Ion Exchange and the Swelling of Ion-exchange Resins

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The review deals with the modern hypotheses concerning the physicochemical properties of ion-exchange resins and their effects in the interaction between resins and solvents and solutes, mainly electrolytes. The problems associated with the permeability of resins, the steric accessibility of the functional centres, and their screening are discussed. Particular attention has been devoted to the interaction between resins and solvents. The thermodynamic conditions of such interaction (the changes in the integral and differential thermodynamic functions of swelling) have been elucidated. The isotherms for the absorption of water vapour have been discussed as a function of the content of the cross-linking agent, the ionic form of the resin, and the hydrophilicity of the matrix. In the section dealing with the comparison of the isotherms for the absorption of water vapour by resins with different degrees of cross-linking, attempts to describe them on the basis of osmotic concepts are discussed. The methods of the osmotic theory have been examined in detail: the characteristics of the hydration of ion-exchange resins which follow from the analysis of the differential and integral free energies of swelling and also from data derived by other methods, such as infrared and nuclear spin resonance spectroscopy. Certain model approaches to the study of the selectivity of ion exchange with participation of the solvent have been described. The thermodynamic methods for the analysis of the relation between the selectivity and swelling of resins are quoted.
The bibliography includes 126 references.

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I. POROSITY, PERMEABILITY, AND SWELLING OF ION-EXCHANGE RESINS

Ion-exchange sorption and chromatography which originated on the basis of mineral and certain natural organic ion exchangers have assumed considerable importance following systematic studies on the synthesis of ion-exchange resins. The formation of a wide variety of cross-linked polymers containing acid or basic functional groups gave rise to insoluble acids, bases, and amphoteric compounds and salts capable of the absorption and exchange of various types of ions or the absorption of electrolytes from solutions. The possibility of modifying the structure of the matrix of a three-dimensional polymer and the properties and positions of acid–base groups and other active groups led to the creation of highly specific ion-exchange resins absorbing preferentially particular types of ions from solution. Ion exchange on resins takes place in heterogeneous systems incorporating a gel-like phase consisting of the grains of the swollen resin and the external solution. The capacity of the ions present in solution to reach all the functional groups in the resin and to exchange with the ions reversibly bound to the functional groups (counterions) is determined by the permeability of the gel phase of the resin grains to the ions undergoing sorption and desorption. Precisely in this sense one speaks of the porosity of the resin within the three-dimensional network or the microporosity, these terms being understood as the permeability to mobile ions. In the exchange of inorganic and organic ions of low molecular weight there is interaction with all the centres regardless of their positions in the bulk of the grains.

However, other cases are known where only part of the exchange centres are accessible to the ions absorbed. We encounter such phenomena in the absorption by resins of ions having large molecular weights, in particular organic ions[1,2]†. In the sorption of the triply charged streptomycin ions (M = 580 conventional units) on carboxylic acid resins, the exchange capacity of the sorbents is found to increase with the swelling coefficient, but the total ion exchange capacity of the resins with respect to metal ions cannot be attained. This phenomenon is attributed to the fact that the sorption of the streptomycin ion is accompanied by the screening of part of the exchange centres of the cation exchanger[4] because the dimensions of the organic ions exceed the average distance between adjacent functional groups. The same tendency is observed with the sextuply charged neomycin ions (mycerin, M = 720 conventional units): the sorption capacity increases with the swellability of the resins, but the total exchange capacity cannot be attained. When the sorbent grains are considerably comminuted, which usually leads to a sharp increase in capacity when the functional centres are sterically inaccessible, only a slight increase in the exchange capacity of the resin with respect to neomycin is noted. On the other hand, ion-exchange resins (even resins with relatively low swellability) with reduced exchange capacity absorb large organic ions at all the functional groups. Thus carboxy-phenolic resins with reduced exchange capacity sorb streptomycin and neomycin at all the functional centres regardless of the swelling coefficient[5].

A similar phenomenon was observed in the sorption of nucleotides on ion-exchange resins. The sorption capacity of Dowex-1 with respect to ATP, AMP, and UMP depends little on the content of the cross-linking agent in the resin and hardly changes over a certain range (1–8% of divinylbenzene).[6] It is much lower than the total exchange capacity of the resins with respect to small ions, i.e. a

†The phenomenon of the inaccessibility of part of the sorption centres to inorganic ions has been observed on zeolites[3].

large part of the active centres do not participate in the exchange processes. Partial deamination of the resin and the associated decrease of the total exchange capacity lead to a sharp increase of the relative exchange capacity with respect to the nucleotides. In the cases considered part of the exchange centres are screened, which makes them inaccessible to interaction with the ions in solution.

Another example of the dependence of the equilibrium properties of ion-exchange resins on their structure is the problem of the correspondence between ionic dimensions and the dimensions of the effective channels in which ions can migrate. This phenomenon is widespread and is sometimes called the phenomenon of ionic sieving (by analogy with molecular sieving in the separation of materials); it is revealed both in the dependence of the sorption capacity with respect to the given ion on the swellability of the resin and in the dependence of the sorption capacity of the given resin with respect to ions of different dimensions. Thus the sorption capacity with respect to singly charged cations of tetracycline antibiotics increases with the swellability of sulphonated resins and almost reaches the total exchange capacity with respect to metal ions (Fig. 1). Similar phenomena occur also in anion exchange.

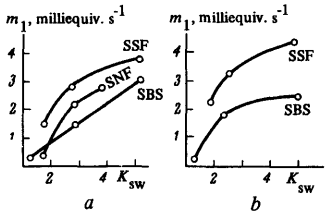


Figure 1. Dependence of the absorption capacity of sulphonated resins with respect to aureomycin (a) and terramycin (b) on resin swellability; K_{SW}—the swelling coefficient in the initial ionic form.

On increase in the swelling coefficients of anion exchangers, there is an increase in the sorption capacity with respect to the singly charged penicilin ion (M = 244 conventional units).[7] The dependence of the sorption capacity with respect to the singly charged novobiocin anion (M = 612 conventional units) on the swelling coefficient of the FAF resin is also described by an S-shaped curve. Screening of part of the sorption centres in the sorption of large organic ions and the inaccessibility of the sorption centres cannot be always unambiguously distinguished. The problem of the correspondence of the physicochemical properties of ion-exchange resins and the characteristics of the chemical and steric structures covers a wide range of phenomena and is one of the central problems in the theory of ion exchange. The solution of this problem involves the determination of quantitative relations between the properties of the initial components of the reaction mixture and those of the copolymers formed under the chosen conditions. At the present time the problem cannot be solved in a general form, although parts of it are susceptible to quantitative studies. The principal feature of the problem is the hypothesis of channels or pores through which the substances sorbed by the resin migrate. There exist ion-exchange materials, for example mineral and synthetic zeolites, which have channels which are homogeneous with respect to size and regular in shape. Zeolites are aluminosilicates and the characteristics of their structure are associated with the tetrahedral coordination of oxygen around aluminium and silicon and also the strength of the bonds between these elements and oxygen. In cross-linked organic polyelectrolytes such homogeneity of the channels cannot be achieved because of the different reactivities of the monomers, their complex dependence on the conversion, and also the possibility of various orientations of the polymer chains as a result of the rotation of methyl and other groups. The channels along which sorption of substances by ion-exchange resins takes place cannot be characterised in detail. Average characteristics such as porosity and permeability have been adopted for their description. The porosity P is the fraction of the volume of the resin grain occupied by pores, i.e.

$$P = \frac{v_1}{v_2},$$

where v_1 and v_2 are the pore volume and the total volume of the resin grain. For some resins, v_1 and v_2 change relatively little on hydration‡. The porosity of such resins has been called the intrinsic porosity.

Swelling resins can also be characterised by the porosity P, but the latter is not a constant. In the dry state $P \simeq 0$ and in the swollen state it can be extremely high and can exceed the value of P for intrinsically porous ion-exchange resins. This porosity has been called the latent porosity. The concept of "permeability" has been introduced in the study of liquid flow through membranes and filters formed from finely disperse materials. In this case the permeability is characterised by the permeability coefficient which enters into D'Arcy's linear filtration law. The permeability of ion-exchange resin grains cannot be defined in this simple form due to the lack of an evident analogy with the phenomenon of liquid flow and the complexity of the conditions in which the diffusion of substances absorbed takes place. Therefore it is now usual to speak of the permeability of disperse ion-exchange materials in the sense that it characterises their capacity to absorb substances. A measure of the permeability of an ion-exchange resin is the amount of substance absorbed under the given conditions. Thus porosity characterises mainly the sorbent, while permeability characterises its interaction with the medium§. The permeability of ion-exchange resins depends on the type of substance absorbed. Therefore the permeability to the solvent, for example, may differ from the permeability to ions. The permeability of ion exchangers depends on the amount of cross-linking agent and its nature. Thus when 20% of divinylbenzene is used in the synthesis of KU-2 sulphonated styrene resin, the product has a swelling coefficient of 1.3–1.4. A similar low swellability of the analogous SBS sulphonated styrene resin is achieved by the introduction of 70% of butadiene (divinyl). Three cross-linking agents

‡Ion-exchange resins may be hydrated both without a significant change in grain volume (resins with a large content of the cross-linking agent, macroporous resin) and with a considerable change in this volume. In the latter case hydration is frequently referred to as swelling. In the literature on ion exchange the term "swelling" is used as a synonym for "hydration".

§In resins with latent porosity the porosity and permeability characterise only the interaction between the resin and the medium.

are most widely used: divinylbenzene (*o*-, *m*-, and *p*-isomers), butadiene, and triazine. A copolymer with the most regular structure is formed when one of the pure isomers of divinylbenzene is used as the cross-linking agent. We believe that ion exchangers with butadiene or triazine as cross-linking agents have a less regular structure [8].

Table 1. Physicochemical methods for the investigation of the structure of ion-exchange resins.

Method	Object of study	References
Application of the theory of capillary condensation	Dowex-50 in H^+-form	9
	KB-4 in H^+-form	10
	macronetwork carboxylic acid resins in H^+-form	10
Measurement of the steric accessibility of functional centres to organic ions with increase in their dimensions	KMT, KB-4, KFU, KFUh	2
	macroporous resins	2
	Wofatit	11
	Amberlyst IR-45	12
	Levatit MII	12
	SBS, KU-2, Permutit	2
	KRS, KRF	13
Depression of the freezing point of the solvent in resins	phenolsulphonic acid resin	14
Determination of the specific absorbing surface by BET method, the porosity, and the average pore diameter	macronetwork resins	10
	macroporous resins	15
	SG-1, AN-2F, EDE-10P, AV-17	15
	skeletons of macroporous resins	16
	macroporous resins	15
Determination of microhardness	SG-1 x 5, AN-2F	17
Electron microscope method	Dowex-50 resins	18
	macroporous resins	19
X-Ray diffraction	Amberlyst 15	20
	KU-1, KU-2, KB4P2	21
Microradiographic study of resin sections	AN-2F, SG-1	17
Optical properties in transmitted and reflected polarised light beams	Carboxylic acid resins	17
	DK-3, DKR, SG-1TS, SG-1P x 5, SG-1 x 5	
Absorption spectra in the visible region	resins saturated with dyes	22, 23
Reflection spectra in the visible region	metal complexes with carboxylic and sulphonic acid cation exchangers	24, 25
Ultraviolet spectroscopy	phenolsulphonic acid, polyethylene-polyamine, and styrene resins	26, 27
Infrared spectroscopy	water in resins	28-31
	structure of styrene resins	32-34
Nuclear magnetic resonance	structure of water in styrene resins	33, 35-39
	anion exchangers in F^--form	40, 41
Electron spin resonance	cation exchangers in Cr- and Mn-forms	42-44
Measurement of magnetic susceptibility	cation exchangers in Fe-form	45
	anion exchangers in OH^-- and Cl^--forms	46
	resins with complex cations and anions	47

The number and relative positions of the functional centres have a significant influence on the permeability of resins. This phenomenon was discussed above (see p. 1257).in connection with the problem of the inaccessibility and screening of functional centres. Numerous methods developed earlier for mineral sorbents are used to estimate the permeability and porosity of ion-exchange resins. Mineral sorbents are in most cases intrinsically porous and their porosity can be investigated both in the dry state and in the presence of a solvent in the pores. A similar approach is unfortunately inapplicable to all types of ion-exchange resins, since, on swelling of resins with latent porosity, the permeability changes. To investigate the structure of ion-exchange resins, it is best to use methods which permit the estimation of the dimensions of the "expanded" regions between three-dimensional networks in the presence of maximum swelling of the resins, since it is then possible to compare the results with those for their permeability under ordinary conditions. It is noteworthy that none of the methods employed at present to estimate the porosity or permeability of resins is absolute. The choice of a particular method depends both on the characteristics of the given problem and on the individual characteristics of the sorbents. Various methods for the investigation of the structure of ion-exchange resins are listed in Table 1 and have been described in a number of reviews [4,74].

Figure 2 presents graphical models of ion-exchange sorbents with different porosities and permeabilities. Until recently the structural type A, characterised by an alternation of expanded and contracted regions in the polymer network, was most widely used. It should be noted that we are dealing with swelling ion-exchange resins and therefore structure A represents the state of the resin containing a solvent. When the latter is removed, the polymer chains close up and the differences between regions with different cross-linking densities are to a large degree smoothed out. In the dry state the packing density of the polymer chains is such that the resin hardly absorbs neutral gas molecules (see Table 2).

In the swollen state ion exchangers of this type are characterised by considerable intramolecular permeability. Almost all their functional centres are accessible to inorganic ions. However, when the degree of cross-linking of resins increases, the functional groups may become screened and sterically inaccessible. A steric model of the styrene–divinylbenzene cation-exchange resin of this structural type was proposed by Grubhofer [18].

If x is the molar percentage of the cross-linking agent (divinylbenzene), then the number of ethylene groups per

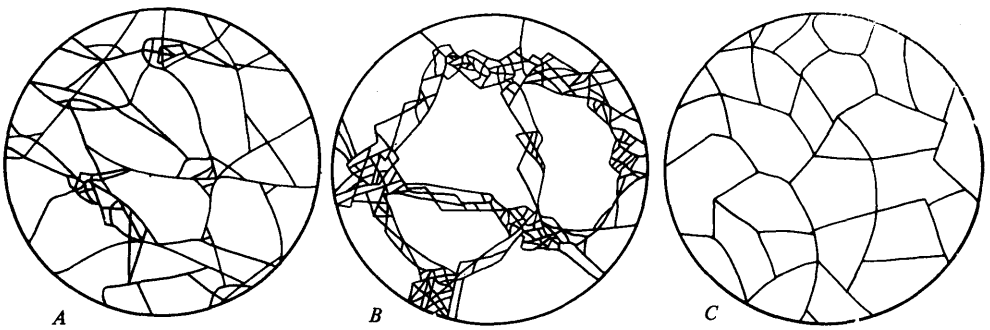


Figure 2. Graphical models of resins of different structural types: A) resin of Dowex-50 type; B) macroporous resin; C) macronetwork resin.

cross-link between the points of attachment of the latter is $y = \frac{1}{2}(100/x + 1)$. The distance between two branching points in the network [taking into account the thickness of the benzene ring (4.5 Å), the length of two carbon–carbon bonds in the phenyl group (2×1.5 Å), and the size of a single monomer unit (2.2 Å)] is

$$a(\text{Å}) = 2.2y + 7.5.$$

Table 2. Internal surfaces of various sorbents.

Sorbent	Form of sorbent	$\bar{d}$, nm	Area of channels, $m^2 g^{-1}$	Refs.
CaA zeolite	Ca		1640	48
NaX zeolite	Na		1400	48
Silica gel	—		507	49
Macroporous resins:				
Amberlyst 15	Na		42.5	50
Amberlyst XN-1001	Cl		62.9	50
KR-1	Pb, Cr	300	3.0	19
KR-2	Pb, Cr	79	31.0	19
AR-1	$PtCl_6$	160	3.2	19
Ordinary resins:				
Amberlyst IR-120	Na		0.1	50
Amberlyst IRA-400	Cl		0.1	50
Macronetwork resins:				
Carboxylic acid cation exchanger	H, Na		<0.1	10, 5
Sulphonic acid cation exchanger	H, Na		<0.1	10, 5

The angle between the main chain and the cross-link is assumed to be 90°. To obtain the dimensions of the cell accessible to the diffusion of ions, it is necessary to subtract from the resulting cell diameter the thickness of the polystyrene chain, i.e. 15 Å. Grubhofer's results for a high content of cross-linking agents in resins agree well with independent estimates of their cell dimensions, and for low contents of the cross-linking agents they agree with data obtained by the electron microscope study of the same specimens in the dry state. This shows that the model describes correctly the fundamental structural characteristics of resins based on styrene and divinylbenzene, despite the fact that it is undoubtedly a very rough approximation, disregarding a whole series of phenomena which obtain in the formation of copolymer structures (the presence of amorphous regions, non-uniform sulphonation, intertwining of chains, etc.).

An unusual type of porosity arises in the synthesis of resins where an inert component (including polymers) is used in the copolymerisation process [52–55]. Resins of this type are called macroporous. They are distinguished by a considerable heterogeneity of structure and are characterised by the presence of regions with higher and lower matrix densities (Fig. 2*B*). The macroporosity of a resin differs significantly from the permeability within the three-dimensional network. The channels in a macroporous sorbent, which have a large internal area, exist also in the unswollen polymer (Table 2). Such channels are absent from ordinary ion-exchange resins. Comparison of the structures of macroporous and ordinary resins with maximum moisture content shows that in the first case there are pores whose dimensions are several times greater than the "expanded" regions between the networks in ordinary resins. When macroporous resins are hydrated, their degree of swelling changes insignificantly. Owing to regions with high matrix density, macroporous resins are distinguished by considerable mechanical strength. The porosity of resins of this type may be characterised as intrinsic porosity.

Certain physicochemical characteristics of the resins are given in Table 2. KR-2 cation-exchange resin was obtained using additives of lower molecular weight than for KR-1 cation exchanger, as a result of which it has a higher surface area, but the average dimensions of its pores are smaller.

It is interesting that cases intermediate between macroporous and ordinary resins are possible; these resins are characterised by latent porosity. Thus AR-1 anion-exchange resin exhibits all the features of a macroporous resin and yet is capable of swelling. Electron diffraction shows that the structures of macroporous resins consist of agglomerates of quasispherical particles with interconnecting cavities between them. The microspherical particles of macroporous resins consist of a gel similar in properties to the gel of ordinary resins, but containing a much higher amount of the cross-linking agent and consequently having a much higher matrix density. The active centres can be located both on the surface of the microspherical particles and within them. Therefore diffusion coefficients measured in macroporous resins are a result of the superposition of the diffusion of ions in the system of cavities and in the gel of the microspherical particles. Similarly the absorption of a solvent by macroporous resins must be regarded as occurring both in the microspherical particles and in the spaces between them. Kunin [56] showed that the absorption of a solvent by macroporous resins takes place in two stages. Initially the microspheres are hydrated and then the spaces between them are filled, the fraction taken up by the microspheres in the cases which he investigated amounting to 28–30% of the total amount of the solvent absorbed. Experimental proof of the occurrence of this phenomenon is provided by the dependence of the amount of mercury which can be forced into the resin on the content of the solvent $\bar{n}_W$. Up to a certain value of $\bar{n}_W$, the porosity either does not change or increases somewhat, but, after the attainment of a critical value, it falls sharply. Evidently a significant cause of the decrease of the porosity is the end of the hydration and swelling of the microspherical particles and the appearance of the solvent between them. The results of experiments in which mercury is forced into the resin also show that the pore dimensions change in the swelling of macroporous resins: large pores become still larger and smaller pores decrease further in size. This phenomenon may be explained by the competition between the processes involving the swelling of the microspherical particles and their deformation on swelling.

The microspherical particles in macroporous resins may be regarded as having latent porosity. In the exchange of small inorganic ions all the functional centres of macroporous resins are accessible. With organic ions, the permeability falls sharply. This may be attributed to the steric inaccessibility to organic ions of the functional centres within the bulk of the microspherical particles and the accessibility of those on the surface of the particles. The phenomenon of steric inaccessibility to tetraethylammonium, triethylbenzylammonium, Methylene Blue, and Crystal Violet ions has been observed in macroporous ion-exchange resins where the capacity due to the functional centres on the surface of microporous particles amounted to 40–50% of the capacity with respect to inorganic ions. On further increase of ionic size, the permeability of the resin changes relatively little [2]. The presence of heterogeneous regions is reflected also in the kinetic properties of macroporous resins. When the functional centres of the microspherical particles are sterically inaccessible, the diffusion coefficient is determined solely by the dimensions

of the macropores. Thus the diffusion coefficients of the ions of quaternary ammonium bases in the macroporous KU-2 resin depend little on the dimensions of the ions in the series tetramethylammonium–triethylbenzylammonium. On the other hand, for ordinary resins of a similar type the rates of diffusion within the same group of ions decrease significantly with increase in their size.

A number of papers have been published recently on the methods of synthesis and the properties of new types of resins with enhanced permeability. Thus, when a telogen is used as a diluent, there is a possibility of breaks in the main chain [57]. The permeability of resins of this kind is higher due to the formation of "defects" in the main chain and due to the dilution of the monomer mixture. A method has been developed for the synthesis of sulphonic acid and carboxylic acid cation exchangers with larger dimensions of the interchain spaces as a result of the use of cross-linking agents with different chain lengths. *NN'*-Alkylenedimethacrylamides proved to be suitable for this purpose [4,10,58-60]. The elementary unit of KMDM macronetwork resins has the following structure.

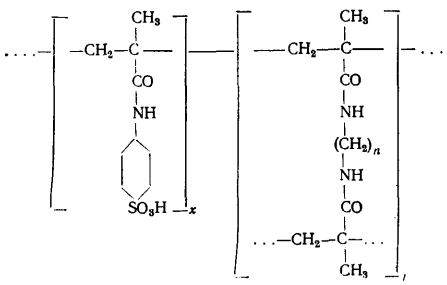


Table 3. Mutual diffusion coefficients of Methylene Blue and streptomycin ions in resins.

Sorption of Methylene Blue on KU-2 sulphonic acid resin (H^+-form, 40°C)		Sorption of streptomycin on KMDM-6* carboxylic acid resin (Na^+-form, 20°C)	
degree of saturation F	diffusion coefficient $10^{10}D$, $cm^2 s^{-1}$	degree of saturation F	diffusion coefficient 10^7D, $cm^2 s^{-1}$
0	1.7	0.23	1.1
0.13	1.6	0.35	1.1
0.40	0.5	0.51	1.3
0.62	0.25	0.86	1.3
0.80	0.35	0.95	1.2

*Cross-linking agent—hexamethylenedimethacrylamide.

The permeability of such resins may be altered both by changing the content of the cross-linking agent and by changing the length of its chain. Macronetwork resins probably have a structure of type *C* (Fig. 2), which is called isoporous. With suitable "pore" dimensions in these resins, there is a possibility in the latter only of the screening of functional centres. The high permeability of such resins to organic ions is reflected, in particular, in their capacity to sorb rapidly ions of large molecular weight. The diffusion coefficient of streptomycin ions in the grains of this resin is not only very high but also it does not decrease during the sorption process (Table 3).

Until recently it was suggested that a cross-linking three-dimensional polyelectrolyte capable of swelling may be regarded as a system with highly elastic properties in which thermal density fluctuations take place [61]. On this basis, the hypothesis was put forward that the incorporation of ions into the grains of the swollen resins may be associated not only with the presence of permanent pores of channels but also with the presence of fluctuating expanded regions in the polymer network. Then the conformational properties of the polymer network can be calculated on the basis of Flory's theory of polymer solutions, one of the results of which is a decrease of the entropy of the network on swelling. However, in a study of the thermodynamics of the exchange of quaternary ammonium ions for Na^+ ions on cross-linked sulphonated polystyrene resins (containing 8% of divinylbenzene), Boyd and Larson [62] observed that, when the resin is converted into the quaternary ammonium-form, its volume increases but the network entropy increases also instead of decreasing. The study of the elastic characteristics of films of sulphonated phenol–formaldehyde resins also showed [63] that the entropy of their extension is positive. These experimental findings and also the value of Young's modulus of ion-exchange resins, which is 10^8–10^{-9} dyn cm^{-2}, i.e. higher by a factor of ten than the value of Young's modulus of rubbers, led to the conclusion [64] that ion-exchange resins of certain types behave as if they were polymers in the vitreous state. Then one may expect that the mobility of the polymer network is fairly low and network density fluctuations under the influence of thermal motion cannot lead to significant changes in the shape of the "pores".

II. INTERACTION OF ION-EXCHANGE RESINS WITH SOLVENTS

a. Methods for the Investigation of the Interaction of Ion-Exchange Resins with Solvents

The study of the solvation of ion-exchange resins¶ is important both for the investigation of their physicochemical properties (structure, amount of cross-linking agents, hydrophilicity of the fixed groups and counterions, etc.) and for the elucidation of the mechanism of ion exchange. A quantitative characteristic of the interaction of the resin with a solvent is provided by the isotherms for the adsorption of the latter from the vapour phase or from solution (the so called isopiestic lines). Isopiestic lines are usually measured in the vapour pressure range from negligibly low values up to the vapour pressure (p_0) of the pure solvent ($0 \leqslant p/p_0 = \alpha \leqslant 1$). The temperature coefficients of isopiestic lines over the entire range of values of α are also important. The composition of the vapour phase is regulated by solutions of salts [65,66] or sulphuric acid [67], the water vapour pressure above which is known over a wide range of temperatures and concentrations. On the basis of the isopiestic lines and their temperature coefficients (or on the basis of the heats of hydration), it is possible to calculate all the thermodynamic functions characterising the interaction of the resin with the solvent. The application of the thermodynamic method to resins [68,69] has developed largely by analogy with the thermodynamics of the hydration of natural macromolecular compounds [70,71].

Suppose that we have a resin with a specified ionic composition containing a certain amount of absorbed solvent

¶We shall consider only the interaction with water.

$\bar{n}_{1w}$ moles per equivalent of ions) in equilibrium with the vapour of the latter whose pressure is p_1. If the pressure changes, for example increases, there is a corresponding change also in the equilibrium content of the solvent in the resin. The increase in moisture content in the process where sorption does not alter the equilibrium vapour pressure may be represented by the following equation:

$$n_i[\bar{n}_{1w}(p_1)] + n_w(p_2) \rightarrow n_i[\bar{n}_{1w} + \bar{n}_w, (p_2)], \quad (1)$$

where n_i is the amount of ion-exchange resin (in grammes) containing E equivalents of exchange centres and $n_w(p_2) = \bar{n}_w(p_2)$.

The increment of the Gibbs free energy of the system during process (1) is

$$\Phi_{sw} = n_i[\mu_i(p_2) - \mu_i(p_1)] + \bar{n}_{1w}[\bar{\mu}_w(p_2) - \bar{\mu}_w(p_1)] = n_i\Delta\mu_i(p_2, p_1) + \bar{n}_{1w}RT\ln\frac{p_2}{p_1}, \quad (2)$$

where Φ_{sw} is the free energy of swelling in process (1) and $\bar{\mu}_w(p_2) = \mu_w(p_2)$. The change in the composition of the vapour phase may be neglected in the derivation of Eqn. (2), because swelling can always be studied under conditions such that the change in the number of moles of water in the vapour phase is very small, with a small resin sample, or under conditions such that this change is compensated by the evaporation of part of the solvent from the electrolyte maintaining the given vapour pressure. The change in the free energy of the vapour is then zero (at T = const. and p = const.) and therefore makes no thermodynamic contribution to the swelling process. On the other hand, the Gibbs–Duhem equation applies to the equilibrium system (at a pressure p_2):

$$n_i d\mu_i + (\bar{n}_{1w} + \bar{n}_w)\, d\bar{\mu}_w = 0, \quad (3)$$

$$d\mu_i = -\frac{(\bar{n}_{1w} + \bar{n}_w)}{n_i}\, d\bar{\mu}_w. \quad (4)$$

According to Eqn. (4), the change in the chemical potential of the ion-exchange resin when the equilibrium vapour pressure changes from p_1 to p_2 is

$$\mu_i(p_2) = \mu_i(p_1) = -\int_{\mu_w(p_1)}^{\mu_w(p_2)} \frac{(\bar{n}_{1w} + \bar{n}_w)}{n_i}\, d\mu_w. \quad (5)$$

Since $\bar{n}_{1w}$ is independent of the pressure p_2, it follows that

$$\mu_i(p_2) - \mu_i(p_1) = -\frac{\bar{n}_{1w}}{n_i}RT\ln\frac{p_2}{p_1} - \int_{\bar{\mu}_w(p_1)}^{\bar{\mu}_w(p_2)} \frac{\bar{n}_w}{n_i}\, d\mu_w.$$

On substituting the change in the chemical potential of the resin determined from Eqn. (6) in Eqn. (2), we obtain

$$\Phi_{sw} = -\int_{\ln\alpha_1}^{\ln\alpha_2} \bar{n}_w RT\, d\ln\alpha, \quad (7)$$

where $\alpha = p/p_0$ and p_0 is the vapour pressure of the pure solvent. To facilitate the comparison of the free energies of swelling of various resins, it is necessary to select standard states for the resin and solvent vapour; usually one chooses the dry resin and the vapour over the pure solvent ($p = p_0$). Then swelling is measured from the state where $p_1 = 0$. The free energy of the transfer of n_w moles of the solvent from the vapour at a pressure p_0 to the vapour at a pressure p_2 is

$$\Phi_{sw_2} = n_w[\mu_w(p_2) - \mu_w(p_0)] = n_w RT\ln\alpha. \quad (8)$$

Thus the change in the free energy of swelling of the resin from the chosen standard states to the specified mixed state is

$$\Phi_{sw} = \Phi_{sw_1} + \Phi_{sw_2} = \bar{n}_w RT\ln\alpha - RT\int_0^{\alpha} \bar{n}_w\, d\ln\alpha = RT\int_0^{n_w} \ln\alpha\, dn_w. \quad (9)$$

We may note that the value of Φ_{sw} calculated by Eqn. (9) corresponds to a hypothetical swelling process where in the equilibration of the dry resin ($p = 0$) with the vapour of the pure solvent ($p = p_0$) the equilibrium vapour pressure decreases to $p_2 > p_0$. Φ_{sw_1} corresponds to the process in a humidifier where p_2 = const. Eqn. (9) thus corresponds to the following free energy difference [68,69]:

$$\Phi_{sw} = \bar{n}_w\bar{\mu}_w(p_2) + n_i\mu_i(p_2) - n_w\mu_w(p_0) - n_i\mu_i(p=0) = \bar{n}_w[\bar{\mu}_w(p_2) - \mu_w(p_0)] + n_i[\mu_i(p_2) - \mu_i(p=0)]. \quad (10)$$

Comparison of Eqns. (9) and (10) shows that the first term in the former characterises the change in the state of the solvent and the second the change in the state of the resin during the sorption process. Similar equations can be written also for the heat of sorption [assuming that $\bar{h}_w(p_2) = h_w(p_2)$]:

$$H_{sw} = \bar{n}_w[\bar{h}_w(p_2) - h_w(p_0)] + n_i[h_i(p_2) - h_i(p=0)], \quad (11)$$

where $\bar{h}_w$ and h_i are the partial heats of sorption of the solvent and of the swelling of the resin. The partial quantities referring to the solvent can be found in the following way:

$$\bar{h}_w(p_2) - h_w(p_0) = \frac{\partial\left(\frac{H_{sw}}{n_i}\right)}{\partial\left(\frac{\bar{n}_w}{n_i}\right)}. \quad (12)$$

On combining Eqns. (11) and (12), we obtain the difference between the partial heats $h_i(p_2) - h_i(p=0)$ characterising the swelling of the resin:

$$h_i(p_2) - h_i(p=0) = \frac{H_{sw}}{n_i} - \frac{\bar{n}_w}{n_i}\cdot\frac{\partial\left(\frac{H_{sw}}{n_i}\right)}{\partial\left(\frac{\bar{n}_w}{n_i}\right)} = -n_e^2\frac{\partial\left(\frac{H_e}{n_e}\right)}{\partial n_e}, \quad (13)$$

where $\bar{n}_e = \bar{n}_w/n_i$ is the equivalent moisture content of the resin and $H_e = H_{sw}/n_i$ the equivalent heat of sorption of the solvent.

Subdivision of the experimental heat of sorption of the solvent into components associated with the change in the thermodynamic state of the resin (the matrix or the ions and counterions fixed on the matrix) and the solvent permits the estimation of their relative contributions and thereby provides quantitative data for the elucidation of the thermodynamic effects of the swelling process. Additional information can also be obtained by comparing the changes in the Gibbs free energies and enthalpies of swelling:

$$\bar{\mu}_w(p_2) - \mu_w(p_0) = \bar{h}_w(p_2) - h_w(p_0) - T[\bar{S}_w(p_2) - S_w(p_0)], \quad (14)$$
$$\mu_i(p_2) - \mu_i(p_0) = h_i(p_2) - h_i(p_0) - T[S_i(p_2) - S_i(p_0)].$$

Eqns. (14) and (15) permit the determination of the partial entropies of sorption of the solvent and of swelling of the resin ($\bar{S}_w$, S_i). The determination of the partial thermodynamic quantities of Eqns. (12)–(15) is possible when the heats of sorption are measured together with the sorption isotherms of the solvent [frequently called "isopiestic" lines, the term reflecting the sorption mechanism defined by Eqn. (1), since the vapour pressure then remains unchanged]. Calorimetric determination of the heat of sorption of the solvent is most advantageous, since

it is then possible to obtain the most accurate values of the enthalpy of swelling as a function of the equilibrium amount of solvent absorbed. From the experimental standpoint, the following procedure for the determination of this function is convenient. Initially it is necessary to measure the integral heat of sorption when the dry resin is mixed with an excess of the solvent. Then the resin is equilibrated with the vapour of the solvent and the heat of mixing with an excess of the solvent is determined for this state. The difference between the two heats represents the heat of conversion of the dry resin into the partially hydrated state corresponding to the chosen vapour pressure. By varying the equilibrium vapour pressure, it is possible to obtain a curve relating H_{SW} to the content of the solvent in the resin. However, this relation can also be calculated provided that the isopiestic lines for the given resin are available at several temperatures. It is known that the heat of a chemical reaction which is independent of temperature (if it does vary with temperature, then the average heat in the given temperature range is employed) may be calculated from the temperature variation of the Gibbs free energy:

$$H_{sw} = -T^2 \frac{\partial \frac{\Phi_{sw}}{T}}{\partial T} \qquad (16)$$

When the temperature changes, the free energy of swelling changes too, since this involves a change in the content of the solvent in the resin. For further discussion, it is convenient to introduce the concept of the isosteric heat change H_{IS}, i.e. the heat change occurring when the solvent is redistributed between the resin and the vapour on changing the temperature but the total amount of solvent remains constant:

$$H_{is} = -T^2 \frac{\partial^2}{\partial T\, \partial \bar{n}_w} \left[\frac{\Phi_{sw}}{T}\right] . \qquad (17)$$

It is easy to show that

$$H_{is} = \left.\frac{\partial H_{sw}}{\partial \bar{n}_w}\right|_{T,p} . \qquad (18)$$

The isosteric heat change can be conveniently determined from two isopiestic lines corresponding to different temperatures on the basis of the following equation:

$$H_{is} = \frac{RT_1T_2}{T_2 - T_1} \ln \left.\frac{\alpha_1}{\alpha_2}\right|_{\bar{n}_w} , \qquad (19)$$

where $T_2 > T_1$ and α_2 corresponds to the temperature T_2. If H_{IS} is determined for different values of $\bar{n}_W$, then the integral heat of sorption H_{SW} may be determined as follows [see Eqn. (18)]:

$$H_{sw} = \int_0^{\bar{n}_w} H_{is}\, d\bar{n}_w . \qquad (20)$$

The calculation of H_{SW} by Eqns. (16) and (20) should in principle yield the same enthalpies of swelling, but in the second case the results are more accurate, since there is an additional computational operation in Eqn. (16) involving integration.

The change in the solvent content of the resin with temperature in the range of several tens of degrees is small, which of course leads to a low accuracy in the determination of the enthalpy of swelling from the temperature variation of Φ_{SW}. In consequence of the condition $\bar{n}_W$ = const., H_{SW} can be calculated down to the smallest swellability in the given temperature range (as a rule it corresponds to the highest temperature).

Together with the development of thermodynamic techniques for the investigation of ion-exchange resin solvation, physical methods are being increasingly employed at the present time: NMR and infrared spectroscopy, methods based on the study of the dielectric properties of the resins, etc. The principal conclusions arrived at on the basis of these methods are described below.

b. Characteristics of the Interaction of Ion-Exchange Resins with Solvents

The isotherms for the absorption of water by an ion-exchange resin depend on the type (types) of counterions, the content of the cross-linking agent, the hydrophilicity of the matrix and the cross-linking agent, and also on the characteristics of the steric structure of the resin matrix. According to Brunauer's classification [72], they can be assigned to the second type, characterised by multilayer adsorption without capillary condensation, With increase of the relative humidity of the vapour phase, the isotherms are nearly linear in the vicinity of zero [pressure ? (Ed. of Translation)]. For sulphonated polystyrene ion-exchange resins saturated with alkali metal or alkaline earth metal ions, the slopes of these curves are particularly high [68]. They are somewhat lower for sulphonated resins containing Ag^+ ions [68] and also organic ions. A sharp change in the isotherms in this region is characteristic of certain carboxylic acid resins in the H^+-form [4] and also for anion exchangers [76]. In the region of intermediate values of α the slope of the $\bar{n}_W - \alpha$ curve decreases compared with the first section but, as a rule, it is higher the higher is its value in the first section. The overall absorption of solvent along both sections of the isotherms is lower (sometimes much lower) than the maximum absorption of the solvent by the resin at $\alpha = 1$. Therefore the greatest change in swelling occurs in the region of relative humidity close to unity. The slopes of the isotherms in this region are also various. The following two series illustrate the variation of the swellability with the type of ion and α:[68]

$\alpha = 1$; $Mg^{2+} > H^+ > Li^+ > Na^+ > Ca^{2+} > NH_4^+ > K^+ > Ba^{2+} > Ag^+ \approx (CH_3)_4N^+$

$\alpha = 0{,}29$; $Mg^{2+} > H^+ > Ca^{2+} > Li^+ > Ba^{2+} > Na^+ > (CH_3)_4N^+ > NH_4^+ > K^+ > Ag^+$.

A change in the content of the cross-linking agent in the resin has the greatest effect along the third section of the isotherms: with increase in the degree of cross-linking, the swellability falls sharply. At lower values of α two opposed results have been noted: the swellability of resins with a high degree of cross-linking is lower for some resins [72,73] and higher for others [64,74,75] than for less cross-linked analogues (in this case the swelling isotherms at low and high values of α are reversed). Gregor [69] was the first to describe the reversal of the isotherms and explained it qualitatively. According to his hypothesis, in the region of low values of α in resins with a low content of cross-linking agents there is more intense interchain interaction, which reduces the degree of swelling. Because of its rigidity, the cross-linking agent limits this interaction, which leads to the reversal of isotherms. It is interesting to note that the isotherms for the absorption of solvents by non-cross-linked polyelectrolytes are also below the isotherms for the cross-linked analogues at low values of α and above them at high values. The reversal of isotherms is shown particularly clearly for macronetwork ion-exchange resins, which is evidently favoured by the interaction between the amide groups of the cross-linking agent and the monomer. It is noteworthy that,

in the hydration of macronetwork resins, data confirming Gregor's hypothesis were obtained: a change in the chain length of the cross-linking agent while retaining its relative content leads to the reversal of the isotherms[4]. The effect of the structural characteristics of resins on swellability may be followed in the usual sulphonated cation-exchange resins of the polymerisation type (macronetwork[75] and macroporous[76]) as examples. For the same content of cross-linking agent in KU-2 resin and in a macronetwork resin, their isotherms virtually merge in the first two regions of α values but differ significantly in the third, where there is a characteristic, particularly sharp rise for macronetwork resins, as a result of which the maximum swellabilities of the resins at $\alpha = 1$ differ severalfold. This phenomenon is associated with the large dimensions of the unit cell of the macronetwork resins and the smaller number of physical nodes in its structure. The isotherms for macroporous resins resemble those for macronetwork resins. They are also characterised by a sharp increase of swellability at α close to unity, but in this case the rise is not due to the formation of a homogeneous internal solution but is probably caused by capillary condensation in the pores of these resins. At lower values of α the hydration of macroporous resins takes place in the more condensed parts of the matrix†, i.e. as in the usual resins with a high content of cross-linking agent. The presence in the resin matrix of other types of hydrophilic centres influences all three sections of the isotherm for the absorption of solvent. Thus the presence of phenolic groups in KU-1 sulphonated cation exchanger appreciably enhances the equivalent content of the solvent in it compared with Dowex-50 × 2 resin (Na^+-form). On the other hand, the presence of amide groups in sulphonated cation exchangers has an insignificant effect on solvent absorption isotherms. The description of the factors influencing the shape of the isotherms for the absorption of solvent by resins shows that their quantitative representation by the function $\bar{n}_W = \varphi(\alpha)$ over the entire range of variation α is exceptionally difficult. Some authors proposed empirical equations describing the adsorption of water in narrow ranges of α. Recently the applicability of the BET equation to the adsorption of water in the region $0 < \alpha < (0.5-0.7)$ [77,78] has been extensively investigated. In this connection, it must be noted that the possibility of representing adsorption isotherms over a narrow range of α by the linear relation

$$\frac{\alpha}{v(1-\alpha)} = \varphi(\alpha)$$

is not sufficient proof that the adsorption mechanism is identical with that underlying the BET theory. It is necessary that the constants C and v_m (in the two-parameter equation) should lie within certain ranges consistent with the physical nature of the process. The second condition is that the measured temperature variation of the constant C should agree with the predictions of the theory. These problems were examined in greater detail by Flood[79].

The difference in the isotherms for the absorption of solvent by resins may be attributed to the different degrees of swelling of the resins in the three regions of the isotherms. The analysis of these effects is based mainly on the variation of the free energies of swelling with α (see p. 552).

†In Kunin's microspheres[56].

The difference in the isotherms for resins containing various amounts of the cross-linking agent may be formally based on osmotic theory in which it is assumed that the components in the resin phase are under a higher pressure $(p_0 + \pi)$ than in solution (p_0).[64,68] This postulate, which constitutes the basis of the osmotic theory of ion exchange, has not been confirmed experimentally and must be regarded as hypothetical. One of its consequences is that the introduction of the cross-linking agent is equivalent to an increase of the pressure π. The pressure π is calculated from the isotherms for the absorption of water vapour by resins containing different amounts of the cross-linking agent. According to the osmotic theory, the chemical potential of the solvent in the resin may be represented thus:

$$\bar{\mu}_w = \bar{\mu}^0_w(T, p_0 + \pi) + RT \ln \bar{a}_w, \tag{21}$$

where $a_W \neq \varphi(\pi)$. Evidently

$$\frac{\partial \bar{\mu}^0_w(T, p_0+\pi)}{\partial \pi} = \frac{\partial^2 \Phi}{\partial n \partial n_s} = \bar{v}^0_w, \tag{22}$$

where $\bar{v}^0_W$ is the partial molar volume of the solvent in the standard state of the resin:

$$\bar{\mu}^0_w(T, p_0+\pi) = \bar{\mu}^0_w(T, p_0) + \int_{\pi=0}^{\pi} \bar{v}^0_w d\pi. \tag{23}$$

On expanding the partial molar volume of the solvent in series in terms of π, we obtain

$$\bar{\mu}^0_w(T, p_0+\pi) = \mu^0_w(T, p_0) + \int_{\pi}^{\pi} \left[\bar{v}^0_w(p_0) + \pi \frac{\partial \bar{v}_w(p_0)}{\partial \pi} + \right.$$
$$\left. + \frac{1}{2!}\pi^2 \frac{\partial^2 \bar{v}_w(p_0)}{\partial \pi^2} + \ldots\right] d\pi \simeq \bar{\mu}^0_w(T, p^0) + v^0_w\left(1 - \varkappa \frac{\pi}{2}\right)\pi = \bar{\mu}^0_w(T, p_0) + \pi \hat{w}^0_s, \tag{24}$$

where κ is the compressibility of water and v^0_W the partial molar volume of water in the standard state at a pressure $\pi/2$. Therefore the expression for the chemical potential of the solvent in the cross-linked resin assumes the following form:

$$\bar{\mu}_w(T, p_0+\pi) = \bar{\mu}^0_w(T, p_0) + \pi \hat{w}^0_w + RT \ln \bar{a}_w. \tag{25}$$

At equilibrium with the vapour of the solvent ($\bar{\mu}_W = \mu_W$)

$$\bar{\mu}^0_w(T, p_0) + \pi \hat{w}^0_w + RT \ln \bar{a}_s = \mu^0_w(T, p_0) + RT \ln \bar{a}. \tag{26}$$

If the standard chemical potentials of the solvent in the resin and in the vapour are chosen the same ($\bar{\mu}^0_W = \mu^0_W$), then

$$\pi \hat{v}^0_w + RT \ln \bar{a}_w = RT \ln \bar{a}. \tag{27}$$

Assuming that in a weakly cross-linked resin $\pi = 0$, we have

$$RT \ln \tilde{a}_w = RT \ln \tilde{a}, \tag{28}$$

$\tilde{\alpha}$ being the relative vapour pressure of the solvent in equilibrium with the weakly cross-linked resin. We may note that an equation of type (22) can be applied not only to the standard chemical potential of the resin but also to the chemical potential of the resin with any solvent content (it is then necessary to satisfy also the condition of a constant moisture content in resins with different values of π):

$$\bar{\mu}_w(T, p_0+\pi) = \bar{\mu}_w(p_0) + \pi \hat{w}^0_w \text{ when } x_w = \text{const} \tag{29}$$

or, taking into account Eqns. (25) and (28) and putting $\bar{\mu}_W(p_0) = \tilde{\mu}_W(p_0)$:

$$\bar{\mu}^0_w(p_0) + \pi \hat{w}^0_w + RT \ln \bar{a}_w = \tilde{\mu}^0_w(p_0) + RT \ln \tilde{\alpha} + \pi \hat{v}^0_w$$
$$\text{when } \bar{x}_w = \tilde{x}_w. \tag{30}$$

For the above choice of standard states, we obtain‡

$$\bar{a}_w = \tilde{a}_w \text{ when } \bar{x}_w = \tilde{x}_w \quad (31)$$

or

$$\bar{f}_w = \tilde{f}_w \text{ when } \bar{x}_w = \tilde{x}_w . \quad (32)$$

Then it follows from Eqns. (27) and (28) that

$$\pi = \frac{RT}{\hat{v}_w^0} \ln \frac{\bar{\alpha}}{\tilde{\alpha}} \text{ when } \bar{x}_w = \tilde{x}_w . \quad (33)$$

Eqn. (33) is the starting point for the determination of the osmotic pressure. Since $\hat{v}_w^0$ corresponds to the partial molar volume of the pure solvent, it can be determined from tabulated data. Sometimes another expression is used for the pressure π:

$$\pi = \frac{RT}{v_w} \ln \frac{\bar{\alpha}}{\tilde{\alpha}} \text{ when } \bar{x}_w = \tilde{x}_w , \quad (34)$$

where v_w is the partial molar volume of the solvent in the swollen (cross-linked) resin.

Eqn. (34) is associated with another form of the expression for the chemical potential of the solvent in the resin, different from Eqn. (21):

$$\bar{\mu}_w(T, p_0 + \pi) = \bar{\mu}_w^0(T, p_0) + RT \ln \bar{x}_w \bar{\gamma}_w(p_0 + \pi) . \quad (35)$$

The possibility of this approach was first pointed out by Holm [81]. The principal difference between Eqns. (21) and (35) is due to the choice of different ideal reference systems§. In the first case it [the reference system? (Ed. of Translation)] is defined at the same pressure $p_0 + \pi$ as that of the components of the cross-linked resin and in the second case at a constant pressure p_0 (x_w is almost independent of π):

$$\frac{\partial \bar{\mu}_w(T, p_0 + \pi)}{\partial \pi} = RT \frac{\partial \ln \bar{\gamma}_w}{\partial \pi} = v_w , \quad (36)$$

where v_w is the partial molar volume of the solvent in the swollen cross-linked resin. It follows from Eqn. (36) that

$$RT \ln \bar{\gamma}_w(p_0 + \pi) = RT \ln \gamma_w(p_0) + \int_{\pi'}^{\pi} v_w d\pi \quad (37)$$

where $\bar{x}_w$ = const. In the region of not unduly low values [pressures (Ed. of Translation)], we have $\alpha \bar{v}_w$ = const. [82] and then

$$\bar{\gamma}_w(p_0 + \pi) = \bar{\gamma}_w(p_0) e^{\frac{\pi v_w}{RT}} \text{ when } \bar{x}_w = \text{const} . \quad (38)$$

At equilibrium between the cross-linked resin and the pure solvent

$$\bar{\mu}_w^0(p_0) + RT \ln \bar{a}_w(p_0 + \pi) = \mu_w^0(p_0) + RT \ln \bar{\alpha} \quad (39)$$

or

$$\bar{a}_w(p_0 + \pi) = \bar{\alpha} \quad (40)$$

when the standard chemical potentials are assumed to be equal in both phases. An analogous expression is obtained for the non-cross-linked resin:

$$\tilde{a}_w(p_0) = \tilde{\alpha} . \quad (41)$$

At equilibrium with vapour of the same composition

$$\frac{\bar{a}_w(p_0 + \pi)}{\tilde{a}_w(p_0)} = \frac{\bar{x}_w}{\tilde{x}_w} \cdot \frac{\bar{\gamma}_w(p_0 + \pi)}{\tilde{\gamma}_w(p_0)} = 1 . \quad (42)$$

‡Condition (31), based on osmotic theory, constitutes essentially the mathematical statement of the postulate indicated above.

§An ideal reference system is a system whose chemical potential satisfies the equation $\mu_i = \mu_i^0 + RT \ln x_i$.

Then using Eqn. (38) we obtain

$$\frac{\bar{x}_w}{\tilde{x}_w} \cdot \frac{\bar{\gamma}_w(p_0 + \pi, \bar{x}_w)}{\tilde{\gamma}_w(p_0, \tilde{x}_w)} = \frac{\bar{x}_w}{\tilde{x}_w} \cdot \frac{\tilde{\gamma}_w(p_0, \bar{x}_w)}{\tilde{\gamma}_w(p_0, \tilde{x}_w)} \cdot e^{-\frac{\pi v_w}{RT}} . \quad (43)$$

The moisture contents to which the activity coefficients correspond are indicated in Eqn. (43). We may note that in the derivation of Eqn. (43), as in Eqn. (30), the fundamental condition of the osmotic theory was employed, i.e.

$$\bar{\gamma}_w(p_0, \bar{x}_w) = \tilde{\gamma}_w(p_0, \bar{x}_w) .$$

Eqn. (43) can also be written as follows [see Eqns. (40) and (41)]:

$$\frac{\bar{a}_w(\bar{x}_w)}{\tilde{a}_w(\bar{x}_w)} = \frac{\bar{\alpha}(\bar{x}_w)}{\tilde{\alpha}(\bar{x}_w)} \cdot e^{-\frac{\pi v_w}{RT}} , \quad (44)$$

which is identical with Eqn. (34).

Comparison of Eqns. (33) and (34) shows that the osmotic pressure depends on the method of calculation, while the chemical potential does not. Compensation is achieved by means of different activity coefficients.

To determine the osmotic pressure in the resin phase, use is also made of the distribution of non-electrolytes between the solvent and the resin (the method of Ginzburg and Cohen). [83] Using Eqn. (25) for a solvent and a non-electrolyte, we obtain

$$\pi(v_w^0 - v_e^0) = RT \ln \frac{\bar{m}_e}{m_e} \frac{\bar{f}_e}{f_e} \cdot \frac{f_w}{\bar{f}_w} = RT \ln \left[K_e \frac{\bar{f}_e f_w}{f_e \bar{f}_w} \right] , \quad (45)$$

where K_e is the partition coefficient¶, $\bar{m}_e$ and m_e are the molalities of the non-electrolyte in the resin and in the external solution, and $\bar{f}_e$, f_e, $\bar{f}_w$, and f_w are the activity coefficients of the non-electrolyte and the solvent in the resin and in the solution respectively. It was found that, for a number of non-electrolytes (sucrose, glucose, arabinose, mannitol, raffinose, glycerol, and ethylene glycol), $\ln K_e$ is directly proportional to $v_w^0 - v_e^0$. The slope of the plot of $RT \ln K_e$ against $v_w^0 - v_e^0$ yields the osmotic pressure when the ratio $\bar{f}_e f_w / f_e \bar{f}_w$ varies insignificantly with $v_w^0 - v_e^0$. The osmotic pressures obtained in this way are fairly consistent with the values given by Eqn. (33), but they do exceed them by a factor of 2–3. This method must be regarded as an independent procedure for the determination of π, since it does not involve the postulates of the osmotic theory.

The qualitative description of the form of the solvent absorption isotherm shows that osmotic pressure increases with the content of the cross-linking agent in the range of relatively high values of α. The reversal of solvent absorption isotherms at low values of α is explained by the supporters of the osmotic theory as an effect of negative osmotic pressure, since it is believed that in this case π is zero in the reference ion-exchange resin (resins containing 0.5–2% of the cross-linking agent are usually chosen as a reference [62,64]).

The linear variation of the osmotic pressure with the equivalent volume of the resin V_e is also of interest [64]. Such relations have been found for Dowex-50 cation-exchange resins saturated with alkali metal ions and also for Dowex-1 anion-exchange resins saturated with halide ions [64]. In the exchange of tetraethylammonium and sodium ions on Dowex-50 × 8 Boyd and Schwarz [117] also observed a linear relation of the type

$$\pi = a \Delta V_e + b \quad (46)$$

¶The partition coefficient was found from the retention volumes of the non-electrolytes in a column experiment.

with the constants $a = 1.05$ cm^3 mole^{-1} atm^{-1} and $b = -239$ cm^3 mole^{-1}. It is nowadays believed[64] that relations of type (46) indicate that the resin may be regarded as a solid elastic body or as an elastomer. Putting Eqn. (46) in the form

$$\pi = k(V_e - V_e^0) = B\frac{\Delta V_e}{V_e^0}, \quad (47)$$

where V_e^0 is the value of V_e at $\alpha = 0$ and B is a constant which has the dimensions of the modulus of elasticity, it is possible to calculate from B an effective Young's modulus for resins. The values of Young's modulus for Dowex-50×8 and Dowex-1×6 resins are both 2.2×10^8 dyn cm^{-2}, which is higher by almost a power of ten than the values of Young's modulus for elastic polymers (in particular rubbers). We believe that another explanation of Eqn. (46) is also possible, not involving the characteristics of the elastic deformation of the polyelectrolyte network but associated with the characteristics of resin hydration in the region where $\alpha \to 1$ [at low moisture contents a and b in Eqn. (46) begin to vary with moisture content]. In this region of α values the slope of the solvent absorption isotherms and in particular the derivative $\partial n_w/\partial \ln \alpha$ varies relatively little with moisture content (a) and with the ionic form of the resin (b). Therefore, for each resin, it is possible to find a range of α values ($\alpha^* < \alpha < 1$) in which the following approximation is valid:

$$\Delta \bar{V}_e = \int_0^{\bar{n}_w} \bar{v}_w\, dn_w = \int_{-\infty}^{\ln \bar{\alpha}} \bar{v}_w \frac{\partial \bar{n}_w}{\partial \ln \bar{\alpha}} d\ln \alpha = \Delta v_e + \int_{\ln \bar{\alpha}^*}^{\ln \bar{\alpha}} \bar{v}_w \frac{\partial \bar{n}_w}{\partial \ln \bar{\alpha}} d\ln \alpha \simeq$$

$$\simeq \Delta v_e^0 + \overline{\bar{v}_w \frac{\partial \bar{n}_w}{\partial \ln \bar{\alpha}}} \cdot \ln \frac{\bar{\alpha}}{\bar{\alpha}^*} = \simeq v_e^0 + \beta \frac{v_w \pi}{RT} + \beta \ln \frac{\bar{\alpha}}{\bar{\alpha}^*} \simeq C + \gamma \pi, \quad (48)$$

where $\beta = v_w \dfrac{\partial \bar{n}_w}{\partial \ln \bar{\alpha}}$, γ, and C are constants, and Δv_e is the value of ΔV_e corresponding to the value of α at which the condition $\beta \simeq$ const. begins to hold.

If in the range of relative moisture contents considered $\partial \bar{n}_w/\partial \ln \bar{\alpha}$ and $\bar{v}_w$ are relatively constant, then Eqn. (48) is equivalent to Eqn. (47). The following comments may be made on these conditions: (a) the steepness of the isotherms for the absorption of solvents by resins saturated by univalent ions is the same for many resins in the vicinity of $\alpha = 1$;[68] the steepness of the solvent absorption isotherms changes on transition to polyvalent ions and also to organic ions[68,122,123]; thus it has been shown[73] that equations of type (46) for the Ba^{2+}- and H^+-forms of KU-2 resin have different constants a and b; (b) since the partial molar volume of the solvent in resins near $\alpha = 1$ changes relatively little with the moisture content of the resins[124], $\bar{v}_w \dfrac{\partial \bar{n}_w}{\partial \ln \bar{\alpha}}$ may indeed be regarded as constant in this region.

The significance of the concept of osmotic pressure in the resin is very important in the osmotic theory. According to one view this is a real pressure in the resin[64,85]. Subsequently it has been stated that the pressure π is merely a measure of all those changes in the system which are introduced by cross-linking[84]. Attempts have been made to associate π with capillary pressure[76]. In this case the strain in the polymeric skeleton of the sorbent is regarded as a response to capillary pressure, arising in consequence of the curvature of the outer surface of the resin grains.

In all cases the pressure π arises from the use of the relation between the chemical potential and the external pressure. The identity of the measure of the network effect with a real hydrostatic pressure is thereby asserted. So far there has been no experimental proof of the existence of an excess pressure in the resin compared with the solution. The method of Ginzburg and Cohen also does not provide a proof of the existence of the osmotic pressure, since the latter is used in the calculation. The application of the osmotic theory to isotherms for the absorption of solvents by resins with different degrees of cross-linking does not lead to an understanding of the essential feature of the swelling process. This is because a relation between the pressure π and the hydration mechanism has not been established. Somewhat greater advances have been made in the analysis of relations between the differential and integral free energies and α, the type of counterions, and the degree of cross-linking of the resins. When α (or $\bar{n}_w$) increases from zero, the integral free energies of swelling increase sharply but remain negative. The greatest changes occur in the absorption of the first solvent molecules, after which the free energies of swelling vary relatively little. However, it is precisely in this region that the resin absorbs the greatest amount of solvent. (This applies to an equal degree to integral and differential thermodynamic functions of swelling.) At high values of α, H_{sw} and S_{sw} for certain resins have a weak maximum, i.e. the changes in them with increasing α in the vicinity of $\alpha = 1$ are positive. The variation of the thermodynamic functions of swelling H_{sw} and S_{sw} with increase of α or $\bar{n}_w$ is explained at the present time mainly in the same way as the concentration dependence of the heats and entropies of hydration of crystalline salts[86].

The principal energy effects are the hydration of the fixed functional groups in the matrix and the counterions ($H_h < 0$ and $S_h < 0$) and also the dissociation of the fixed group–counterion pair ($H_d > 0$, $S_d > 0$). Since the overall values of H_{sw} and S_{sw} are negative, it is reasonable to suppose that the hydration effect exceeds the dissociation effect. The influence of the second effect prevails when α is close to unity in those cases where

$$\frac{\partial H_{sw}}{\partial \alpha} > 0 \text{ and } \frac{\partial S_{sw}}{\partial \alpha} > 0.$$

It should be borne in mind that in the swelling of resins the thermodynamic functions H_h, S_h, H_d, and S_d refer to interionic interactions only when the thermodynamic characteristics of the hydration and dissociation of the non-ionogenic parts of the polymer (Φ_{hm}, H_{hm}, S_{hm}, Φ_{dm}, H_{dm}, S_{dm}) are treated independently. It was shown above that interchain interaction may be considerable even in somewhat swollen resins (the reversal of isopiestic lines). In dry resins this interaction is probably even more pronounced and can lead to an ordered arrangement of the polyelectrolyte chains. This is indicated in particular by electron microscope photographs of dehydrated resins obtained by Kargin et al.[87] and also the data of Laskorin et al.[17]

It is of great interest to establish a relation between the thermodynamic functions of swelling and the degree of order in the arrangement of chains in dry resins.

In the description of the dependence of Φ_{sw}, H_{sw}, and S_{sw} on α, it is usual also to indicate two further factors determined by the high molecular weight of the resin—the increase in the strain of the matrix on swelling and the mixing of the polymer chains with the solvent. The experimental methods for the determination of these effects are lacking; they can be estimated qualitatively with the aid of the theory of the swelling of cross-linked polyelectrolytes of Rice and Harris[88]. When the dehydrated cross-linked polyelectrolytes and the pure solvent are chosen as

the standard states, both contributions are negative. Calculations show that the contributions of these components (of the conformational entropy and enthalpy of swelling H_{SW} and S_{SW}) are indeed low [89]. For example, in the swelling of Dowex-50 cation-exchange resin in the K^+-form (from the dry resin to the resin with the maximum degree of swelling) the conformational free energy is −0.43 and −0.81 kcal equiv.$^{-1}$ for divinylbenzene contents of 3 and 15% respectively, which amounts to 10 and 20% of the integral free energy of swelling. Thus the integral free energy of swelling Φ_{SW} is affected by at least five factors.

$$\Phi_{sw} = \Phi_h + \Phi_d + \Phi_{con} + \Phi_{hm} + \Phi_{dm} \qquad (49)$$

However, at present it is possible to determine experimentally only Φ_{SW}, so that the contributions of each separate effect remain unknown†. This is one of the main obstacles to the development of a theory of swelling of cross-linked polyelectrolytes, since it makes it impossible to obtain quantities necessary to simulate the individual effects and to test them. Further accumulation of experimental data in this field is necessary.

Ion-exchange resins have come to be regarded as electrolytes with a high concentration of ions set up by their fixation on the matrix. It is interesting to note some similarity and also a difference in the thermodynamic functions of the hydration of resins and crystalline salts (using heat as an example): 1. H_{SW} changes sharply on sorption of the first solvent molecules and then the variation is slight. The heat of solution in water of a crystalline salt varies relatively little with dilution in the region close to the saturated solution. On the other hand the heats of solution of salts in organic solvents are much more exothermic and their variation with concentration is also more pronounced. Possibly the effect of the organic resin matrix is identical with the effect of the organic solvent. 2. The relation between the enthalpies and entropies of hydration of salts is close to linearity [90]. Fig. 3 shows that there is also a linear relation between H_{SW} and S_{SW} for resins in water. Points corresponding to a given degree of cross-linking of the resins in different ionic forms and also points corresponding to resins with different contents of the cross-linking agent but in the same ionic form are plotted on this curve. We may note that the thermodynamic functions of the swelling of Dowex-50 resins depends little on the degree of cross-linking while those for macronetwork resins depend on cross-linking to a much greater extent. With increase in the degree of cross-linking of macronetwork resins and Dowex-50 resins, the absolute values of H_{SW} and S_{SW} increase. The thermodynamic functions H_{SW} and S_{SW} for non-cross-linked polymethylstyrenesulphonic acid and its sodium salt exceed the corresponding thermodynamic functions for cross-linked resins (up to 15% of divinylbenzene). Nevertheless these values are consistent with the relations presented in Fig. 3. The existence of relations of a similar form between the enthalpies and entropies of swelling of resins and of the hydration of crystalline salts shows that there is a profound analogy between these processes. As far as we are aware, these relations have not been explained.

†Analogous problems occur in the theory of electrolyte solutions at moderate and high concentrations where the concentration variation of the heats and entropies of hydration is also determined by a number of separate factors [86].

The mechanism of the absorption of water vapour by ion-exchange sorbents has also been investigated by analysing the differential free energies, enthalpies, and entropies of swelling. The differential thermodynamic functions of swelling have been used most successfully for the analysis of the mechanism of the interaction with the solvent, particularly in the region of low values of α.

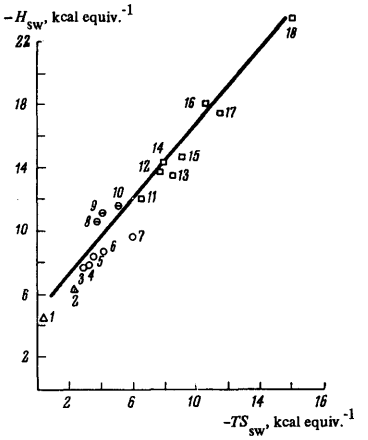


Figure 3. Relation between the enthalpies and entropies of swelling of resins in water: 1) Dowex-50 × 3, K^+; 2) Dowex-50 × 15, K^+; 3) Dowex-50 × 1, Na^+; 4) Dowex-50 × 3, Na^+; 5) Dowex-50 × 8, Na^+; 6) Dowex-50 × 15, Na^+; 7) KU-2, Na^+; 8) Dowex-50 × 0.5, H^+; 9) Dowex-50 × 3, H^+; 10) Dowex-50 × 8, H^+; 12) KU-2, H^+. Macronetwork resins with different amounts of cross-linking agent: 11) decamethylenedimethacrylamide (DMDMA), 16%, H^+; 13) DMDMA, 16%, Na^+; 14) hexamethylenedimethacrylamide (HMDMA), 9%, Na^+; 15) ethylenedimethacrylamide (EDMA), 16%, H^+; 16) HMDMA, 16%, Na^+; 17) EDMA, 16%, Na^+; 18) HMDMA, 41%, Na^+.

The work of Gluekauf and Kitt [91] largely initiated these investigations. The hydration of ion-exchange resins is regarded as a stepwise adsorption process. Analysis of the thermodynamic functions of the sorption of water shows that the first water molecule is sorbed exclusively by an SO_3^- group fixed on the matrix. Such a mechanism of the absorption of water has been attributed to all the salt-forms of sulphonated resins. The scatter of the differential thermodynamic functions of different salt-forms is probably due to different interactions between the non-hydrated cations and the hydrated groups. It has also been shown that the second and subsequent hydration shells are formed as a result of the hydration of the cation.

The enthalpy and entropy components for the sorption of the first, second, and subsequent solvent molecules per functional group of the resin have been calculated from the temperature variation of the water vapour absorption isotherms. Analysis of the heats and entropies of solvent absorption led to the following conclusions. If there is one molecule per active group, then its interaction with the counterion and also the interaction of the counterion with the water molecule is not a linear function of the ionic radius alone, i.e. is not purely Coulombic. For large ions

such as Ag^+ and Cs^+, these interactions may depend in addition on factors such as polarisation. The addition of a second water molecule probably loosens somewhat the structure of the sorption complex and weakens the polarisation interactions occurring over short distances. Beyond this point Coulombic interaction becomes typical for the entire series of alkali metal ions. Later these methods were criticised both from the standpoint of the validity of the thermodynamic description of the hydration of resins and from the standpoint of the reliability of the experimental data[89,92]. The inflections in the plots of the thermodynamic functions obtained from the temperature variation of the isotherms were not confirmed by calorimetric measurements on similar resins[89,92-94]. We may note that for all the ionic forms investigated by Gluekauf and Kitt[91] the error in the determination of the differential thermodynamic functions is approximately the same and yet the curves for different ionic forms differ significantly. The H^+-, Ba^+-, and Ca^{2+}-forms of the resins do not show inflections, while for the Li^+-, Ag^+-, Na^+-, K^+-, NH_4^+-, and Cs^+-forms the inflections in the thermodynamic functions are fairly pronounced. Recently the inflections in the differential thermodynamic functions for certain types of sorbents have been observed also by calorimetric methods[95,97]. Nevertheless, final conclusions concerning the presence or absence of inflections in the differential thermodynamic functions of swelling would be premature, since in all the studies of which we are aware no estimate was made of the reliability of these functions when inflections are present.

The mechanism of the hydration of ion exchangers has been vigorously investigated also by a wide variety of physical methods. The study of the infrared spectra of thin films (up to 5 μm) of sulphonated polystyrene led to the conclusion[29,30] that the hydration of the salt-forms of sulphonated resins begins with the interaction of water with the counterion. On combining with a first water molecule, the cation becomes somewhat removed from the fixed group in the sorbent. The subsequent hydration shells are formed both between the counterion and the fixed group and in the space surrounding both ions. These findings are based mainly on the study of the stretching and deformation vibrations of sorbed water molecules. However, direct investigation of the frequencies of interionic vibrations[96] in films of polyvinylsulphonic [polyethylenesulphonic ? (Ed. of Translation)] acid and its salts shows that, on absorption of the first solvent molecule, the distance between ions changes relatively little. The interionic distance increases but this change is insufficient for the incorporation of water molecules between the ions. It was also shown that the water of hydration does not participate in ionic vibrations, i.e. there is no rigid binding of water molecules. On this basis, it was concluded that ion pairs and not individual ions are hydrated in ion-exchange films. Thus there exist different explanations of the mechanism of primary hydration. The reason for this remains obscure. With decrease in crystallographic ionic radius (from Rb^+ to Li^+ and from Ba^{2+} to Mg^{2+}), the interaction of ions with water molecules intensifies. The splitting of asymmetric stretching vibrations of the SO_3^- group and in particular the independence of this splitting of moisture content for all counterions shows that in all cases the counterion is located asymmetrically in the pyramidal structure of the sulphonato-group, namely in the vicinity of one of the oxygen atoms. The following counterions have been examined[29,30]: H^+, Li^+, Na^+, K^+, Rb^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, NH_4^+, $(CH_3)_4N^+$ and $(C_2H_5)_4N^+$. In the hydration of the hydrogen-forms of sulphonated resin films aggregates of several hydrogen-bonded water molecules having the general formula $H_{4n+3}O_{2n+1}$ (n is independent of the relative moisture content) are formed. For all moisture contents, hydronium ions are also distributed asymmetrically in relation to the sulphonato-group, the proton being capable of migrating readily from one water molecule in the aggregate to another. Judging from the differential thermodynamic functions, the mechanism of the primary hydration of carboxylic acid cation exchangers[98] in the H^+-form is similar to the mechanism of the hydration of the salt-forms of sulphonated resins discussed above[96]. After the formation of the primary hydration shell, polymolecular condensation of water takes place. On the other hand, the mechanism of the hydration of the salt-forms of carboxylic acid cation exchangers is probably similar to the mechanism of the hydration of the salt-forms of sulphonated cation-exchange resins proposed by Gluekauf and Kitt[91].

The NMR method has been used to characterise moisture absorption by hydrogen-forms of Dowex-50 resin with different degrees of cross-linking[33,35-39]. Quantitative information about the state of water in resins has been obtained from chemical shifts and changes in signal width. A decrease in the moisture content of resins leads to an increase of signal width and its maximum is displaced towards lower field strengths. This shift is different for resins with different amounts of the cross-linking agent. The chemical shift depends also on the presence of hydrogen bonds in the sorbed water. Therefore at a low moisture content, when the normal structure of water breaks down due to the vigorous interaction of water molecules with the polar groups of the solvent, the resonance band is displaced towards lower field strengths as in ordinary water on increase of temperature. The chemical shift towards higher magnetic field strengths is proportional to the number of benzene rings and to the increase of the distance between the sulphonato-group and the molecules of water of hydration. The width of the resonance absorption band for sorbed water is much higher than for pure water (20–100 Hz compared with 0.5 Hz) but is less than for ice. This means that water molecules in the resin phase are in a state of rapid albeit restricted motion. The increase in absorption band width has been attributed to the inhomogeneity of the magnetic field of the resin grains. At low moisture contents not all the active groups of the resin can be hydrated to an equal extent and therefore different chemical shifts are possible. Then the observed resonance band will consist of bands corresponding to several different states of the water molecules, which is the reason for its broadening. Together with the absorption band due to sorbed water, an absorption band due to the water between the grains is also observed. The disappearance of this second band on reducing the moisture content of resins and the reversible sharpening and smoothing out of the bands on lowering and raising the temperature respectively show that there is exchange between the protons of the water in the resin and outside. The kinetics of this exchange have been investigated using heavy water and the results have been interpreted by the method of Boyd and Soldano[99]. The diffusion coefficient proved to be of the order of 800×10^{-6} cm^2 s^{-1}. The NMR method enables the heterogeneity of resins to be quantitatively characterised. The presence of a single narrow absorption band due to internal water indicates a high degree of homogeneity of the materials employed. This homogeneity must be regarded as indicating a constant time-average environment of the molecules of sorbed water. Since one cannot exclude the possibility of the presence in resin

grains of density gradients of the cross-linking agent or concentration gradients of the active groups, this result may be evidence of rapid exchange between water molecules in different states. The exchange within grains is considered, since it has been shown by the same method that the exchange of water molecules between grains is much slower.

Thus the narrow resonance absorption line may be due to kinetic causes (migration of water molecules and structural features of the resins such as a constant density of the cross-linking agent and of the concentration of active groups throughout the bulk of the grain. By studying the temperature variation of the half-width of the resonance band, it is possible to distinguish both components in individual cases, since the first of these depends on the change in temperature and the second does not.

III. FREE ENERGY OF ION EXCHANGE

There have been many studies where the ion-exchange equilibria between inorganic and also between organic and inorganic ions were investigated [100–105]. The nature of the ion has a significant effect on the selectivity of its absorption: factors which are dominant in the first case may be secondary in the second. These studies, in particular by Boyd and coworkers [101,102], confirm the qualitative hypotheses concerning the principal effects which determine the thermodynamic selectivity (electrostatic interaction, different structure of the hydration shells of ions in the resin compared with the solution, effect of solvent structure on the interaction between ions, effect of resin matrix, etc.). Among these qualitative concepts, mention should be made of the theories of Daimond [107], Eisenman [108], and Izmailov [109]. Further development of these concepts requires, however, a knowledge of the thermodynamic functions associated with the different states of the solvent in the resin and in solution. In this connection it is necessary to consider the methods of calculation of the thermodynamic functions associated with the changes in the hydration of resins during ion exchange.

Experimental data show that in ion exchange the state of equilibrium depends on the change in the degree of swelling and hence on the factors which determine the interaction between the resin and the solvent. When the selective absorption of ions is determined by the reduction of the enthalpy of the system, i.e. when the electrostatic interaction with the fixed group increases, their interaction with the solvent is weakened. When Li^+ ions are displaced by other alkali metal ions from Dowex-50 resin, the selectivity increases on going from Na^+ to Cs^+ ($\Delta H^0 < 0$) and the swellability of the resin decreases steadily. Since the affinity of the carboxy-group for the proton is particularly high, the swellability of carboxylic acid cation exchangers in the H^+-form is much lower than that of the salt-forms. The selective sorption of quaternary ammonium ions and a number of other organic cations on Dowex-50 resins is also accompanied by a decrease of the swelling of the resin [62]. In those cases where the decrease of the free energy of ion exchange is due to an entropy increase, the swellability of the resin may decrease to a smaller extent, while in some others it can increase [110]. In the early theory of ion exchange (Gregor [80], Gluekauf [111]) it was assumed that the change in the degree of swelling of the resin in ion exchange determines entirely its specificity. The effect of swelling on selectivity in this theory is taken into account quantitatively in two ways: in terms of the osmotic work $\pi\Delta v_i$ (π is the swelling pressure and Δv_i the difference between the partial molar volumes of the resinates) and also to some extent in terms of the activity coefficients of the resinates. In the two methods of choosing a reference system in the osmotic theory (see Section II), there is a possibility of two formally different expressions for the thermodynamic ion-exchange equilibrium constant‡. If the reference states in the solution § and in the resin are chosen at different pressures (in solution $p = 1$ atm and in the resin $p = \pi$), the following expression is obtained [81] for K_B^A:

$$RT \ln K_B^A = \int_{p_0}^{p_0} [z_B v_A^0 (p, m_A, m_B) - z_A v_B^0 (p, m_A, m_B)]\, dp, \qquad (50)$$

where

$$K_B^A = \frac{\bar{a}^{z_A}_B}{\bar{a}^{z_B}_A} \frac{a^{z_B}_A}{a^{z_A}_B} = \tilde{K}_B^A \frac{\bar{\gamma}^{z_A}_B}{\bar{\gamma}^{z_B}_A} = \tilde{\tilde{K}}_B^A \frac{\bar{\gamma}^{z_A}_B}{\bar{\gamma}^{z_B}_A} \cdot \frac{\gamma^{z_B}_A}{\gamma^{z_A}_B},$$

$$RT \ln \tilde{\tilde{K}}_B^A = RT \ln \frac{\gamma^{z_A}_B}{\gamma^{z_B}_A} - RT \ln \frac{\bar{\gamma}^{z_A}_B}{\bar{\gamma}^{z_B}_A} (\pi, m_A, m_B) + \int_{p_0}^{p_0+\pi} (z_B v_A^0 - z_A v_B^0)\, dp \simeq$$

$$\simeq RT \ln \frac{\gamma^{z_A}_B}{\gamma^{z_B}_A} - RT \ln \frac{\bar{\gamma}^{z_A}_B}{\bar{\gamma}^{z_B}_A} (\pi, m_A, m_B) + \pi [z_B v_A^0 - z_A v_B^0]. \qquad (51)$$

Here v_B^0 and v_A^0 are the partial molar volumes of the resinates in the standard state. In this equation the swellability of the resin influences two terms—the last and the penultimate. The term $RT \ln (\bar{\gamma}^{z_A}_B / \bar{\gamma}^{z_B}_A)$ takes into account also the interaction of the ions with the resin and with one another. On the other hand, when all the reference states are chosen at the same pressure, for example, atmospheric, then the following expression is obtained for K_B^A (the standard states of all the components are the same ¶):

$$\ln K_B^A = 0,$$

$$RT \ln \tilde{\tilde{K}}_B^A = RT \ln \frac{\gamma^{z_A}_B}{\gamma^{z_B}_A} - RT \ln \frac{\bar{\gamma}^{z_A}_B}{\bar{\gamma}^{z_B}_A} (p_0, m_A, m_B) + \int_{p_0}^{p_0+\pi} (z_B v_A - z_A v_B)\, dp \simeq$$

$$\simeq RT \ln \frac{\gamma^{z_A}_B}{\gamma^{z_B}_A} - RT \ln \frac{\bar{\gamma}^{z_A}_B}{\bar{\gamma}^{z_B}_A} (p_0, m_A, m_B) + \pi [z_B v_A - z_A v_B]. \qquad (52)$$

In Eqn. (52) the activity coefficients in the resin phase are independent of pressure and consequently of the swelling of the given cross-linked resin. The effect of swellability on selectivity is associated with the last term on the right-hand side. However, this term also takes partially into account the deviation of the system from ideality. Thus in none of the cases is it possible to distinguish the component which depends entirely on the change in swellability during ion exchange†. The quantities v_B^0 and v_A^0 in Eqn. (51) correspond to the partial molar volumes of the hydrated resinates at infinite dilution and can be estimated approximately from the corresponding values for the low-molecular electrolytes which are suitable models for

‡Holm [81] showed that both equations can be obtained from a more general equation with a different choice of reference states.

§The reference state in solution corresponds to infinite dilution.

¶For a more general case, see Holm [81].

†As pointed out correctly by Holm [81], for the same reason the osmotic free energy and the energy of interionic interaction introduced by Boyd [82] are not independent.

resins. In order to find the osmotic work from Eqns. (51) and (52), it is necessary to employ isopiestic measurements (which determine πv_W) and also pyknometric measurements (which determine v_W and Δv_i). When Eqn. (52) is used, it is possible to indicate a simpler method for the determination of osmotic work, involving isopiestic data only. For many resins, there is a relation (in some cases linear) between the swelling pressure π and the equivalent resin volume V_e:[64]

$$\pi = F(V_e) \quad . \tag{53}$$

According to the definition of the equivalent volume,

$$z_A z_B dV_e = (z_B v_A - z_A v_B)\, d\theta_A + z_A z_B v_W dn_W \,, \tag{54}$$

where v_A, v_B, and v_W are the partial molar volumes of the resinates A and B and the solvent and θ_A is the equivalent fraction of the ions A in the sorbed state. Hence it can be shown [112] that

$$\pi(z_B v_A - z_A v_B) = z_A z_B \int_0^{\bar{n}_W} \frac{\partial w_W}{\partial \theta_A} dn_W \quad . \tag{55}$$

The integral on the right-hand side of the equation can be calculated provided that the absorption isotherms for the vapour of the given and reference resin are known for several ionic compositions.

In the osmotic theory there are several methods for the calculation of the activity coefficients of the resinates (and also their ratios) from the solvent absorption isotherms. A large group of studies (Gluekauf, Gregor, Soldano, and others) deals with the determination of the dependence of the osmotic coefficient of the solvent in the resin on the molality of the counterions, the calculation by the Gibbs–Duhem equation of the activity coefficients of the mono-ionic forms, and their combination of determine the activity coefficients of ions in resins having a mixed composition [100,111,113,115]. Soldano showed [114] that the Harned rule does not apply to the resin phase and an empirical relation with the molality in the resin has been proposed for the interaction coefficients, on the basis of which it proved possible to obtain satisfactory agreement between the calculated and experimental $\overset{\approx}{K}{}^{A}_{B}$ in the exchange of a series of univalent and divalent ions. Boyd's method [82] is more rigorous from the thermodynamic standpoint. For subsequent discussion, it is convenient to consider the derivation of Boyd's equation by a method somewhat different from that employed in the original paper [112].

If the resin is regarded as a three-component system (two counterions and the solvent), the McKay relation becomes

$$\left.\frac{\partial \ln \bar{a}_B}{\partial \bar{n}_W}\right|_{\bar{n}_A, \bar{n}_B} = \left.\frac{\partial \ln \bar{a}_W}{\partial \bar{n}_B}\right|_{\bar{n}_A, \bar{n}_W}, \tag{56}$$

$$\left.\frac{\partial \ln \bar{a}_A}{\partial \bar{n}_W}\right|_{\bar{n}_A, \bar{n}_B} = \left.\frac{\partial \ln \bar{a}_W}{\partial \bar{n}_A}\right|_{\bar{n}_B, \bar{n}_W}. \tag{57}$$

Eqns. (56) and (57) are now multiplied by z_A and z_B respectively. On subtracting Eqn. (57) from Eqn. (56) and remembering‡ that

$$\frac{\bar{a}_B}{\bar{a}_A} = \frac{\bar{m}_B \bar{\gamma}_B}{\bar{m}_A \bar{\gamma}_A} = \frac{\bar{x}_B \bar{\gamma}_B}{\bar{x}_A \bar{\gamma}_A}, \tag{58}$$

where $\bar{m}_B$ and $\bar{m}_A$ are the molalities of the counterions, $\bar{\gamma}_B$ and $\bar{\gamma}_A$ the molal activity coefficients, and $\bar{x}_B$ and $\bar{x}_A$ the equivalent fractions, we obtain the following equation:

$$\left.\frac{\partial \ln \dfrac{\bar{\gamma}^{z_A}_B}{\bar{\gamma}^{z_B}_A}}{\partial \bar{n}_W}\right|_{\bar{n}_A, \bar{n}_B} = z_A \left(\frac{\partial \ln \bar{a}_W}{\partial n_B}\right)_{\bar{n}_A, \bar{n}_W} - z_B \left(\frac{\partial \ln \bar{a}_W}{\partial \bar{n}_A}\right)_{\bar{n}_B, \bar{n}_W} . \tag{59}$$

We shall now convert the independent variables $\bar{n}_B$, $\bar{n}_A$, $\bar{n}_W$ to the variables $\bar{\theta}_B$, $\bar{\theta}_W$, and n, where

$$\bar{\theta}_B = \frac{\bar{n}_B z_B}{\bar{n}_A z_A + \bar{n}_B z_B} = \frac{\bar{n}_B z_B}{n} = \text{equivalent fraction of the ion B in the resin} \tag{60}$$

and

$$\bar{\theta}_W = \frac{\bar{n}_W}{\bar{n}_A z_A + \bar{n}_B z_B} = \frac{\bar{n}_W}{n} = \text{equivalent content of the solvent} \quad (\bar{n} = \bar{n}_A z_A + \bar{n}_B z_B). \tag{61}$$

It can be shown [125] that

$$z_A \left(\frac{\partial \ln \bar{a}_W}{\partial \bar{n}_B}\right)_{\bar{n}_A, \bar{n}_W} - z_B \left(\frac{\partial \ln \bar{a}_W}{\partial \bar{n}_A}\right)_{\bar{n}_B \bar{n}_W} = \frac{z_A z_B}{n} \left(\frac{\partial \ln \bar{a}_W}{\partial \theta_B}\right)_{\bar{\theta}_W, \bar{n}} . \tag{62}$$

Then we obtain from Eqn. (59), taking into account Eqn. (62),

$$\left.\frac{\partial \ln (\bar{\gamma}^{z_A}_B / \bar{\gamma}^{z_B}_A)}{\partial \theta_W}\right|_{\theta_B n} = z_A z_B \left(\frac{\partial \ln \bar{a}_W}{\partial \theta_B}\right)_{\theta_B n} . \tag{63}$$

We shall now consider Eqn. (63) under the condition n = const., i.e. when the exchange capacity is constant [taking into account Eqn. (40)]:

$$\ln \frac{\bar{\gamma}^{z_A}_B}{\bar{\gamma}^{z_B}_A} = \ln \frac{\bar{\gamma}^{z_A}_B}{\bar{\gamma}^{z_B}_A}(\text{отсч}) + z_A z_B \int_{\theta_{W(\text{ref.})}}^{\bar{\theta}_W} \frac{\partial \ln \alpha}{\partial \theta_B} d\theta_W \,, \tag{64}$$

where $\theta_{W(\text{ref})}$ is the equivalent content of the solvent in the reference state of the resin (for example in the resin swollen to the maximum extent). The integral on the right-hand side of Eqn. (64) is equal to the integral J_R in Boyd's paper [82]§ to within a numerical multiplier:

$$\int_{\theta_{W(\text{ref.})}}^{\bar{\theta}_n} \frac{\partial \ln \bar{a}_W}{\partial \bar{\theta}_B} d\theta_W = \frac{\partial}{\partial \bar{\theta}_B} \left[\int_{\bar{\theta}_{W(\text{ref.})}}^{\bar{\theta}_W} \ln \bar{a}_W d\theta_W \right]_{\bar{\theta}_W, \bar{\theta}_{W(\text{ref.})}} = - \int_0^{\ln \bar{a}_W} \frac{\partial \bar{\theta}_W}{\partial \bar{\theta}_B} d \ln a_W =$$

$$= 55.51 \int_0^{\ln \bar{a}_W} \frac{\partial \frac{1}{m}}{\partial \bar{\theta}_A} d \ln a_W = 55.51\, J_R . \tag{65}$$

The integral J_R [or the integral in Eqn. (64)] is calculated from isopiestic data for several ionic compositions of the resin. In Eqn. (52) the apparent ion-exchange equilibrium constant $\overset{\approx}{K}{}^{A}_{B}$ at $\pi = 0$ depends on the ratio of the activity coefficients of the cross-linked resin [$\ln (\bar{\gamma}^{z_A}_B / \bar{\gamma}^{z_B}_A)(p_0 m_A m_B)$]. If it is assumed, as in the osmotic theory, that they can be equated to the activity coefficient of the non-cross-linked resin having the same ionic composition, i.e:

$$\ln \frac{\bar{\gamma}^{z_A}_B}{\bar{\gamma}^{z_B}_A}(p_0, m_A, m_B) = \ln \frac{\tilde{\gamma}^{z_A}_B}{\tilde{\gamma}^{z_B}_A}(p_0, m_A, m_B) , \tag{66}$$

then substitution of Eqns. (64) and (66) in Eqn. (52) yields

‡In Boyd's theory the molal concentration scale is employed.

§In Boyd's paper [82] there is a misprint: the sign on the right-hand side of Eqn. (7e) and of the integrals in the subsequent equations should be reversed. This misprint was eliminated from Boyd's subsequent papers [116,117]. Nevertheless it has found its way into certain monographs on ion exchange (see, for example, Helfferich [100]).

the required relation between $\tilde{\tilde{K}}^{A}_{B}$ and a function of the swellability of the cross-linked resin:

$$RT\ln\tilde{\tilde{K}}^{A}_{B}=RT\ln\frac{\bar{\gamma}^{z_A}_{B}}{\bar{\gamma}^{z_B}_{A}}-RT\ln\frac{\tilde{\gamma}^{z_A}_{B}}{\tilde{\gamma}^{z_B}_{A}}\ (\text{ref.})+z_Az_B\int_{\bar{\theta}_{w(\text{ref.})}}^{\bar{\theta}_w}\left(\frac{\partial\ln\tilde{a}_w}{\partial\bar{\theta}_B}\right)_{\theta_w,\pi}d\theta_w+$$
$$+\pi[z_Bv_A-z_Av_B]. \qquad (67)$$

The effect of the swellability of the cross-linked resin is shown in the quantities π, $\bar{\theta}_w$, v_A, and v_B. The term $RT\ln(\bar{\gamma}^{z_A}_{B}/\bar{\gamma}^{z_B}_{A})$ (ref.) is determined by applying Eqn. (67) to a weakly cross-linked resin, from the absorption isotherm of which the integral $J_R(\bar{\theta}_w=\bar{\theta}_{w(\text{ref})},\ \pi=0)$ is calculated:

$$RT\ln\tilde{\tilde{K}}^{A}_{B}\ (\text{ref.})=RT\ln\frac{\bar{\gamma}^{z_A}_{B}}{\bar{\gamma}^{z_B}_{A}}-RT\ln\frac{\tilde{\gamma}^{z_A}_{B}}{\tilde{\gamma}^{z_B}_{A}}. \qquad (68)$$

The ratio of the activity coefficient in the external solution is the same in Eqns. (67) and (68) if the apparent ion-exchange equilibrium constants $\tilde{\tilde{K}}^{A}_{B}$ and $\tilde{\tilde{K}}^{A}_{B}$ (ref.) are determined for the case where the cross-linked and the weakly cross-linked reference resins are in contact with the same solutions. Substitution of Eqn. (68) in Eqn. (67) gives

$$RT\ln\tilde{\tilde{K}}^{A}_{B}=RT\ln\tilde{\tilde{K}}^{A}_{B}\ (\text{ref.}))+\int_{\bar{\theta}_{w(\text{ref.})}}^{\bar{\theta}_w}\left(\frac{\partial\ln\bar{a}_w}{\partial\bar{\theta}_B}\right)_{\theta_w,\pi}d\theta_w+\pi[z_Bv_A-z_Av_B]. \qquad (69)$$

Eqn. (69) permits the calculation from a combination of isopiestic and pyknometric data [and for systems obeying Eqn. (53) isopiestic data alone] of the ratio of the apparent ion-exchange equilibrium constants for the cross-linked and reference resins: $\tilde{\tilde{K}}^{A}_{B}/\tilde{\tilde{K}}^{A}_{B}$ (ref.). To determine $\tilde{\tilde{K}}^{A}_{B}$ for the cross-linked resin, it is also necessary to determine experimentally $\tilde{\tilde{K}}^{A}_{B}$ (ref.). It is important to note that, when $\tilde{\tilde{K}}^{A}_{B}$ (ref.) and the integral J_R are known for any one reference resin, it is possible to calculate $\tilde{\tilde{K}}^{A}_{B}$ for any resin which obeys condition (66). When Eqn. (51) is used, it is also possible to arrive at Eqn. (69) with the aid of the following relation between the activity coefficients of the components and pressure:

$$RT\frac{\partial\ln\bar{\gamma}_i(\pi)}{\partial p}=v_i-v_i^0\frac{\partial p_r}{\partial p}, \qquad (70)$$

where p_r is the pressure in the system in the reference state. In Eqn. (51) it is assumed that the reference states are chosen at the same pressures as those present in the real system. In ion-exchange resins such a pressure is the osmotic pressure. Combination of the integrals in Eqn. (70) for counterions A and B leads to the following relation:

$$RT\ln\bar{\gamma}^{z_A}_{B}/\bar{\gamma}^{z_B}_{A}(\pi,m_A,m_B)=RT\ln\bar{\gamma}^{z_A}_{B}/\bar{\gamma}^{z_B}_{A}(p_0,m_A,m_B)+$$
$$+\int_{p_0}^{p_0+\pi}(z_Av_B-z_Bv_A)\,dp-\pi(z_Av_B^0-z_Bv_A^0). \qquad (71)$$

When Eqn. (71) is substituted in Eqn. (51), Eqn. (69) is obtained. Therefore the methods for the determination of $\pi\Delta v_i$ and $RT\ln[(\bar{\gamma}^{z_A}_{B}/\bar{\gamma}^{z_B}_{A})(p_0,m_A,m_B)]$ described above have a direct bearing on the analysis of the selectivity of ion exchange from the standpoint of this version of the osmotic theory. Boyd suggested that condition (66) applies to ion-exchange resins of a single type, for example sulphonated polystyrene resins cross-linked with divinylbenzene¶. Comparison of the values of $\tilde{\tilde{K}}^{A}_{B}$ calculated by Eqn. (69) and found experimentally shows that the methods of the osmotic theory give a satisfactory quantitative representation of the variation of the apparent ion-exchange equilibrium constant with the degree of cross-linking of the resin (or its swellability). At present such comparisons have been made both for low values of $\pi\Delta v_i$ together with high contributions of the activity coefficients (exchange of alkali metal ions on Dowex-50 cation exchangers [82], exchange of halide anions on anion exchangers [116]) and for high values of $\pi\Delta v_i$ together with relatively smaller contributions of the activity coefficients (tetramethylammonium–sodium exchange on sulphonated polystyrene resins). It is interesting that in the latter case the theory predicts the reversal of selectivity, which is observed experimentally. In all cases the discrepancy between the theory and experiment increases with the degree of cross-linking of the resin. No attempt has been made to treat this discrepancy quantitatively.

Together with the osmotic theory, other methods have been developed, among which particularly interesting are the formally thermodynamic methods unrelated to any models or assumptions apart from those which follow from the nature of thermodynamic laws. Such are the methods of Bonner and Davidson [118,119] and Gaines and Thomas [120,121]. Despite the fact that the first method does not take the solvent into account while the second does involve an estimate of its contribution, both methods yield virtually identical activity coefficients and ion-exchange equilibrium constants. If can be readily shown that the reason for this lies in the nature of the standard states of the resins (pure monofunctional forms in equilibrium with an infinitely dilute solution or pure solvent). When other standard states are employed, the thermodynamic contribution of the solvent increases. Although the choice of standard chemical potentials is in principal arbitrary, it is nevertheless useful to choose them so that the contribution of each component involved in the method is convenient for experimental estimation. Only then is it possible to compare the changes of the individual effects when the type of ion, the type of resin, etc. are varied, i.e. it is possible to obtain a quantitative relation with models. We believe that the choice of dehydrated monofunctional forms of ion-exchange resins as the standard states satisfies these requirements. We shall examine the calculation of the activity coefficient and ion-exchange equilibrium constant for this choice of standard states. To do this, Eqn. (63) is applied to a cross-linked resin remembering that in this case the activity of the solvent in the resin is assumed equal to its activity in the vapour phase regardless of the content of the cross-linking agent. Integration of Eqn. (63) from the state of the dehydrated resin ($\bar{\theta}_w=0$) to the state of the resin swollen to the maximum extent in the solvent gives

$$\ln\frac{\bar{\gamma}^{z_A}_{B}}{\bar{\gamma}^{z_B}_{A}}=\ln\frac{\bar{\gamma}^{0z_A}_{B}}{\bar{\gamma}^{0z_B}_{A}}+z_Az_B\int_0^{\bar{\theta}_w}\frac{\partial\ln\alpha}{\partial\bar{\theta}_B}d\theta_w\qquad\bar{\theta}_B=\text{const},\ \bar{n}=\text{const}, \qquad (72)$$

where $\bar{\gamma}_B$ and $\bar{\gamma}_A$ are the activities [activity coefficients] of the counterions in the swollen resin with the ionic composition defined by $\bar{\theta}_A$ and $\bar{\theta}_B$ and $\bar{\gamma}^0_B$ and $\bar{\gamma}^0_A$ are the

¶In some cases a resin of a different chemical type may serve as a reference. If such substitution is permissible, the scope of the osmotic theory becomes wider.

activities [activity coefficients] of the counterions in the dehydrated resin of the same ionic composition.

The integral in Eqn. (72) may be transformed using the rule governing the differentiation of a definite integral with respect to a parameter and also Eqn. (9):

$$\ln\frac{\bar{\gamma}_B^{z_A}}{\bar{\gamma}_A^{z_B}} = \ln\frac{\bar{\gamma}_B^{0z_A}}{\bar{\gamma}_A^{0z_B}} + z_A z_B \frac{1}{RT}\frac{\partial\left(\frac{\Phi_{sw(n_w)}}{n}\right)}{\partial\bar{\theta}_B}\bigg|_\alpha - \frac{\partial\bar{\theta}_w}{\partial\bar{\theta}_B}\bigg|_{\bar{a}_w} \cdot \ln\bar{a}_w z_A z_B \,. \quad (73)$$

On substituting Eqn. (73) in the expression

$$-RT\ln\tilde{K}_B^A = -RT\ln K_B^A + RT\ln\frac{\bar{\gamma}_B^{z_A}}{\bar{\gamma}_A^{z_B}} \quad (74)$$

we have the following equation for $\tilde{K}_B^A$:

$$-RT\ln\tilde{K}_B^A = -RT\ln K_B^A + RT\ln\frac{\bar{\gamma}_B^{0z_A}}{\bar{\gamma}_A^{0z_B}} + z_A z_B\Delta\Phi_{sw} - RT z_A z_B\frac{\partial\bar{\theta}_w}{\partial\bar{\theta}_B}\bigg|_\alpha \ln\alpha, \quad (75)$$

where $\Delta\Phi_{sw}$ is the differential free energy of swelling during ion exchange $[\Delta\Phi_{sw} = \partial(\Phi_{sw}/n)/\partial\theta_B|_\alpha]$. The term $(\partial\theta_w/\partial\theta_B)\ln\alpha$ becomes zero when ion-exchange equilibrium in an infinitely dilute solution is considered ($\alpha = 1$). In more concentrated solutions it remains small. This term takes into account the deviation of the state of water in the system from its standard state. $\Delta\Phi_{sw}$ is calculated from isopiestic data for the cross-linked resin at several ionic compositions. It is noteworthy that in Eqn. (75) the term $RT\ln(\bar{\gamma}_B^{0z_A}/\bar{\gamma}_A^{0z_B})$ takes into account the interaction effects in the absence of solvent in the resin, while the term $[\Delta\Phi_{sw} - RT\ln\alpha(\partial\bar{\theta}_w/\partial\bar{\theta}_B)_\alpha] = \Delta\Phi_s$ represents the change in all interactions due to the solvent. In order to find the term $RT\ln(\bar{\gamma}_B^{0z_A}/\bar{\gamma}_A^{0z_B})$, we shall examine the state of the dehydrated resin of mixed ionic composition. This can be regarded as a two-component system, i.e. we have

$$\bar{n}_A\, d\ln\bar{\gamma}_A^0 + \bar{n}_B\, d\ln\bar{\gamma}_B^0 = 0 \,. \quad (76)$$

This equation will be solved simultaneously with the differential of Eqn. (75):

$$d\ln\bar{\gamma}_B^0 = -\frac{\bar{\theta}_A}{z_A}d\ln\tilde{K}_B^A - \frac{z_B\bar{\theta}_A}{RT}d\Delta\Phi_s \,, \quad (77)$$

$$d\ln\bar{\gamma}_A^0 = \frac{\bar{\theta}_B}{z_B}d\ln\tilde{K}_B^A + \frac{z_A\bar{\theta}_B}{RT}d\Delta\Phi_s \,. \quad (78)$$

When the dehydrated monoionic forms of resins are chosen as standard states (here we shall use a symmetrical comparison system [126]), we obtain

$$\lg\bar{\gamma}_B^0 = -\frac{\bar{\theta}_A}{z_A}\ln\tilde{K}_B^A(\theta_A) - \int_1^{\bar{\theta}_B}\frac{\ln\tilde{K}_B^A}{z_A}d\theta_B - \frac{z_B\bar{\theta}_A}{RT}\Delta\Phi_s - \frac{z_B}{RT}\int_1^{\bar{\theta}_B}\Delta\Phi_s\, d\theta_B, \quad (79)$$

$$\lg\bar{\gamma}_A^0 = \frac{\bar{\theta}_B}{z_B}\ln\tilde{K}_B^A(\theta_A) - \int_0^{\bar{\theta}_B}\frac{\ln\tilde{K}_B^A}{z_B}d\theta_B + \frac{z_A\bar{\theta}_B}{RT}\Delta\Phi_s - \frac{z_A}{RT}\int_0^{\bar{\theta}_B}\Delta\Phi_s\, d\theta_B \,. \quad (80)$$

Substitution of Eqns. (79) and (80) in Eqn. (75) yields

$$-\Delta\Phi^0 = RT\ln K_B^A = RT\int_0^1\ln\tilde{K}_B^A\, d\theta_B + z_A z_B\int_0^1\Delta\Phi_s\, d\theta_B \,. \quad (81)$$

At equilibrium in very dilute solutions

$$-\Delta\Phi^{0*} = RT\ln K_B^A = RT\int_0^1\ln\tilde{K}_B^A\, d\theta_B + z_A z_B[\Phi_{sw}(\theta_B=1) - \Phi_{sw}(\theta_B=0)] \,. \quad (82)$$

Thus when dehydrated monoionic forms are chosen as standard states, the contribution of the solvent to selectivity is proportional to the difference between the free energies of swelling of the resins in the pure monoionic forms. Table 4 lists the thermodynamic quantities associated with the exchange of triethylbenzylammonium and sodium ions on KU-1 and Dowex-50 × 2 resins, from which it is evident that, with this method of calculation, the standard free energy of ion exchange becomes more negative. This increase is necessary to compensate the thermodynamically unfavourable effect involving the displacement of the solvent from the resin during ion exchange.

Table 4. Thermodynamic functions of swelling and the exchange of triethylbenzylammonium (TEBA) and Na^+ ions on Dowex-50 and KU-1 resins.

	θ_{TEBA}	Φ_{sw}/n, kcal equiv.$^{-1}$	$\Delta\Phi_{sw}$, kcal equiv.$^{-1}$	$\tilde{\tilde{K}}^{Na}_{TEBA}$	$\ln K^{Na}_{TEBA} = \int_0^1 \ln\tilde{\tilde{K}}^{Na}_{TEBA}\, d\theta_{TEBA}$	$\Delta\Phi^0 = -RT\ln K^{Na}_{TEBA}$, kcal equiv.$^{-1}$	$\Delta\Phi^{0*} = \Delta\Phi^0 + \Phi_{sw}[\theta_{TEBA}=1] - \Phi_{sw}[\theta_{TEBA}=0]$
Dowex-50 × 2	0	4.7	4.0	—	1.7	−1.0	−2.0
	0.14	4.2	2.4	7.4			
	0.23	4.1	1.2	5.8			
	0.48	3.9	0.6	3.6			
	0.95			2.0			
	1.0	3.7	0.3				
KU-1	0	8.7	7.5	—	5.6	−3.4	−7.0
	0.15	7.7	6.0	450			
	0.32	6.8	4.5	230			
	0.40	6.6	2.8	180			
	0.95			20			
	1.0	5.1	2.2	—			

Note. The values of $\tilde{\tilde{K}}^{Na}_{TEBA}$ at $\theta_{TEBA} = 0$ and $\theta_{TEBA} = 1$ were obtained by extrapolation. It was assumed that $\gamma_{TEBA}/\gamma_{Na} = 1$ under the experimental conditions (μ = 0.1 M).

Thus the lowering of the selectivity with respect to ions on reduction of the degree of cross-linking of resins is determined to a large degree by the thermodynamically unfavourable contraction of the resin and the decrease of its solvent content, which are in many cases larger for more readily swelling sorbents. We arrived at similar conclusions in the study of other systems [122,123]. We may note that the use of Eqns. (75), (79), and (80) permits the calculation of $\tilde{\tilde{K}}_B^A$ from isopiestic data for the given resin having several compositions and also from the ion-exchange isotherm for the resin. It is, however, possible to reduce the calculation of $\tilde{\tilde{K}}_B^A$ for a cross-linked resin to a calculation from isopiestic data for another resin of a different type with a different amount of cross-linking agent, since there exists the following expression relating the values of $\Delta\Phi_s$ for resins cross-linked to a different extent [125]:

$$\Delta\Phi_s - \Delta\Phi_s(\text{ref.}) = \int_0^{\theta_w}\frac{\partial(\pi v_w)}{\partial\theta_B}d\theta_w + RT\int_{\theta_w(\text{ref.})}^{\theta_w}\frac{\partial\ln\alpha}{\partial\theta_B}d\theta_w \,. \quad (83)$$

For systems in which $\pi = F(V_e)$ [see Eqn. (53)],

$$\Delta\Phi_s - \Delta\Phi_s(\text{ref.}) \simeq \pi\Delta v_l + RT\int_{\theta_w(\text{ref.})}^{\theta_w}\frac{\partial\ln\alpha}{\partial\theta_B}d\theta_w \,. \quad (84)$$

If it is assumed that the ion-exchange equilibrium constant K_B^A is independent of the degree of cross-linking [Eqn. (52) of the osmotic theory is based on a similar assumption], then, combining different expressions, it is possible to obtain an equation for the determination of $\tilde{\tilde{K}}_B^A$ for the

given resin from $\approx{K}^{A}_{B}$ (ref.) for the reference resin from its isopiestic data at several compositions and the maximum swellability of the given resin at several compositions. Thus, within the framework of the formal thermodynamic method too, it is possible to calculate independently the apparent ion-exchange equilibrium constants.

The structural characteristics of ion-exchange resins are shown in particular in the phenomena of the steric inaccessibility and the screening of sorption centres, while the hydration properties of resins also have a significant influence on their selectivity with respect to different ions. Systematic accumulation of experimental data on the relation between the selectivity and swellability of ion-exchange resins of different structures is necessary for further development of theories in this field.

REFERENCES

1. G. V. Samsonov, "Sorbtsiya i Khromatografiya Antibiotikov" (The Sorption and Chromatography of Antibiotics), Izd. Akad. Nauk SSSR, Moscow, 1960.
2. G. V. Samsonov, L. V. Dmitrenko, and V. S. Yurchenko, Symposium, "Sintez i Svoistva Ionoobmennykh Materialov" (The Synthesis and Properties of Ion-Exchange Materials), Izd. Nauka, 1968, p. 169.
3. R. M. Barrer, L. V. C. Rees, and M. Schamsuzzoha, J. Inorg. Nucl. Chem., 28, 629 (1966).
4. V. S. Yurchenko, G. I. Kil'fin, K. B. Musabekov, V. A. Pasechnik, and G. V. Samsonov, Symposium, "Izbiratel'naya Ionoobmennaya Sorbtsiya Antibiotikov" (Selective Ion-Exchange Sorption of Antibiotics), Trudy Leningrad. Khim.-Farm. Inst., No. 25, 121 (1968).
5. G. V. Samsonov and A. B. Petushina, Symposium, "Vydelenie i Ochistka Antibiotikov" (Isolation and Purification of Antibiotics), Trudy Leningrad. Khim.-Farm. Inst., No. 7, 28 (1959).
6. L. V. Dmitrenko, V. S. Pirogov, and G. V. Samsonov, Symposium, "Termodinamika Ionnogo Obmena" (Thermodynamics of Ion Exchange), Izd. Nauka i Tekhnika, Minsk, 1968, p. 162.
7. G. V. Samsonov, V. V. Vvedeneeva, L. N. Zav'yalova, and T. A. Vikhoreva, Symposium, "Voprosy Fermentatsii i Ochistki Antibiotikov" (Problems of the Fermentation and Purification of Antibiotics), Trudy Leningrad. Khim.-Farm. Inst., No. 15, 93 (1962).
8. G. V. Samsonov and L. V. Dmitrenko, Symposium, "Termodinamika Ionnogo Obmena" (Thermodynamics of Ion Exchange), Izd. Nauka i Tekhnika, Minsk, 1968, p. 178.
9. E. Blasius, H. Pittack, and M. Negwer, Angew. Chem., 68, 671 (1956).
10. V. A. Dinaburg, G. V. Samsonov, K. M. Genender, V. A. Pasechnik, V. S. Yurchenko, G. E. El'kin, and S. F. Belaya, Zhur. Prikl. Khim., 41, 891 (1968).
11. K. Gärtner, R. Griessbach, and E. Anton, Kolloid. Z., 175, 123 (1961).
12. A. Narebska and J. Kotecka, Roczniki Chem., 39, 1305 (1965).
13. E. P. Trostyanskaya, S. B. Makarova, I. N. Murashko, and E. V. Egorov, Symposium, "Sintez i Svoistva Ionoobmennykh Materialov" (The Synthesis and Properties of Ion-Exchange Materials), Izd. Nauka, Moscow, 1968, p. 17.
14. R. Schlögl and H. Schurig, Z. Elektrochem., 65, 863 (1961).
15. B. N. Laskorin, A. P. Yuzhin, and L. A. Strelkov, see Ref. 13, p. 34.
16. A. A. Tager, M. V. Tsilipotkina, A. B. Pashkov, E. B. Makovskaya, and E. I. Lyustgarten, Plastmassy, No. 3, 23 (1966).
17. B. N. Laskorin, P. V. Pribytkov, L. P. Vodolazov, and T. G. Kononova, see Ref. 13, p. 152.
18. N. Grubhofer, Macromol. Chem., 30, 96 (1959).
19. Z. Pelzbauer and V. Forst, Coll. Czech. Chem. Comm., 31, 2338 (1966).
20. B. Chu and D. N. Tan Creti, J. Phys. Chem., 71, 1943 (1947).
21. Yu. M. Marchevskaya, O. D. Kurilenko, V. R. Klochkov, and A. A. Shpigun, Ukrain. Khim. Zhur., 31, 1161 (1965).
22. Z. V. Zhidkova and I. I. Men'shova, Zhur. Fiz. Khim., 39, 545 (1965) [Russ. J. Phys. Chem., No. 3 (1965)].
23. Z. V. Zhidkova, Zhur. Fiz. Khim., 39, 1823 (1965) [Russ. J. Phys. Chem., No. 8 (1965)].
24. V. N. Tolmachev, L. A. Lomako, and N. A. Klyucha-reva, Ukrain. Khim. Zhur., 31, 321 (1965).
25. M. Fujimoto and G. Körtum, Ber. Bunsenges. Phys. Chem., 68, 488 (1964).
26. B. Calmanovici, Mater. Plast., 2, 369 (1965).
27. B. Calmanovici, Mater. Plast., 3, 199 (1966).
28. Yu. M. Marchevskaya, O. D. Kurilenko, and S. V. Gerei, Ukrain. Khim. Zhur., 31, 717 (1965).
29. G. Zundel, H. Noller, and G.-M. Schwab, Z. Elektrochem., 66, 122 (1962).
30. G. Zundel, H. Noller, and G.-M. Schwab, Z. Elektrochem., 66, 129 (1962).
31. G. Zundel, A. Murr, and G.-M. Schwab, Z. Phys. Chem., 35, 199 (1962).
32. A. Strasheim and K. Buijs, Spectrochim. Acta, 17, 388 (1961).
33. J. E. Gordon, J. Phys. Chem., 66, 1150 (1962).
34. R. Hart and R. Janssen, Macromol. Chem., 43, 242 (1961).
35. R. H. Dinius and G. R. Choppin, J. Phys. Chem., 68, 425 (1964).
36. D. Reichenberg and I. J. Lawrenson, Trans. Faraday Soc., 59, 141 (1963).
37. R. H. Dinius and G. R. Choppin, J. Phys. Chem., 66, 268 (1962).
38. R. H. Dinius, M. T. Emerson, and G. R. Choppin, J. Phys. Chem., 67, 1178 (1963).
39. J. E. Gordon, Chem. Ind., 267 (1962).
40. N. Ishibashi, T. Seyama, W. Sakai, and Yu. Ishii, J. Electrochem. Soc. Japan, 31, 752 (1963).
41. P. M. Borodin, M. K. Nikitin, and E. N. Sventitskii, Zhur. Strukt. Khim., 6, 188 (1965).
42. M. Konstantinesku, O. Konstantinesku, and I. Pascaru, Rev. Phys. Acad. Rep. Populaire Romaine, 7, 367 (1962).
43. M. Konstantinesku, O. Konstantinesku, and I. Pascaru, Studii si cercetari fiz. Acad. RPR, 13, 631 (1962).
44. O. Konstantinesku, I. Pascaru, and M. Konstantinesku, Rev. Rom. Phys., 9, 705 (1964).
45. C. E. A. Brownlow, Nature, 194, 175 (1962).
46. G. L. Starobinets and S. D. Kulkina, Zhur. Fiz. Khim., 39, 3089 (1965).
47. T. Nortia, Suomenkemistilehti, B38, 171 (1965).
48. M. M. Dubinin, Symposium, "Prirodnye Sorbenty" (Natural Sorbents), Izd. Nauka, Moscow, 1967, p. 5.
49. M. M. Dubinin, E. D. Zaverina, and L. V. Radushkevich, Zhur. Fiz. Khim., 21, 1351 (1947).
50. R. Kunin, J. Amer. Chem. Soc., 84, 305 (1962).
51. K. B. Musabekov, A. Sh. Genedia, G. E. El'kin,

V. A. Dinaburg, V. A. Pasechnik, and G. V. Samsonov, "Tezisy Dokladov na XIV Konferentsii IVS" (Abstracts of Reports at the Fourteenth Conference of the Institute of Macromolecular Compounds), Izd. Nauka, Leningrad, 1967.
52. R. Kunin, E. F. Meitzner, and N. M. Bortnik, J. Amer. Chem. Soc., 84, 305 (1962).
53. K. A. Kun and R. Kunin, J. Polymer. Sci., B2, 389, 587 (1964).
54. J. Seidl and J. Malinsky, J. Chem. Prum., 13, 97 (1963).
55. J. R. Millar, D. G. Smith, W. E. Marr, and T. R. E. Kressman, J. Chem. Soc., 2740 (1964).
56. K. A. Kun and R. Kunin, J. Polymer. Sci., 16C, 1475 (1967).
57. E. B. Trostyanskaya, A. S. Tevlina, and F. A. Naumova, Vysokomol. Soed., 8, 1240 (1963).
58. A. A. Vansheidt, V. A. Dinaburg, K. M. Genender, and S. N. Korobeinikova, USSR P. 168 427 (1963); Byull. Izobret., No. 4 (1965).
59. K. B. Nusabekov and V. A. Dinaburg, USSR P. 215 504 (1968); Byull. Izobret., No. 13 (1968).
60. B. N. Trushin, A. B. Davankov, V. M. Laufer, and A. B. Belousova, Zhur. Prikl. Zhur., 41, 1293 (1968).
61. A. A. Tager, Vysokomol. Soed., 2, 994 (1960).
62. G. E. Boyd and Q. V. Larson, J. Amer. Chem. Soc., 89, 6038 (1967).
63. D. Koshel and R. Schlögl, Z. Phys. Chem., 11, 137 (1957).
64. G. E. Boyd and S. A. Soldano, Z. Elektrochem., 57, 162 (1953).
65. J. E. Vincent and K. E. Bristol, Ind. Eng. Chem., 17, 465 (1945).
66. L. E. Copeland and J. C. Hayes, J. Amer. Concrete Inst., 52, 633 (1956).
67. International Critical Tables of Numerical Data in Physics, Chemistry and Technology", London, 1928.
68. H. P. Gregor, B. R. Sundheim, K. M. Held, and M. H. Waxman, J. Coll. Sci., 7, 511 (1952).
69. M. H. Waxman, B. R. Sundheim, and H. P. Gregor, J. Phys. Chem., 57, 969 (1953).
70. H. B. Bull, J. Amer. Chem. Soc., 66, 1499 (1944).
71. A. D. McLaren and J. W. Rowen, J. Polymer Sci., 7, 289 (1951).
72. S. Brunauer, "The Adsorption of Gases and Vapours" (Translated into Russian), Inostr. Lit., Moscow, 1948.
73. L. K. Arkhangel'skii, Symposium, "Fiziko-khimicheskie Svoistva Rastvorov" (Physicochemical Properties of Solutions), Leningrad. Gos. Univ., 1964, p. 188.
74. J. Stamberg, Chem. Listy, 62, 153 (1968).
75. K. B. Musabekov, V. A. Pasechnik, and G. V. Samsonov, Izv. Akad. Nauk Kazakh. SSR, Ser. Khim., No. 5, 64 (1968).
76. G. Dickel and K. Bunzl, Z. phys. Chem., 39, 198 (1963).
77. A. M. Kirgintsev and A. V. Luk'yanov, Symposium, "Ionity i Ionnyi Obmen" (Ion-Exchange Resins and Ion Exchange), Izd. Nauka, Moscow, 1966, p. 31.
78. E. F. Nekryach, N. V. Gorokhovskaya, L. P. Avramchuk, and O. D. Kurilenko, "Ionity i Ionnyi Obmen" (Ion-Exchange Resins and Ion Exchange), Izd. Nauka, Moscow, 1966, p. 40.
79. E. A. Flood, "Solid-gas Interface", New York, 1967, Vol. 1.
80. H. P. Gregor, J. Amer. Chem. Soc., 73, 642 (1951).
81. L. W. Holm, Arkiv Kemi, 10, 151 (1956).
82. G. E. Boyd and G. E. Myers, J. Phys. Chem., 60, 521 (1956).
83. B. Z. Ginzburg and D. Cohen, Trans. Faraday Soc., 60, 185 (1963).
84. L. K. Arkhangel'skii and E. A. Materova, Symposium, "Fiziko-Khimicheskie Svoistva Rastvorov" (Physicochemical Properties of Solutions), Izd. Leningrad. Gos. Univ., 1964, p. 163.
85. G. Dickel, Z. Phys. Chem., 25, 233 (1960).
86. K. P. Mishchenko, "Voprosy Termodinamiki i Stroeniya Vodnykh i Nevodnykh Rastvorov Elektrolitov" (Problems of the Thermodynamics and Structure of Aqueous and Non-Aqueous Electrolyte Solutions), Izd. Khimiya, Leningrad, 1968.
87. V. A. Kargin, M. E. Bogdanov, and E. P. Cherneva, Vysokomol. Soed., 429 (1968).
88. S. Rice and F. E. Harris, Z. Phys. Chem., 8, 207 (1956).
89. D. Dolar, S. Lapanje, and Paljik, Z. Phys. Chem., 34, 360 (1962).
90. B. E. Conway and J. O'M. Bockris in "Modern Aspects of Electrochemistry" (Translated into Russian), Inostr. Lit., Moscow, 1958, p. 63.
91. E. Gluekauf and P. Kitt, Proc. Roy. Soc., A228, 322 (1955).
92. S. Lapanje and D. Dolar, Z. Phys. Chem., (Frankfurt), 21, 376 (1959).
93. S. Lapanje and D. Dolar, Z. Phys. Chem. (Frankfurt), 18, 11 (1958).
94. N. G. Peryshkina, N. I. Sudarikova, and V. S. Soldatov, Symposium, "Sintez i Svoistva Ionoobmennykh Materialov" (The Synthesis and Properties of Ion-Exchange Materials), Izd. Nauka, Moscow, 1968, p. 187.
95. E. F. Nekryach, O. D. Kurilenko, and A. V. Dumanskii, Dokl. Akad. Nauk SSSR, 165, 611 (1965).
96. K. K. Kal'nin'sh, "Programma XV Nauchnoi Konferentsii IVS" (The Programme of the Fifteenth Scientific Conference of the Institute of Macromolecular Compounds), Leningrad, 1968.
97. G. Dickel, H. Degenhart, K. Haas, and J. W. Hartman, Z. Phys. Chem., 20, 121 (1959).
98. K. Gärtner and J. Giesemann, Z. Phys. Chem., 228, 129 (1965).
99. G. E. Boyd and B. A. Soldano, J. Amer. Chem. Soc., 75, 6105 (1953).
100. F. Helfferich, "Ionenaustauscher" (Translated into Russian), Inostr. Lit., Moscow, 1962.
10 . G. E. Boyd, F. Vaslow, and S. Lindenbaum, J. Phys. Chem., 68, 590 (1964).
102. F. Vaslow and G. E. Boyd, J. Phys. Chem., 70, 2507 (1966).
103. V. S. Soldatov and G. L. Starobinets, Symposium, "Issledovanie Svoistv Ionoobmennykh Materialov" (Studies on Ion-Exchange Materials), Izd. Nauka, Moscow, 1964, p. 36.
104. G. V. Samsonov and B. V. Moskvichev, Izd. Akad. Nauk SSSR, Ser. Khim., 742 (1967).
105. D. Reichenberg, "Ion Exchange" (Edited by Marinsky), p. 227.
106. B. Chu, D. C. Whitney, and R. M. Daimond, J. Inorg. Nucl. Chem., 24, 1405 (1962).
107. R. M. Daimond and D. C. Whitney, see Ref. 105, p. 277.
108. G. Eisenman, Biophys. J. Suppl., 2, 259 (1962).
109. N. A. Izmailov, "Elektrokhimiya Rastvorov" (Electrochemistry of Solutions), Izd. Khimiya, Moscow, 1966.

110. G. E. Boyd, F. Vaslow, and S. Lindenbaum, J. Phys. Chem., 71, 2214 (1967).
111. E. Gluekauf, Proc. Roy. Soc., A214, 207 (1952).
112. G. E. El'kin, V. A. Pasechnik, and G. V. Samsonov, Symposium, "Termodinamika Ionnogo Obmena" (Thermodynamics of Ion Exchange), Izd. Nauka i Tekhnika, Minsk, 1968, p. 111.
113. B. A. Soldano, Q. V. Larson and G. E. Myers, J. Amer. Chem. Soc., 77, 1339 (1955).
114. B. A. Soldano and D. Chesnut, J. Amer. Chem. Soc., 77, 1334 (1955).
115. B. A. Soldano and Q. V. Larson, J. Amer. Chem. Soc., 77, 1331 (1955).
116. G. E. Boyd, S. Lindenbaum, and G. E. Myers, J. Phys. Chem., 65, 577 (1961).
117. A. Schwarz and G. E. Boyd, J. Phys. Chem., 69, 4268 (1965).
118. O. D. Bonner, W. J. Argersinger, and A. W. Davidson, J. Amer. Chem. Soc., 74, 1044 (1952).
119. W. J. Argersinger, Jnr., A. W. Davidson, and O. D. Bonner, Trans. Kansas Acad. Sci., 53, 404 (1950).
120. G. L. Gaines and H. C. Thomas, J. Chem. Phys., 21, 714 (1953).
121. G. L. Gaines and H. C. Thomas, J. Chem. Phys., 23, 2332 (1955).
122. G. V. Samsonov and V. A. Pasechnik, Zhur. Fiz. Khim., 36, 2727 (1962) [Russ. J. Phys. Chem., No. 12 (1962)].
123. V. A. Pasechnik and G. V. Samsonov, Symposium, "Issledovanie Svoistv Ionoobmennykh Materialov" (Studies on the Properties of Ion-Exchange Materials), Izd. Nauka, Moscow, 1964, p. 44.
124. L. K. Arkhangel'skii, A. A. Voevodina, and E. A. Materova, Vestnik Leningrad. Gos. Univ., No. 22, 102 (1961).
125. G. E. El'kin, V. A. Pasechnik, and G. V. Samsonov, Symposium, "Izbiratel'naya Ionoobmennaya Sorbtsiya Antibiotikov" (Selective Ion-Exchange Sorption of Antibiotics), Trudy Leningrad. Khim.-Farm. Inst., No. 25, 92 (1968).
126. I. Prigogine and R. Defray, "Treatise on Thermodynamics", Vol. 1, "Chemical Thermodynamics" (Translated into Russian), Izd. Nauka, Novosibirsk, 1966.

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