very useful since the formation of the resin film on the surface of the dyed fabric may effectively shield the dyestuff by selective absorption of the radiation responsible for degradation. A resin film using guanidine carbonate has also been found very effective. Recently, a plastic based on sym. dimethyl glycol has been found quite useful in ensuring better stability of basic dyestuffs like Methasol Aurine AS[8]. Some of these treatments are quite restrictive and hence no method can be universally recommended.

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Ion-Exchange

R. R. Pandit*

IN 1856, J. Thomas Way[1], a consulting chemist to the Royal Agricultural Society of England discovered that the apparent bodily removal of ammonia from aqueous solutions on passing through certain soils was really an exchange with the calcium of a particular type of silicate occurring in these soils. Eichorn discovered that this exchange was reversible. Subsequent researches on the cation-exchange properties of the soils and humus materials led to the commercial application of zeolites and acid-treated coal to water-softening and to the development of synthetic gel zeolites. However, till 1935 the application of ion-exchange was limited to the field of water-softening only. This was not because the phenomenon was not well understood but because of the limitations of the then available ion-exchange materials—the main limitations being their low capacity and chemical instability under extreme pH conditions.

A new era in the field of ion-exchange dawned with the discovery by Adams and Holmes[2] in 1935 that resins of the phenol-formaldehyde class exhibited ion-exchange properties. The advantages of these synthetic resins were not only the higher operating efficiency, better mechanical, chemical and thermal properties but also that they could be made with " tailor-made " properties to suit any particular application by selecting proper reactants for the polymerisation reaction. Since 1935, the advance has been very rapid and the ion-exchange principle has been applied so very extensively in the field of technology that ion-exchange is now considered as a unit operation.

The phenomenon of ion-exchange can be defined as the exchange of ions that occurs on contacting an ionic solid with an electrolyte. The ionic solid is called the ion-exchanger. Ion-exchangers are

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*Research student, Chemical Engineering Section, Dept. of Chemical Technology.

classified according to their abilities of exchanging cations or anions. Examples of the cation-exchangers are the zeolites and modified phenol-formaldehyde resins. Cation-exchangers can again be classified into two classes: (i) Sodium exchangers and (ii) Hydrogen exchangers according to their ability of exchanging respectively sodium ions or hydrogen ions for the heavy metal ions in the contacting solution. When the exchanging capacity of these materials is exhausted the sodium exchangers can be regenerated with strong brine (NaCl) solution and the hydrogen exchangers by dilute acids. These reactions are stoichiometric and can be represented as:

Action of sodium-exchanger.

$$2\,\mathrm{Na.R} + \mathrm{CaSO_4} \rightleftharpoons \mathrm{CaR_2} + \mathrm{Na_2SO_4}$$

Action of hydrogen-exchanger

$$\mathrm{HR} + \mathrm{NaCl} \rightleftharpoons \mathrm{NaR} + \mathrm{HCl}$$

Where Na.R is the sodium salt of a cation-exchanger and HR is the hydrogen form of a cation-exchanger.

Anion exchangers are mostly acid-adsorbents. Only recently true anion exchangers have been synthesized which exchange hydroxyl ions (OH) for other anions in the solution. The anion exchangers can be regenerated by dilute alkalis. Examples of anion exchangers are the amine formaldehyde resins.

The affinity or the exchange-capacity of an ion-exchanger varies from ion to ion. Two empirical rules are :

(i) At low concentrations of aqueous solutions and ordinary temperatures, the extent of exchange increases with the increasing valence of the exchanging ion : $\overset{\cdot}{\mathrm{Na}} < \overset{\cdot\cdot}{\mathrm{Ca}} < \overset{\cdot\cdot\cdot}{\mathrm{Al}} < \overset{\cdot\cdot\cdot\cdot}{\mathrm{Th}}$ *i.e.* $\overset{\cdot\cdot}{\mathrm{Ca}}$ will replace $\overset{\cdot}{\mathrm{Na}}$ from the resin and so on.

(ii) At low concentrations of aqueous solutions, ordinary temperatures and constant valence, the extent of exchange increases with increasing atomic number : $\overset{\cdot}{\mathrm{Li}} < \overset{\cdot}{\mathrm{Na}} < \overset{\cdot}{\mathrm{K}} < \overset{\cdot}{\mathrm{Rb}}$ *i.e.* $\overset{\cdot}{\mathrm{K}}$ will replace $\overset{\cdot}{\mathrm{Na}}$ on a resin and so on.

At higher concentrations the exchange will depend on the activity of the ions in solutions and the affinities of the ions for the resin. The total exchanging capacity of an ion-exchanger depends on the pH and concentration of the solution. The variation in the affinity of the ion-exchanger can be utilised to separate a mixture of ions of the same type in a solution.

The phenomenon of ion-exchange has been explained by double layer theory of colloids. Like colloids, the surfaces of ion-exchange agents have been pictured as consisting of two layers of electric charges—an inner fixed layer *e.g.* the anionic groups, aluminosilicate group in zeolites or the sulfonic, hydroxyl (phenolic) and carboxyl groups in synthetic resins, and an outer diffuse mobile layer of charges *e.g.* sodium or hydrogen ions in the above cases. There exists an equilibrium between these two. If the concentration of the ions in the external solution is changed by the addition of a foreign electrolyte, the equilibrium is upset and a new one is established. New ions enter into the diffuse layer replacing some of the ions previously held there. In order that the law of electroneutrality is satisfied, the exchange must be stoichiometrc. Since ion exchange is controlled by electrostatic forces, the adsorbability of various ions will depend on the relative charges and ionic radii† of the two ions entering into the exchange, hence the ready adsorption of the ions of higher valence in dilute solutions. In order to overcome this affinity, during regeneration, the activities of the sodium

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†Ions behave like spheres of definite size. The distance between the lattice planes of a crystal of electrolyte which is usually measured by X-ray diffraction technique is considered as the sum of the ionic radii of the two ions.

and hydrogen ions have to be increased using stronger solutions of these ions. The variation in the affinities for the ions of the same valence is explained to be due to hydration of the ions in aqueous solutions. The ions of the metals of higher atomic number are less hydrated and have smaller ionic radii and hence tend to displace ions of larger ionic radii. The exchange capacity of an ion-exchanger varies with pH and concentration because the extent of the double layer varies with pH and concentration.

Commercial Ion-Exchange Agents :—

The basic commercial requirements of an ion-exchanger are :

i) low solubility,
ii) hydrophilic character,
iii) high capacity, and
iv) physical and chemical stability.

Inorganic Ion-exchangers :—

The chief among these are the naturally available green-sand and synthetic alumino-silicates (artificial zeolite). These are still used on a large scale for water-softening. However the disadvantage is that these can only be used for waters of definite pH range, since disintegration of the silicate lattice occurs in acidic waters and they impart silica to waters of low silica contents, especially at higher pH. These are cation-exchangers which exchange Ca and Mg for Na^+ ions. There is no satisfactory inorganic anion exchanger.

Organic Exchangers :—

Earlier researches on the exchange-adsorbent properties of humus substances led to the development of sulfonated products of peat, lignite and brown coal. These were the first hydrogen-exchangers. In this case there is no fear of silica pickup when employed for water-softening but they tend to impart colour to the water at higher alkalinity.

Researches of Adams and Holmes indicated that modified phenol-formaldehyde—especially those from polyhydric phenols or tannin-formaldehyde resins, were far superior cation-exchangers. Later it was found that increased exchange capacity, particularly at low pH, is obtained by the incorporation of strongly acidic groups such as aryl or alkyl sulfonic acids, into the resin lattice. This is effected by condensation of a phenolic body with formaldehyde and sodium sulfite or by a condensation of sulfonic acids of aromatic hydroxy compounds with formaldehyde.

Synthetic resins which exhibited anion-exchange or acid-adsorbent properties were at first prepared by condensing aromatic amines such as aniline and m-phenylene diamine with formaldehyde, or by the reaction of a polyamine, phenol and formaldehyde. A more basic anion-exchange resin has been prepared from guanidine formaldehyde and phenol, phenol being added for the purpose of improving physical properties.

Recently, co-polymers of styrene and divinylbenzene have been used as a base material. Sulfonation of this polymer produces a high capacity and more durable cation-exchanger. Nitration and subsequent reduction of the same base yield a stable but weakly basic acid-adsorbent resin. A carboxylic type of cation-exchange resin has been prepared by incorporating maleic anhydride into the polymer and then hydrolysing the resulting product.

APPLICATIONS

The phenomenon of ion exchange can be utilized to achieve the following:—

(i) Removal of undesirable ionic impurities from solutions ; e.g. Water softening and deionisation.

(ii) Recovery of valuable substances

from solutions or the concentration of ionic substances ; e.g. recovery of copper from copper alloy pickle wastes or waste cuprammonium liquors.

(iii) Separation and fractionation of electrolytes ; e.g. separation of rare earths.

(iv) Use as catalysts.

Water-softening :—

This is one of the major applications of ion-exchange. The hardness producing ions, Ca and Mg, are removed and exchanged for sodium ions by passage through a column of cation-exchanger. The cation-exchanger is regenerated with brine. The exchangers generally used are natural and artificial zeolites; though synthetic resins are gradually replacing them because of their superior qualities.

Deionisation :—

It is apparent that the use of a hydrogen-exchanger results in the replacement of all cations by H ions and the neutral salts are converted to the corresponding acids. Similarly the use of an anion-exchanger adsorbent results in the complete removal of free acids. Thus, the passage of water through a double system of hydrogen and anion-exchanger removes all dissolved salts and results in the production of water having conductance comparable to that of conductivity water.

Sugar-Manufacture[3] :—

Sucrose has a significantly higher solubility in high ash content syrups. Hence ion-exchange has been utilised for the removal of mineral matter which is generally composed of salts of sodium and potassium, from the juice. It was found that ion-exchange resins (a double system of hydrogen and anion-exchangers) not only remove the ash but also weakly ionised nitrogen compounds, many color bodies and even some colloids. The efficiency of removal of impurities can be gauged from the following:

Total nitrogen removal	56%
Total non-sugar removal	84%
Ash removal	94%

The advantage of the treatment of the juice by ion-exchange is the increased extraction of sucrose due to elimination of impurities (from 81% to 90%) and hence a decrease in the amount of molasses. The other advantage is the decrease in the scaling of heat transfer surfaces.

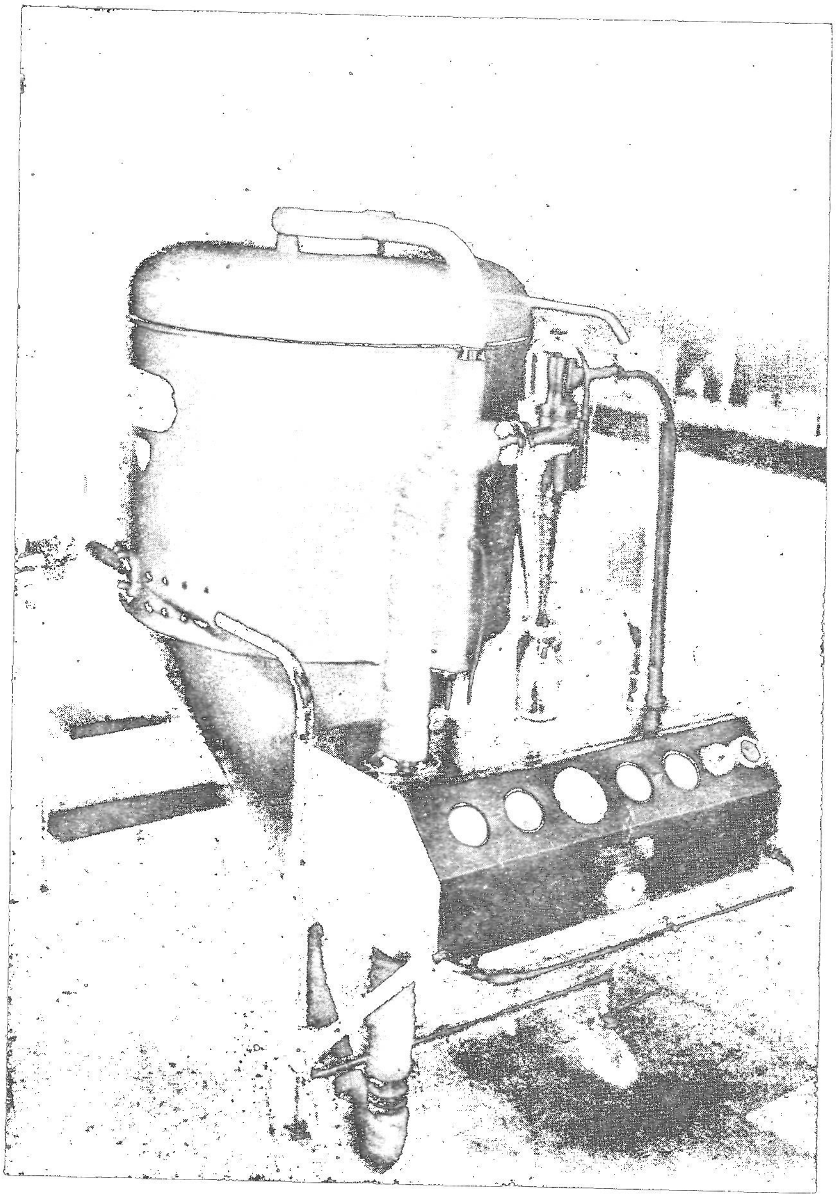
Revovery of metals :—

Over 17 tons of copper were recovered per day[4] from cuprammonium wastes in a Rayon plant in Germany, by ion-exchange. The copper is usually removed as the diammonium complex with a cation-exchange resin and after exhaustion of the resin, the recovery of the copper and regeneration of the resin is carried out by means of sulfuric acid. It was reported that the recovered copper sulfate was extremely pure and better for dissolving cellulose than the copper oxychloride initially used.

Copper and chromium in copper alloy pickle wash water are now concentrated 25 fold by taking up these metal cations on a carbonaceous zeolite exchanger (sulfonated coal) and subsequently regenerating with normal sulfuric acid.

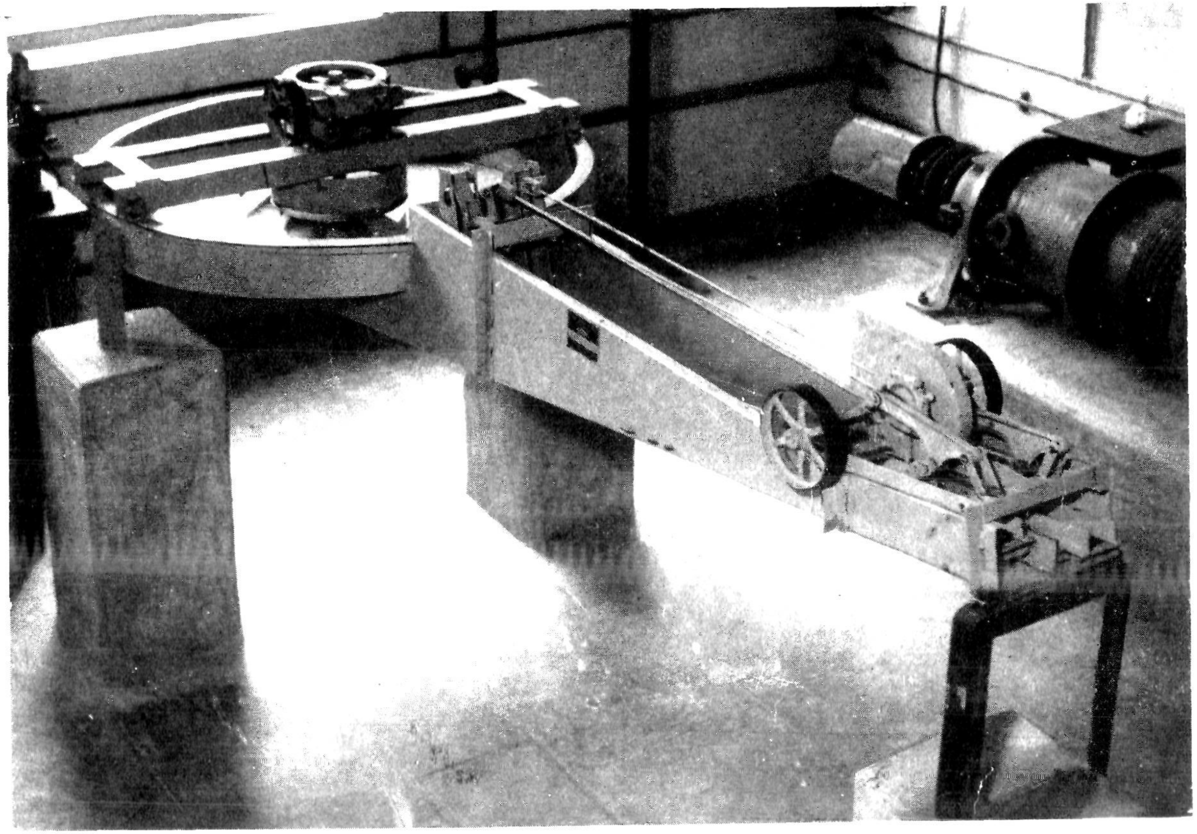
Recovery of organic compounds :—

Nicotine is now recovered from the exhaust gases of cigarette tobacco dryers by scrubbing the gases with water or dilute acids and passing this nicotine solution through a cation-exchanger operating on hydrogen cycle. The nicotine is removed by treating the exhausted exchanger with ammoniacal alcohol.



SPRAY DRIER
(Chemical Engineering Section)

Photo by: C. B. WADIKAR



"DORR" CLASSIFIER
(*Chemical Engineering Section*)

Photo by: C. B. WADIKAR

Tartaric acid from winery still slop is now recovered by exchange adsorption on an anion-exchanger in chloride form. Brine is used as a regenerant. Concentration of the tartrate in solution is thus increased 15-18 times over that in the original slop.

At one time, citrus fruit and pine-apple cannaries in U.S.A. were faced with the problem of disposing of the waste sugar solutions containing 6-8% sugar. However, now the waste solution is demineralised by ion-exchange and the effluent can be concentrated to syrups and reused. At the same time the citric acid, one of the impurities taken out by ion-exchange, is recovered as a by-product.

Separation of Rare Earths :—

One of the greatest achievements in the field of inorganic chemistry in recent years is the separation of rare earths by ion-exchange method. By older methods of purification, thousands of fractional crystallisations were required to get a relatively pure sample of one of the rare earths. For example, G. Urbain[5] had to crystallise the rare earth salt 15,000 times to purify ytterbium from lutecium. However, it is now possible to achieve the separation and recovery of macro quantities of rare earths of spectroscopic purity in a matter of weeks by adsorption on a cation-exchanger like Amberlile IR 1 or Dowex 50 (modified phenol methylene sulfonic resins) and subsequent elution with citric acid-ammonium citrate solution at controlled pH. The rare earths form complexes with the citrate ions. If the pH is suitably adjusted, competition is set up for the rare earth ions between the citrate complexes and the active centres of the resin. Therefore, if a solution of rare earth in citric acid-ammonium citrate solution is allowed to trickle over the resin column, each rare earth ion is adsorbed and desorbed many times. Since the equilibrium constants for the rare earth citrate complexes vary slightly among the different rare earths, their rates of travel down the column differ sufficiently to lead to their separation. Repeated cycles in the columns effectively achieve the separation in a short time. In the Manhatten project[6] wherein this work was originally carried out, pure rare earth salts up to 1 kilogram quantities were prepared by using 24 columns (8′ high and 4″ diameter) and a few gallons of citrate solution in a time of about two months.

Pharmaceuticals :—

Ion-exchange has been successfully tried for the separation of amino-acids. Recovery and purification of streptomycin have been achieved on an industrial scale using ion-exchange technique. It is also used for the purification of alkaloids, vitamins and hormones.

Catalytic properties of Ion-exchange resin :—

The strongly acidic sulfonic cation-exchange resins have been found effective catalysts for estehification as well as for most homogeneous or heterogeneous acid-catalysed reactions. The strongly basic anion-exchange resins have been found effective basic catalysts e.g. for aldol condensations. The advantages of the ion-exchange resins as catalyst over the conventional soluble acids and bases are:

(i) the resulting products are not contaminated by the catalyst.
(ii) the catalyst can be used over and over again.
(iii) they may frequently cause fewer side reactions.

Above are only a few applications of ion-exchange. In a small elementary article like this, it is not possible to enumerate all of them. However, they are sufficient to indicate the wide scope of application of this technique of ion-exchange. There is a possibility that this technique may help us to obtain pure water from sea water and if this can be achieved, it will be of the greatest consequence for the welfare of humanity in general.

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Some Aspects of Drug Resistance

H. R. ALIMCHANDANI*

THE exact mechanism of drug action is, as yet only imperfectly understood. The majority of drugs used in the treatment of infections exert their effect primarily by inhibiting the formation or utilisation of certain metabolites essential for the multiplication of the parasite. With such cases, it frequently happens that on repeated exposure to a drug, especially at sublethal concentrations, micro-organisms become resistant to it. In recent years considerable work has been done to elucidate the mechanism by which micro-organism may become drug resistant. Knowledge gained on the mode of acquirement of drug resistance has to some extent enabled the adoption of methods to deal with drug-resistant microbes.

Postulated mechanisms by which drug resistance has been explained are outlined below :

Prevention of drug from reacting site of action :—

A number of organisms develop resistance to toxic agents by becoming impermeable to them. Trypanosomes become resistant to the inhibitory action of basic dyes presumably by modification in cell-membrane ; resistant trypanosomes are no longer stained by basic dyes. Quite often micro-organisms are known to develop capsules which protect them from lethal agents.

Inactivation of drug :—

Certain organisms acquire resistance to drugs by developing a capacity to destroy or detoxicate them. A few penicillin-resistant organisms are so by virtue of the fact that they elaborate an enzyme penicillinase which destroys it. The tubercle bacillus is resistant to crystal violet because it possesses a mechanism to inactivate it. Pyrithiamine is a powerful analogue antagonist of thiamine. Instances are known where a microbial strain could become resistant to pyrithiamine by developing a capacity to split pyrithiamine into two non-toxic parts. One of the postulated mechanisms by which micro-organisms become resistant to sulpha drugs is by acetylating them ;

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*Demonstrator, Food Technology Section.