

Ion Exchange Chromatography

Amongst the various chromatographic methods, the most frequently used methods are ion exchange chromatography as well as gas chromatography. The former has very wide applications in Inorganic Chemistry while the latter is very useful in the separation of organic compounds. The cleancut separation of chemically similar elements like rare earths, or zirconium and hafnium or niobium tantalum was possible by ion exchange chromatography. The softening or deionisation of water was facilitated by the ion exchange process. The task of removal of total salt concentration and removal of interfering ions, separation of ions from nonelectrolytes or isolation of trace concentration of precious metals was possible by ion exchange methods. The principal advantage of ion exchange method over other methods of separation is that this procedure is simple, rapid and inexpensive. For instance, the resin can be reutilised after regeneration. These resins are easily available in any particle size with varying exchange sites. Most of them are insoluble in water and therefore can be packed into the column, which permit reasonable flow rate of the solution provided appropriate particle size of resin is selected.

MECHANISM OF ION EXCHANGE

The various explanations which have been put forward to explain the exchange mechanism can be grouped into three theories:

- (a) Crystal lattice exchange
- (b) Double layer
- (c) Donnan membrane

(a) According to crystal lattice theory, Pauling and Bragg drew an analogy between ion exchange resin and ionic solids. In ionic solids, the constituents of the crystal lattice are present as ions instead of molecules. A crystal of KCl contains K^+ Cl^- ions, each ion being surrounded by a fixed number of ions. When placed in a medium of high dielectric constant such as water, the net attractive forces binding the ion to the crystal are reduced to such an extent that exchange of this ion for another ion in solution becomes quite feasible. Such exchange depends upon the nature of forces binding the ion to the crystal, concentration of exchanging ions, size of the two ions, accessibility of lattice site and solubility effects. Now if $NaNO_3$ is added to KCl solution, K^+ exchanges with the Na^+ ion and Cl^- with the NO_3^- ion. This exchange is similar to the

exchange of crystal lattice ions and ions of an electrolyte solution. The mechanism of ion exchange in resins, although noncrystalline, is quite similar to the exchange of a crystal lattice ions. The resin is a high molecular weight insoluble polymer *i.e.*, electrolyte. The functional groups - HSO_3 , - COOH , - OH are responsible for exchanging ions. The capacity of the sulphonic type resin can be stated by knowing the sulphur content of the resin. The exchange of ions with these resins occurs throughout the entire gel structure of the resin and is not merely restricted to surface effects. In anion exchange resins, exchange is due to covalent absorption of acid. They are polyamines, the amine content of the resin is the measure of the total exchange capacity.

) In double layer theory, the electrokinetic properties of colloids have been extended to ion exchange systems to interpret the various factors involved. The Helmholtz double layer consists of two rigid electrical layers at the surface of a colloid, similar to the plates of a condenser. According to Gouy and Stern, the double layer actually consists of an inner fixed layer which is diffuse and mobile outer layer of charges. The charged layers originate from absorbed ions which may be quite different from ions present in the inner layer and influence the electrokinetic properties of the colloidal system. The concentration of ions in the outer diffuse layer is related to the concentration and pH of the external solution. On addition of a foreign ion to the external solution, new ions will enter the outer layer replacing some of the ions previously held in this layer. A new equilibrium is set up and the overall exchange is stoichiometric. Exchange at the crystal lattice centre and in a double layer is only somewhat similar. The relation between the theoretical total exchange capacity and pH or concentration is not the same for the two systems. In the former, it is assumed that there are a few exchange sites which must be satisfied independent of pH and concentration change, but in the latter exchange, this does not apply as the capacity of different double layers depends both on pH and concentration (Fig. 12.1).

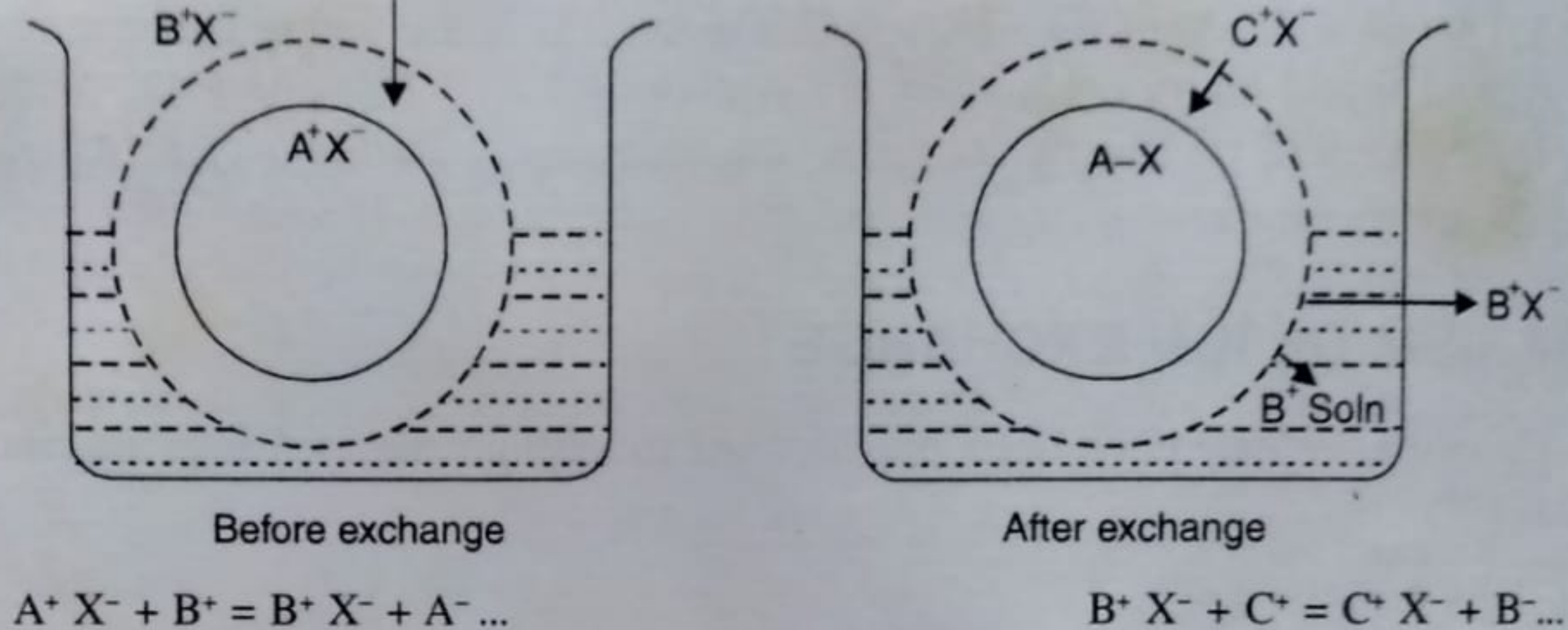
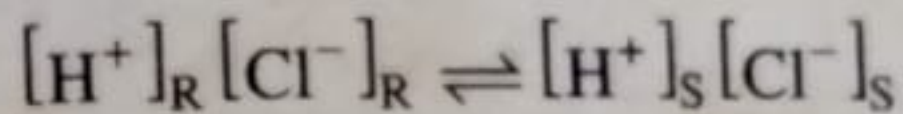
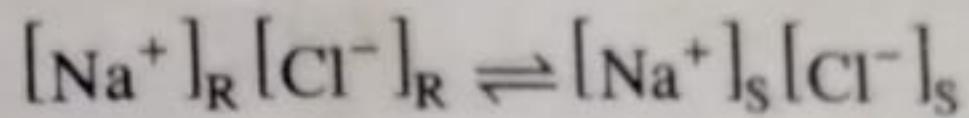
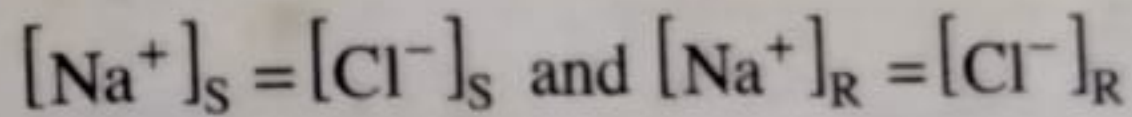


Fig. 12.1 Double layer theory

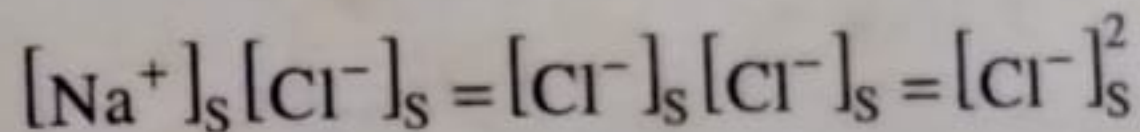
(c) Finally the Donnan membrane theory deals with unequal distribution of ions on two sides of a membrane. One side contains an electrolyte whose ions cannot penetrate through the membrane. In ion exchange equilibria, the interface between solid and liquid phases may be considered as a membrane. The nondiffusible ion is the colloidal micelle to which the exchangeable ions are attached e.g. NaCl in contact with cation exchange resin (H^+ form). Equilibrium is set up as in a heterogeneous reaction between the solution phase and the resin phase wherein $H_2^+R^-$ denotes the resin and the subscripts R and S indicate the resin and solution phases respectively. Hence we have



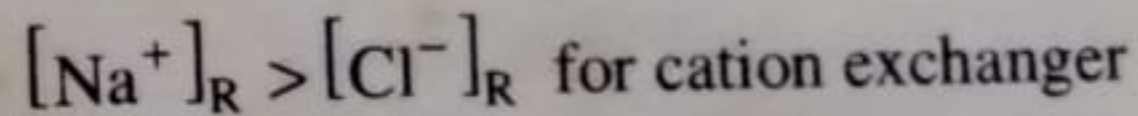
To maintain electroneutrality



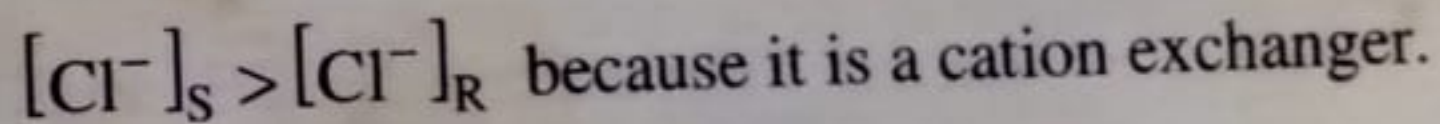
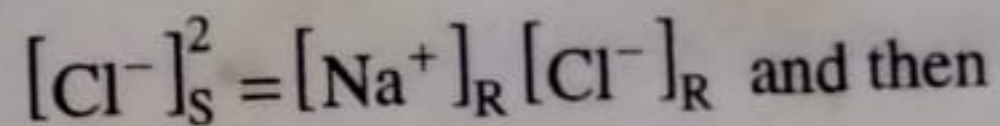
Hence



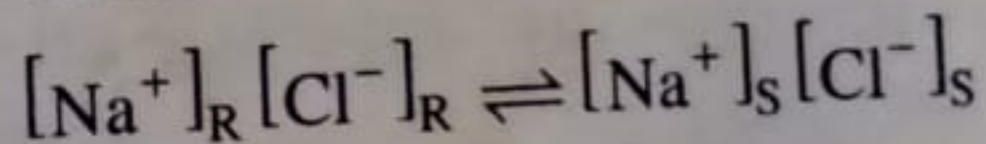
Now if



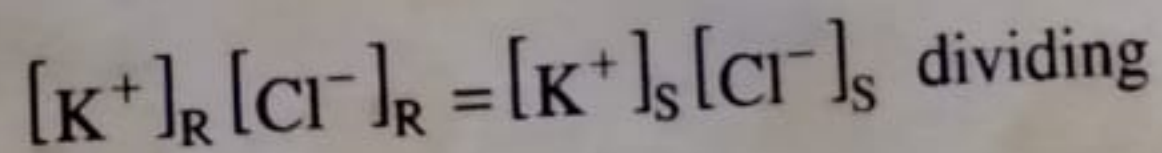
and



Thus activity of NaCl is greater on the side that is free of nondiffusible ions in the solution phase. Now if a second cation K^+ is added to the system the following conditions must hold.



and



$$\frac{[\text{Na}^+]_{\text{R}}}{[\text{K}^+]_{\text{R}}} = \frac{[\text{Na}^+]_{\text{S}}}{[\text{K}^+]_{\text{S}}}$$

CHARACTERISTICS OF ION EXCHANGE RESINS

We would consider both cation and anion exchange resin from the view point of their physical and chemical properties. Such properties include: (i) color, density, (ii) particle size, (iii) presence of functional group, (iv) exchange capacity, (v) selectivity, (vi) degree of cross linking (vii) porosity, (viii) swelling, (ix) rate of exchange, (x) chemical resistance, (xi) effect of temperature, (xii) effect of media.

(a) *Color*: The color of resin is generally brown for strong resins, but few are colorless e.g. Dowex 50W-X8. For anion exchange resin color varies from pale yellow to brown. The density of dry cation exchange resin is 1.4 gm/ml while that of anion exchange resin is 1.2 g/ml but for wet resin density always increases from 1.1-1.3 g/ml. On an average they contain water 40-60%

- (b) *Particle size*: This is most critical as it influences the plate height (HETP) as well as total number of plates (N) in the column. With smaller grain size exchange is always better though it is slow. Mesh size varies from 16-400 (US standard) or (1.168-0.038 mm). Polystyrene resins are generally available in circular beads. For all practical purposes one uses 20-50 mesh size resins during columnar work for metal separations.
- (c) *Nature of functional group*: Depending upon presence of the active group they are classified into four categories viz. strongly and weakly acidic cation exchange resins and strongly and weakly basic anion exchange resins. Such information can be obtained experimentally by potentiometric titration. We obtain curves as shown in Fig. 12.8 and Fig. 12.9. Here in Fig. 12.8, Amberlite IR-120 is strongly acidic cation exchange resin while Amberlite IRC-50 is weakly acidic cation exchange resin. Similarly in Fig. 12.9 Amberlite IRA-400 is strongly basic while Amberlite IR4B is weakly basic ion exchange resin.

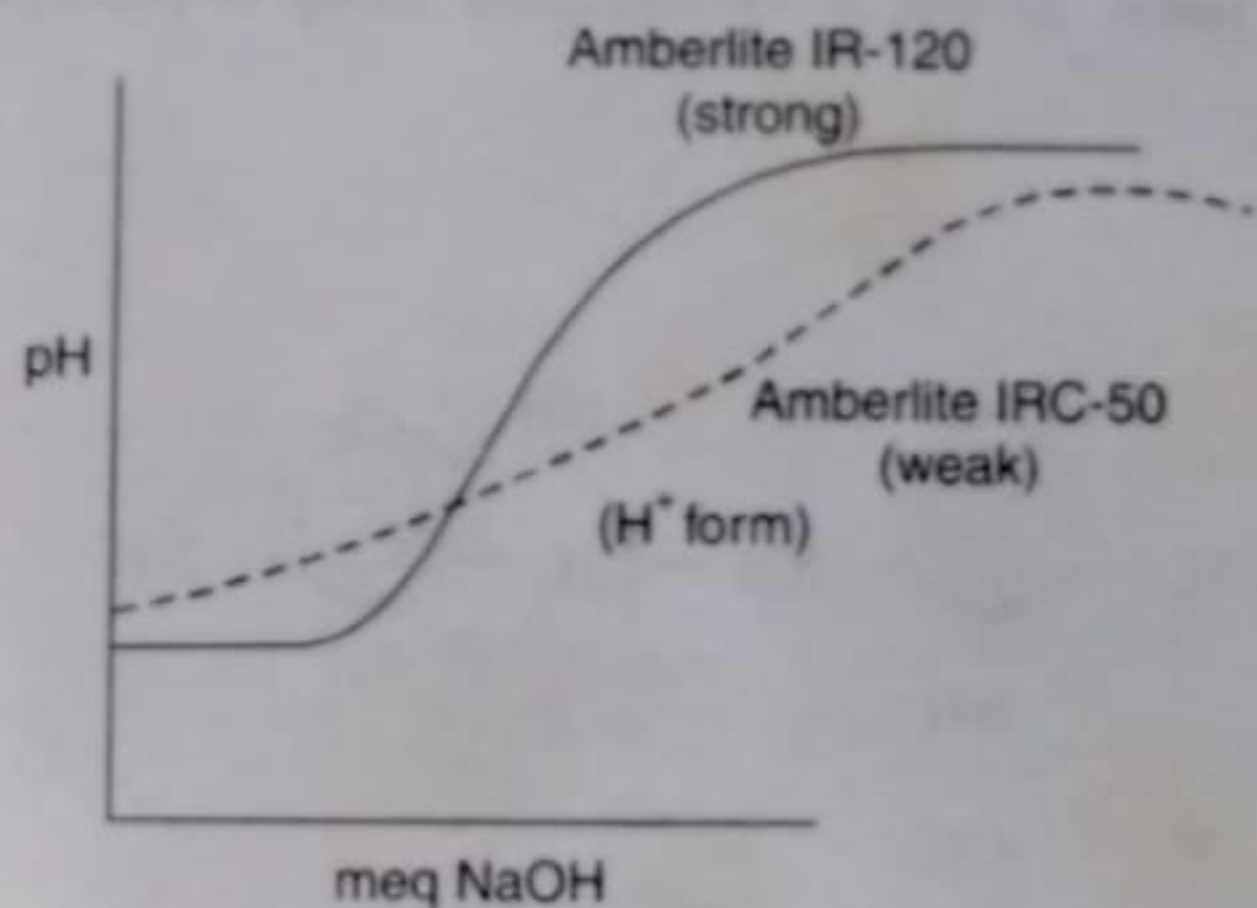


Fig. 12.8 Titration pattern

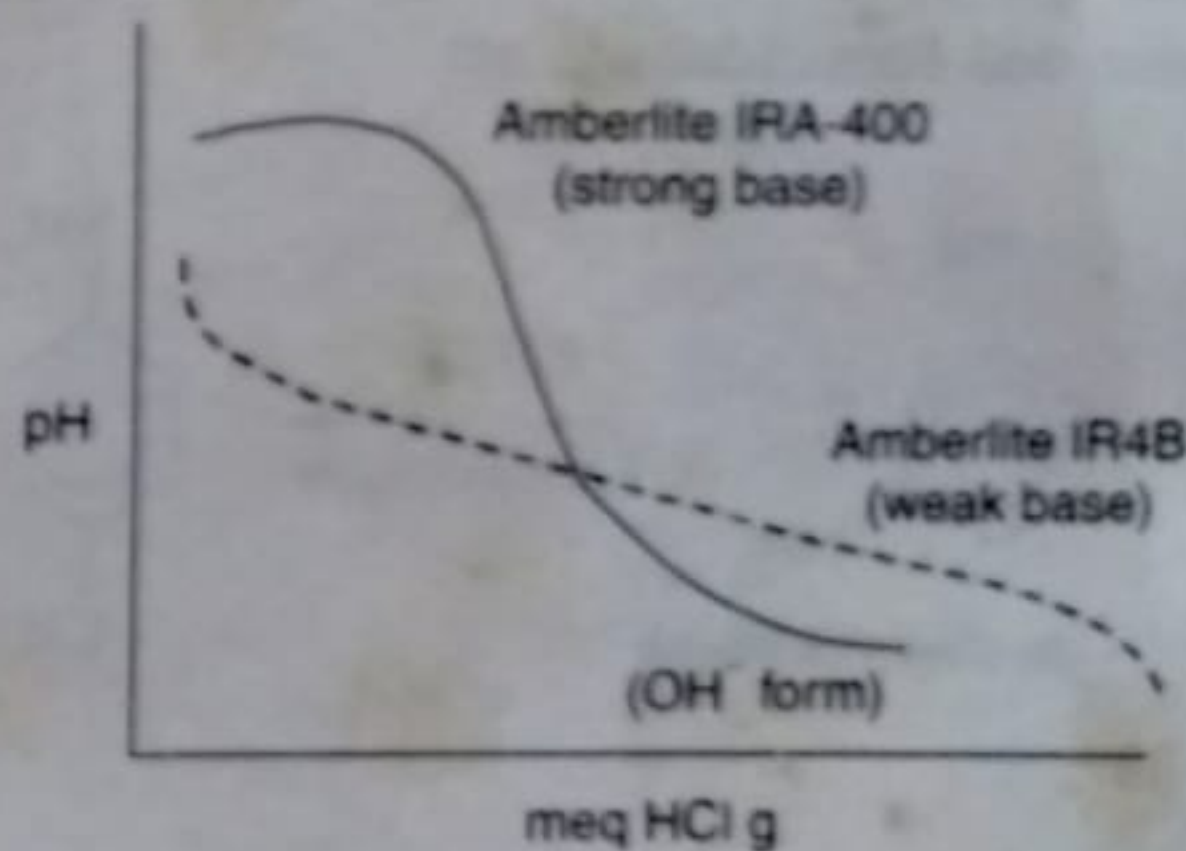
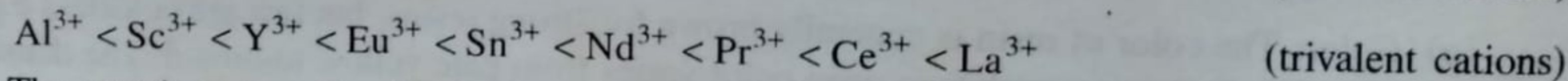
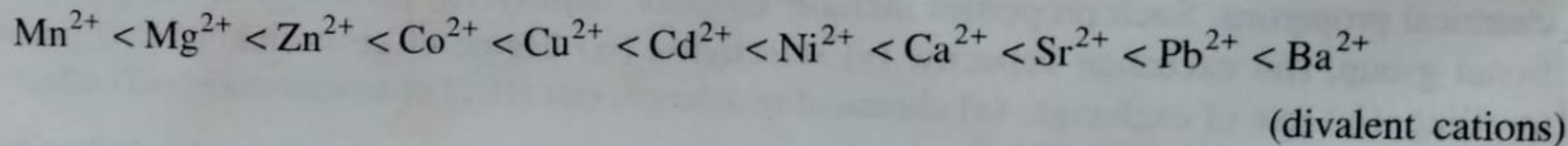
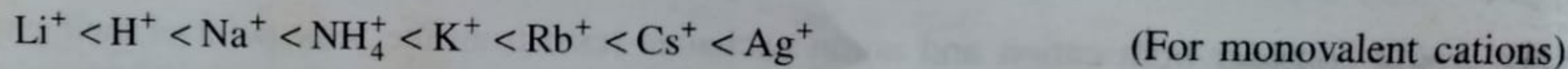


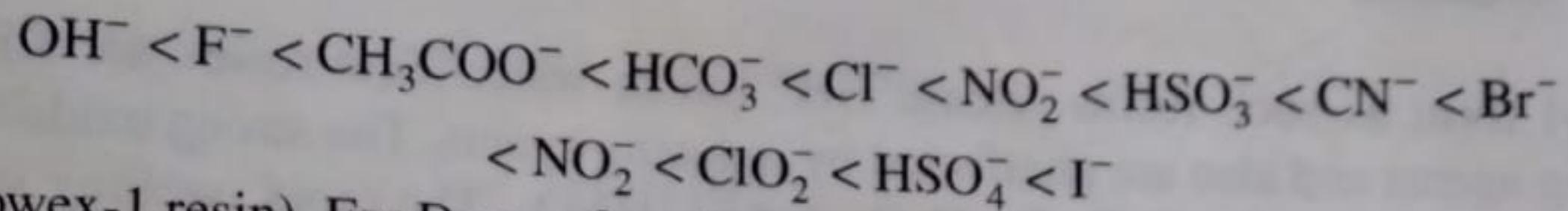
Fig. 12.9 Titration pattern

d) *Capacity*: The total exchange capacity means the total amount of exchangeable ions per unit weight of resin (dry/wet). It is obtained by acid–base titration. The salt splitting capacity is the amount of H^+/Na^+ released by known weight of cation exchange resin while salt splitting capacity of anion exchange resin is the amount of liberated base by unit weight or unit volume. It is related to dissociation constant of active groups. For strongly acidic or strongly basic resin the salt splitting capacity and total capacities are identical. The washing effect must be also considered in relation to capacity. The breakthrough capacity usually depends on the pH, grain size, column size, flow rate in column.

e) *Selectivity*: The different ions are sorbed at different strength e.g. multivalent ions are strongly held in comparison to mono or divalent ions by cation exchange resin. The order of sorption for cation resin is:



The sorption strength of resin increases with decreasing diameter of hydrated cation. It also depends upon kind of active group present and phenomena of complexation. The weakly basic resins are good for multivalent anions. The order for sorption of anions on resin is:



(e.g. Dowex-1 resin). For Dowex 2 resin order is slightly altered for OH^- ion. Here the valency, diameter of hydrated ion, strength of acid and structure of ion decides the selectivity scale. For weakly basic anion exchange resin the order is: $\text{HCO}_3^- < \text{CH}_3\text{COOH} < \text{F}^- < \text{Cl}^- < \text{SCN}^- < \text{Br}^- < \text{I}^- < \text{NO}_3^- < \text{OH}^-$.

(f) *Cross linking and swelling*: One can vary crosslinking from 1-16%. When the resin is immersed in solution, it swells and gets saturated with that solution. The swelling decreases with increasing crosslinkages and decreasing size of hydrated species (Table 12.1) is shown.

Table 12.1 Swelling of cation exchange resin

% DVB	Swelling (mg of water per mill equi. of resin)					
	Ionic radii ($^{\circ}\text{A}$) \rightarrow	9.0 (H^+)	6.0 (Li^+)	4.2 (Na^+)	3.0 (K^+)	2.5 (Cs^+)
4		417	357	303	294	233
8		219	196	172	167	144
16		128	119	99	95	86

Table 12.2 Swelling of anion exchange resin

% DVB	Swelling (mg of water per mill equi. of resin)				Resin capacity	
	Ionic radii ($^{\circ}\text{A}$)	3.5 (F^-)	3.0 (Cl^-)	3.0 (Br^-)		3.0 (I^-)
4		345	264	181	85	3.47
8		185	139	100	67	3.10
16		128	114	87	65	1.91

The resin with low (%DVB) can swell more readily than with high %DVB (Table 12.2). The mechanical resistance is good and it has better selectivity. Low pore size give low swelling and low rate of exchange. On an average good resin contains 8% DVB. Otherwise this is mentioned as Dowex 50W-X12 (meaning 12% DVB). The swelling is measured by weighing, the saturated resin with solution followed by driving out solution out of resin on centrifuge in vacuum and weighing resulting dry resin. The difference between the two figures gives swelling capacity of the resin.

- (g) *Porosity*: Resins as a rule are porous. Porosity determines its selectivity. Pore size is obtained by vapour pressure measurement. For resins, the pore size varies from sample to sample hence mean value is accepted for actual pore size.
- (h) *Resistance*: Let us consider chemical resistance of resin. Most of the styrene based resin are safe in strong acid or strong base; but condensation type of resin (e.g. phenol formaldehyde) are affected by alkalies. So also anion resin containing $-\text{COOH}$ group. The deciding strength is $>1 \text{ M}$ for base. The storage of anion exchange resin must be done in the chloride and not in

hydroxyl form as such resins release OH^- ion in water. Few resins are affected by strong oxidising agents and also are unaffected by reducing agents. The strong oxidising agents which attack resin are KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, H_2O_2 , hot conc. HNO_3 . The rapid swelling spoils these resin. Those resin beads with large size ($20\text{-}60^\circ\text{A}$) split readily in small pieces.

- (i) *Rate of Exchange:* On immersing resin in solution, an equilibrium is established between resin and the hydrophilic solution. Such rate of exchange depends on size of exchanging ion and grain size of the resin as the process of the diffusion is in continuous operation during exchange reaction.
- (j) *Effect of temperature:* At high temperature, the resin tends to pulverise with loss in swelling and splitting of active groups. Polystyrene base resin are stable even at high temperature. Anion exchange resins are more sensitive to high temperature. The selectivity for ions decreases with rise in temperature, but diffusion is accelerated for ions with temperature. On thermal heating, one can observe loss of crosslinking and also loss of the ionogenic groups. Thus it loses % DVB at 50°C . For OH^- anion exchange resin loss of ionogenic group is significant ($\sim 15\%$ loss). They dissociate in following manner
- (a) $\text{CH}_2\text{N Me}_3\text{OH} \rightarrow \text{CH}_2\text{OH} + \text{NMe}_3$ (60%)
- (b) $\text{CH}_2\text{N Me}_3\text{OH} \rightarrow \text{CH}_2\text{NMe}_3 + \text{MeOH}$ for anion exchange resin. Weak base anion exchange resin are more stable at high temperature.
- (k) *Resins in nonaqueous solvents:* Solvents like methanol, acetone, acetic acid, benzene, pyridine all have definite effect on swelling capacity of resin. It depends upon polarity and dielectric constant of the solvent. The exchange capacity lowers as few adsorb better in these solvents. Water behaviour is altogether different with the mixtures of solvents. Selectivity can be improved in non aqueous solvents.
- (l) *Exchange characteristics:* The electroneutrality is followed and accordingly equivalent amount of cation/anion are exchanged. It is a stoichiometric exchange. The exchange reactions are invariably reversible. The conversion to suitable form (H^+ with hydrochloric acid for cation) or (OH^- with ammonia and not sodium hydroxide for anion) is rapid. After conversion resin should be thoroughly washed with deionised water before further use for exchange reactions. Chelating resins like Dowex A-1 are useless as their conversion reactions are extremely slow.