CHAPTER I

SECTION A.

INTRODUCTION AND REVIEW OF PREVIOUS WORK

A heterogeneous system is characterized by the simultaneous presence of a number of distinct phases. The separate phases may be solid, liquid or gas. There may be heterogeneous systems consisting of two or more solid or liquid phases or combination of solid, liquid and gas phases. Thus, the number of equilibria possible in heterogeneous systems is very large and the scope of study of such equilibria is wide and of varied interest to scientific workers in chemistry and allied fields. The present investigation includes topics of interest in connection with the equilibrium at the interface of several exchangers of inorganic origin and aqueous solutions of different electrolytes both organic and inorganic. Kaolinite, montmorillonite, vermiculite, illite, silica gel and hydrated alumina are used as the solid phases.

The interactions at the solid liquid interface under consideration may be considered to take one of several forms. The electrolytes may be adsorbed partially or completely in which case the situation is essentially the same as molecular adsorption. The change may, however, exhibit a different picture as well. The ions of one sign are held by the solid matrix with a strong force and the ions of opposite sign, the so-called counter ions are held loosely in a diffuse or secondary layer. In the latter case the ions may be displaced by similar ions. This is the familiar ion-exchange process. In resins, zeolites, aluminosilicates etc. the primary ions are essential components of the solid matrix.

As adequate knowledge of the architecture of these exchangers are necessary for satisfactory interpretation of the equilibrium data, the structure of the minerals are briefly described first.

Architecture of exchanger Minerals:

Clay minerals viz. kaolinite, montmorillonite, illite, vermiculite, chlorite and mixed layer-lattice type minerals have been identified in the vast majority of natural soils. The correlation between the structure and exchange properties of these minerals has been established from a crystallo-chemical point of view on the basis of the important contributions of Pauling (198), Bragg (31), Gruner (95), Brindley (30), Hofmann (110), Marshall (161), Hendricks and others (105),(171),(117),(176),(13),(243),(92),(174). From these studies clay minerals are recognised to consist essentially of two units. One is composed of two layers of closely packed oxygens or hydroxyls in the centre of which aluminium or magnesium ion is arranged in such a manner that the six oxygens or hydroxyls are in octahedral coordination with the metal ion. With aluminium in the octahedral position only two thirds of the possible positions are filled to balance the structure. It is the gibbsite structure having the bulk formula $Al_2(OH)_6$. When magnesium is present in octahedral coordination all the possible positions are filled up giving the brucite structure having the bulk formula $Mg_3(OH)_6$.

The other unit is the tetrahedral silica layer. Silicon atom is placed in the cavity formed by four oxygen atoms such that the latter are in tetrahedral coordination with it. The silica tetrahedra are joined together in the a, b directions, through oxygen, to form a hexagonal network which is repeated indefinitely to form a sheet. The tips of all the tetrahedra are in the same direction.

Kaolinite:

Kaolinite is composed of a single silica tetrahedral sheet and a single octahedral sheet combined in a unit so that the tips of the silica tetrahedra and one of the layers of the octahedral sheet form a common layer. All the tips of the silica tetrahedra point in the same direction and towards the centre of the unit made of the silica and octahedral sheets. These sheets which are continuous in the a, b directions are stacked one above the other in the c-direction. During stacking the oxygens of the tetrahedral layer are placed very close to the hydroxyls of the octahedral layer, so that the sheets are held tightly by hydrogen bonding as a result of which very little expansion in the c-direction is possible.

Montmorillonite:

According to the currently accepted concept, montmorillonite is composed of units made up of two silica tetrahedral sheets with a central alumina octahedral sheet. All the tips of the tetrahedra point in the same direction and towards the centre of the unit. The tetrahedral and the octahedral sheets are combined so that the tips of the tetrahedra of each silica sheet and one of the hydroxyl layers of the octahedral sheet form a common layer. The atoms common to the tetrahedral and octahedral layers become O instead of OH.

The minerals of this group are also developed by the stacking of these unit sheets one above the other in the c-direction. During stacking the O layers of one unit are close to the O layers of the other unit, so that there is an excellent cleavage between the sheets. Polar molecules can enter the space between the sheets causing expansion of the axis in the c-direction. Isomorphous substitution of other metal ions for silicon and aluminium in both the tetrahedral and octahedral layers is known to occur. Complete replacement of aluminium by iron and magnesium is found in the minerals nontronite and saponite respectively. Substitution in the tetrahedral layer in montmorillonite does take place, but to a limited extent.

Vermiculite:

It consists of alternate stacking of mica and water layers. Isomorphous replacement of Al for Si always takes place in the tetrahedral layer and replacement of the Fe for Mg or Al in the octahedral layer is limited. In natural vermiculites the net resulting charge deficiency is balanced primarily by Mg^{2+} and to some extent by Ca^{2+}. These ions are held as exchangeable ions in between the mica layers. It has also been suggested that these exchangeable ions are responsible for the orientation of water molecules. The Mg^{2+} are present in octahedral grouping with six water molecules causing the existence of two layers of water molecules, but with K^+ in place of Mg^{2+} the thickness of the water layer is monomolecular. The c-axis expansion is limited to the thickness of two water molecules.

Illite:

The micas exhibit a bewildering variety of composition in which isomorphous replacements may occur in the octahedral layer such as replacement of octahedral Al^{3+} by Mg^{2+} as in illite, the excess negative charge in part may be balanced by the substitution of OH for O. Both Fe^{2+} and Fe^{3+} may also replace some of the octahedral Al^{3+}. Only 15% of the Si are replaced by Al. They are distinguished from mica by relatively small content of K and a large percentage of water.

Silica Gel:

It is a pure mineral being an important constituent of natural clays. The molecular unit is SiO_2, and the tetrahedral unit coordination group is $[SiO_4]$. It polymerises into chains, networks and frameworks which form the fundamental basis of all silicates. The structural principles in quartz, tridymite and cristobalite are based on variations of the frameworks with the same tetrahedral pattern. The bonding in SiO_2 is intermediate between ionic and covalent. The mesomeric character of bonding in silicates makes it possible for structural interpretations to be made, both from ionic and homopolar principles. The oxygen atoms at the tips of the silicon tetrahedra on the external surfaces capture hydrogen to form OH. The hydrogen of the hydroxyl is exchangeable with other cations.

Hydrated Alumina:

Hydrated alumina exists as three types of tri-hydrates ($Al_2O_3,3H_2O$)- gibbsite, bayerite and horstrandite; two monohydrates (Al_2O_3,H_2O)- boehmite and diaspore, and two anhydrous varieties, two of which corundum and alumina are known to occur in nature. Gibbsite is the most stable hydrated form at low temperatures (below 150°C), and is present in naturally occuring bauxite, together with boehmite, and also in naturally occuring clays. The simple structure of gibbsite consists of double layers of hydroxyl groups, enclosing the aluminum atom in octahedral coordination. Successive groups are stacked so that the hydroxyl groups of one unit are directly above those of the next. As regards the hydroxyl groups, the sequence is of closest packing, open packing and so on. Gibbsite forms hexagonal plates with ready cleavage in the plane of the layers. The hydrogen of the hydroxyls are exchangeable with other cations, at pH $<$ iso-electric point and at pH $>$ iso-electric point the hydroxyls are exchangeable with other anions (231),(232). Thus hydrated alumina is an example of an amphoteric ion-exchanger mineral. The detailed nature of the surface hydroxyl groups of alumina is a problem on which the last word is yet to be said.

Ion-Exchange

Excellent reviews (193),(31),(93),(30),(110),(161),(105),(171),(117),(176),(13),(243),(92),(174) are now available on the ion-exchange characteristics of the above minerals. In view of the great fundamental and practical importance in the present investigation, the causes of cation exchange capacity of the clay minerals are enumerated below:

(1) Broken bonds around the edges of the silica-alumina units give rise to unsatisfied charges which are balanced by adsorbed cations. The number of broken bonds, hence the exchange capacity due to this cause, increase as the particle size decreases. In kaolinite, broken bonds are the major cause of exchange capacity.

(2) Substitution within the lattice of trivalent aluminium for quadrivalent silicon in tetrahedral sheets and of ions of lower valency, particularly of magnesium for aluminium in the octahedral sheets results in unbalanced charges in the structure of some clay minerals. In montmorillonite and vermiculite this cause contributes to 80 percent of the total exchange capacity. There is very little isomorphous replacement in Illite and practically no such contribution to the exchange capacity in kaolinite.

(3) The hydrogen of exposed hydroxyls are also replaced by a cation which is exchangeable. This is also believed to account for part of the exchange capacity of the minerals.

The exchange capacities of silica gel and hydrated alumina, as pointed out earlier (P4,5) are considered to be due to the third cause.

Systematic studies of cation exchange in pure minerals were carried out by Page and Baver (197), Bar and Tendorloo (7), Hendricks and Alexander (104), Schachtschabel (218), Mukherjee (188) and others. Most of those investigations were based upon exchange equilibria, selectivity etc. with simple inorganic ions. Exchange reactions involving clay minerals with organic compounds have also been established by different scientists (225),(82),(83),(111). Small organic cations are seen to be taken up by the aluminosilicates upto the extent corresponding to cation exchange capacity, while larger ions may be adsorbed in excess, being held up by van der Waals and/or hydrophobic forces. It has been observed that the sorption of organic molecules takes place on the surface of the aluminosilicate of the fixed lattice group viz. kaolinite, while they penetrate between the unit layers of expanding lattice group of minerals viz. montmorillonite, vermiculite etc. Exchange studies with complex ions are also known (166),(173),(154),(44),(52),(51).

The measurement of the base (cation) exchange capacity (b.e.c.) when combined with other methods, is useful in the identification of clays and related ion-exchangers, details of which has been discussed in Ch. I, pp 6-33. The b.e.c. is known to be dependent upon the (i) nature of the clay mineral, (ii) its particle size, (iii) concentration and nature of the exchanging and exchangeable cations, (iv) temperature, (v) pH and (vi) anions, when they change the pH or in some way interact with the exchanger matrix or the exchanging cations. In view of these controlling factors, an accurate determination of the exchangeable cations or the b.e.c. is rendered difficult. Numerous methods are in vogue (126),(203),(202). The specificity of the effect of cations on the exchange capacity of clay minerals have been shown by Mitra (180) Mukherjee (186) and by Jenny and coworkers (118). The order of ease of entry by exchange was $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+ < H^+$ and $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+} < La^{3+} < Th^{4+}$, which is the normal lyotrope series (84),(118). It has also been shown that titrations carried out in the presence of salts give higher value than those in which the base alone is used.

There is considerable variation in the strength of binding of a given cation by different exchangers, but in certain cases, a given mineral shows different affinities for a given cation. This was demonstrated by Weigner and Mitchell and later extended to clay minerals by Weigner and Renold (244). Later this was demonstrated for montmorillonite and kaolinite by Ganguly and Mukherjee (74), and for hydrated alumina by Churms (45) and Peri (204). Certain other complications also arise, when the anion associates with the exchanging cations in solution (Cf. pp 34). The whole situation is therefore one of confusion. The b.e.c. values determined are obviously dependent upon the experimental technique employed.

Also the fixation effect of cations in clay minerals is a process in which considerable attention has been drawn. The fixed cation is rendered non-exchangeable when part of the entering ions become fixed, the total exchange capacity of the clay is apparently increased. This property was shown to be characteristic of montmorillonite (121) and illite groups (33). The dominant factor in fixation processes is the ionic size. Ions which are of such size that they fit into the 'holes' in the exchanger matrix, show the strongest tendency to become fixed, e.g. K^+, Cs^+, NH_4^+ etc.

The exchange of an inorganic ion for organic ions was studied by Barrer in a series of papers (10). The sorption properties of montmorillonite was seen to change with the adsorption of quaternary ammonium ions $(CH_3)_4N^+$ and $(C_2H_5)_4N^+$. Due to adsorption of these ions the lamellae of the clay minerals are opened and increased amounts of oxygen is adsorbed in the inter-lamellar space. Organic cationic dyes are also known to exchange on the surface of clay minerals, and other exchangers. The sorption of methylene blue was studied by many workers (34),(18), (6),(207),(112),(58). Most of these studies were related to surface area measurements. The sorption of crystal violet and malachite green were also studied on various minerals (196),(230),(160),(150),(239),(135). These workers have also shown that when the dye molecules are present in solution as micelles (generally as micelles of 10 to 100 molecular units) the observed exchange capacity is increased.

The physico-chemical aspects of many exchange reactions with different exchangers especially of inorganic origin are still unknown in their fundamental details. This constitutes one of the objectives of the present investigation. The relevant literature has been reviewed in the next few sections of this chapter.

SECTION B.

Poly-functional exchangers

The existence of exchange spots with different bonding energies in mica was reported by Mitra (182) on the basis of potentiometric titration experiments. Shaw (232) and Grim (90) believe that in illites the broken bonds developed on the lateral surface contribute to a large extent towards their base exchange capacities (b.e.c). It is now recognised that physical accessibility of the exchange spots is one of the limiting factors which determine b.e.c. Certain specificities in the exchange behaviour of clay minerals which have been traced to their characteristic lattice configurations have also been pointed out by Mitra (180). Mukherjee and Mitra (186),(187) attempted to explain the dibasic character of kaolinite and tri-basic character of H-muscovite and illite (183) in the light of the conceptions of the electrical double layer and the primary and secondary adsorption of ions, postulated by Mukherjee (184) as well as from the lattice structure of minerals (91),(162),(191). Ganguly and co-workers have shown the tri-basicity of montmorillonite by potentiometric tritrations in non-aqueous media (77). The role of Al in exchange reactions was studied by Mukherjee and Chatterjee (185) and Marshall (162) and others. Harward and Coleman (99) showed that the double end points obtained with electrometric titrations of montmorillonite were due to H-Al clays rather than exchangeable hydrogen of different dissociations. High frequency titration of H-resin treated bentonite, illite and kaolinite (140) indicated that H-resin treatment results in the immediate appearance of some Al on the exchange complex. A hypothesis that it may be associated with broken bond cation exchange sites is suggested. The investigations of Roy and Das (214), Chakravarti (40),(41),(43) and Adhikari (1) on the electro-chemical properties of clay mineral mixtures also furnish important observations in the line for characterisation and identification purposes.

The base exchange of hydrogen laden silica gel, mica, kaolinite and montmorillonite was determined by Ganguly (73). In general, the exchange spots on the surface of the layer structure minerals are not of uniform character. There are definite energy levels of interaction, and the bonding energies are ruled by the nature and location of the atoms inside the lattice. Ganguly found a decreasing order of the acid function for silicon, aluminium and magnesium in their bonding to the H ions in the hydroxyl groups. In kaolinite structure, Ganguly and Mukherjee (76) distinguish two exchangeable positions, in bentonite and mica three of these. According to I. Martin, R. Glaeser and J. Mering (166 a) the acidity of hydrogen montmorillonite in fresh samples is typically a protonic one, but in this state the hydrogen is rapidly exchanged by aluminum. This ageing effect is highly sensitive to temperature. Evidently, the Al^{3+} ions change their positions to those of the hydrogen ions from the edges and corners of the crystals. Whereas the common Al-montmorillonite is similar in its reactions to Ca-montmorillonite, the protonic modification shows similarities with Na-montmorillonites.

In recent years it has been established both by theoretical and experimental results that the exchange sites on the surface of pure silica gel and hydrated alumina are of more than one type. The origin of such inhomogeneous surfaces are said to be due to crystal defects. The surface hydroxylation of silica was studied by Armistead, Tyler, Hambleton, Mitchell and Hockey (3) by thermo-gravimetric methods of de Boer and Vleeskens (57) and infra-red studies were carried out by others (4),(68),(56). Their results suggest that the surface hydroxylation of fully hydroxylated silicas correspond to a surface containing about 4.6 hydroxyl groups per 100 A^{o2} of the total surface area. Of these about 1.4 ± 0.1 hydroxyl groups exist as single non-hydrogen bonded species (i.e. 1.4 A-type sites/100 A^{o2}). The remaining 3.2 hydroxyls exist as pairs (1.6 ± 0.1 B-type sites/100 A^{o2}). Referring to published infra-red data this model is in accordance with the assignment of "high frequency" (3750 cm^{-1}) absorption band to the single hydroxyl species and the assignment of 3550 cm^{-1} absorption band to the hydrogen bonded surface species. A non-exchange band centered at 3650 cm^{-1} observed in freshly prepared silicas corresponds to hydrogen bonded internal or bulk hydroxyls. Peri and Hensley (205) on the basis of their researches on a theoretical model, concluded that different types of hydroxyls do exist (205),(206),(201),(3),(4).

Further support for the presence of two distinct types of hydroxyls on the surface of silica comes from the work of Tylor, Hambleton, Mitchell and Hockey (3).

Our knowledge regarding the disposition of hydroxyls on the surface of hydrated alumina is rather meagre. Much remains to be learned about the details of surface hydration, the creation of high energy sites upon dehydration, and the significance of various types of isolated hydroxyl groups on the surface of alumina. Experimental evidence in this regard stems mainly from infra-red spectroscopic studies involving hydration, dehydration, and sorption and desorption of NH_3 and CO_2 on alumina surface (203),(247),(132),(206),(204). A theoretical model has been developed by Peri (204) to account for the surface hydration properties of γ-alumina. This model postulates the existence of different types of hydroxyls on the alumina surface.

At surface coverages greater than about 10% of monolayer, according to Peri, some hydroxyl ions are said to have one or more hydroxyl ions as nearest neighbours, and inter hydroxyl hydrogen bonding is assumed to occur between them. Since both protons in a pair of adjacent hydroxyls cannot simultaneously form bonds, this should give rise to an isolated hydroxyl infra-red band. The influence of the adjacent (hydrogen bonded) hydroxyl cannot be assessed exactly. Hydrogen bonded hydroxyl groups produce broad bands at frequencies below those of isolated hydroxyl groups. In highly hydrated systems, hydrogen bonding would be expected to be extensive on the model surface although an isolated band or bands would be expected to persist.

In the midst of this speculation regarding the nature of the exchange sites on the alumina surface certain facts established must be reckoned with - a) that more than one type of exchangeable hydroxyl (or proton) does exist on the surface (204) and (b) sorption of solvent and ion-exchange in the pores of alumina is significant as compared to sorption on the external surface (209), (45).

In the present thesis the experimental data obtained from adsorption measurements involving [illegible] Tl^+, has been presented and compared in the light of the above knowledge, on exchangers H-bentonite, silica gel and hydrated alumina.

SECTION C.

Thermodynamic Quantities, theoretical models and formulations in ion-exchange equilibria.

Theoretical Models:

Several approaches (189) both qualitative and quantitative have been made to understand the equilibria between an ion-exchanger and ions in solution. Experiments were conducted in which concentrations of ions were varied, the results suggesting an exponential relationship between the ions adsorbed (or desorbed) and concentration of the exchanging cation. Limitations have been tacitly accepted in most mathematical treatments of exchange reactions. Thus (a) the simultaneous presence of both cation and anion exchange reactions in a given system have been considered rarely, (b) the exchange capacity of the cation or anion exchanger has been assumed to be constant, though cases are known where the exchange capacity varies markedly with the pH and the nature of the exchanging ion, (c) simple stoichiometric equivalence between ions taken up and released is generally assumed to be present; deviations are usually explained in terms of simultaneous adsorption of molecules or formation of complex ions, (d) finally, perfect reversibility is taken for granted.

// On this basis the Freundlich and Langmuir adsorption equations were proposed. The original form of the Freundlich equation is

$$\frac{x}{m} = KC^{1/p}.$$

where x is the amount adsorbed, m the weight of the material taken and C the equilibrium concentration of the electrolyte; K and 1/p are constants. Wiegner (244) used this equation in 1912.

The two main weaknesses with regard to this equation is that it does not flatten out at higher values of C, as a system with a fixed exchange capacity should, secondly, while Wiegner showed that the position of equilibrium is independent of volume, the Freundlich equation shows a variation in exchange with variation of the total volume. The second objection was however overcome by Jenny in 1926 from his equation

$$\frac{x}{m} = K. \left(\frac{c}{a-c}\right)^{1/p}$$

With the flexibility afforded by the two constants, good agreement is often obtained with experimental data over a limited range. However, Marshall (165) has shown that it was superior as regards K, but 1/p varied erratically. A similar type of equation to the Langmuir's, with only one constant was proposed by Vageler (235) but it could not account for the variability of equilibrium with volume.

The first use of the law of mass action in formulating ionic exchange as a completely reversible reaction was made by Ganssen (73). Kerr (127) investigated specific mass action equations for monovalent, monovalent and monovalent-divalent exchanges; these took the forms:

$$\frac{(\bar{X}) . (Y^{+})}{(\bar{Y}) . (X^{+})} = K_1; \qquad \frac{(\bar{X})^2 . (Y^{+2})}{(\bar{Y}) . (X^{+})^2} = K_2$$

the bar indicates the ion in the exchanger phase.

The constants K_1 , K_2 are termed as selectivity coefficients. The ionic terms represent concentrations in equilibrium solutions. But owing to a lack of knowledge about the activities of the ionic species in the exchanger phase the equilibrium constant could only be evaluated qualitatively or empirically. Bauman (17) and Gregor (88) pointed out the difficulties in terms of swelling and volume change particularly of the resins. The model introduced by Gregor, although thermodynamically less well-defined brings out clearly the physical action of the swelling pressure. A more rigorous application of the law of mass action has been made by Boyd and his Co-workers (26) in which the "solid solution" idea of Vanselow (236) has been the basis on the assumption that the ion-exchange is a "solid-solution" process.

A more elaborate use of the mass action principle in which clay substrates are treated as bi-functional with respect to single cations has been tried by Garrels and Christ (79) and by Blackmon (24). The data examined were the potentiometric titration curves of Marshall and co-workers. In this treatment the exchangeability of a given ion upon a given type of site is assumed to be independent of the proportion of sites occupied and of the nature of complementary ions present. This assumption has been disproved later form a consideration of statistical models. However, doubts regarding the application of the principle of law of mass action were first clearly expressed by Weigner and co-workers (245) in 1933. In order to explain some of their experimental results they postulated the existence of lossely and firmly bound ions on the surface of the same exchanger. Without the necessary information regarding the surface characteristics of the silicates which Wiegner used for his work he had to invoke the idea of the existence of micro-pores, edges and cleavages.

In 1936 Jenny (119) developed the first statistical thermodynamical model of exchange reactions on monofunctional surfaces. He assumed that the counter-ions compensating the framework surplus charge are located in a diffuse double layer at the colloid surface. Every counter-ion is coordinated to an exchange site and oscillates within certain volume, characteristic of the ion and its interaction with the colloid particle. Other counter ions from the solution are able to penetrate into this oscillation volume. The probability of ion-exchange occurring at a given site is calculated from the probability that a competing counter ion will enter the oscillation volume. Multivalent counter-ions occupy several neighbouring sites. The Fowler-Guggenheim (66) theory of adsorption for mono-molecular layer was adapted by Davis (54),(55) to this model, for the case of multiply charged ions. Later the Davis statistical treatment was extended by Sakai (217). The equation derived includes an interaction energy term characteristic of differences in the mode of occupancy of neighbouring sites. Sakai claims success in applying his equation to ion-exchanger gels also. Krishnamoorthy and Overstreet (143) applied the statistical method as has been used by Fowler (65) and Guggenheim (94) in the case of gas adsorption on a solid surface. The attempts to understand ion-exchange reactions on the basis of the electrical double layer, as postulated by Mukherjee (184) yields no doubt qualitative results but the concept in many respects, conforms better with observations. He assumed two categories of exchangeable ions, the osmotically active ions which constitute the mobile part of the double layer and the osmotically inactive ones constituting the immobile part of the double layer. The interpretation of the electro-chemical properties of clays in terms of these two categories of ions has been in many ways very fruitful. The relationship of crystalline structure of clays, their electrochemical properties and ion-exchange characteristics have been studied in their fundamental details by Mukherjee and Mitra (186), Mitra and Bagchi (161), Ganguly and Mukherjee (75) and Chakravarti (40).

Kielland's Model:

The first attempt to describe ion-exchange equilibria by a theoretical equation which accounts for deviations from the regular pattern was given by Kielland (131). He introduced the use of "solid-phase activity coefficients". Kielland followed Vanselow (237) in treating the hetero-ionic form of the ion-exchanger as a "solid-solution" of the components AR and BR (where R symbolises the structural unit of the exchanger). For the exchange of univalent ions

$$AR + B \rightleftharpoons BR + A$$

the mass action law in its general form is,

$$\frac{\bar{a}_{AR} \cdot a_B}{\bar{a}_{BR} \cdot a_A} = K = \text{Constant} \quad \ldots \quad (1)$$

where K is the thermodynamic equilibrium constant. Kielland assumed a van der Waals type of equation of state and obtained the following relations for the rational activity coefficients in the solid:

$$\ln \bar{f}_{AR} = c \cdot \bar{N}_{BR}^2 \; ; \; \ln \bar{f}_{BR} = c \cdot \bar{N}_{AR}^2 \quad \ldots \quad (2)$$

$\bar{f}_{iR}$ = rational activity coefficient of the component iR;

$\bar{N}_{IR} = \dfrac{\bar{n}_{iR}}{(\bar{n}_{AR} + \bar{n}_{BR})}$ = mole fraction of the component

iR in the solid; c is an empirical constant.

The selectivity coefficient $\underline{K}$ is obtained as

$$\ln \underline{K} = \ln K + c(\bar{N}_{AR}^2 - \bar{N}_{BR}^2) \quad \ln \frac{A}{B} \qquad \ldots \quad (3)$$

This relationship was given a sounder theoretical treatment by Barrer.

Barrer's Model:

Barrer (8) by the use of statistical thermodynamics, has derived an equation which is remarkably successful in describing the behaviour of most regular and irregular systems with and without phase transition. The assumptions of Barrer are as follows:-

(i) When two entering ions, B, occupy adjacent crystal sites in the A-rich lattice, an additional change in the free energy of the crystal occurs.

(ii) This change is negligible when ions A, B occupy adjacent sites relative to the state when A, A ions occupy adjacent sites.

(iii) The change in energy is additive with respect to the number of pair B, B independently of whether these pairs are in clusters or isolated.

(iv) Apart from this energy change, all other interactions between the energy change and the partition functions of ions A and B in the framework, and of the framework may be neglected.

(v) The distribution of ions on sites is assumed random.

(vi) The amount of intra-crystalline water is taken as un-altered by exchange.

In irregular systems in which accommodation of the larger ions become more and more difficult as conversion progresses, occupancy of two neighbouring sites? by two large ions is evidently less favourable than occupancy by one large and one small or by two small ions. At constant overall ionic composition (eg. zeolites) there is a characteristic difference in energy between the occupancy of two neighbouring sites by two ions B and by two ions A and B or two ions A. This energy may be written as $2E_V/Z$, where E_V is an (positive or negative) interaction energy and Z is the coordination number of the lattice. A statistical distribution of the exchange sites occupied by two ions B is assumed. The number of these pairs is $Z\bar{n}_B/2\bar{n}_Z$ ($\bar{n}_B$ = number of counter ions B in the zeolite; $\bar{n}_Z$ = number of exchange sites). In this way, a simple expression giving the total partition function of the zeolite can be obtained. By differentiation of this expression and use of the equilibrium condition, the following relation is found

$$\ln \frac{\bar{n}_A \cdot a_B}{\bar{n}_B \cdot a_A} = \ln \frac{\bar{j}_A(T)}{\bar{j}_B(T)} + \frac{\mu_A^0 - \mu_B^0}{kT} + \frac{\bar{E}_A - \bar{E}_B}{kT}$$

$$\frac{2\bar{n}_B}{\bar{n}_Z} \cdot \frac{E_V}{kT} \qquad \ldots (4)$$

where $\bar{j}_i$ = partition function of species i in the exchanger;

$\bar{E}_i$ = energy of species i in the exchanger;

μ_o i = standard chemical potential of species i.

After substituting equivalent ionic fractions

$\bar{x}_i = \dfrac{\bar{n}_i}{\bar{n}_A + \bar{n}_B}$ one can write Eqn (1) in the form

$$\ln \underline{k} = \ln \frac{\bar{x}_A \cdot a_B}{\bar{x}_B \cdot a_A} = \ln K + c\,(1 - 2\,\bar{x}_B) \quad \ldots (5)$$

The quantity K is the rational thermodynamic equilibrium constant, and $\underline{k}$ the corrected selectivity coefficient.

// Comparison with Eqn (1) shows that

$$\ln K = \ln \frac{\bar{j}_A(T)}{\bar{j}_B(T)} + \frac{\mu^{\circ}_A - \mu^{\circ}_B}{kT} + \frac{\bar{E}_A - \bar{E}_B}{kT}$$

$$+ \frac{(\bar{n}_A + \bar{n}_B)}{\bar{n}_z} \cdot \frac{E_V}{kT} = \text{Constant.}$$

and that the constant **c** is,

$$c = - \frac{\bar{n}_A + \bar{n}_B}{\bar{n}_z} \cdot \frac{E_V}{kT}$$

// From Eqn (5) we have a straight line upon plotting ln $\underline{k}$ versus $(1 - 2\bar{x}_B)$ the slope being equal to **c**, and the intercept giving the value of ln K. // The second term on the right hand side of Eqn (5) arises from the gain or loss in free energy resulting from interaction between the neighbouring sites occupied by ions B. In "regular" systems this term is zero since no interaction occurs. // In irregular systems in which occupancy of two neighbouring sites by two ions B is unfavourable, the constant **c** is negative.

Abstract Thermodynamic Method:

An abstract thermodynamic treatment of ion-exchange equilibria has a certain resemblance to Kielland's approach except that no assumptions are made. This treatment was developed first by Argensinger, Davidson and Bonner (2),(21),(30),(153) and by Högfeldt, Ekedahl and Sillén (61),(114),(113) and was presented in its most complete form by Gaines and Thomas (72). It requires no model with particular properties and uses only thermodynamic relations.

Ion exchange is pictured as a heterogeneous reaction involving the electrolytes AY and BY and the resinates AR and BR. Thus the components of the system are the resinates, the electrolytes and the solvent. The treatment consists essentially in the calculation of the thermodynamic equilibrium constant and the activity coefficients in the ion-exchanger from experimental measurements of the selectivity coefficients under various conditions. To this aim the Gibbs-Duhem equation is used. For the sake of simplicity solvent and electrolyte sorption effects are disregarded and the counter ions are regarded as univalent. The ion exchanger phase is regarded as a solid solution of the resinates AR and BR. The mole fractions of the latter in the solid are defined by

$$\bar{N}_{AR} \equiv \frac{\bar{n}_{AR}}{\bar{n}_{AR} + \bar{n}_{BR}} \quad ; \qquad \bar{N}_{BR} \equiv \frac{\bar{n}_{BR}}{\bar{n}_{AR} + \bar{n}_{BR}} \quad \ldots \quad (6)$$

where n_i = number of moles of species i in the exchanger.

The thermodynamic equilibrium constant K of the ion-exchange process is given by

$$\frac{\bar{a}_{AR} \cdot a_{BY}}{\bar{a}_{BR} \cdot a_{AY}} = K \qquad \ldots (7)$$

As the standard and reference states for AR and BR, the monoionic A form and B form respectively, of the ion-exchanger are chosen, so that

$$\bar{N}_{AR} = 1, \quad a_{AR} = 1, \quad \bar{f}_{AR} = 1$$

and

$$\bar{N}_{BR} = 1, \quad a_{BR} = 1, \quad \bar{f}_{BR} = 1 \qquad \ldots \quad (8)$$

The rational equilibrium constant K and the corrected selectivity coefficient k are interrelated by

$$k \equiv \frac{\bar{N}_{AR} \cdot a_{BY}}{\bar{N}_{BR} \cdot a_{AY}} = K \cdot \frac{\bar{f}_{BR}}{\bar{f}_{AR}} \qquad \ldots \quad (9)$$

Differentiation of Eqn (6) yields

$$d \ln K = d \ln \bar{f}_{BR} - d \ln \bar{f}_{AR} \qquad \ldots \quad (10)$$

The application of Gibbs-Duhem equation to the ion-exchanger phase gives

$$\bar{N}_{AR} \cdot d \ln \bar{f}_{AR} + \bar{N}_{BR} d \ln \bar{f}_{BR} = 0 \qquad \ldots \quad (11)$$

By combination of these equations, use of $\bar{N}_{AR} + \bar{N}_{BR} = 1$ and $d \bar{N}_{AR} + d \bar{N}_{BR} = 0$ and partial integration under the restriction (5) one obtains

$$\ln \bar{f}_{AR} = - \bar{N}_{BR} \cdot \ln K + \int_{\bar{N}_{BR}}^{1} \ln K \cdot d \bar{N}_{AR} \qquad \ldots \quad (12)$$

and, $\ln K = \int_0^1 \ln \underline{k} \; . \; d\,\bar{N}_{AR}$ ... (13)

The activity coefficients and the rational thermodynamic equilibrium constant can be calculated by graphical integration according to eqns (9) and (10). The numerical values of these rational quantities cannot be compared to the corresponding molal quantities because of different choice of the standard and reference states. It may be emphasized that the rational equilibrium constant, in contrast to the molal equilibrium constant is characteristic of the selectivity of the ion-exchanger.

Pauley's Model:

Pauley (199) has intepreted selectivities in ion-exchange equilibria in the language of a very simple model. Its essential feature is the electrostatic attractions between the counter ions and the fixed ionic groups. It is assumed that all the counter ions in the ion-exchanger are found at their distance of closest approach to the fixed ionic groups. Writing AR and BR for the pairs of fixed ionic groups and counter ions at the distance of closest approach, one can split the exchange of A for B into the two processes:

$$AR \rightarrow A + R \quad \ldots \quad (14)$$

$$R + B \rightarrow BR \quad \ldots \quad (15)$$

Coulomb's law (without any correction) leads to the following results for the above processes:

$$\Delta G_1^0 = \int_{a_A^0}^{\infty} \frac{e^2}{r^2\epsilon} \cdot dr = \frac{e^2}{a_A^0 \cdot \epsilon} \quad \ldots \quad (16)$$

and

$$G_2^0 = \int_{\infty}^{a_B^0} \frac{e^2}{r^2 \cdot \epsilon} \cdot dr = - \frac{e^2}{a_B^0 \cdot \epsilon} \quad \ldots \quad (17)$$

where ΔG_1^0 and ΔG_2^0 are the free energy changes for the processes (14) and (15); e = electronic charge;

ϵ = dielectric constant; r = distance from centre of fixed charge; a_1^0 = distance of closest approach between counter ion 1 and fixed ionic group. Hence the overall free energy change is

$$\Delta G^0 = \Delta G_1^0 + \Delta G_2^0 = \frac{e^2}{\epsilon} \cdot \left(\frac{1}{a_A^0} - \frac{1}{a_B^0} \right) \quad \ldots \quad (18)$$

and the thermodynamic equilibrium constant K is

$$\ln K = - \frac{\Delta G^0}{kT} = \frac{e^2}{kT\epsilon} \left(\frac{1}{a_B^0} - \frac{1}{a_A^0} \right) \quad \ldots \quad (19)$$

Therefore, a linear relationship should hold between ln K and $1/a_1^0$. The model leads qualitatively to preference of the ion-exchanger for counter ion with the smaller a^0 value and counter ion of higher valency (51).

Thermodynamic Formulations:

Direct attempts to measure heat changes have met with little success. For ions of the same valency this situation is evident from the fact that though heat of adsorption values are known to be smaller than 2K Cals/mole, values greater than 1 K Cal/mole are seldom met with; of course in exceptional cases values as high as 10 K Cals/mole are on record.

A more promising approach to thermo-chemical quantities is through study of the variation in apparent equilibrium constant with temperature. The method was followed by Marshall and Mukherjee to good effect (190). The temperature dependence of equilibria is in general related to the standard enthalpy change, the standard free energy change and the entropy change. The temperature dependence of ion-exchange equilibria is given by the thermodynamic relationships (28),(60)

$$\frac{(d \ln K)}{dT} = \frac{\Delta H^0}{RT^2}$$

and $\Delta G^0 = -RT \ln K$ and the thermodynamic equilibrium constant and selectivity are interrelated by

$$K = k \cdot \left(\frac{\bar{f}_A}{f_A}\right)^{|z_B|} \cdot \left(\frac{f_B}{\bar{f}_B}\right)^{|z_A|} \cdot \left(\frac{\bar{a}_W}{a_W}\right)^{h} \cdot \left(\frac{\bar{a}_{AY}}{a_{AY}}\right)^{g} \left(\frac{a_{BY}}{\bar{a}_{BY}}\right)^{f}$$

where K is the rational thermodynamic equilibrium constant, and ΔH^0 and ΔG^0 the standard enthalpy and free energy changes of the ion exchange $\bar{A} + B \rightarrow \bar{B} + A$; $\bar{f}_i$ and f_i are the activity coefficients in exchanger and solution and $\bar{a}_i$, a_i the activities in exchanger and solution phases respectively; h,g,f are moles of solvent, AY, BY sorbed (or desorbed).

Experiments carried out at two different temperatures enable the calculation of the heat of adsorption or enthalpy of the reaction ΔH from the use of the integrated Clausius-Clayperon equation:

$$\Delta H = \frac{R \cdot T_1 T_2}{T_1 - T_2} \cdot \ln \frac{C_1}{C_2}$$

where C_1 and C_2 are the amounts of adsorbate in the solution phase at temperatures T_1 and T_2 corresponding to the same amount retained in the solid phase at the two different temperatures. Then from the relation

$\Delta F = \Delta H - T \Delta S$, since $\Delta F = 0$

at equilibrium, we have $\Delta S = \Delta H/T$. Here ΔH, ΔF and ΔS are the partial molal quantities, characterising the aqueous phase in adsorption. Barshad (14) has measured ΔH directly by differential thermal analysis. Application of the Gibbs-Duhem equation, $n_W\, d\bar{F}_W + n_W\, d\bar{F}_m = 0$ etc, those provides a means of passing from the three quantities ΔF, ΔH and ΔS to corresponding values for the exchanger phase.

In most cases, selectivity results from association or aggregation processes such as complex formation in the ion-exchanger or solution, ion-pair formation, solvation etc. These processes are usually discouraged by an increase of temperature. Hence the selectivity should be expected to decrease with increase of temperature. From general thermodynamic considerations also, the process of ion-exchange should be an exothermic one as it is associated with a decrease of free energy and entropy. This is often, but not always the case (23), (22), (46), (59), (139), (140), (169). No interpretation for exceptional behaviour has yet been advanced.

Ion-exchange processes are often accompanied by other processes which result in considerable changes in entropy (46),(151),(224). The more important contribution to the "driving force" of ion-exchange, i.e. to the free energy change, stems from the entropy change given by Δ S. This term arises mainly from the entropy of mixing, configurational entropy changes of the matrix and from changes in order of solvent molecules resulting from the formation and degradation of aggregates and solvation shells. The interpretation of entropy is thus still somewhat speculative. However, considerable amount of work have been done with respect to heat changes associated with the hydration and dehydration of the exchanger matrix, and it has been recognised that the process of exchange of cations for protons involves exchange across a fixed layer of water molecules on the exchanger surface (12),(157),(152),(149),(213),(243),(64),(223). It has also been established that water plays a very important role in exchange processes, since the hydration energy of exchangers ranges from tens of thousands of calories downwards. In this respect the contributions of Low, Martin, Lawrence, Rai Puri et al, Marshall and others need careful consideration.

Thermodynamics of the exchange of Tl(I) on synthetic ion-exchange resins have been carried out by Starobinets and Soldatov (237) and by Bonner and Pruett (23).

In the present thesis the exchange data obtained with bentonite, silica gel and aluminium hydroxide and the inorganic cation Tl in solutions of $TlClO_4$ and TlCl have been applied to some of the well known models viz, the abstract thermodynamic method, Kielland and Barrer's models and the model of Pauley. Attempt has also been made to evaluate the heat of adsorption, the free energy changes and entropy changes from adsorption studies at different temperatures.

SECTION D.

Polarography of insoluble substances:

The versatility of the polarograph has been amply demonstrated, ever since the invention of the polarograph as an electro-analytical tool. The great majority of polarographic work has been done to this day, with electro-active substances in true solution. Studies on polarography of suspensions of gases and solids are also known, though quite scanty in comparison with those of the former.

The versatile technique was also extended for studies in the domain of macro-molecules. Thus Kolthoff, Brdicka, Stricks and others (228), (136a), (179) used it for studies on proteins. Stricks and Chakravarti (228) applied it to study the interaction of sulphydryl groups present in proteins with ethyl mercury chloride. Chakravarti (39) also noticed a shift of half wave potential of the reduction wave of $Coen_3Cl_3$ when a small amount of a stable suspension of bentonite or illite is added to the experimental solution. Similar shifts of half-wave potential have also been observed in complex forming reactions by different workers (257). Thus the shift in half-wave potential is considered as an index of complexation.

Hicks (179) has shown that various insoluble substances in the form of a suspension undergo direct reduction at the dropping mercury cathode. Majer (153) suggested that the transport of positive charges of colloidal micelles results in the depolarisation of the dropping mercury cathode; the reduction of the micelles seemed to be very much probable. These findings were confirmed by the results of study of suspensions of carbon blacks made by Hallum and Drushel (93). They stated that the chemi-sorbed oxygen on the surface of carbon particles is responsible for the reduction current and showed that with suspensions of certain types of carbon black in dimethyl formamide it was possible to obtain well reproducible polarographic waves. Micka (179) showed that in stirred suspensions of active charcoal a relatively great reduction current flows through the polarographic cell, while in a quiet suspension no current is observed, which is quite in contrast to normal polarographic work in true solutions. He has divided substances investigated into four classes. Firstly, suspensions of materials, such as activated charcoal and oxides like manganese oxide and cuprous oxide; these gave irregular waves, not at all reproducible. Secondly, fresh precipitates, such as sulphides of lead and mercury ; these gave good waves with a sharp and reproducible maximum. The potential at which current was maximum was characteristic of each precipitate. The third class consisted of suspensions like silver chloride and silver oxide, with which the currents decreased on standing. This was attributed to the alteration of the state of the particles due to ageing. Finally, the fourth class of substances included insoluble materials, such as barium and lead sulphates. These gave no currents. It has been stated that strong adsorption on the electrode surface is necessary if reproducible polarographic wave is to be obtained, and that the current is a function of the potential of the dropping mercury electrode. The most striking and important result of this work is that substances of equal chemical composition but of different crystallographic constitution behave differently. Such distinction without the aid of X-ray analysis, had never been possible before. It brought to light the important role of the type of the crystal lattice in the polarographic behaviour of suspensions.

The polarographic study of some other physico-chemical aspects associated with suspensions are also reported in literature. Measurement of the rate of attainment of equilibrium with finely divided solids have been attempted by Tyler and Karchmer (233) and by Vodenhal and Markel (240). The former deals with the rate of attainment of an ion-exchange reaction equilibrium, and uses a shielded dropping mercury cathode. The latter method is based upon the polarographic determination of the unreacted ion in the heterogeneous system. He also studied the effect of the degree of cross-linking on sulphonated catexes of the naphthalene-phenol-formaldehyde type, and also the influence of the degree of acidity on the rate of attainment of equilibrium. The results of these workers were improved by Zagorski (250) who developed a new type of cell especially suited for the measurement of surface areas of finely divided solids in suspension. The method was based upon the rate of dissolution of a solid in suspension. Zagorski's technique also made possible the study of heterogeneous kinetics, i.e. the adsorption of polarographically active substances in suspension of adsorbent, where the adsorbent is inactive. The curve of adsorption was found to have an opposite direction to the curve of dissolution, and its slope and shape indicate the accessibility of pores. This was checked for the adsorption of methylene blue on Fuller's earth. The method has severe limitations and hence has not found universal application.

Oscillographic polarography with suspensions was carried out by Kalvoda using alternating current at 50 c/s (123). It was observed that the colour of a substance has a certain significance; some white substances are not reducible, e.g., tin (IV) oxide, tantalum (V) oxide, titanium (IV) oxide, zinc sulphide. Reducibility was also found to depend upon the size of the cation constituting the insoluble compound particle. Thus it was found that freshly prepared precipitate of elementary sulphur is more active than an old sulphur or sulphur flowers.

However, no effect was observed upon the reduction potential due to differences in particle size. Taking into consideration colour and size effects, predictions were made regarding the reducibility of certain substances, e.g., copper (II) oxide, mercury (II) selenide, etc., which are easily reducible.

In the present thesis certain polarographic studies have been carried out with suspensions of cation-exchangers viz., bentonite, vermiculite, illite, kaolinite, silica gel and Al(OH)$_3$, on which is adsorbed some electro-active ion like Tl or Coen$_3^{3}$ or methylene blue cation.