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THERMOCHEMISTRY OF ION EXCHANGE
IN POROUS CRYSTALS

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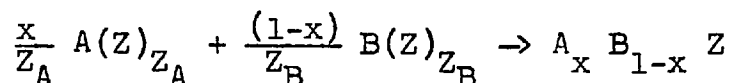
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ABSTRACT

Exchanges involving the ion pairs Na - Li, Na - K, Na - Rb, Na - Cs, Na - Ag, Na - Tl, Na - Ca, Na - Sr and Na - Ba have been studied in the zeolites chabazite and Linde Sieve Y. The Na - NH_4 and Na - Pb exchanges have also been studied in chabazite. The variation of the standard heat of ion exchange with the extent of exchange has been measured calorimetrically at 25°C. The standard heat of complete ion exchange, ΔH° , involving 1 equivalent of each of the reactants and products in their standard states has been found to be in the range 0 to 3 kcals/gm. eq. In the exchanges involving only univalent ions, ΔH° was negative when the ion of larger crystallographic radius entered the zeolite, whereas in the uni-divalent exchanges ΔH° was positive when the divalent ion entered the zeolite, except for the Na - Ba exchange in Linde Sieve Y which had a small negative heat.

From the equilibrium isotherms the standard free energies of exchange and the activity coefficients of the components in the exchanger have been calculated. Limited exchange has been observed in several of the exchange systems, and an attempt has been made to correlate these limits with the distribution of cation position in the exchangers.

The thermodynamic data for the exchanges have been used to evaluate the free energy, heat and entropy changes for the formation of the mixed exchanger from its components i.e. the reaction represented by



involving x equivalents of $A(Z)_{Z_A}$, $1-x$ equivalents of $B(Z)_{Z_B}$ and 1 equivalent of the mixed exchanger $A_x B_{1-x}(Z)$. A comparison of these functions has been made with those corresponding to ideal behaviour. The results indicate that the mixed exchanger cannot be regarded as an ideal solid solution of its components.

Comparisons have been made with isotherms obtained in these systems by other workers and with isotherms involving other zeolites.

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INTRODUCTION

The process of ion exchange between a solid exchanger and an electrolyte solution has been extensively studied in recent years and a great deal of experimental data obtained. However, the exchange process and the effect of the solvent are not fully understood and no adequate theory of ion exchange has been formulated. Ion exchange in organic resins is further complicated by the volume changes which occur in the resins during exchange. These volume changes do not arise in certain of the inorganic ion exchangers e.g. the zeolites, and these exchangers are therefore more suited to a fundamental study of ion exchange as a solid state reaction.

The determination of the thermodynamic data for these ion exchange reactions can lead to a better understanding of the exchange process. Comparisons can also be made with the predictions of theoretical models.

The determination of the heats of ion exchange by observing the temperature dependence of the thermodynamic equilibrium constant has proved unsatisfactory since these heats are small (< 3 kcal/gm. eq.). Consequently heats of ion exchange must be measured calorimetrically where this method is possible.

The crystalline exchanges used in this work are

- a) the naturally occurring zeolite chabazite and
- b) the synthetic zeolite NaY. The ion exchange equilibrium properties of these zeolites have been investigated to some extent (49) (59), although no attempts have been made to determine the heats of ion exchange. NaY has the same framework structure as NaX, whose exchange properties have already been investigated in these laboratories (15), but differs in the number of cations per unit cell. Thus a comparison can be made of the effect of the framework charge density on the heats of ion exchange.

1.1. Structure of Aluminosilicates

The silicate materials are all based on the tetrahedral SiO_4^{4-} unit. The various classes of silicate minerals can be formed by the joining of the tetrahedral unit to none, one, two, three or four other units. The zeolites, which are members of a class of silicates known as the tectosilicates, are based on a structure in which each SiO_4^{4-} tetrahedron is linked to four other tetrahedra thus forming a three dimensional framework. This framework has the composition $(\text{SiO}_2)_n$; and consequently no residual charge.

Isomorphous replacement of the Si^{4+} by Al^{3+} results in the formation of a group of minerals known as the aluminosilicates. To preserve electroneutrality cations must occupy the interstices of the framework. However, it is not possible to replace all the silicon by aluminium; the extent of substitution being governed by Loewenstein's Rule (1). From several observations on aluminosilicates Loewenstein concluded that not more than 50% of the available Si^{4+} could be replaced by Al^{3+} , if the Al^{3+} is to retain its tetrahedral configuration. Thus, if two aluminium ions are neighbours to the same oxygen, then at least one of them must have a co-ordination number greater than four.

The variety of frameworks found amongst the tectosilicates is due to the different arrangements of the linked SiO_4^{4-} and AlO_4^{5-} tetrahedra. These tetrahedra form polyhedra, which can be stacked in various co-ordinations, by sharing faces, etc. in different ways to form large intracrystalline cavities and channels which occur regularly within the crystal. The cations and any water present are located in these cavities and channels. Several types of polyhedra have been found in zeolites e.g.

- a) cubooctahedron, built from twenty-four tetrahedra. This unit is found in sodalite and is commonly called the sodalite cage. It is also the building unit of the synthetic zeolites A, X and Y.
- b) cubic cages, built from eight tetrahedra by the sharing of oxygen atoms. This type is found in NaA.
- c) hexagonal prism - built from twelve tetrahedra in two parallel six-membered rings. This is the building unit of the zeolites, chabazite, gmelinite and levynite (2).

The zeolites have been classified according to morphological properties; three-dimensional framework, lamellar and fibrous zeolites were accordingly distinguished. Typical members of each class are:

- a) three dimensional framework; NaA, NaX, NaY, chabazite,

gmelinite.

- b) Lamellar zeolites; stilbite and heulandite.
- c) Fibrous zeolites; natrolite, thomsonite, edingtonite and scolecite.

More recently, Meier (3) has identified seven groups of zeolites on the basis of their framework structures. They are named after representative members of each group. The seven groups are therefore analcime, natrolite, chabazite, phillipsite, heulandite, mordenite and faujasite.

The three dimensional framework zeolites are much less prone to structural changes during ion exchange reactions than members of the lamellar and fibrous classes. They can be dehydrated by heating under vacuum without any collapse of the framework, although Smith et al (4,5) have observed small changes in the rhombohedral lattice parameters of calcium chabazite on dehydration. When dehydrated the zeolites develop large capacities for the sorption of neutral molecules. The sizes of these molecules, and also of cations involved in ion exchange, which can enter the crystals are governed by the diameters of the narrowest apertures through which these molecules or ions must pass. This molecular sieve effect has been used for the separation of normal and branched chain hydrocarbon isomers (6).

The stacking of the various polyhedra of SiO_4^{4-} and

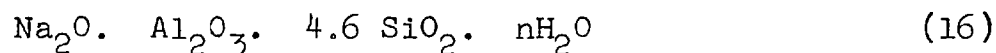
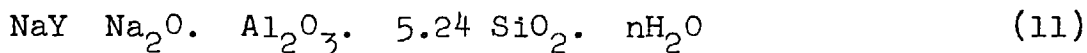
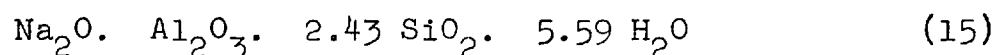
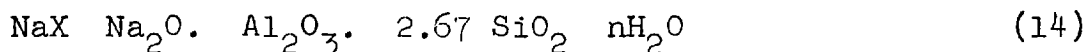
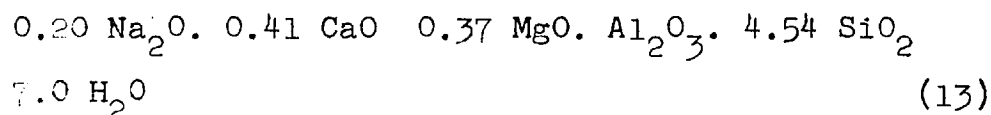
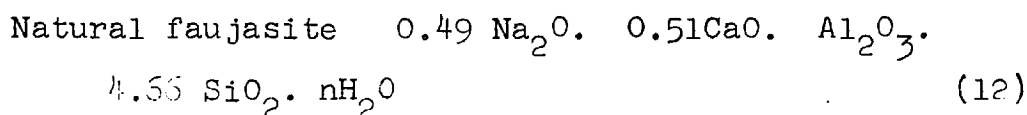
AlO_4^{5-} in different arrangements leads to a variety of channels within the crystals. In faujasite (7) the intersecting channels are identical with the arrangement of bonds in diamond; whereas in NaA(8) the channels intersect mutually at right angles. In the case of sodalite (9) the channels radiate from the centre to the corners of the cubic unit cell. Not all zeolites have channel systems which are intersecting e.g. in cancrinite the channels run adjacent to one another, and at their points of closest approach are interconnected by eight membered rings.

The channel dimensions may vary periodically along their lengths, and of course between one exchanger and another. e.g. for the sodalite-nosean feldspaths the maximum and minimum diameters are $6.6\text{\AA}$ and $2.2\text{\AA}$ respectively, whereas in faujasite the corresponding values are $12\text{\AA}$ and $9\text{\AA}$. Barrer (10) has introduced a graded series of aluminosilicates on the basis of their degree of openness:-

Faujasite	>	NaA	>	Chabazite		>	Mordenite	>	Levynite
				Gmelinite					
		Phillipsite					Analcite, sodalite,		
>			>						
		Harmotome					ultramarine, nosean, cancrinite		

1.2. Structure of NaX and NaY

NaX and NaY are synthetic zeolites manufactured by the Linde Air Products Co. Ltd. of the United States. They are synthetic forms of the rare zeolite faujasite in which the silica/alumina ratio can be varied between 2.1 and 5.2 (11), the X form having the ratio between 2.1 and 3.0, whereas in the Y form the ratio varies from 3.0 to 5.2. Several analyses of faujasite, NaX and NaY have been reported:-



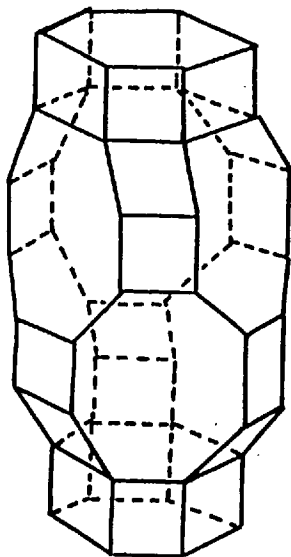
In all these analyses there exists a balance between the number of cations and the charge on the framework. However, in certain cases (17), (18), a deficiency of Na^+ has been reported. To compensate for this deficiency, hydronium ions, H_3O^+ have been introduced into the lattice.

Numerous attempts have been made to detect this ion by infra-red spectroscopy (21) (22) (24). The infra-red

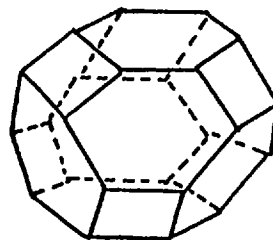
stretching frequency of H_3O^+ is in the range $1700\text{-}2800\text{cm}^{-1}$, but no absorption bands corresponding to this ion have been observed in the samples studied. However, for the dehydrated zeolites, infra-red stretching frequencies in the range $3450\text{-}3700\text{cm}^{-1}$ have been observed by several experimenters (21-24). This range corresponds to the -OH group stretching frequencies, and it is believed that it is due to the existence of surface hydroxyl groups.

The structural unit of faujasite (and hence of NaX and NaY) is the cubo-octahedral aluminosilicate cage consisting of 24 Si/Al atoms and 36 oxygen atoms. This polyhedron was first observed in sodalite and is called the sodalite cage, Fig. 1(b). These sodalite cages are stacked in the faujasite structure in the same way as the carbon atoms in diamond. They are joined together by the bridging of oxygen atoms across the six-membered oxygen rings thus outlining a hexagonal prism (25), (26). This arrangement of sodalite cages forms a very open framework with large cavities in it, Fig. 1(c). These cages are 26-hedra and have 'free' diameters of $12\text{-}13 \text{ \AA}^0$. They are interconnected by windows outlined by 12-membered $(\text{Si, Al})_{12} \text{O}_{12}$ rings which measure $10\text{-}12 \text{ \AA}^0$ across from centre to centre of two opposing oxygen atoms. Thus in the faujasite structures there are three types of cages:

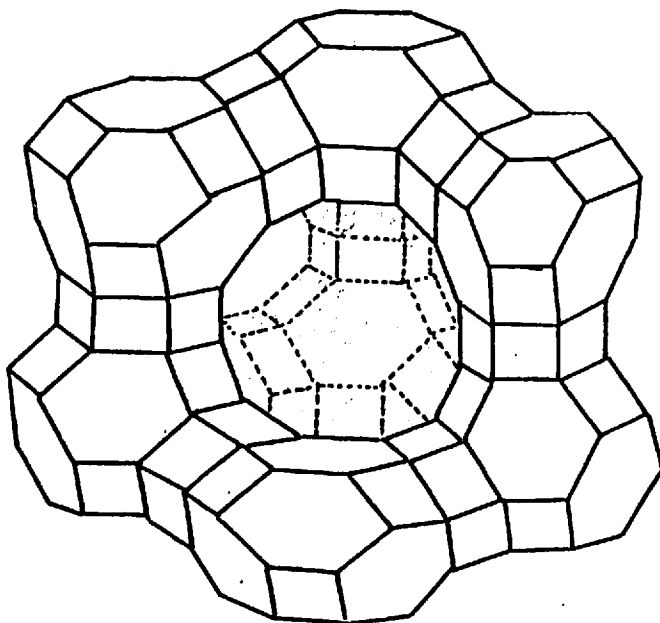
a) the very large 'supercages' of free diameter $12 \text{ \AA}^0$

Diagrams of the cavities in ZeolitesFig.1

(a) Chabazite



(b) Sodalite



(c) Faujasite

with twelve-membered oxygen rings leading to four other similar cavities.

- b) Sodalite cages of free diameters $6.6\text{\AA}$.
- c) Hexagonal prisms of free diameters 2 to $2.5\text{\AA}$.

In the cubic unit cell of natural faujasite, NaX and NaY, there are eight supercages, eight sodalite cages and sixteen hexagonal prisms. The unit cell parameters of these forms are $24.67\text{\AA}$, $24.93\text{\AA}$ and $24.67\text{\AA}$ for faujasite, NaX and NaY respectively (13). Little change in this parameter is observed on ion exchange (14).

1.3. Cation positions in NaX and NaY

The number of cations in the unit cell is dependent on the silica/alumina ratio. For the X type zeolite there are around 86 monovalent ions per unit cell, whereas in the more siliceous Y zeolite this number is reduced to around 54. Broussard and Shoemaker (25) have investigated the hydrated NaX structure using X-ray diffraction and three dimensional Fourier analysis. They have located 16 Na^+ ions in the hexagonal prisms; 32 Na^+ ions were thought to be located near the open six-membered rings of the sodalite cages, and the remainder were assumed to be randomly distributed in the large cages. The six-membered rings of the sodalite cages were found to be distorted in an analogous way to cyclohexane in

the chair form. Three types of cation sites have been classified by Breck (27); type I are those inside the hexagonal prisms, type II are near the open six-membered rings of the sodalite cages, and type III are on the walls of the channels next to the four-membered rings. The major difference between the X and Y zeolites is the non-occupancy of the type III sites in NaY.

Kasai (28), in his electron spin resonance studies of NaY, has defined four types of sites in the crystal. Type I is at the centre of the hexagonal prisms; type II is outside the cubooctahedron next to an open $(\text{Si}, \text{Al})_6 \text{O}_6$ hexagonal ring. Type I' and II' sites are both inside the cubooctahedron and are mirror images of the type I and II sites respectively across the hexagonal plane.

1.4. Structure of Chabazite

Chabazite is a naturally occurring zeolite found in several parts of the world e.g. Bay of Fundy, Nova Scotia; Kyogle, N.S.W.; Oregon U.S.A. The silica/alumina ratio of chabazite depends on its source e.g. that of Nova Scotian origin has a ratio of approximately five. Analyses of this sample

0.91 CaO. 0.10 Na₂O. Al₂O₃. 4.87 SiO₂. 7.10 H₂O (49)
0.87 CaO. 0.17 Na₂O. Al₂O₃. 5.00 SiO₂. 6.75 H₂O (33)

also show that the predominant cation is the calcium ion.

The structure of chabazite was investigated initially by Wyart (29) using X-ray technique. His rhombohedral (almost cubic, $\alpha = 94^{\circ}21'$) structure was composed of four membered and six membered oxygen rings, which provide maximum apertures of $\sim 3.0\text{\AA}$ diameter. However, Kington and Laing (30) have found that argon (diameter $3.94\text{\AA}$) and methane (diameter $4.24\text{\AA}$) were relatively easily adsorbed on to chabazite. Consequently the structure has been reinvestigated by Dent and Smith (31) and Nowacki (32). They, independently, have proposed a new structure built up of double six membered oxygen rings forming one cage per unit cell. Each cage has six octagonal, two hexagonal and twelve quadrilateral faces; and is connected to the six neighbouring cages by eight membered oxygen rings permitting sorption in all directions, but limiting it by the octagonal (non-planar) apertures of minimum width of about $3.9\text{\AA}$. Fig. 1(a).

1.5. Cation Positions in Chabazite

Ducros and Rimsky (34) consider that they have located Ca^{2+} ions in natural chabazite near the centres of the hexagonal prisms. Their X-ray diffraction studies were not able to locate positions for the Na^{+} ions, which could not be in the same positions as the Ca^{2+} ions since two Na^{+} ions are required to replace one Ca^{2+} ion.

However, they supposed that the Na^+ ion was found at equal distances from certain of the four Si or Al atoms forming the square rings.

Extensive investigations of the crystal structure of both dehydrated and hydrated Ca-chabazite have been made by Smith et al. (4) (5). X-ray diffraction and electron density measurements were used to locate the positions of the atoms and molecules in the structure. In the dehydrated sample, the positions of the calcium ions were revealed by the occurrence of peaks that could not be explained by Si, Al or O atoms. It was found that the peaks were not high enough for calcium ions and it was necessary to assign fractional atoms on the basis of a statistical distribution. Peaks equivalent in electron density to 0.6 Ca atoms at the origin of the unit cell, and to 0.35 Ca atoms at each of two positions on the triad axis near the centres of the six membered rings, have been located. A third type of site has also been postulated to occur on the inside walls of the cavities. The three types of sites have been designated Ca_1 , Ca_2 , Ca_3 respectively. Upon hydration of the sample Smith et al. (5) observed little change in the unit cell length ($a = 9.42\text{\AA}$ as opposed to $9.37\text{\AA}$ for the dehydrated form), but a change of about 2° was observed for the rhombohedral angle. The six membered rings were found to be more

regular, and the eight membered rings more circular, than in the dehydrated form. Assignment of observed electron density peaks to the water molecules and calcium ions was not straightforward. Smith postulates four types of sites in the hydrated crystals:-

- a) at the centre of the eight membered rings with distances to the oxygen of $3.30\text{\AA}$ or higher. This position is most probably occupied by water molecules.
- b) on the triad axis but displaced $1\text{\AA}$ away from the centre of a six membered ring. Although this site is occupied by a calcium ion in the dehydrated sample, Smith has assigned a water molecule to this site in the hydrated sample.
- c) a two-fold set of positions on the triad axis has also been assigned to water molecules.
- d) twelve small peaks each containing two or three electrons. These peaks have been interpreted as a statistical distribution of molecules on a twelve-fold general position. These sites are most probably associated with the framework of the main cage.

Exchange of bivalent ions by univalent ions will obviously change the ion positions. The site at the origin of the di-trigonal prism can only be entered through a six-membered ring whose 'free' aperture is about $1.3\text{\AA}$ in radius. Consequently, certain of the large monovalent

ions e.g. Cs^+ and possibly Rb^+ would encounter difficulty in exchanging with these sites. The six-membered rings would be available for all cations, though the larger ones would have to lie displaced from the ring towards the centre of the large cavity.

The effect of cations on the sorption properties of chabazites with varying Si:Al ratios has been investigated by Barrer and Baynham (35). However, their interpretation of the results was based on the incorrect sodalite structure of Wyart. Smith (36) has re-interpreted their results on the revised structure. He considers that a) many, perhaps all, of the potassium and rubidium atoms can be placed in the eight-membered rings; b) the first two sodium and calcium atoms can be placed in the six-membered rings or in the hexagonal prisms, and subsequent ones in or near the eight-rings. However, cation blocking of sorption will only occur for those atoms and molecules that do not interact significantly with the cations. Highly polar molecules, such as water, will link with the cations and move with them into the cavities thus forming their spheres of hydration.

1.6. Water in Zeolites

All zeolites have a certain amount of water associated with their structures, the amount depending on temperature and pressure. In some cases e.g. faujasite, the water constitutes as much as 28% of the total weight of the hydrated crystals. The positioning of water molecules inside zeolite structures is not well understood. One view is that water occupies certain definite sites in the crystal structure in a similar way as in the salt hydrates. A second view is that it is freely mobile. Most probably the true state of water is some intermediate between these two extremes. Glemser (102) has suggested that in the relatively compact zeolites such as analcite and natrolite the water molecules are in fixed positions, whereas in the more open zeolites chabazite, heulandite and stilbite, part of the water is mobile. Smith (5), in his X-ray work on hydrated calcium chabazite has placed some of the water molecules in fixed positions. For the most open zeolite known, faujasite, which has 260 water molecules per unit cell, the water acts as a continuous fluid (26).

Dehydration curves, at constant pressure, have been used to investigate the state of water in crystals. Three types of isotherms have been found for zeolites:-

- a) Stepped curves, characteristic of hydrate formation

- b) Smoothly continuous curves
- c) Continuous curves with definite steps.

Certain types of isobars can be identified with certain types of zeolites e.g. the fibrous zeolites, scolecite, natrolite and thomsonite have stepped dehydration curves (103); stilbite, a lamellar zeolite, has a dehydration curve which is continuous but with definite steps (103); whereas the three-dimensional framework zeolites chabazite (33) and faujasite have smooth dehydration curves.

The effect of cations on the water retentivity of chabazite was investigated by Barrer and Langley (33) using differential thermal analysis and thermogravimetric analysis. The order of retentivity of water by the various cationic forms of chabazite was $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$, suggesting an association between the cations and the water molecules. Also the divalent ions show a greater retentivity than do the univalent ions of comparable radii ($\text{Ca} > \text{Na}$, $\text{Ba} > \text{K}$). Differential thermal analysis has shown that for Li, Sr, Ba chabazites, the water is given off in more than one stage, analogous to the situation for the fibrous zeolites.

2. Ion exchange in crystalline exchangers

The earliest recorded observations of ion exchange are those due to Thompson (37) and Way (38) well over a hundred years ago. Thompson observed that calcium was present at the bottom of a column of soil through which ammonium chloride solution had been passed. In 1876, Lemberg (39) demonstrated the reversibility of ion exchange when he converted leucite $K_2O \cdot Al_2O_3 \cdot 4SiO_2$ to analcite $Na_2O \cdot Al_2O_3 \cdot 4SiO_2$ by treatment with sodium chloride solution and then back to leucite with potassium chloride solution. Cation exchange by fusion with salts was attempted by Steiger (40) in 1902. Silver forms of chabazite and analcite were obtained by fusion of the zeolites with silver nitrate at $250^\circ C$. Ammonium forms of chabazite, heulandite and thomsonite were prepared by heating the zeolites with ammonium chloride (41). Clarke (42) in 1905 prepared fully exchanged NH_4 , Ag, Tl, Sr, Ba forms of analcite, but considerable salt occlusion was observed with chabazite. Zotch (43) compared the exchange properties of various zeolites on the basis of their affinity for the ammonium ion, which was in the order Scolecite < Harmotome < Heulandite < Stilbite < Chabazite. Hey and Bannister (44) prepared several exchanged forms of the minerals thomsonite, natrolite, edingtonite and scolecite by fusion with low melting salts. Barrer (45)

investigated the ion exchange properties of mordenite and found partial exchange with Li^+ , Na^+ , K^+ , Ca^{2+} , Ba^{2+} by hydrothermal methods. A NH_4^+ rich mordenite was obtained by treatment with ammonium chloride at temperatures greater than 250°C . The exchange properties of analcite and chabazite were compared by Barrer (46). He found that whereas most monovalent ions exchanged freely on chabazite, caesium was excluded from the analcite crystals. This 'ion sieve' effect was attributed to the more open structure of chabazite. In this work four methods of ion exchange were used; percolation, hydrothermal, fusion with a salt of low mp, and vapour phase using a volatile salt.

In their investigation of analcite Barrer and Hinds (47) demonstrated the non-reversibility of exchange isotherms. There was evidence of limited mutual solid solubility of the end members in the exchanges involving the ion pairs Na-K, Na-Tl and K-Tl, and the isotherm for the Na-K exchange exhibited marked hysteresis i.e. the equilibrium positions in the exchange were dependent on the initial composition of the exchanger. This hysteresis was attributed to the growth of one solid phase by nucleation in or on a second. The presence of two coexistent solid phases was shown by X-ray methods. A lead-rich form of analcite was prepared, and from the % increase

in weight of the crystals, Barrer and Hinds concluded that lead entered the crystal as the complex ion $\text{Pb}(\text{OH})^+$.

Although ultramarine is unstable under hydrothermal conditions, Barrer and Raitt (48) have obtained quantitative data for the Na-Li exchange, and found that the mass action quotient was reasonably constant. This quotient was also found to be constant for the Na-Ag exchange in chabazite (49). The other uni-univalent exchanges Na-Rb, Na-Tl, K-Ag were satisfactorily represented by

$$\log K = \log \frac{B_z(1-B_s)}{B_s(1-B_z)} + C(1-2 B_z) \text{ where } K \text{ and } C \text{ are}$$

constants and B_z , B_s are the equivalent cation fractions of ionic species B in zeolite and in solution respectively. Chabazite samples rich in H^+ , Li^+ , Mg^{2+} , Sr^{2+} , NH_4^+ , Co^{2+} , Ni^{2+} and Pb^{2+} were also prepared, but N Me_4^+ and N Et_4^+ were excluded from the crystal by the ionic sieve effect.

The above equation also describes the Na-Li exchange in basic cancrinite (9). Barrer and Falconer found three types of isotherms in their investigations of basic cancrinite, basic sodalite and analcite:-

(a) ideal form obeying the law of mass action $K = \frac{B_z(1-B_s)}{B_s(1-B_z)}$,
(Na-Li, Na-K, Na-Ag and Li-K in basic sodalites);

(b) a sigmoid form obeying the equation

$$\log K = \log \frac{B_z(1-B_s)}{B_s(1-B_z)} + C(1-2 B_z) \quad \text{and}$$

(c) a form exhibiting hysteresis (Na-Ag and Li-Ag in basic cancrinite and K-Rb in analcite).

Na A is a synthetic zeolite manufactured by the Linde Molecular Sieve Co. Its exchange properties were investigated initially by Barrer and Meier (50) and later by Barrer, Rees and Ward (51). Its unit cell composition may be represented as $\text{Na}_{12} [12\text{AlO}_2 \ 12\text{SiO}_2] \ \text{NaAlO}_2 \cdot 28.6 \ \text{H}_2\text{O}$. All thirteen Na^+ ions could be replaced by Ag^+ , but only twelve by Tl^+ . This was interpreted as two types of sites existing in the crystal. Several exchanges were performed using the alkyl ammonium ion RNH_3^+ . As the size of the group R increased in the sequence methyl, ethyl, n-propyl, n-butyl, the relative exchange capacities decreased 0.43, 0.29, 0.12, 0.06 respectively. The order of affinity amongst the monovalent ions was found to be $\text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Li}^+ > \text{Cs}^+$. With the exception of Li^+ , the affinity decreases as the crystallographic radius increases. Similar exchanges using polystyrene resins (52) (53) have shown the opposite behaviour - the affinity of the ion increases as the crystallographic radius of the ion increases. The affinity sequence of Barrer, Rees and Shamsuzzoha (15) for monovalent ion exchanges on NaX is $\text{Rb}^+ > \text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ which, with the exception of Rb^+ is the same as that observed with organic resins. The affinity of the ions for the resin increased

with decreasing distance of closest approach of the ions as expressed by the Debye Hückel parameter a_0 , a conclusion previously reached by Boyd et al. (54). A linear relationship between $\log_{10} K$ and $1/a_0$ for uni-univalent exchanges was shown by Kressmann and Kitchener (55). However, a_0 is not an independent constant since its value depends on the concentration used in its calculation.

The ion exchange properties of the synthetic zeolites A and X have also been investigated by Federov and co-workers (57) (58). They have obtained overall affinity sequences amongst the monovalent ions on the basis of the value of the thermodynamic equilibrium constant. However, their affinity sequences are not in good agreement with those of Barrer et al. (15) (51). This might possibly be due to the fact that they have based their calculations on a different exchange capacity of the zeolites. This was equal to its capacity with respect to the less readily sorbed of the given two ions.

Much information is now available on the ion exchange properties of zeolites. It is of interest to compare the various affinity sequences observed on different zeolites, and also by different experimenters on the same zeolites. Amongst the monovalent ions the following affinity sequences have been derived on the values of the thermodynamic equilibrium constant K_{Therm} .

Basic Sodalite	(9)	$\text{Ag} > \text{Na} > \text{Li} > \text{K}$
Chabazite	(49)	$\text{Tl} > \text{Ag} \approx \text{Rb} \approx \text{K} > \text{Na}$
Faujasite	(14)	$\text{Ag} > \text{Tl} > \text{K} > \text{Na}$
NaA	(51)	$\text{Na} > \text{K} > \text{Rb} > \text{Li} > \text{Cs}$
	(57)	$\text{K} > \text{Na} > \text{Rb} > \text{Cs} > \text{Li}$
NaX	(15)	$\text{Rb} > \text{Cs} > \text{K} > \text{Na} > \text{Li}$
	(58)	$\text{K} > \text{Na} > \text{Rb} > \text{Cs} > \text{Li}$
	(59)	$\text{Na} > \text{Cs} > \text{Rb} \approx \text{K} > \text{Li}$
NaY	(59)	$\text{Tl} > \text{Cs} > \text{Rb} > \text{Ag} > \text{K} > \text{Na} > \text{Li}$

Variation of the affinity sequences observed by different experimenters on the same zeolite is due to the variable limits of exchange defined by the different experimenters. For example, the Na-Rb and Na-Cs exchanges on NaX have been studied by Barrer et al. (15) and by Sherry (59). Both sets of experimenters found that only $\sim 66\%$ of the sodium could be replaced by these ions. Barrer has taken this as the limit to exchange and has calculated K_{Therm} accordingly. Sherry, on the other hand, has extrapolated his isotherm to 82% exchange which he considers to be the maximum limit to exchange. Consequently, different affinity sequences have been obtained.

An attempt at predicting ion exchange selectivity among the monovalent ions has been put forward by Eisenmann (56). He suggested that the primary variable controlling cation specificity is the field strength of the anionic

site. He has considered the anionic sites to be represented as monopolar sites of radius r^- . By varying this anionic parameter he has derived eleven selectivity series among the Group IA ions. A limitation to the theory is that it is based on only one type of site in the solid phase. This may be correct in the case of glasses, to which the theory was originally applied, but it is known that most zeolites have more than one type of cationic site. This heterogeneity of sites leads to sigmoidal isotherms, selectivity reversals and ion sieve effects which have been found in several exchanges in zeolites.

As already mentioned the aluminosilicate structures, having robust three-dimensional frameworks, should in certain cases be free from dimensional changes associated with exchange. This behaviour has been studied by X-ray powder photography for faujasite (14), NaA (8), ultramarine (48) and analcite (72). The cubic unit cell dimensions of ion exchanged forms of the above zeolites are summarized in Table 1. The greatest percentage change in the unit cell dimensions occur in the most compact structures. In ultramarine the maximum change in the unit cell is $\sim 5^\circ$, while in NaA and faujasite it is only of the order of 1° .

TABLE 1

Cubic Unit Cell dimensions of various cationic forms of
some crystalline exchangers

Cationic Form	Ion Radius A ^o	Ultramarine	Analcite	NaA	Faujasite
Li	0.78	8.77	13.5	12.11	-
Na	0.95	9.05	13.66	12.27	24.89
K	1.33	9.25	13.79	12.28	25.03
Rb	1.49	-	-	12.31	-
Cs	1.69	-	13.66	12.30	-
Ag	1.26	8.97	13.7	12.28	24.91
Tl	1.49	9.07	-	12.29	25.06
Ca	0.99	-	-	12.23	24.87
Sr	1.13	-	-	12.24	25.01
Ba	1.35	-	-	-	24.98

Mono-divalent ion exchanges have not been studied so extensively as mono-monovalent exchanges. The earlier work of Barrer and Sammon (49) on chabazite and Barrer and Meier (50) on NaA have shown a greater affinity of the zeolites for the divalent ions, but no attempts were made to derive thermodynamic data. The NaA zeolite was later investigated by Barrer, Rees and Ward (51) who obtained a value of -0.14 kcal/gm.eq. for the free energy of the Na-Ca exchange. Although calcium was the preferred ion,

the reaction was found to be endothermic with a standard heat of exchange of 2.1 kcal/gm.eq. Consequently a large positive entropy change was associated with this exchange. A possible explanation of this effect is that the concentration of the ions in the internal aqueous phase of NaA approaches 25N, whereas in the external solution it is only 0.1N. Thus changes in the degree of hydration of the ions can be expected on exchange. Barrer, Rees and Shamsuzzoha (15) have also found the free energy and standard heats of exchange to have opposite signs for the exchanges involving the ion pairs Na-Ca, Na-Sr and Na-Ba on NaX. No attempts were made by them to obtain values of $T\Delta S^\circ$ since the measured heats of partial exchange were associated with points which were not at true equilibrium. A subsequent slow process was found to occur. A notable feature of mono-divalent exchange is the non-linearity of plots of $\log_{10}$ (selectivity coefficient) against cationic composition. In several instances these curves were found to exhibit maxima.

Mono-divalent and di-divalent ion exchanges have also been studied by Ames (73), involving the cations Na^+ , Ca^{2+} , Sr^{2+} on the synthetic zeolite type A, and the natural zeolites erionite, phillipsite and clinoptilolite. Standard free energies of exchange have been derived for the Na-Ca, Na-Sr and Ca-Sr exchanges on erionite,

phillipsite and clinoptilolite. These values have been found to be positive in all cases except the Na-Sr and Ca-Sr exchanges on clinoptilolite. The effect of temperature on the Na-Ca exchange on phillipsite was found to be negligible thus showing the reaction enthalpy to be small. This was assumed to be the case for all the other exchanges. Plots of $\log$ (selectivity coefficients) against cationic composition were non-linear although no maxima occurred. In the case of the Ca-Sr exchange on type A zeolite, however, a straight line was obtained, and consequently the Kielland coefficient was calculated ($C = -0.094$). This constant has the same sign as those found for uni-univalent exchanges, and its small value suggests almost ideal behaviour in the solid phase.

The existence of maxima observed in Kielland plots obtained by Barrer et al. (15) (51) has been questioned by Sherry (92). The Na-Ba exchange on NaX has been studied. As well as observing a different limit to exchange from that of Barrer, Sherry found that a graph of $\log_{10} K_c$ against Ba_z continuously decreased with increasing Ba_z . This is in direct contrast to that of Barrer et al. (15), who found this function to increase continuously with increasing Ba_z . Sherry has interpreted this as the non-establishment of equilibrium for the results of Barrer et al. although the time of contact

between solid and solution was the same in both cases (4 days).

The only work involving trivalent ion exchange on zeolites is that of Ames, who has determined exchange isotherms for the ion pairs Na-Ce, Na-Sr, Ce-Sr and Na-Y on the synthetic zeolite NaX (93). The isotherms were subjected to a thermodynamic treatment, thus enabling the free energies of exchange to be evaluated. The multivalent ions were found to exhibit very high affinities for the exchanger, the affinity sequence being $\text{Ce}^{3+} > \text{Sr}^{2+} > \text{Y}^{3+} > \text{Na}^+$. None of the isotherms was found to be ideal, and plots of $\log_{10}$ (selectivity quotient) against cationic composition were found to decrease with increasing cationic composition of the ingoing ion. The effect of temperature on the Na-Ce exchange was studied, and it was found that the selectivity increased with increasing temperature. However, no attempt was made to determine the heat of exchange from these observations. More recently Ames (94) has extended trivalent ion exchange to a synthetic heulandite-clinoptilolite zeolite of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 11.5. The exchanges $\text{H}_3\text{O}^+ - \text{Ce}^{3+}$ and $\text{NH}_4^+ - \text{Ce}^{3+}$ were studied. It was found that the zeolite was hydronium-ion selective, greater than 90% cerium in the solution being required to load an appreciable amount of cerium on the zeolite. In the exchange involving

ammonium ion, however, the preferred ion was cerium. No attempt was made to derive the free energy of exchange from the ion exchange data.

2.1. Cation Exclusion in Ion Exchangers

Several investigations of ion exchange in crystalline exchangers have shown that complete exchange of one ion by another is not possible. This 'ion sieve' effect is summarized in Table 2.

TABLE 2

Exchanger	Exchanged	Not exchanged
Ultramarine (48)	K^+	Cs^+
Analcite (47)	Rb^+	Cs^+
Basic Cancrinite (9)	Rb^+	Cs^+
Chabazite (49)	Cs^+	NMe_4^+
Faujasite (14)	NMe_4^+	NEt_4^+

Most of the exchanges studied have used zeolites initially in the Na form. Na^+ (crystallographic radius $0.95A^\circ$) should readily pass through all apertures found in zeolites. Several reasons can be put forward to explain this 'ion sieve' effect.

a) Steric effect. The cation entering the crystal might have a diameter greater than that of a window in the crystal. For example, in NaX and NaY there are sixteen

Na^+ ions siting in the hexagonal prisms. Access to these sites is through six-membered rings of free diameters $\sim 2.5\text{\AA}$. Rb^+ and Cs^+ with cation diameters of $2.96\text{\AA}$ and $3.38\text{\AA}$ respectively are therefore not exchanged with these Na^+ ions. It is possible that at higher temperatures further exchange could occur. Below 100°C Cs^+ will not displace Na^+ from analcite (60), while at 200°C the exchange proceeds slowly (61).

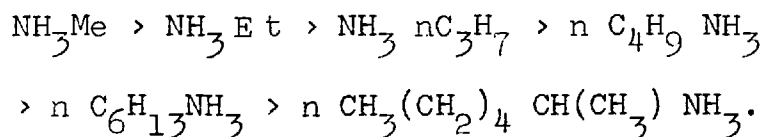
b) Volume effect. In their investigations of alkyl ammonium ion exchange on NaX, Barrer et al. (14) found the % exchange to decrease with increase in size of the alkyl groups. Table 3 summarises their results.

TABLE 3

Ion	Exchange Sol.	Cationic Composition	Unit Cell Edge
NH_4^+	2N - NH_4Cl	$92^\circ/\text{oNH}_4 + 8^\circ/\text{oNa}$	24.9
NH_3^+Me	2N- NH_3MeCl	$58^\circ/\text{oNH}_3\text{Me} + 42^\circ/\text{oNa}$	24.9
NH_2Me_2^+	1N- $\text{NH}_2\text{Me}_2\text{Cl}$	$37^\circ/\text{oNH}_2\text{Me}_2 + 63^\circ/\text{oNa}$	24.9
NHMe_3^+	2N- NHMe_3Cl	$28^\circ/\text{oNHMe}_3 + 72^\circ/\text{oNa}$	24.9
NMe_4	1N- NMe_4Cl	$23^\circ/\text{oNMe}_4 + 77^\circ/\text{oNa}$	25.0
NH_3Et^+	2N- NH_3EtCl	$50^\circ/\text{oNH}_3\text{Et} + 50^\circ/\text{oNa}$	24.9
NEt_4^+	1N- NEt_4Cl	No exchange	

Complete exchange of Na^+ by NMe_4^+ could never occur, because this would require 86 cations per unit cell, whereas approximately 33 NMe_4^+ cations would fill all the available interstitial volume in the non-swelling crystal.

A similar series of decreasing ion exchange has been found on NaA(8). For this zeolite the amount of exchange is



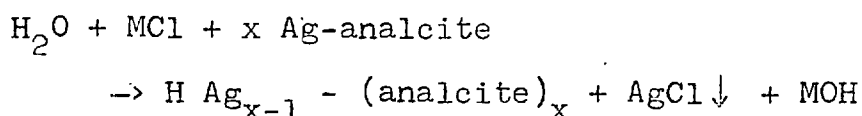
No exchange was observed with NMe_4^+ and NEt_4^+ . Hexyl and heptyl ammonium ions, with lengths greater than the channel diameters were believed to pass through the $4.5 \text{ \AA}$ windows lengthways. However, the space inside the crystal was insufficient for all Na^+ to be replaced.

c) A third type of ion sieve effect is that found in basic cancrinite (9). Although Cs^+ has a diameter less than that of the channels, it has been found to be excluded from the crystal. The most probable explanation is that ion exchange requires a 'two-way traffic' and cannot take place in a 'one-way street'. The channels in cancrinite are not interconnected and are too narrow for a Cs^+ ion to pass another ion.

d) Valency effect. Barrer and Sammon (49) found that

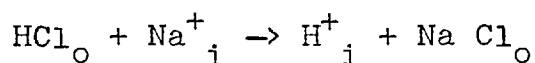
lanthanum ($r^{3+} = 1.15 \text{ \AA}$) was excluded from crystals of chabazite when the zeolite was treated with aqueous lanthanum nitrate solution. Cation exclusion on the basis of crystal ionic radii could not account for this since Rb($r^{+} = 1.48 \text{ \AA}$) readily enters the chabazite framework. A valency effect was proposed to explain this exclusion. In such an exchange as $3\text{Na}^{+} \rightleftharpoons \text{La}^{3+}$, there would be a local excess of positive charge at the site occupied by La^{3+} , and local excess of negative charge at the sites vacated by two of the Na^{+} ions. This charge disbalance leads to an energetically unfavourable situation in the crystal.

One important consequence of the ion sieve effect is the possibility of obtaining hydrogen zeolites in neutral or alkaline solutions. When Ag-analcite was heated to $\sim 100^{\circ}\text{C}$ with caesium chloride it was established that while no Cs^{+} left the solution some silver chloride was precipitated (60). When the experiment was repeated with trimethyl-ammonium chloride and silver analcite, up to 60% of the total silver in the analcite was precipitated as chloride, while an equivalent amount of alkali appeared in solution. This behaviour was attributed to hydrogen ion exchange



A similar behaviour has been noted in ultramarine (48), cancrinite (9) and chabazite (49).

Hydrogen-ion exchange associated with a sieve action towards anions was observed when certain outgassed feldspathoids - basic sodalite, nosean and cancrinite - were exposed to dry hydrogen chloride at moderate temperatures (95). In this case hydrogen ions migrated into the crystals while sodium ions diffused out. Consequently, sodium chloride formed externally on the crystals. The Cl^- ion and HCl molecule are both too large to diffuse as such in the sodalite lattice. The openings through which Cl^- or HCl would require to pass have 'free' diameters of $\sim 2.2 \text{ \AA}^0$; the diameters of Cl^- and of Cl^- in HCl are each about $3.6 \text{ \AA}^0$. Thus the overall equation for this reaction is



where the subscripts 'o' and 'i' denote outside and inside the crystal respectively.

An analytical application of ion-sieve action is in the separation of Cs^+ from other alkali metal ions. It has been found that the analcite framework is open enough to admit ions of Li, Na, K and Rb, but not that of Cs. Thus Ag-analcite has been studied as a reagent for separating Cs^+ from the other ions (60). At 100°C it was found that Na^+ could be quantitatively removed from Cs^+

without any incorporation of any Cs^+ in the crystal. Thus a Na^+ free aqueous caesium solution remained. Separations between $\text{K}^+ - \text{Cs}^+$ and $\text{Rb}^+ - \text{Cs}^+$ were not so successful since a small amount of Cs^+ was incorporated into the crystal.

2.2. Thermochemistry of Ion Exchange

The first recorded calorimetric measurements of the heats of ion exchange which were not complicated by heats of neutralization of acidic groups were made by Coleman (62) on the polystyrene sulphonate resins Amberlite IR-100 and IR-120. He used an isothermal calorimeter maintained at 30°C , and measured temperature changes using a Beckman thermometer. The results obtained can be regarded as no more than qualitative in nature since no attempts were made to correct the heats to some standard state. The heats of ion exchange were found to be of the order of 1 kcal/gm.eq. of resin for the ion pairs $\text{Li} - \text{K}$, $\text{Na} - \text{K}$, $\text{NH}_4 - \text{K}$, $\text{Ca} - \text{K}$, $\text{Ca} - \text{Ba}$, and $\text{Ca} - \text{Mg}$.

Cruikshank and Meares (52) have made some very accurate measurements of the heats of ion exchange on resins, using a non-adiabatic calorimeter maintained at 25°C . A thermistor in conjunction with a Wheatstone bridge and deflection galvanometer were used to measure temperature changes. The experimental heats were corrected

to obtain standard heats of ion exchange. They defined their standard states as infinite dilution with water for the solution phase, and pure resin in equilibrium with an infinitely dilute solution of the exchangeable ion for the resin. For the uni-univalent exchanges, the standard free energies, heats and entropies were found to have the same sign. It was considered that the substitution of the more preferred ion into the resin resulted in an increased interionic attraction with a corresponding decrease in both internal energy and entropy. The decrease in internal energy was always sufficient to outweigh the decrease in entropy in determining the sign of the standard free energy ΔG° . All the exchanges studied were found to occur with a decrease in resin volume. However, the work of swelling is small and never more than 10% of the standard heat of exchange ΔH° . A systematic investigation of the effect of crosslinking for a given ion pair $H \rightarrow K$ showed that both free energy and heat of exchange increased in magnitude, although their difference $T\Delta S^\circ$ was fairly constant. It was suggested that the variation of ΔG° , ΔH° and $T\Delta S^\circ$ was largely due to hydration effects of the hydrogen ions.

Only one exchange involving a divalent ion was studied i.e. the H - Sr exchange on ZeoKarb 225 - a polystyrene sulphonate resin crosslinked with 10% divinyl

benzene. Although Sr^{2+} showed a much greater affinity for the resin than the hydrogen ion, the accompanying heat of exchange was small (-264 cal/gm.eq.). This was accounted for by the swelling work involved in exchange, so that the preference for the ion of higher valence was not in this case the result of a strong electrostatic interaction as suggested by Duncan (64) for the Na - Ba exchange.

Mono-multivalent ion exchange has been studied more thoroughly by Flett and Meares (65) on the polystyrene sulphonate exchanger Dowex 50 crosslinked with 8% DVB. As in their previous work the heats have been corrected to the standard state of infinite dilution for the solution and pure resin in equilibrium with an infinitely dilute solution of the exchangeable cation for the resin. From their results it was clearly shown that the replacement of any alkali metal cation, excluding lithium, by a bi- or tri-valent cation was endothermic to the extent of 1 - 2 kcal/gm.eq. Replacement of monovalent ions by multivalent ions produces considerable changes in electrostatic energy which contributes to the heat of exchange. When a resin is loaded with monovalent ions, every fixed charge may be imagined to be paired with a counter ion situated at its distance of closest approach. This results in short range electroneutrality in the

resin. However, replacement of several monovalent ions by a multivalent ion produces a situation whereby one fixed charge has a net positive charge and others a net negative charge. Short range electroneutrality therefore does not exist and the electrostatic energy is greater than in the univalent case.

The effect of cross linking on the degree of exchange has been further investigated by Boyd and Vaslow (71), using Na - Ag exchange on Dowex 50. Increase in the degree of crosslinking produced an increase in the affinity of the resin for Ag^+ : A corresponding increase in the entropy of exchange was also observed. A notable feature of all the exchanges at different DVB content was the approximate constancy of the mass action quotient with the degree of exchange, thus indicating ideal behaviour of the components of the solid phase. Since Na^+ and Ag^+ have very similar hydrated radii, the electrostatic interaction between these ions and the fixed ionic charges should be similar. Consequently the heats of ion exchange were expected to be small. This was found to be the case, the largest heat (-0.34 kcal/gm.eq.) being associated with the resin with the greatest amount of crosslinking. For a resin of 1% DVB content, no heat of exchange was observed. Any changes in electrostatic interaction were counterbalanced by changes in internal energy due to

swelling which is present for resins of low degree of crosslinking.

Extensive measurements of the heats of ion exchange on the surface of the clay mineral montmorillonite have been made by Martin and Laudelout (66) using a Calvet microcalorimeter. Uni-univalent cation exchanges only were studied. The heats of exchange were found to become more negative for the reaction $\text{Na} \rightarrow \text{A}$ as the crystallographic radius of the cation A increased. A similar behavior was noted for alkali metal ion exchange on NaA (51) and NaX (15).

Barrer, Rees and Ward; and Barrer, Rees and Shamsuzzoha have investigated the heats and ion exchange equilibria of NaA and NaX respectively with Li^+ , K^+ , Rb^+ , Cs^+ and Ca^{2+} on both zeolites and Sr^{2+} , Ba^{2+} with NaX only. Standard heats of exchange for the reaction

$$\text{Z}_B \text{ A Cl}_{\text{Z}_A} + \text{Z}_A \text{ B(Z)}_{\text{Z}_B} \rightarrow \text{Z}_B \text{ A(Z)}_{\text{Z}_A} + \text{Z}_A \text{ B Cl}_{\text{Z}_B}$$

were obtained by (a) measuring the heat associated with a pure cationic form B(Z)_{Z_B} in equilibrium with water at 25°C , where B^{Z_B+} is the exchangeable cation and Z is the anionic framework, and a chloride solution ACl_{Z_A} containing the exchangeable cation A^{Z_A+} , and (b) for the heat associated with the same equivalent amount of zeolite A(Z)_{Z_A} in equilibrium with water at 25°C , and a chloride solution BCl_{Z_B} . The same equilibrium state was reached

in each experiment by the adjustment of the initial molalities so that the total molality of A^+ and B^+ ions at equilibrium was the same in each experiment. The algebraic difference between the experimental values, when adjusted to a reaction involving one gram-equivalent of exchanger, and corrected to the standard states chosen, gave the standard heat of ion exchange. The standard states were the same as those defined by Cruikshank and Meares (52).

Their results for uni-univalent ion exchange only on both zeolites show that the exchange reaction is exothermic when the ion of larger crystallographic radius enters the crystal, and that the magnitude of the heat of ion exchange also increases with increasing crystallographic radius of the in-going ion. Only in the case of NaX (15), however, do the signs of the heats of exchange agree with the signs of the free energies. In the case of NaA, the measured enthalpies and energies of exchange of the ion pairs Na - K, Na - Rb, Na - Cs have opposite signs. Consequently a large negative entropy change is associated with these exchanges, and this large entropy change outweighs the enthalpy change in determining the sign of the free energy. Thus in the case of the Na - K, Na - Rb, Na - Cs exchanges in NaA, although Na^+ is the preferred ion in all cases, the enthalpies are negative

when the Na^+ is being replaced by the other counter ion.

For uni-divalent exchanges on NaX and NaA, involving the ion pairs Na - Ca and Na - Sr, the reverse situation is found. In these cases the divalent ion is the one preferred by the zeolite, although the exchanges are found to be endothermic. Consequently a positive entropy change is associated with these exchanges. This can be interpreted by the changes in the degree of hydration of the divalent ion when this ion enters the crystal, since the divalent ion has to shed its 'solvation sheath' when it passes through the apertures in the crystal, although it can regain it to a certain extent when inside the cavities of the crystal.

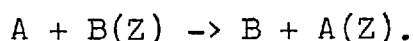
Only in the case of the Na - Ba exchange on NaX has it been found that the enthalpy and entropy of exchange have the same sign (both negative), although the enthalpy of exchange (-0.11 kcal/gm.eq.) is the smallest that has been observed for any ion pair exchange on zeolites. Even so, this exchange has a positive entropy change in agreement with all the other uni-divalent exchanges observed.

2.3. The Indirect Determination of the Heat of Ion Exchange

Many attempts have been made to determine the heat of ion exchange indirectly by means of the Van't Hoff isochore

$$\frac{d \ln K_{aB}^A}{dT} = \frac{\Delta H^{\circ}}{RT^2}$$

where K_{aB}^A is the thermodynamic equilibrium constant and ΔH° is the standard enthalpy change for the ion exchange



Ion exchange reactions occur generally with little evolution or uptake of heat. Accordingly the temperature dependence of ion exchange equilibria is small. Kraus and Raridon (67) have investigated ion exchange equilibrium at temperatures between 0°C and 200°C on Dowex 50 resin, and have obtained thermodynamic data for exchanges involving H^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Be^{2+} , Ba^{2+} , Ca^{2+} , Zn^{2+} , La^{3+} and Eu^{3+} . Plots of $\log K_{aB}^A$ against $\frac{1}{T}$ were not linear indicating that ΔH° varied with temperature. Certain exchanges e.g. Na - H, Ba - H, Co - H and Zn - H, which were found to be exothermic at low temperatures, were found to be endothermic at higher temperatures. No explanation of this behaviour has yet been advanced.

Thomas and co-workers (68) have studied ion exchange

equilibria on the clay minerals attapulgite and montmorillonite over a range of temperatures. They have obtained standard free energies, heats and entropies of exchange for the Cs - Li, Cs - Na, Cs - K exchanges on attapulgite, and Cs - Sr, Cs - Y, Cs - Ce exchanges on montmorillonite. Among the uni-univalent ion exchanges on attapulgite, the free energies, heats and entropies of exchange were found to have the same signs for a particular exchange. The order of affinity was $\text{Cs} > \text{K} > \text{Na} > \text{Li}$, a sequence found in several zeolites and organic resins. Heats of exchange were found to be negative when an ion of larger crystallographic radius replaced a smaller one in the solid.

Uni-divalent and uni-trivalent ion exchanges on montmorillonite were found to be highly endothermic when the polyvalent ion entered the solid. Corresponding entropies of exchange were positive, and were explained in terms of disordering of water molecules as the polyvalent ion enters the clay structure, since water orientated about a polyvalent ion in solution is lost in the exchange for caesium.

The effect of temperature on ion exchange equilibria in several zeolites has been investigated eg. Na - Ag, Na - Tl exchange in chabazite (49), Na - Li in basic canrinite (9) and Na - K in faujasite (10). No attempts were made to evaluate the heats of ion exchange and it

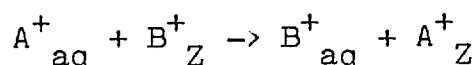
was concluded that the heats in these zeolites were small. However, Ames (69) has attempted to measure the heats of exchange of the Na - K and Na - Cs exchanges in NaX by studying the equilibria at 25^oc and 70^oc. He reports standard heats of exchange of -200 cal/mole and 200 cal/mole for these exchanges respectively, as compared with the calorimetric evaluated figures of -1250 and -1660 respectively. The Na - K ion exchange in NaX has also been studied by Huang et al. (70) at 30^oc and 60^oc. They have derived a value of -993 cal/gm. eq. for the standard heat of exchange for this ion pair exchange with water as the solvent. Heats of exchange in methanol and ethanol were also measured for the Na - K exchange in NaX. The heat of exchange in ethanol was found to be similar to that in water, but in methanol it was found to be much more exothermic. However, due to the discrepancies in the measured heats by observing the temperature dependence of ion exchange equilibria it seems advisable to measure heats of ion exchange by a calorimetric method where this method is possible.

2.4. Theories of the Heat of Ion Exchange

Attempts at measuring the heats of ion exchange from ion exchange equilibria measurements at different temperatures have shown that this quantity is small. This has

been confirmed by direct calorimetric measurements (15) (51) - the standard heats of ion exchange being of the order of 1 - 2 kcal/gm. eq. of exchanger.

Barrer and Falconer (9) have presented a simple picture of the ion exchange process in crystalline exchangers, which can account for the small heats of ion exchange that have been observed. The ion exchange is regarded as an interchange of ions between two dielectric media, otherwise structureless. Thus for the ion exchange reactions



(where the subscripts Z and aq denote in the zeolite and solution respectively), the energy of reaction ΔU is given by

$$\Delta U = U_{A^+_Z} + U_{B^+_{aq}} - U_{B^+_Z} - U_{A^+_{aq}}$$

where $U_{A^+_Z}$ and $U_{A^+_S}$ are the energies of the ion A in the solid and solution respectively. Similarly for ion B. The energy of a sphere of charge Ze and radius r in a medium of dielectric constant ϵ is

$$U = \frac{(Ze)^2}{2r\epsilon}$$

If the dielectric constants are respectively ϵ_S and ϵ_Z for the aqueous phase and the zeolitic medium, then the energy of reaction ΔU is

$$\Delta U = \frac{(Z_A e)^2}{2r_A \epsilon_Z} + \frac{(Z_B e)^2}{2r_B \epsilon_S} - \frac{(Z_B e)^2}{2r_B \epsilon_Z} - \frac{(Z_A e)^2}{2r_A \epsilon_S}$$

where r_A , r_B are the radii of the exchanging ions A and B respectively. For mono-monovalent exchange $Z_A = Z_B = 1$, and the equation reduces to

$$\Delta U = \frac{e^2}{2} \left(\frac{r_B - r_A}{r_A r_B} \right) \left(\frac{\epsilon_S - \epsilon_Z}{\epsilon_S \epsilon_Z} \right)$$

This shows that the nearer r_B and r_A , or ϵ_S and ϵ_Z approach each other the smaller will be the value of ΔU . Using values of $\epsilon_S = 80$ and $\epsilon_Z = 20$ and crystallographic ionic radii, Barrer and Falconer have calculated values of ΔU for several ion pairs. These are summarized in the following table.

TABLE 4

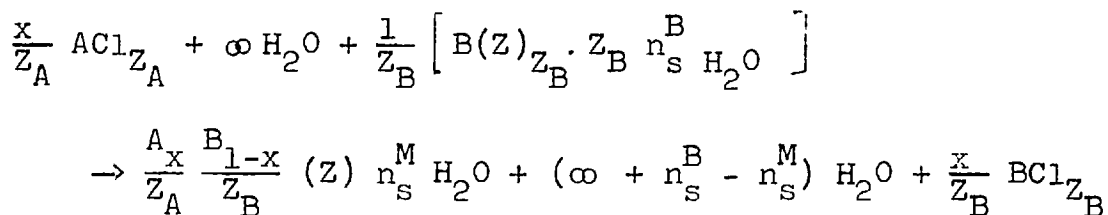
Calculated energies of exchange between inert dielectrics

<u>Ion</u>	<u>Radius A⁰</u>	<u>Exchange</u>	<u>ΔU kcal/gm.eq.</u>
Li ⁺	0.78	Li → Na	-1.5
		Li → Rb	-3.7
Na ⁺	0.95	Na → K	-1.7
K ⁺	1.33	K → Li	+3.2
		K → Rb	-0.5
Rb ⁺ (or Tl ⁺)	1.49	Na → Rb	-2.0
Ca ²⁺	0.98	$\frac{1}{2}$ Ca → Na	-6.0

(The ion on the right in $A \rightarrow B$ is the one entering the exchanger).

However, this model of the ion exchange process is a very simplified one as it neglects changes in the degree of hydration of the ions as they are involved in the ion exchange process, and also assumes complete homogeneity of the exchange sites. A further consideration is that fixed values of the dielectric constants have been used for all cationic forms of the exchanger. Also the dielectric constant of the aqueous phase has been taken as that of bulk water. However, the dielectric constant of the medium immediately surrounding an ion is not the same as that of the bulk medium. Nevertheless, the theory has explained how the major part of the energy of exchange arises. Strictly the energy change is the free energy change and should be corrected for an entropy change in order to derive a value of the heat of ion exchange. However, better agreement has been found to exist between the measured heats of exchange and the calculated energy change than between the measured free energy and the calculated energy change.

An attempt has been made by Barrer, Rees and Shamsuzzoha to correlate the heats of exchange with differences in the heats of hydration of the ions (15). The ion exchange reaction may be represented by



where all the reactants and products are in their standard states. Thus, for the reaction when an ion A of valence Z_A replaces sodium in the zeolite

$$\Delta H = (\Delta H_{\text{Na}}^{\circ} - \frac{1}{Z_A} \Delta H_A^{\circ})_S + (\frac{1}{Z_A} \Delta H_A^{\circ} - \Delta H_{\text{Na}}^{\circ})_Z$$

where $\Delta H_{\text{Na}}^{\circ}$ and ΔH_A° are the standard heats of solvation of gaseous Na and entering ion A respectively, and the subscripts S and Z represent the aqueous and zeolite phases respectively. The first term in the above equation can be calculated from tables of thermodynamic data. Thus, using the measured value of the standard heat of ion exchange, the second term can be evaluated. These values are given below for the exchanges in NaX.

Cation	Li	K	Rb	Cs	Ca	Sr	Ba
$(\Delta H_{\text{Na}}^{\circ} - \frac{1}{Z_A} \Delta H_A^{\circ})_S$	+26.1	-20.2	-26.1	-36.0	+93.4	+75.8	+58.9
$(\Delta H_{\text{Na}}^{\circ} - \frac{1}{Z_A} \Delta H_A^{\circ})_Z$	+24.3	-19.0	-23.8	-33.5	+92.3	+74.0	+59.0
kcal/gm.eq.)							

Except for the $\text{Na}^+ \rightarrow \frac{1}{2} \text{Ba}^{2+}$ exchange, the sign of all values of ΔH° are the same as the signs of the differences in solvation heats of gaseous ions in aqueous solutions.

Also differences in heats of solvation of the gaseous ions in the zeolite are numerically close to the same differences in the aqueous solutions, thus showing the similarity between the zeolite medium and the aqueous solution.

3. Theoretical treatment of ion exchange equilibria

The following symbols will be used in this thesis:-

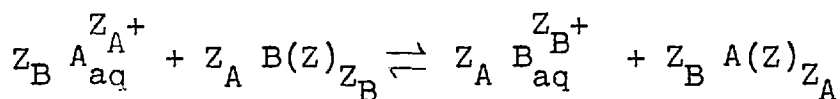
A, B	exchangeable cations
(Z)	1 equivalent of exchanger anion
Z_A, Z_B	valencies of cations A, B respectively
Y	univalent anion
$A(Z)$	1 equivalent of exchanger in A-form
$A_x B_{1-x}(Z)$	1 equivalent of mixed exchanger
x	extent of exchange in equivalents occurring in 1 equivalent of exchanger
n_A, n_B	number of moles of A and B in exchanger
A_Z	equivalent cation fraction of A or equivalent fraction of $A(Z)_{Z_A}$ in exchanger
$X_{A(Z)_{Z_A}}$	mole fraction of $A(Z)_{Z_A}$ in exchanger
	$X_{A(Z)_{Z_A}} = \frac{n_A}{n_A + n_B}$
A_s	equivalent cation fraction of A in solution
n_s	number of moles of solvent in exchanger
n_s^A	number of moles of water in 1 equivalent of pure exchanger $A(Z)_{Z_A}$ in its standard state
n_s^B	number of moles of water in 1 equivalent of pure exchanger $B(Z)_{Z_B}$ in its standard state

- n_s^M number of moles of water in 1 equivalent of mixed exchanger $A_x B_{1-x}(Z)$ in its standard state
- $f_{A(Z)_{Z_A}}, f_{B(Z)_{Z_B}}$ activity coefficients of $A(Z)_{Z_A}$, $B(Z)_{Z_B}$ respectively in exchangers
- $\gamma_{\pm AY_{Z_A}}, \gamma_{\pm BY_{Z_B}}$ mean activity coefficients of AY_{Z_A} , BY_{Z_B} respectively in solution
- γ_s ratio of mean activity coefficients in solution
- K mass action quotient
- $$K = \frac{A_Z}{B_Z} \cdot \frac{B_s}{A_s} \text{ for uni-univalent exchanges}$$
- K_a thermodynamic equilibrium constant
- $(A_Z)(B_Z)$ activities of A and B in exchanger
- $(A_s)(B_s)$ activities of A and B in solution
- μ chemical potential
- m molality of solution
- $j_A(T), j_B(T)$ partition functions of ions A and B in the exchanger
- $n_s^{A(v)}$ number of moles of water in 1 equivalent of pure exchanger $A(Z)_{Z_A}$ in equilibrium with water vapour over pure water at 25°C
- $n_s^{M'}$ number of moles of water in 1 equivalent of mixed exchanger $A_x B_{1-x}(Z)$ in contact with its equilibrium solution containing the exchanging cations at a finite concentration

N	number of equivalents of electrolyte in solution
v	number of moles of water in solution
m_A	molality of ACl_{Z_A} in solution
ΔH°	standard heat of ion exchange involving 1 equivalent of exchanger
ΔH°_x	standard heat of partial ion exchange involving 1 equivalent of exchanger
ΔH_x	experimentally measured heat of ion exchange involving 1 equivalent of exchanger
ϕ_{BZ}°	apparent equivalent heat content of pure exchanger - zeolite framework and exchangeable cations - in its standard state
ϕ_{BZ}^v	apparent equivalent heat content of pure exchanger - zeolite framework and exchangeable cations - in equilibrium with water vapour over pure water at 25°C
$\phi'_{(A,B)Z}$	apparent equivalent heat content of mixed exchanger $A_x B_{1-x}(Z)$ - zeolite framework and exchangeable cations - in contact with its equilibrium solution containing a finite concentration of the exchangeable cations
$\phi_{ACl}^{m_A}$	apparent molar heat content of ACl_{Z_A} at a molality m_A

- $\phi_{Acl}^{m_A}$ relative apparent molal heat content of ACl_{Z_A}
at a molality m_A
- H_s^o standard molal heat content of water
- ΔH_{BZ}^W a heat of wetting, involving 1 equivalent of
the pure exchanger $B(Z)_{Z_B}$ equilibrated
with water vapour over pure water at $25^\circ c$
- $\Delta H_{(A,B)Z}^W$ a heat of wetting, involving 1 equivalent of
the mixed exchanger $A_x B_{1-x}(Z)$ equilibrated
with water vapour over pure water at $25^\circ c$
- $\Delta H_{(A,B)Z}^E$ a heat of equilibration, involving 1 equivalent
of the mixed exchanger $A_x B_{1-x}(Z)$ equili-
brated with water vapour over pure water
at $25^\circ c$

The ion exchange equilibrium between a cation exchanger and an electrolyte solution can be represented by the equation:



Several equations, assuming different models for the exchange systems, have been used to describe ion exchange equilibria. However, since these equilibria have been studied in a variety of substances, e.g. zeolites and organic resins where exchange takes place inside the exchanger, and in clays, where in some cases the exchange

takes place on the surface of the exchanger, the various models proposed have only limited applications and have been successful when applied to particular systems. Thus only theories based on models assuming a rigid three-dimensional framework will be considered in this section. A review of models proposed for ion exchange equilibria in which swelling effects are taken into consideration is given by Helfferich (74). In non-swelling exchangers the exchange equilibria have been approached in several ways:-

- a) Empirically; by analogy with adsorption isotherms of gases on solids, and by a kinetic approach.
- b) By considering ion exchange equilibrium as a Donnan membrane equilibrium
- c) By formulation of ion exchange equilibria according to the law of mass action
- d) By considering ion exchange as a statistical distribution of ions amongst the available sites.

3.1. a) Empirical Equations. Equations derived by analogy with adsorption of gases on solids. Equations derived kinetically.

The early attempts at representing ion exchange equilibria were mainly empirical. The equations

$$\frac{A_Z}{B_Z} \cdot \left(\frac{B_S}{A_S} \right)^{\text{const}} = \text{constant} \quad 3.1.1$$

$$\text{and } A_Z \left(\frac{B}{A_S} \right)^{\text{const}} = \text{constant} \quad 3.1.2$$

have been proposed by Rothmund and Kornfeld (75a) and Wiegner and Jenny (75b) respectively.

An analogy to the adsorption of gases on solids has been used by Vageler (19) who proposed the equation

$$A_Z = \text{constant } (A_S)^{\text{constant}} \quad 3.1.3$$

However, all of the above equations have no theoretical basis and are of little value in understanding the mechanism of the ion exchange process.

Boyd, Schubert and Adamson (54) have proposed a more acceptable treatment of the ion exchange process as an adsorption process. By analogy with the Langmuir equation for the adsorption of two gases from a binary gaseous mixture, the equation for the adsorption of the ion A^+ from dilute electrolyte solution is given by

$$\left(\frac{x}{m} \right)_{A^+} = \frac{k b_1 c_{A^+}}{1 + b_1 c_{A^+} + b_2 c_{B^+}} \quad 3.1.4$$

where $\left(\frac{x}{m} \right)_{A^+}$ is the amount of ion A adsorbed per gram of exchanger; c_{A^+} , c_{B^+} are respectively the equilibrium concentrations of ion A, B in solution; and k , b_1 , b_2 are constants. When all the sites are filled in order to establish electroneutrality this equation reduces to

$$\left(\frac{x}{m} \right)_{A^+} = \frac{k b_1 c_{A^+}}{b_1 c_{A^+} + b_2 c_{B^+}} \quad 3.1.5$$

Gapon (76) has assumed that ion exchange equilibria are reversible, and that the rate of adsorption of a cation on the surface of the exchanger was proportional to the concentration of that cation in solution and to the amount of the other ion in the solid. At equilibrium the rates of adsorption of the two cations were equal, thus enabling the following equations to be derived:

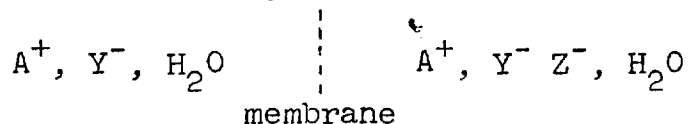
$$\frac{m_{A^+}}{m_{B^+}} = K \cdot \frac{[A^+]}{[B^+]} \quad \text{for a 1:1 exchange}$$

$$\text{and } \left[\frac{m_{A^{2+}}}{m_{B^+}} \right]^{\frac{1}{2}} = K \cdot \frac{[A^{2+}]}{[B^+]}^{\frac{1}{2}} \quad \text{for a 1:2 exchange}$$

where m_i represents the molality of species i in solution, and $[A_i]$ is the amount of the species i in the solid.

3.2. Ion exchange equilibrium treated as a Donnan membrane equilibrium

Electrolyte sorption equilibria have a resemblance to equilibria in systems such as



in which a membrane permeable for all species except for Z^- is between two solutions AY and $AY + AZ$. The behaviour of membrane systems such as above was first

studied by Donnan (77) in 1911.

Ion exchange equilibrium has been treated as a Donnan membrane equilibrium by Bauman and Eichhorn (78), the exchanger network being regarded as the semi-permeable membrane and the anionic groups of the exchanger being the non-diffusible anions. At equilibrium the chemical potentials of electrolytes AY and BY are the same in both phases, thus

$$\mu_{AY_S} = \mu_{AY_Z} \text{ and } \mu_{BY_S} = \mu_{BY_Z} \quad 3.2.1$$

The term μ_{AY_S} can be replaced by

$$\mu_{AY_S} = \mu_{AY_S}^0 + RT \ln (A_S)(Y_S) \quad 3.2.2$$

where (A_S) , (Y_S) indicate the activities of A and Y respectively in the solution phase. Similar equations can be derived for μ_{AY_Z} , μ_{BY_Z} , μ_{BY_S}

Substitution leads to

$$(A_S)(Y_S) = (A_Z)(Y_Z) \quad 3.2.3$$

$$(B_S)(Y_S) = (B_Z)(Y_Z) \quad 3.2.4$$

$$\text{Thus } \frac{(A_Z)}{(B_Z)} \cdot \frac{(B_S)}{(A_S)} = 1 \quad 3.2.5$$

Replacing activities by concentrations and activity coefficients, this reduces to

$$\frac{A_Z}{B_Z} \cdot \frac{B_S}{A_S} \cdot \frac{f_{A(Z)}}{f_{B(Z)}} \cdot \frac{\gamma_{B(s)}}{\gamma_{A(s)}} = 1 \quad 3.2.6$$

For dilute solutions, if the ratios of the activity coefficients are constant then

$$\frac{A_Z}{B_Z} \cdot \frac{B_S}{A_S} = K \quad 3.2.7$$

which is identical to the simple form of the law of mass action (vide section 3.3).

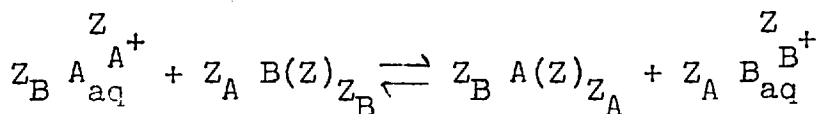
The Donnan membrane theory of exchange has been used extensively in studies of resin exchangers. However, no account of the change in free energy associated with the swelling of resins during ion exchange was taken in the above treatment. Gregor (79) has considered the exchanger as a swelling gel in which an equilibrium is set up between the swelling pressure and the matrix forces in the exchanger, and has derived the relation

$$RT \ln \frac{A_Z}{B_Z} \cdot \frac{B_S}{A_S} = \pi (\bar{V}_B - \bar{V}_A) \quad 3.2.8$$

for a uni-univalent exchange where π is the swelling pressure within the exchanger and $\bar{V}_A$, $\bar{V}_B$ are the partial molar volumes of the hydrated ions. However, Gregor's theory is inapplicable to some crystalline exchangers since they undergo no swelling when immersed in aqueous solutions of salts.

3.3. Ion Exchange Equilibria according to the Law of Mass Action

The law of mass action expression for the generalized ion exchange reaction



is

$$K_a = \frac{(A_Z)^{Z_B} \cdot (B_S)^{Z_A}}{(B_Z)^{Z_A} \cdot (A_S)^{Z_B}} \quad 3.3.1$$

For uni-univalent exchanges $Z_A = Z_B = 1$, so this reduces to

$$K_a = \frac{(A_Z)}{(B_Z)} \cdot \frac{(B_S)}{(A_S)} \quad 3.3.2$$

In terms of concentrations and activity coefficients this may be written

$$K_a = \frac{A_Z}{B_Z} \cdot \frac{B_S}{A_S} \cdot \frac{f_{AZ}}{f_{BZ}} \cdot \frac{\gamma_{Bs}}{\gamma_{As}} \quad 3.3.3$$

$$= K \cdot \frac{f_{AZ}}{f_{BZ}} \cdot \frac{\gamma_{Bs}}{\gamma_{As}} \quad 3.3.4$$

The selectivity coefficient K is obtained from ion exchange equilibrium data. In order to determine the thermodynamic equilibrium constant K_a the activity coefficients of the ions in the solution and exchanger have to be known. The single ion activity coefficients are

strictly indeterminate although the ratio of the coefficients in one phase is determinate. However, the ambiguities associated with single ion activity coefficients can be avoided by taking the pure exchangers $A(Z)_{Z_A}$ and $B(Z)_{Z_B}$ as the components in the solid phase. The solid phase at equilibrium can be regarded as a non-ideal solution of the pure components, and consequently the activity of each component can be related to its mole fraction multiplied by an activity coefficient, $F_{A(Z)_{Z_A}}$. Thus

$$K_a = \frac{X_{A(Z)} F_{A(Z)}}{X_{B(Z)} F_{B(Z)}} \cdot \frac{m_{BY}}{m_{AY}} \cdot \frac{\gamma_{\pm BY}^2}{\gamma_{\pm AY}^2} \quad 3.3.5$$

for a uni-univalent exchange

and

$$K_a = \frac{X_{A(Z)_2} F_{A(Z)_2}}{X_{B(Z)_2} F_{B(Z)_2}} \cdot \frac{m_{BY}^2}{m_{AY_2}} \cdot \frac{\gamma_{\pm BY}^4}{\gamma_{\pm AY_2}^3} \quad 3.3.6$$

for a uni-divalent exchange.

In the case of uni-univalent exchanges several simplifying assumptions can be made with regard to the activity coefficients in the solution and exchanger phases. For dilute solutions, the ratio of the activity coefficients, $\gamma_s = \gamma_{\pm BY}^2 / \gamma_{\pm AY}^2$ should be nearly constant and equal to one for different ratios of the exchanging ions in solution. Also if it is assumed that the ratio

of the activity coefficients in the solid phase,

$\gamma_Z = F_{A(Z)}/F_{B(Z)}$ is constant, then equation 3.3.5 reduces to the simple form of the law of mass action,

$$K = \frac{A_Z}{B_Z} \cdot \frac{B_S}{A_S}$$

The selectivity coefficient has been found to be constant for several exchanges, e.g. Na - Tl exchange in NaA (50), and the Na - Ag exchange in Chabazite (49). However in most cases it has been found that the selectivity coefficient was dependent on cationic composition e.g. K - Ag exchange in chabazite. In these cases the assumption that γ_Z is constant is not valid.

Activity coefficients in electrolytic solutions

The activity coefficients of the electrolytes used in equations 3.3.5 and 3.3.6 should strictly be the activity coefficients of one electrolyte in the presence of a second, and not the values of the activity coefficients of the single electrolytes in solution at the same molality as the mixed electrolytes at equilibrium. Very few measurements of the activity coefficients of electrolytes in solution containing two electrolytes have been made. Marshall and Gupta (80) used a direct potentiometric method to determine the activities of the electrolytes involved in ion exchange equilibria with clays, but this method is not generally applicable.

However, the activity coefficient $(\gamma_{\pm})_{AY}$ of an electrolyte AY in the presence of a second electrolyte BY can be evaluated approximately from an expression derived by Glueckauf (81)

$$\log(\gamma_{\pm})_{AY} = \log(\overline{\gamma_{\pm}})_{AY} - \frac{[B]}{4I} \left[K_1 \log(\overline{\gamma_{\pm}})_{AY} - K_2 \log(\overline{\gamma_{\pm}})_{BY} - \frac{K_3}{1 + \frac{1}{I} I^{1/2}} \right] \quad 3.3.7$$

where $(\overline{\gamma_{\pm}})_{AY}$ is the activity coefficient of the single electrolyte AY in a solution at an ionic strength equal to the ionic strength I of the solution of the mixed electrolytes, $[B]$ is the concentration of the ion B and K_1 , K_2 , K_3 are constants whose values depend on the valencies of the ions A, B, Y. For a solution involving only monovalent ions, Glueckauf's expression reduces to

$$\log \frac{(\gamma_{\pm})_{AY}}{(\gamma_{\pm})_{BY}} = \frac{1}{2} \log \frac{(\overline{\gamma_{\pm}})_{AY}}{(\overline{\gamma_{\pm}})_{BY}} \quad 3.3.8$$

$$\text{or } \frac{(\gamma_{\pm}^2)_{BY}}{(\gamma_{\pm}^2)_{AY}} = \frac{(\overline{\gamma_{\pm}})_{BY}}{(\overline{\gamma_{\pm}})_{AY}} = \gamma_s \quad 3.3.9$$

It is this ratio that is substituted in equation 3.3.5 for the thermodynamic equilibrium constant for mono-monovalent cation exchange.

For a solution of two electrolytes where the valency

of the ions A and B differ, and where there is a common anion, the activity coefficients of the respective electrolytes in the presence of one another have to be calculated directly from Glueckauf's expression.

Activity coefficients in the solid phase

Since the two components of the exchanger phase normally form continuous solutions, attempts have been made to relate the activities of the components to some function of their concentration in the exchanger. If a linear relationship is assumed to exist between the activity of each component and its concentration, then this leads, together with the stipulation that γ_s is constant, to the simple form of the law of mass action.

Kielland (82) suggested the following semi-empirical equations to describe the activity coefficients in the solid phase

$$\log f_A(Z) = CX_B^2(Z) ; \quad \log f_B(Z) = CX_A^2(Z) \quad 3.3.10$$

when a non-ideal solution is formed, the value of the constant C, which can be positive or negative, depending on the system. Substitution of these expressions in equation 3.3.3 leads to

$$\log K_a = \log K_c + C(1-2A_Z) \quad 3.3.11$$

$$\text{where } K_c = \frac{A_Z}{B_Z} \cdot \frac{B_s}{A_s} \frac{(\gamma^+)_{BY}}{(\gamma^+)_{AY}} \quad 3.3.12$$

$$= \frac{A_Z}{B_Z} \cdot \frac{B_S}{A_S} \cdot \gamma_S \quad 3.3.13$$

$$= K \gamma_S \quad 3.3.14$$

For a uni-univalent exchange where a plot of $\log K_c$ against A_Z is linear, $K_a = K_c$ when $A_Z = 0.5$. When the value of C is zero, equation 3.3.11 reduces to the simple law of mass action. This equation has been found to represent the ion exchange isotherms in several exchanges NaA(51), NaX(15) and chabazite (49).

For some exchanges, the variation of $\log K_c$ with cationic composition A_Z is found to be non-linear. In these cases, if the exchange is between univalent ions, Kielland's relations are not valid. Hogfeldt, Ekedahl and Sillen (83) and Argersinger, Davison and Bonner (84) independently have derived a method for obtaining values for the activity coefficients of the components in the exchanger phase, and the thermodynamic equilibrium constant K_a . The solid phase was considered as a binary solution of the components $A(Z)_{Z_A}$ and $B(Z)_{Z_B}$. The standard states of the components were taken as the pure components $A(Z)_{Z_A}$, $B(Z)_{Z_B}$ in equilibrium with dilute solutions of AY_{Z_A} and BY_{Z_B} respectively. For a uni-univalent exchange

$$K_c = K_a \frac{f_{B(Z)}}{f_{A(Z)}} = K_a \frac{f_{B(Z)}}{f_{A(Z)}} \quad 3.3.15$$

where the activity coefficients associated with the

components of the solid solution expressed in mole fractions $X_A(Z)$, $X_B(Z)$ are identical to those when the composition of the exchanger is expressed in equivalent fractions A_Z , B_Z .

Application of the Gibbs - Duhem equation to the exchange phase gives the relation

$$X_A(Z) d \ln X_A(Z) \cdot F_A(Z) + X_B(Z) d \ln X_B(Z) F_B(Z) = 0 \quad 3.3.16$$

neglecting any changes of water content of the exchanger. From equations 3.3.15 and 3.3.16

$$d \ln F_A(Z) = - X_B(Z) d \ln K_c \quad 3.3.17$$

$$\text{and } d \ln F_B(Z) = X_A(Z) d \ln K_c \quad 3.3.18$$

In order to evaluate the activity coefficients of the components at a particular composition of the exchanger phase, these two equations are integrated noting that when $X_A(Z)$ (or A_Z) = 1, $X_B(Z)$ (or B_Z) = 0, $K_c = K'_c$ and $F_A(Z)$ (or $f_A(Z)$) = 1, and when $X_A(Z)$ (or A_Z) = 0, $X_B(Z)$ (or B_Z) = 1, $K_c = K^0_c$ and $F_B(Z)$ (or $f_B(Z)$) = 1

Thus

$$\log f_A(Z) = - \int_{K_c^0}^{K_c} B_Z d \log K_c \quad 3.3.19$$

$$\log f_B(Z) = \int_{K_c^0}^{K_c} A_Z d \log K_c \quad 3.3.20$$

Thus the activity coefficients of the components in the exchanger phase can be determined from a graph of $\log K_c$ against A_Z . The thermodynamic equilibrium constant K_a can be evaluated from equation 3.3.15 by substitution of the above expressions. Thus

$$\log K_a = \log K_c' - \int_{K_c^0}^{K_c'} A_Z d \log K_c \quad 3.3.21$$

$$= \int_0^1 \log K_c d A_Z \quad 3.3.22$$

For uni-divalent exchanges, i.e. $Z_A = 2$, $Z_B = 1$, equivalent fractions and mole fractions in the exchanger phase are not equal, thus neither will be the activity coefficients of the components associated with these fractions. The expression for the thermodynamic equilibrium constant for uni-divalent exchanges is

$$K_a = \frac{X_{A(Z)_2} \cdot F_{A(Z)_2} \cdot m_{BY}^2 \cdot \gamma_{BY}^4}{X_{B(Z)}^2 \cdot F_{B(Z)}^2 \cdot m_{AY_2} \cdot \gamma_{AY_2}^3} \quad 3.3.6$$

$$= K_c \frac{F_{A(Z)_2}}{F_{B(Z)}^2} \quad 3.3.23$$

$$\text{where } K_c = \frac{X_{A(Z)_2} \cdot m_{BY}^2 \cdot \gamma_{BY}^4}{X_{B(Z)}^2 \cdot m_{AY_2} \cdot \gamma_{AY_2}^3}$$

In this expression the composition of the exchanger phase is expressed in mole fractions and $F_{A(Z)_2}$, $F_{B(Z)}$ are the corresponding activity coefficients of the components in the exchanger phase, associated with the mole fractions $X_{A(Z)_2}$, $X_{B(Z)}$ respectively.

Application of the Gibbs-Duhem equation to the exchanger phase gives the relation

$$X_{A(Z)_2} \cdot d \ln X_{A(Z)_2} \cdot F_{A(Z)_2} + X_{B(Z)} \cdot d \ln X_{B(Z)} \cdot F_{B(Z)} = 0 \quad 3.3.24$$

Combining equations 3.2.23 and 3.3.24, the expressions for the activity coefficients become

$$d \ln F_{A(Z)_2} = - \frac{X_{B(Z)}}{X_{B(Z)} + 2X_{A(Z)_2}} d \ln K_c \quad 3.3.25$$

$$d \ln F_{B(Z)} = \frac{X_{A(Z)_2}}{X_{B(Z)} + 2X_{A(Z)_2}} d \ln K_c \quad 3.3.26$$

Integrating equations 3.3.25 and 3.3.26 noting that when $X_{A(Z)_2} = 1$, $K_c = K_c^1$ and $F_{A(Z)_2} = 1$; and when $X_{B(Z)} = 1$, $K_c = K_c^0$ and $F_{B(Z)} = 1$; thus

$$\ln F_{A(Z)_2} = - \int_{K_c^0}^{K_c} \frac{X_{B(Z)}}{X_{B(Z)} + 2X_{A(Z)_2}} d \ln K_c \quad 3.3.27$$

$$\text{and } \ln F_B(Z) = \int_{K_c^0}^{K_c} \frac{X_A(Z)_2}{K_c^0 X_{B(Z)} + 2 X_{n(Z)}_2} d \ln K_c \quad 3.3.28$$

Thus the activity coefficients in the exchanger phase can be obtained from a graph of $\log K_c$ against cationic composition of the exchanger (expressed in mole fractions) by graphical integration. The thermodynamic equilibrium constant is obtained from

$$\log K_a = \log K_c + \log F_A(Z)_2 - 2 \log F_B(Z)$$

by substitution of the values of the various functions.

The approach of Ekedahl (83) and Argersinger et al. (84) outlined above is quite rigorous apart from the assumption that the effects of water in the exchanger phase do not alter as exchange proceeds. However, as the water contents of the exchangers in their standard states are often not the same, it is necessary to consider water as an additional component and to introduce a term in the Gibbs-Duhem equation to express the variation of the chemical potential of the solvent. This thermodynamic treatment was carried out independently by Gaines and Thomas (85), Hogfeldt (86) and Argersinger (87). The treatments differ slightly, but the treatment of Gaines and Thomas is the most advantageous since it enables calculations of the activity coefficients of the components of the mixed exchanger to be made which

are independent of the concentration of the external solution.

They considered the activity coefficients in the exchanger to be associated with the equivalent fraction of the components $A(Z)_{Z_A}$, $B(Z)_{Z_B}$ of the mixed exchanger. Thus the chemical potential of the component $A(Z)_{Z_A}$ is given by

$$\mu_{A(Z)_{Z_A}} = \mu_{A(Z)_{Z_A}}^{\circ} + RT \ln A_Z f_{A(Z)_{Z_A}} \quad 3.3.29$$

In the solution the chemical potential of the exchanging species was related to the molality of the solution in the normal manner, thus

$$\mu_{A_S} = \mu_{A_S}^{\circ} + RT \ln m_{A_S} \cdot \gamma_{A_S} \quad 3.3.30$$

The standard state chosen for the electrolyte in solution is therefore a solution of unit molality in which the solute has a mean activity coefficient of unity at atmospheric pressure and at all temperatures. This solution is known as the 'hypothetical ideal 1 molal solution'.

The standard state of the water was defined such that its activity at equilibrium was the same in each phase i.e. the activity of the water, a_s , is equal to unity for pure water, and the standard chemical potentials in the three phases, exchanger, liquid and vapour

are all equal.

For the exchanger the standard states were taken as pure exchanger $A(Z)_{Z_A}$ in equilibrium with an infinitely dilute solution of AY_{Z_A} , which is effectively pure water. Thus when $A_Z = 1$ ($a_s = 1$) then $f_A(Z) = 1$, and when $B_Z = 1$ ($a_s = 1$), $f_B(Z) = 1$. At equilibrium the chemical potential of the water is the same in all phases, and the change in free energy is zero. Thus

$$Z_B \mu_{A(Z)_{Z_A}} - Z_A \mu_{B(Z)_{Z_B}} - Z_B \mu_{A_s} + Z_A \mu_{B_s} = 0 \quad 3.3.31$$

Hence the thermodynamic equilibrium constant K_a is given by

$$K_a = \frac{A_Z^{Z_B} \cdot f_{A(Z)}^{Z_B} \cdot m_{BY_{Z_B}}^{Z_A} \cdot \left[\gamma_{BY_{Z_B}}^{+} \right]^{Z_B+1}}{B_Z^{Z_A} \cdot f_{B(Z)}^{Z_A} \cdot m_{AY_{Z_A}}^{Z_B} \cdot \left[\gamma_{AY_{Z_A}}^{+} \right]^{Z_A+1}} \quad 3.3.32$$

(for convenience the valence subscripts in the activity coefficients have not been included). The standard free energy of exchange per equivalent of exchanger, ΔG° is given by

$$\Delta G^\circ = - \frac{RT}{Z_A Z_B} \ln K_a \quad 3.3.33$$

Applying the Gibbs-Duhem equation to the exchanger phase, including a term to express the variation of the chemical potential of the water,

$$n_A d \ln A_Z f_A(Z) + n_B d \ln B_Z f_B(Z) + n_s d \ln a_s = 0 \quad 3.3.34$$

Multiplying equation 3.3.34 by $Z_A Z_B / Z_A n_A + Z_B n_B$ and replacing $Z_A n_A / Z_A n_A + Z_B n_B$ by A_Z , the equation becomes

$$A_Z d \ln A_Z^{Z_B} f_A(Z) + B_Z d \ln B_Z^{Z_A} f_B(Z) + Z_A Z_B n_s d \ln a_s = 0 \quad 3.3.35$$

and therefore

$$Z_A d B_Z + Z_B d A_Z + A_Z d \ln f_A^{Z_B}(Z) + B_Z d \ln f_B^{Z_A}(Z) + Z_A Z_B n_s d \ln a_s = 0 \quad 3.3.36$$

$$\text{As before } K_a = K_c \frac{f_A^{Z_B}(Z)}{f_B^{Z_A}(Z)} \quad 3.3.37$$

$$\text{or } d \ln K_c + d \ln f_A^{Z_B}(Z) - d \ln f_B^{Z_A}(Z) = 0 \quad 3.3.38$$

Combining equations 3.3.36 and 3.3.38,

$$d \ln f_A^{Z_B}(Z) = -(Z_A - Z_B) d B_Z - B_Z d \ln K_c - Z_A Z_B n_s d \ln a_s \quad 3.3.39$$

and

$$d \ln f_B^{Z_A}(Z) = (Z_A - Z_B) d A_Z + A_Z d \ln K_c - Z_A Z_B n_s d \ln a_s \quad 3.3.40$$

On integrating these relations between the limits

of pure exchanger and non-standard states a and b

$$\ln f_{A(Z)}^{Z_B} / f_{A(Z)_a}^{Z_B} = -(Z_A - Z_B)B_Z - \int_{K_c'}^{K_c} B_Z d \ln K_c - Z_A Z_B \int_{a_s(a)}^{a_s'} n_s d \ln a_s \quad 3.3.41$$

and

$$\ln f_{B(Z)}^{Z_A} / f_{B(Z)_b}^{Z_A} = (Z_A - Z_B)A_Z + \int_{K_c^O}^{K_c} A_Z d \ln K_c - Z_A Z_B \int_{a_s(b)}^{a_s'} n_s d \ln a_s \quad 3.3.42$$

where a_s' is the activity of the water in the mixed exchanger phase; $K_c = K_c'$ when $A_Z = 1$, $B_Z = 0$ and $a_s = a_s(a)$; and $K_c = K_c^O$ when $A_Z = 0$, $B_Z = 1$ and $a_s = a_s(b)$. Hence the thermodynamic equilibrium constant is given by

$$\ln K_a = (Z_B - Z_A) + \ln \frac{f_{A(Z)_a}^{Z_B}}{f_{B(Z)_b}^{Z_A}} + \int_0^1 \ln K_c dA_Z - Z_A Z_B \int_{a_s(a)}^{a_s(b)} n_s d \ln a_s \quad 3.3.43$$

where $f_{A(Z)_a}^{Z_B}$, $f_{B(Z)_b}^{Z_A}$ are the activity coefficients of the pure exchangers in the non-standard states a and b. Gaines and Thomas have derived the equation

$$d \ln f_{A(Z)_a}^{Z_B} = Z_A Z_B \int_{a_s=1}^{a_s(a)} \left(\frac{V}{T} - n_s \right) d \ln a_s \quad 3.3.44$$

for the activity coefficients of the exchanger in its non-standard state, where T is the molar volume of the vapour and V is the volume of the exchanger. Generally

for an exchanger $V \ll \tau$ so that $\frac{V}{\tau}$ is small compared with n_s . Therefore

$$d \ln f_{A(Z)_a}^{Z_B} = - Z_A Z_B \int_{a_s=1}^{a_s(a)} n_s d \ln a_s \quad 3.3.45$$

A similar expression exists for $d \ln f_{B(Z)_b}^{Z_A}$. Thus the expressions for the activity coefficients become

$$\begin{aligned} \ln f_{A(Z)_A}^{Z_B} = & -(Z_A - Z_B) B_Z - \int_{K'_c}^{K_c} B_Z d \ln K_c - Z_A Z_B \int_{a_s(a)}^{a'_s} n_s^A d \ln a_s \\ & - Z_A Z_B \int_{a_s=1}^{a_s(a)} n_s^A d \ln a_s \end{aligned} \quad 3.3.46$$

and

$$\begin{aligned} \ln f_{B(Z)_B}^{Z_A} = & (Z_A - Z_B) A_Z + \int_{K_c^0}^{K_c} A_Z d \ln K_c - Z_A Z_B \int_{a_s(b)}^{a'_s} n_s^B d \ln a_s \\ & - Z_A Z_B \int_{a_s=1}^{a_s(b)} n_s^B d \ln a_s \end{aligned} \quad 3.3.47$$

and the expression for the thermodynamic equilibrium constant can be written

$$\ln K_a = (Z_B - Z_A) + \int_0^1 \ln K_c \, dA_Z$$

$$- Z_A Z_B \left[\int_{a_s=1}^{a_s(a)} n_s^A \, d \ln a_s - \int_{a_s=1}^{a_s(b)} n_s^B \, d \ln a_s + \int_{a_s(a)}^{a_s(b)} n_s^M \, d \ln a_s \right]$$

3.3.48

where n_s^A , n_s^B and n_s^M represent the water contents of the pure exchangers $A(Z)_{Z_A}$, $B(Z)_{Z_B}$ and the mixed exchanger $A,B(Z)$ respectively in their standard states.

When applying the above equations to ion exchange reactions in crystalline exchangers, certain simplifying assumptions can be made. As this type of exchanger possesses a rigid framework which is little altered in dimensions upon ion exchange, swelling effects will be negligible. Thus the solvent contents of the pure exchangers will vary negligibly with the activity of the water in solution, and the first two integrals in the brackets of equation 3.3.48 will reduce to

$$n_s^A \ln a_{s(a)} - n_s^B \ln a_{s(b)} \quad 3.3.49$$

Generally ion exchange equilibria data are obtained using solutions of constant total normality in the range 0.1N to 1.0N. In such solutions the activities of the water in solutions of the pure electrolytes at the same normality are approximately the same, so that equation

3.3.49 can be further reduced to

$$(n_s^A - n_s^B) \ln a_s \quad 3.3.50$$

which tends to zero as the equilibrating solutions become more dilute. Also for dilute solutions of constant total normality, the activity of the water in the solutions at equilibrium is almost independent of the mole fractions of the individual ions in solution. Thus the third integral in the brackets of equation 3.3.48 reduces to zero.

If the water contents of the pure exchangers are approximately equal i.e. $n_s^A \approx n_s^B$, the difference between the first two integrals in the square bracket of equation 3.3.48 will be small provided that solutions of constant normality have been used in the ion exchange reactions. If, however, $n_s^A \neq n_s^B$, the term $(n_s^A - n_s^B) \ln a_s$ can be satisfactorily neglected, provided the solutions are dilute, without producing any significant error in the value of K_a . Thus, the expressions for the activity coefficients of the components of the mixed exchanger and the thermodynamic equilibrium constant K_a reduce to

$$\ln f_{A(Z)}^{Z_B} = -(Z_A - Z_B) B_Z - \int_{K'_c}^{K_c} B_Z d \ln K_c \quad 3.3.51$$

$$\ln f_B^{Z_A}(Z) = (Z_A - Z_B)A_Z + \int_{K_c^0}^{K_c} A_Z d \ln K_c \quad 3.3.52$$

$$\ln K_a = (Z_B - Z_A) + \int_0^1 \ln K_c d A_Z \quad 3.3.53$$

In the case of uni-univalent exchanges the expressions of Gaines and Thomas become identical to those of Ekedahl et al. provided dilute solutions are used. However, this is not true for uni-divalent exchanges since Gaines and Thomas have associated activity coefficients with the equivalent fractions of the mixed exchanger, while Ekedahl et al. have associated the activity coefficients with the mole fractions of the mixed exchanger, which are not identical to the equivalent fractions when $Z_A \neq Z_B$.

If the equilibrating solutions employed in the ion exchange determinations are not of constant normality, but increase in strength as the extent of exchange increases, then the values of K_c will not correspond to the same solvent activity. When $A_Z = 0$, the extrapolated value of K_c i.e. K_c^0 will correspond to a solvent activity $a_s(b) = 1$, since very dilute solutions would be used in the determination of the isotherm in this range. When $A_Z = 1$, the extrapolated value of K_c , i.e. K_c' will

correspond to a solvent activity of $a_s(a)$ which will not differ too greatly from unity provided the solutions used in the determination of the isotherm in this range remain fairly dilute. Thus the terms in the square brackets of equation 3.3.48 reduce to

$$n_s^A \ln a_s(a) + \int_{a_s(a)}^{a_s(b)=1} n_s^M d \ln a_s \quad 3.3.54$$

which can rearrange to

$$\int_{n_s^B}^{n_s^A} \ln a_s d n_s \quad 3.3.55$$

where n_s^A , n_s^B are the number of moles of water in one equivalent of the pure exchangers $A(Z)_{Z_A}$, $B(Z)_{Z_B}$ respectively in their standard states. This factor cannot be accurately determined since the activity of the water $a_s(a)$ in a solution corresponding to the extrapolated value of K_c at $A_Z = 1$ is indeterminate. However, some estimate of this term can be made if it is assumed that $a_s(a)$ is equal to the activity of the water in a solution of ACl_{Z_A} at a molality equal to that of the most concentrated solution used in the exchanges. Thus equation 3.3.55 reduces to $(n_s^A - n_s^B) \ln a_s(a)$ 3.3.56

The water contents of the exchangers used in the evaluation of equation 3.3.56 are those for the pure

exchangers in their standard states. These quantities are not known, although the water contents of the pure exchangers when equilibrated with water vapour over saturated ammonium chloride solution are known. Thus equation 3.3.56 can be evaluated using these values for the water contents of the pure exchangers, together with the osmotic coefficients of the respective solutions obtained from the tabulated data of Stokes and Robinson (108). The error contributed by the terms in the square brackets of equation 3.3.48 to the standard free energy of exchange ΔG° is found to be of the order of 6 cal./gm. eq. of exchanger, and this can be neglected in comparison with the error involved in the graphical integration of the integral $\int_0^1 \ln K_c d A_Z$. Thus, even though solutions of varying molalities have been used to determine the exchange isotherms, the contributions made to the value of ΔG° from the varying activities of the solvent in the solutions have been shown to be small.

3.4. Statistical Thermodynamic Treatment of Ion Exchange Equilibria

A statistical thermodynamic treatment of uni-univalent ion exchange has been developed by Barrer and Falconer (9), which can lead to isotherms obeying the

simple mass action law, to sigmoid isotherms, or to isotherms showing limited mutual solubility of the two pure exchange forms. Certain assumptions were made:-

- a) When two entering ions B^+ occupy adjacent sites in an A^+ rich lattice a change in the energy of the crystal occurs.
- b) This change is negligible when ions A^+, B^+ occupy adjacent sites relative to the state when A^+, A^+ ions occupy adjacent sites.
- c) The change in energy is additive with respect to the number of pairs B^+, B^+ independently of whether these pairs are in clusters or isolated.
- d) All other interactions between the energy change and the partition functions of ions A and B in the framework, and of the framework are neglected.
- e) The distribution of ions on the sites is assumed to be random.
- f) The total amount of intracrystalline water is taken as unaltered by exchange.

If ω is an energy term and Z is the co-ordination number of any site, then the energy change when two B type ions occupy adjacent sites is conveniently written as $\frac{2\omega}{Z}$. Then for random distribution, the number of pairs of sites is $\frac{Z N^2}{2N}$ where N is the total number of available sites and N_B is the number of ions of type B

in the crystal. The partition function for the mixed exchanger is

$$Q = \frac{N!}{N_A! N_B! (N - N_A - N_B)!} \left[j_A(T) \exp \frac{E_A}{kT} \right]^{N_A} \left[j_B(T) \exp \frac{E_B}{kT} \right]^{N_B} \times \exp\left(-\frac{\omega N_B^2}{NkT}\right) \cdot Q_L \quad 3.4.1$$

where $j_A(T)$, $j_B(T)$ are the partition functions of the ions A and B respectively in the exchanger; E_A , E_B are the energies of these ions in the crystal relative to those in a reference state, and Q_L is the partition function for all the anionic framework. The free energy A is given by

$$A = -kT \ln Q \quad 3.4.2$$

By use of Stirling's approximation and differentiation, the chemical potentials of the cations in the exchanger can be obtained. Thus

$$\frac{\mu_{BZ}}{kT} = \ln N_B - \ln j_B(T) - \frac{E_B}{kT} + \frac{2N_B \omega}{NkT} \quad 3.4.3$$

and

$$\frac{\mu_{AZ}}{kT} = \ln N_A - \ln j_A(T) - \frac{E_A}{kT} \quad 3.4.4$$

In solution the chemical potentials are given by

$$\frac{\mu_{AS}}{kT} = \frac{\mu_{AS}^0}{kT} + \ln a_{AS} \quad 3.4.5$$

and

$$\frac{\mu_{B_s}}{kT} = \frac{\mu_B^0}{kT} + \ln a_{B_s} \quad 3.4.6$$

At equilibrium in the ion exchange reaction

$$\mu_{A_Z} + \mu_{B_s} = \mu_{B_Z} + \mu_{A_s} \quad 3.4.7$$

Hence

$$\begin{aligned} \ln \frac{N_A}{N_B} \cdot \frac{a_{B_s}}{a_{A_s}} &= \ln \left(\frac{J_{A(T)}}{J_{B(T)}} \right) + \frac{\mu_{A_s}^0 - \mu_{B_s}^0}{kT} + \frac{E_A - E_B}{kT} \\ &+ \frac{2 N_B}{N} \cdot \frac{\omega}{kT} \end{aligned} \quad 3.4.8$$

$$\text{Since } \frac{a_{B_s}}{a_{A_s}} = \frac{B_s}{A_s} \cdot \frac{\gamma_{B_s}}{\gamma_{A_s}} \quad \text{and} \quad \frac{N_A}{N_B} = \frac{A_Z}{B_Z}$$

equation 3.4.8 may be re-written

$$\begin{aligned} \log \left[\frac{A_Z}{B_Z} \cdot \frac{B_s}{A_s} \cdot \frac{\gamma_{B(s)}}{\gamma_{A(s)}} \right] &= \log \frac{J_{A(T)}}{J_{B(T)}} + \frac{1}{2.303} \left[\frac{\mu_{A(s)}^0 - \mu_{B(s)}^0 + E_A - E_B}{kT} \right] \\ &+ \frac{2 B_Z}{2.303} \left(\frac{N_A + N_B}{N} \right) \frac{\omega}{kT} \end{aligned} \quad 3.4.9$$

This is of the same form as 3.3.11, which was derived on the semi-empirical approach of Kielland, where

$$C = \frac{-\omega(N_A + N_B)}{2.303 NkT} \quad 3.4.10$$

The type of isotherm predicted by eq. 3.4.9 depends on the value of the constant C. For negative values

of C, the sign of w is positive, which means that the ions entering the exchanger show a reluctance to occupy adjacent sites. Positive values of C lead to isotherms showing miscibility gaps. In the case when $C = 0$, i.e. $w = 0$, an ideal solution is obtained and the simple law of mass action is obeyed.

The statistical thermodynamic treatment has been extended to uni-divalent exchange by Harvey, Redfern and Salmon (88). Their initial assumptions are similar to those of Barrer and Falconer (9), and hence the grand partition function is

$$Q = g(N_A, N_B) \left[J_A(T) \exp \frac{E_A}{kT} \right]^{N_A} \left[J_B(T) \exp \frac{E_B}{kT} \right]^{N_B} \quad Q_R \cdot \exp -E \quad 3.4.11$$

where Q_R is the partition function of the anionic framework, E is a function of the energy of interaction of B^{2-} , B^{2-} pairs, $g(N_A, N_B)$ is a statistical weight factor, and $A^- B^{2-}$ are the univalent and divalent ions respectively. In order to evaluate the statistical weight factor they have assumed the A^- ions to be charged points, and the B^{2-} ions to be two charge points rigidly joined to form a dumb-bell charge. Z is the number of neighbouring sites around any given site. They have derived an expression for $g(N_A, N_B)$

$$\left[\frac{Z}{N_A + 2N_B - 1} \right]^{N_B} \left[\frac{(N_A + 2N_B)!}{N_A!} \right] \quad 3.4.12$$

Since each B^{2-} ion is indistinguishable and symmetrical the above probability must be divided by $N_B!(2)^{N_B}$.

Also the A^- ions can now fill the remaining sites in one indistinguishable way. Thus the thermodynamic probability becomes

$$\left[\frac{Z/2}{(N_A + 2N_B - 1)} \right]^{N_B} \left[\frac{(N_A + 2N_B)!}{N_A! N_B!} \right] = \left[\frac{Z/2}{N_A + 2N_B} \right]^{N_B} \left[\frac{(N_A + 2N_B)!}{N_A! N_B!} \right] \quad 3.4.13$$

since $N_A + 2N_B \gg 1$.

The energy of interaction for all the B^{2-} , B^{2-} ion pairs was found to be $\frac{\omega N_B^2}{N_A + N_B}$ (similar to that of Barrer and Falconer). Thus the grand partition function becomes

$$Q = \left[\frac{Z/2}{(N_A + 2N_B)} \right]^{N_B} \cdot \left[\frac{(N_A + 2N_B)!}{N_A! N_B!} \right] \cdot \left[j_A(T) \exp \frac{E_A}{kT} \right]^{N_A} \\ \times \left[j_B(T) \exp \frac{E_B}{kT} \right]^{N_B} \cdot \left[\exp \frac{-N_B^2}{N_A + N_B} \cdot \frac{\omega}{kT} \right] Q_R \quad 3.4.14$$

By Stirling's approximation and in conjunction with the expressions for the free energy, $G = -kT \ln Q$ and chemical potentials $\mu_1 = \frac{\partial G}{\partial N_1}$, expressions for the chemical potentials of the ions A^- and B^{2-} can be derived. Using standard expressions for the chemical potentials of the

components of the solutions in the equation

$$\mu_{B_Z} + 2\mu_{A_S} = 2\mu_{A_Z} + \mu_{B_S}$$

then

$$\ln \left[\frac{N_A^2}{N_B(N_A + 2N_B)} \cdot \frac{a_B}{a_A^2} \right] = K' + \frac{\omega}{kT} \cdot \frac{2N_B(N_A + N_B) + N_B^2}{(N_A + N_B)^2} \quad 3.4.15$$

where

$$K' = \frac{2E_A - E_B}{kT} + \ln \frac{j_A^2(T)}{j_B(T)} + \frac{2\mu_{A_S}^0 - \mu_{B_S}^0}{kT} - \ln Z/2 \quad 3.4.16$$

The left hand side of equation 3.4.15 was rewritten

$$\text{as} \quad \ln \left[\frac{N_A^2}{N_B(N_A + 2N_B)} \cdot \frac{a_B}{a_A^2} \right] = \ln \left[\frac{m_B}{m_A^2} \frac{f_2}{f_1^2 c} \cdot 2 \frac{\bar{x}_A^2}{\bar{x}_B} \right] = \theta \quad 3.4.17$$

since $c m_i f_i = a_i$ (where a_i, m_i and f_i are the activity, mole fraction, and activity coefficient of species i , and c = total anion concentration in moles/litre), and $N_A/N_B = 2\bar{x}_A/\bar{x}_B$ and $N_A/N_A + 2N_B = \bar{x}_A$ where $\bar{x}_i$ is the equivalent fraction of species i in the resin.

$$\text{Thus } \theta = \ln \frac{1}{C} \frac{(1 - \bar{x}_B)^2 x_B (2 - x_B)}{\bar{x}_B^2 (1 - x_B)^2} \quad 3.4.18$$

where x_i is the equivalent fraction in solution and

$$C = f_1^2 c / f_2.$$

For the r.h.s. of eq. 3.4.15, on substitution and conversion to molar quantities, one has

$$\begin{aligned} & 2 \frac{E_A - E_B}{RT} + \ln \frac{Q_A^2(T)}{Q_B(T)} + \frac{2 \overline{G_A^0} - \overline{G_B^0}}{RT} - \ln \frac{Z}{2} \\ & + \frac{\bar{x}_B (4 - \bar{x}_B)}{(2 - \bar{x}_B)^2} \cdot \frac{\omega}{RT} \end{aligned} \quad 3.4.19$$

or

$$K + \frac{\bar{x}_B (4 - \bar{x}_B)}{(2 - \bar{x}_B)^2} \cdot \frac{\omega}{RT} \quad 3.4.20$$

where K replaces K' because of the change of units. Thus equation 3.4.15 can be written as

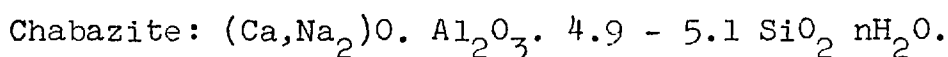
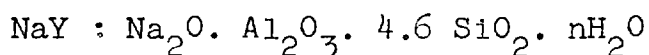
$$\ln \frac{1}{C} \frac{(1-\bar{x}_B)^2 x_B (2-x_B)}{\bar{x}_B 2(1-x_B)^2} = K + \frac{\bar{x}_B (4 - \bar{x}_B)}{(2 - \bar{x}_B)^2} \cdot \frac{\omega}{RT} \quad 3.4.21$$

Harvey, Redfern and Salmon have shown for several uni-divalent anion exchanges that the lower or more negative the value of K, the greater is the preference for the resin of the divalent ion.

4. Materials, Apparatus and Experimental Procedures

4.1. Materials

The crystalline exchangers used in this work were the synthetic zeolite NaY and the naturally occurring zeolite chabazite. NaY is a white crystalline powder obtained from the Linde Co. (U.S.A.), whereas chabazite is obtained as pink crystals from Ward's Natural Science Establishment, New York, and was of Nova Scotian origin. The compositions of these exchangers were approximately known



The chabazite crystals were detached from their rock matrices and separated from the intergrown stilbite and calcite.

Both exchangers were ground and in almost all this work the portion between 150 and 200 mesh was used. The powdered zeolites were washed with distilled water at room temperature to remove any soluble material. To investigate the ion exchange properties of the zeolites it was necessary to obtain them in pure sodium forms. The powdered zeolites were therefore treated with aqueous sodium chloride solutions (0.2M) for several days replacing the solution with fresh sodium chloride solution every two days. Pure NaY was obtained after only two treatments with NaCl solution, but for chabazite it was found necessary to continue

the treatment for several weeks, until it was found that no more calcium came out of the crystals (solution tested with ammonium oxalate solution). The crystals were then washed with distilled water until the filtrate was free of sodium chloride (test with $\text{HNO}_3/\text{AgNO}_3$). The zeolites were dried at 110°C overnight, and then allowed to equilibrate with water vapour over saturated ammonium chloride in a desiccator at room temperature for one week. This procedure was necessary to obtain constant zeolitic water, since the water content of a zeolite is dependent on the humidity of the surrounding atmosphere.

X-ray powder photographs of the zeolites were taken and were found to have only those lines corresponding to the known zeolite structures.

4.1.1. The Preparation of pure cationic forms of the zeolites

Pure cationic forms of the zeolites were prepared by treating the powdered zeolites with concentrated solutions of the appropriate salts in a beaker with continuous stirring overnight. This treatment was repeated several times replacing the solution with fresh solution every 2 - 3 days. As in the preparation of Na-chabazite it was found necessary to continue treatment with the appropriate salt solution for several weeks to obtain a high degree of exchange in the crystal. The chlorides

were used for the preparation of Li, K, Rb, Cs, NH_4 , Ca, Sr and Ba zeolites; the nitrates for the Ag and Pb zeolites and the acetate for the Tl zeolites.

The ion exchanged samples obtained by the above method contained appreciable quantities of included salts. These were readily removed by washing the zeolite samples with several litres of hot distilled water, until no salt was detected in the washings. Finally the zeolites were dried at 110°C overnight, and then allowed to equilibrate with water vapour over saturated ammonium chloride at room temperature for one week.

4.1.2. The Preparation of Na^{22} labelled zeolites

The Na-zeolites were labelled with Na^{22} radioactive tracer in the following manner. About 15 gm of the powdered zeolite (150 - 200 mesh) was stirred overnight with 50 mls of 0.1N sodium chloride solution to which had been added the requisite amount of Na^{22}Cl . The zeolite and solution were separated by filtration, and the radioactive zeolite washed with distilled water until free from chloride (test with $\text{AgNO}_3/\text{HNO}_3$). The zeolite was dried at 110°C and then allowed to equilibrate with water vapour as before. Radioactive samples of other pure cationic forms of the zeolites were prepared in a similar way using the appropriate salt solutions and

radioactive tracer.

In order to determine the amount of radioactivity in the sample of Na^{22} -zeolite a known weight (~ 0.5 gm) was rotated in a sealed tube for 3 - 4 days with 30 mls of inactive sodium chloride solution of known concentration (0.1N). During this time the Na^{22} had distributed itself between the solid and solution phases in direct proportion to the amount of sodium in each phase. The zeolite and solution were separated by centrifuging and the radioactivity of the solution measured. Knowing the amount of sodium in each phase, it was possible to calculate the amount of Na^{22} in the zeolite.

4.1.3. Preparation of solutions

Aqueous solutions were prepared with distilled water. All reagents were of 'Analar' grade with the exception of rubidium chloride, caesium chloride and thallous acetate which were supplied by Hopkin and Williams, and lithium chloride which was supplied by B.D.H. Limited. Standard solutions of sodium, potassium, rubidium, caesium and silver were prepared by dissolving the appropriate amount of the salt, dried at 110°C , in a known amount of water. Solutions of the other salts were made up by volume and then standardized.

Methanolic solutions of sodium iodide and potassium iodide were made by dissolving the appropriate weight

of the salts, dried at 110°C , in dry methanol. The methanol was dried as follows:- Methanol (1 litre) was refluxed with 10 gm of magnesium and 2 gm of iodine for 2 - 3 hours. It was then distilled into a dry receiver, the fraction boiling between $64 - 65^{\circ}\text{C}$ being collected. The above procedure was repeated, and the dry methanol stored in a stoppered flask sealed with picien wax.

4.2. Analytical Procedures

4.2.1. Gravimetric Analysis

The analyses of the zeolites were carried out by the methods given by Groves; Hillebrand et al; and Vogel (89).

Water Content

Water was estimated as the loss of weight of the zeolite upon ignition of the sample at red heat for several hours.

Silica Content

The zeolites were decomposed by the addition of (1:1) HCl to a weighed sample in a platinum dish. The mixture was evaporated to dryness on a steam bath, and the residue treated with concentrated HCl and allowed to stand for a few minutes. Hot distilled water was then added and the mixture allowed to stand on a steam bath for ten minutes. The silica was filtered off and

washed with diluted HCl and hot distilled water. The filtrate and washings were evaporated to dryness in the platinum dish, and the residue dried at 110°C for one hour. The residue was then treated with concentrated HCl, allowed to stand for a few minutes, and then diluted with distilled water. Any additional silica yielded by this treatment was filtered off and washed with diluted HCl and hot water. The combined precipitates were ignited in a platinum crucible, and weighed. The ignited silica was treated with concentrated HF and a few drops of H_2SO_4 , ignited and reweighed. The loss in weight upon ignition was the weight of SiO_2 in the zeolite.

Alumina Content

The combined filtrates and washings from the silica determination were evaporated to 200 ml, and a small amount of HCl added. The solution was boiled and NH_4OH (1:1) was added until the solution was alkaline to methyl red. After further boiling for two minutes, the precipitate was filtered off and washed with hot 2% NH_4Cl , and transferred back to the beaker that was used for the original precipitation. The precipitate was redissolved in diluted hydrochloric acid, diluted to 200 ml, and reprecipitated as before. The precipitate of aluminium hydroxide was filtered off, washed with 2% NH_4Cl and distilled water, and ignited in a platinum crucible and weighed as Al_2O_3 .

Alkaline Earth Content

The combined filtrates from the alumina determination were evaporated to 200 ml. Calcium was precipitated as calcium oxalate upon addition of a slight excess of 5% ammonium oxalate solution to a slightly alkaline solution from the alumina determination. The solution was allowed to stand overnight and the precipitate separated by filtration on a sintered glass crucible. The precipitate was dried at 110°C, and weighed as calcium oxalate monohydrate.

Barium was precipitated as barium sulphate upon addition of a slight excess of H_2SO_4 to the solution from the alumina determination. The solution was allowed to stand for a few hours, and then the BaSO_4 filtered off and ignited in a weighed porcelain crucible. Barium was estimated as the weighing form BaSO_4 .

Strontium was also precipitated as strontium sulphate upon addition of dilute H_2SO_4 to the solution from the alumina determination. An equal volume of ethanol was also added and the solution allowed to stand overnight. The precipitate was filtered on to a sintered glass crucible, washed with 50% EtOH containing a little H_2SO_4 , then with 95% EtOH; dried at 110°C and weighed as SrSO_4 .

Alkali metal content

The combined filtrates from the alumina determination were evaporated to dryness in a platinum crucible. A small amount of diluted H_2SO_4 was added, and the ammonium salts driven off by gentle heating. The residue was dissolved in water, a drop of H_2SO_4 was added and the solution evaporated and finally heated over a Meker burner before weighing. The alkali metals were weighed as their sulphates, from which the alkali content of the zeolite was obtained.

Analyses of Ag, Tl and Pb zeolites

Zeolites containing these ions had to be decomposed with concentrated nitric acid (instead of HCl) and the components were determined in the order SiO_2 , Ag_2O (or Tl_2O or PbO) and Al_2O_3 .

Silver was precipitated with HCl and estimated as AgCl immediately after the separation of the silica. Similarly thallium was determined as TlI which was precipitated with 0.1 N KI solution at 90° . The TlI was filtered off after cooling to 0°C , dried at 110°C and weighed as TlI .

Lead was precipitated as lead molybdate upon the addition of 2% ammonium molybdate solution to the boiling solution. The PbMoO_4 was filtered on to a sintered glass crucible, washed with distilled water and

dried at 110°C . The lead was estimated as PbMoO_4 .

Kjeldahl Determination of Nitrogen

The Kjeldahl method was used to determine the ammonium content of ammonium chabazite.

0.2 gm of the zeolite was decomposed with concentrated sulphuric acid (6 ml) on a steam bath. The cooled product was transferred to a Kjeldahl apparatus and treated with 30 ml of $40^{\circ}/\text{o}$ NaOH (plus 5 ml of $20^{\circ}/\text{o}$ $\text{Na}_2\text{S}_2\text{O}_3$) and mercuric oxide (1.0 gm) as catalyst. The ammonia was steam distilled into 100 mls of $\frac{\text{N}}{100}$ potassium bi-iodate $\text{KH}(\text{IO}_3)_2$, and the excess $\text{KH}(\text{IO}_3)_2$ titrated with $\frac{\text{N}}{100}$ sodium thiosulphate.

A blank determination was also performed, and the 'blank correction' subtracted from the calculated value of the NH_4 content of the zeolite.

Radiochemical Methods of Analysis

In addition to the gravimetric methods, radiochemical methods have been used for the Na, K, Rb, Cs, Ca, Sr, Ba, Ag and Tl forms of the zeolites.

A known weight of any cationic form of a zeolite was equilibrated with a standard solution containing the same cation, to which had been added a negligible weight of the radioactive isotope. Equilibration was performed by rotating the solid and solution in a sealed tube for 3 - 4 days. During this time the radioactivity distributed

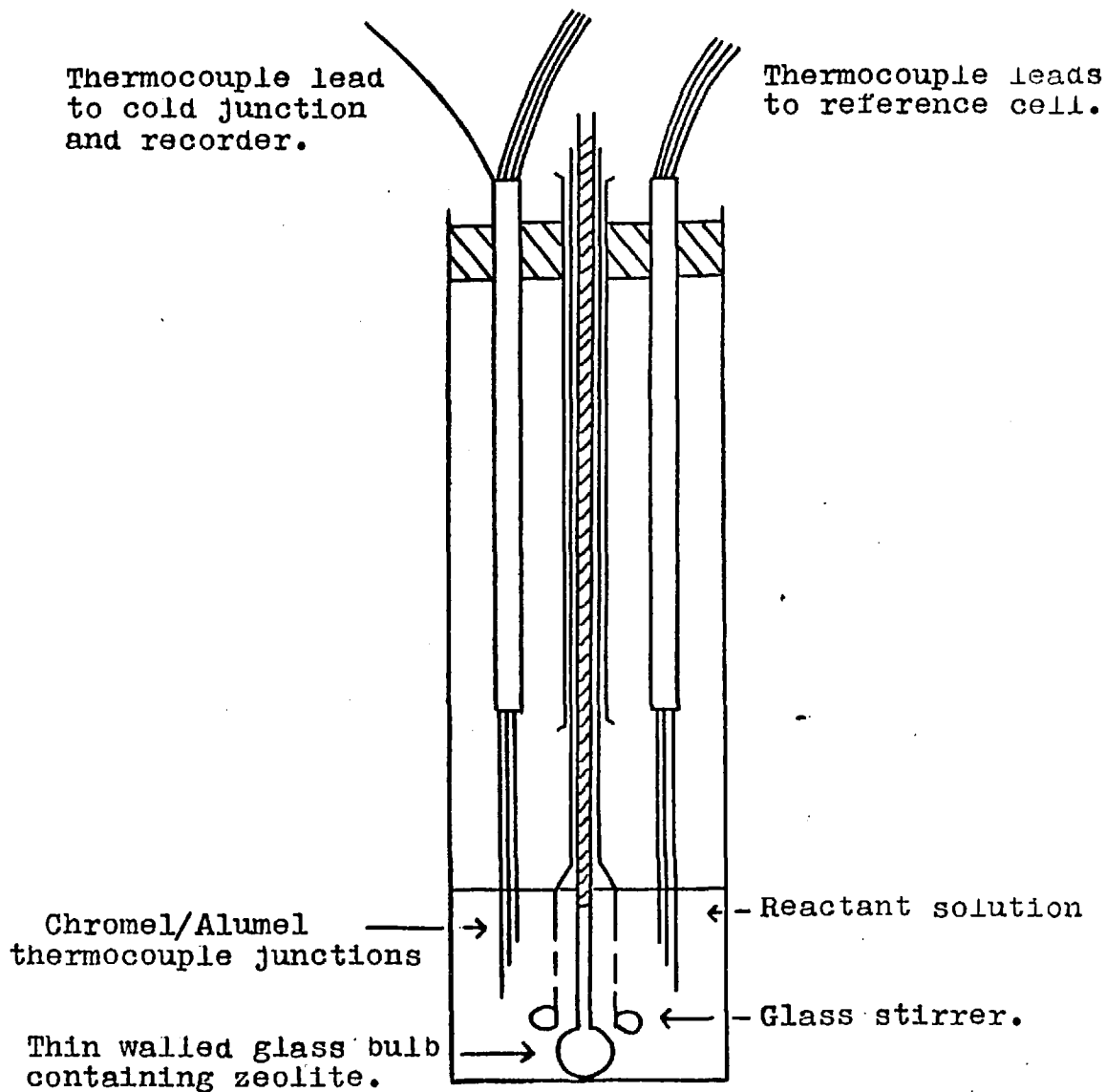
itself in direct proportion to the amount of cation in each phase. The zeolite was separated from the equilibrated solution by centrifuging and the activity in the solution measured. The radioactive isotopes used in this method of analysis were Na^{22} , K^{42} , Rb^{86} , Cs^{134} , Ag^{110} , Tl^{204} , Ca^{45} , Sr^{85+89} and Ba^{133} . In the case of K^{42} corrections had to be made for its short half-life ($t_{\frac{1}{2}} = 12.5$ hours). A sample of the standard K^{42} Cl solution was counted a number of times over a period of a few hours, and also during that time the activity of the equilibrated solution was measured. From a graph of the logarithm of the activity of the standard solution against time, the activity of the standard solution at the particular time at which the equilibrated solution was counted could be obtained.

4.3. The Calorimeter

In this work the temperature changes associated with ion exchange have been measured by two methods:- (a) using a differential thermocouple and (b) using a thermistor in conjunction with a Wheatstone bridge.

4.3.1. Differential Thermocouple

The measurement of the heats of ion exchange using a thermocouple were performed in a calorimeter originally built by Barrer, Rees and Ward (51) and subsequently

Fig.2Diagram of reactant cell

used by Barrer, Rees and Shamsuzzoha (15). The calorimeter was based on that of Borchardt and Daniels (91) and used under near isothermal conditions. A diagrammatic representation of the cell is given in Fig. 2. A similar cell was used as the reference cell except that it contained distilled water instead of the exchanging solution. Temperature changes were measured as the e.m.f. produced by a set of chromel/alumel thermocouples which was recorded as a function of time on a Honeywell strip chart recorder. A detailed description of the apparatus is available in the thesis by Ward (90).

The Theory of Heat Measurement

Let T_o , T_1 , T_2 be the temperature of the bath, reaction cell and standard cells respectively. The equation of heat balance is

$$Cp_r dT_1 = dH + k_r (T_1 - T_o)dt \quad 4.3.1$$

where dH is the increase in enthalpy in time dt , Cp_r the heat capacity of the reactant cell, and dT_1 the rise in temperature of the contents of the reactant cell, and k_r is a constant corresponding to the conduction rate of heat transfer from the reactant cell to the thermostat per unit time and unit temperature difference between the reactant cell and the thermostat. The symbol ΔT can be substituted for the term $T_1 - T_o$, hence

$$dH = Cp_r d(\Delta T) + k_r \Delta T dt \quad 4.3.2$$

Integrating from $t = 0$ to $t = \infty$, Cp_r and k_r being constant

$$\Delta H = Cp_r (\Delta T_{\infty} - \Delta T_0) + k_r \int_0^{\infty} \Delta T dt \quad 4.3.3$$

ΔT_0 and ΔT_{∞} represent the differences between reactant cell temperature and thermostat temperature at times $t = 0$ and $t = \infty$. These are zero since the system is allowed to come to thermal equilibrium before and after exchange. Thus

$$\Delta H = k_r \int_0^{\infty} \Delta T dt \quad 4.3.4$$

The integral $\int_0^{\infty} \Delta T dt$ represents the variation of the temperature difference of the components of the reaction cell and the thermostat, and hence the area under the heat curve observed on the strip chart recorder.

$$\text{Therefore } \Delta H = k_r A \quad 4.3.5$$

Thus any unknown heat can be determined, provided k_r is known, by simply measuring the area under the heat curve. The same volume of the contents of the reactant cell must be used since the value of k_r is dependent on volume.

The effect of fluctuations in bath temperatures

A small change in the temperature of the thermostat dT_o during the course of a calorimetric measurement will produce a fluctuation in the heat transferred from the water bath to the contents of the reaction cell and consequently a change in the temperature of the contents of the reactant cell. Thus the increase in enthalpy of the contents of the reactant cell $Cp_r dT_1$ in a time dt is given by

$$Cp_r dT_1 = dH + k_r (T_o + dT_o - T_1)dt \quad 4.3.6$$

The increase in enthalpy of the contents of the reference cell due to the change in temperature dT_o is given by

$$Cp_s dT_2 = k_s (T_o + dT_o - T_2)dt \quad 4.3.7$$

where Cp_s is the heat capacity of the contents of the reference cell.

Assuming $k_r = k_s$ and $Cp_r = Cp_s$, which are justified if identical cells are used and if they contain the same volume of liquid, and also if the reactant solution is dilute and water is used as the reference liquid, then

$$dH = Cp_r (dT_1 - dT_2) + k_r \Delta T dt \quad 4.3.8$$

which reduces to

$$dH = Cp_r d(\Delta T) + k_r \Delta T dt \quad 4.3.9$$

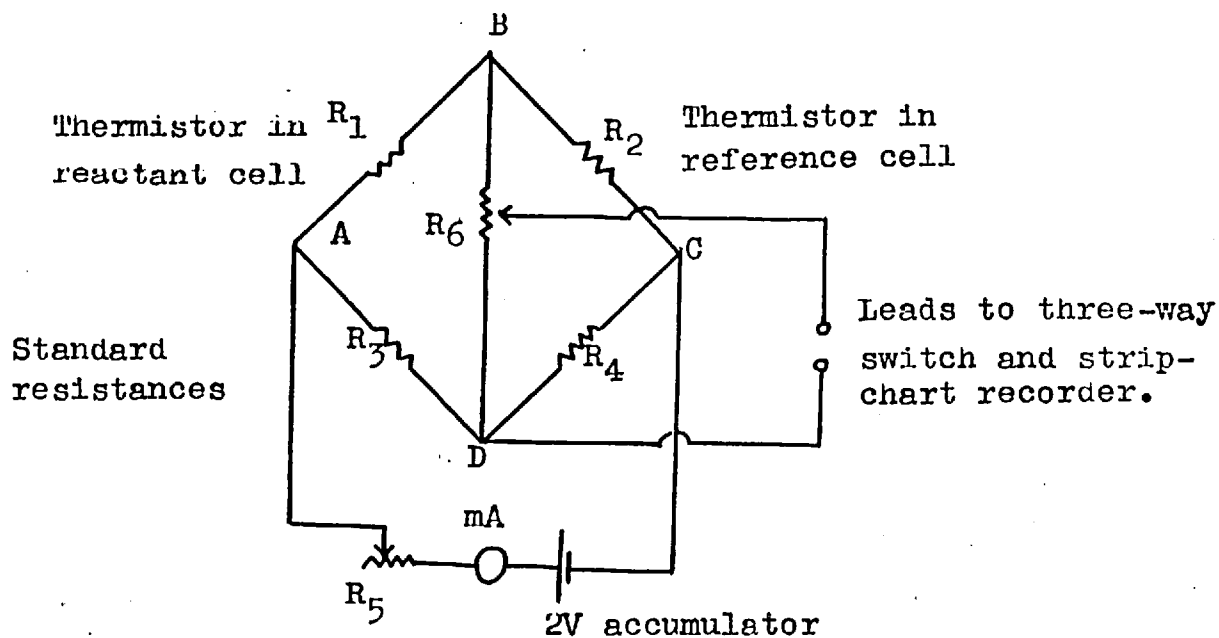
This equation is identical with equation 4.3.2; thus on integrating from $t = 0$ to $t = \infty$

$$\Delta H = k_r \int_0^{\infty} \Delta T dt = k_r A \quad 4.3.5$$

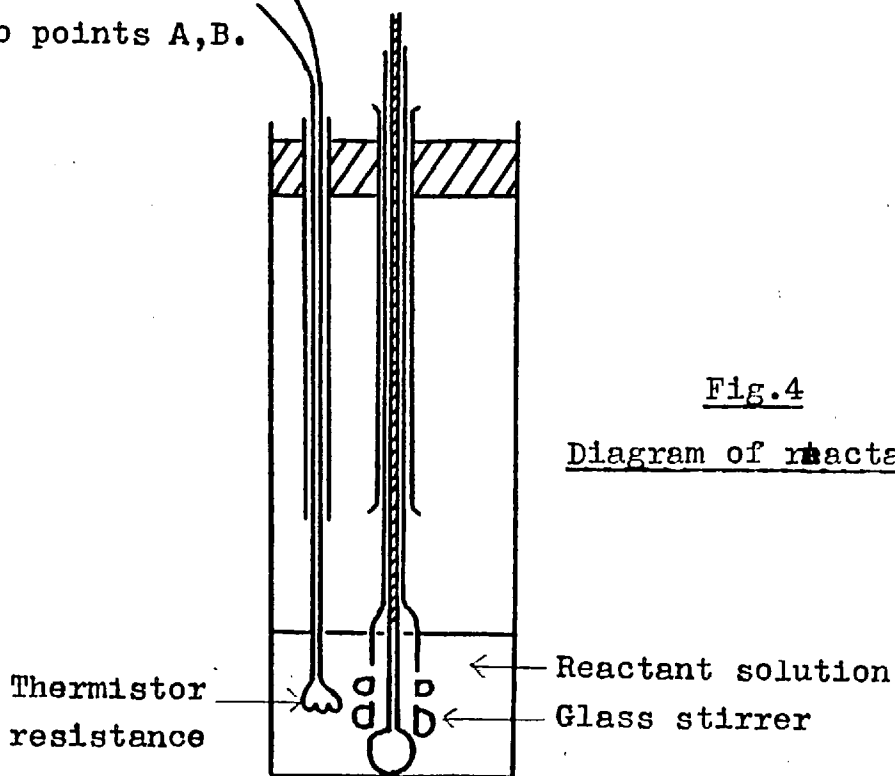
If any fluctuations do occur in the temperature of the water bath during a calorimetric measurement, the area under the heat curve will not be affected provided that the conditions mentioned above are observed.

4.3.2. Thermistor in conjunction with a Wheatstone bridge

A calorimeter was designed in which a thermistor was used in conjunction with a Wheatstone bridge and a strip chart recorder to measure the temperature changes occurring in the reactant cell. The circuit diagram is shown in Fig. 3. R_1 , R_2 are the thermistor resistances in the reactant and standard cells respectively; R_3 , R_4 are decade resistance boxes variable between 0 and 10,000 ohms; and R_5 , R_6 are carbon granule potential dividers of variable resistances 0 to 5000 ohms. The e.m.f. to the whole circuit is provided by a 2V accumulator. The total current in the circuit was maintained constant (indicated by the milliammeter) by adjusting R_5 . The thermistors had resistances of ~ 1.2 k ohms and temperature coefficient of resistances of ~ 40 ohms/ $^{\circ}\text{C}$. R_4 was set at 1.5 k ohms, while R_3 was adjusted to obtain bridge balance. The potential divider R_6 between B and D controlled the sensitivity of the system.

Fig.3 Circuit Diagram.

Thermistor leads
to points A,B.

Fig.4Diagram of reactant cell

Differences in potential existing between points B and D were fed through copper wires, via the potential divider R_6 and a three-way switch to a strip chart recorder. The instrument was a self-balancing potentiometer and balanced any potential differences against that across a slide wire energized by a 1.5 volt dry cell.

At bridge balance no p.d. existed between B and D, hence a straight line along the centre of the strip chart was obtained. If, however, the bridge was thrown slightly out of balance by adjusting R_3 , it was possible to position the 'base-line' near to one edge of the chart. This enabled almost all the width of the chart to be used when determining temperature changes in the reactant cell, as opposed to only 'half-scale deflection' when the 'base-line' was located at the centre of the chart. This had the advantage over the thermocouple that large areas could be obtained, and consequently the error associated with the determination of this area was reduced.

When a temperature change occurs in the reactant cell this produces a change in resistance R_1 . Consequently the bridge is thrown out of its steady state balance, and an e.m.f. exists between B and D. Let α be the temperature coefficient of resistance of the thermistor in the reactant cell. For a small change in temperature of the contents of the reactant cell ΔT , the change in the

resistance of the thermistor R_1 is ΔR_1 where

$$\Delta R_1 = R_1 \alpha \Delta T \quad 4.3.10.$$

If the same notation is used for the temperatures of the reactant cell and water bath, and, as before k_r is the heat transfer coefficient of the reactant cell, then the increase in enthalpy of the contents of the reactant cell is

$$dH = C_{p_r} dT_1 + k_r (T_1 - T_0) dt \quad 4.3.11$$

If ΔT is substituted for the term $(T_1 - T_0)$, then equation 4.3.11 becomes

$$dH = C_{p_r} d(\Delta T) + k_r \Delta T dt \quad 4.3.12$$

Combining equations 4.3.10 and 4.3.12

$$dH = \frac{C_{p_r}}{R_1 \alpha} \Delta R_1 + \frac{k_r}{R_1 \alpha} \Delta R_1 dt \quad 4.3.13$$

The total heat involved in the reaction is obtained by integrating equation 4.3.13 between the limits $t = 0$ and $t = \infty$, C_{p_r} , k_r , α and R_1 being constant:

$$\Delta H = \frac{C_{p_r}}{\alpha R_1} (\Delta R_{1_\infty} - \Delta R_{1_0}) + \frac{k_r}{\alpha R_1} \int_0^\infty \Delta R_1 dt \quad 4.3.14$$

Since the difference in resistances, ΔR_1 , of the resistance of the thermistor is zero at $t = 0$ and $t = \infty$,

$$\Delta H = \frac{k_r}{\alpha R_1} \int_0^\infty \Delta R_1 dt \quad 4.3.15$$

Equation 4.3.15 represents the variation of the resistance difference of the thermistor resistance in the reactant cell with time, which is followed by the strip chart recorder, and the integral $\int_0^{\infty} \Delta R_1 dt$ is the total area A under the heat curve. Thus

$$\Delta H = \frac{k_r}{\alpha R_1} A \quad 4.3.16$$

Since k_r , α , R_1 are all constants, the heat of reaction is directly proportional to the area under the heat curve.

Thus, any unknown heat can be determined simply by measuring the area under the heat curve, provided the ratio $\frac{k_r}{\alpha R_1}$ is known. If this ratio is replaced by a constant K_r , such that

$$\Delta H = K_r A \quad 4.3.17$$

then K_r can be determined by measuring the area under the curve produced for known values of ΔH .

4.4. Experimental Procedure

4.4.1. Calibration

The calibration of the calorimeters was performed by measuring the integral heats of dissolution of varying amounts of pure potassium chloride and sodium chloride in water. The integral heats of solution of these salts in water are known accurately for various concentrations,

and are available from tables compiled by Rossini et al. (96).

The alkali chlorides were dried at 110⁰c for several hours, cooled over phosphoric oxide in a desiccator and weighed into dried, thin-walled glass bulbs. Each bulb was sealed, and fused on to a glass rod which passed through the hollow glass shaft of the stirrer in the reactant cell. The calorimeters were assembled as shown in Figs. 2 and 4; then immersed in the thermostatic bath for several hours to obtain thermal equilibrium. The recorder was switched on about fifteen minutes before breaking the bulb, so as to record the steady state conditions when both reactant and reference cells were at thermal equilibrium. The bulb was broken by applying pressure to the top of the glass rod. The temperature differences existing between the contents of the reactant and reference cells were then recorded on the strip-chart recorder.

Varying amounts of alkali chlorides (0.01 - 0.08 gm) were used in the calibration measurements in order to test the validity of the equation

$$\Delta H = k_r A$$

over as large a range as possible. The area under the curve was determined by transferring the curve to graph paper. A known area of graph paper was cut out and weighed.

The heat curve was also cut out from the graph paper and weighed. The area under the curve was calculated by simple proportions. Three such determinations were made and the area under the curve taken as the mean value. The values obtained for the calibration constants were 0.05180 cal/cm^2 , 0.06358 cal/cm^2 , for the thermocouple systems I and II respectively, as compared with the value of 0.07482 cal/cm^2 obtained by Shamsuzzoha (90) and 0.1201 cal/cm^2 obtained by Ward (90). The thermistor system had a calibration constant of 0.01759 cal/cm^2 , thus making it the most sensitive system of heat detection.

4.4.2. Measurement of the Heat of Bulb Breaking

In order to determine whether any corrections had to be applied to the heat data obtained, attempts were made to measure the heat associated with the breaking of the glass bulb in the calorimeter. The experimental procedure was the same as that used for the calibration measurements except that the glass bulb was empty. Several determinations were carried out, but it was found that the breaking of the bulb produced no heat in the calorimeter even when the most sensitive system, i.e. the thermistor, was used.

4.4.3. Measurement of the Heat of Wetting of Zeolites

The heat of wetting of the pure cationic forms of the zeolite equilibrated with water vapour at 25°C was measured. The zeolite (0.5 gm) was weighed into a thin-walled glass bulb and allowed to equilibrate with water vapour over pure water at 25°C in a vacuum desiccator. The bulb was then sealed and fused onto a glass rod as before. The remainder of the experimental procedure was the same as that used for the calibration experiments. In certain cases heats of wetting were obtained for partially exchanged forms of the zeolites, the same experimental procedure being adopted.

The heats of equilibration of the same partially exchanged zeolites, when immersed in solutions containing the appropriate equilibrium ratio of the exchangeable cations were also measured. In both cases the zeolite was equilibrated with water vapour over pure water at 25°C, and the experimental procedure adopted was the same as that for the determination of the heats of wetting of the zeolite.

The heats of wetting for the pure cationic forms of chabazite and NaY, and also heats of wetting and heats of equilibration of the mixed exchangers are shown in Tables 13 and 14 (vide section 6.4).

4.4.4. Measurement of the Heat of Ion Exchange

The zeolite (0.5 gm), equilibrated with water vapour over saturated ammonium chloride solution at 25°C was weighed into a thin-walled glass bulb. The bulb was placed in a desiccator over pure water, and the desiccator in a thermostat at 25°C. The zeolite was allowed to equilibrate with water vapour over pure water for two days. The glass bulb was then sealed and fused to the glass rod as before. Into the calorimeter was placed 30 ml of the exchanging solution (usually between 0.005 and 1.0 molal). The calorimeter was assembled, immersed in the thermostat and allowed to come to thermal equilibrium. The remainder of the experimental procedure was the same as that for the calibration. The area under the curve was measured by transferring the curve to graph paper, weighing the area produced and comparing this with the weight of a known area of graph paper. Knowing the calibration constant k_r , the heat of ion exchange was calculated.

4.4.5. Ion Exchange Equilibria

To determine the position of equilibrium between a pure cationic form of a zeolite and a solution containing a second exchangeable cation, several experiments were conducted in which the solid and solution were left in contact with each other for periods of time much greater than the ten minutes allowed in the calorimeter experiments.

The pure cationic form of the zeolite was rotated in sealed glass tubes with the same volume of the exchanging solution as was used in the calorimeter experiments i.e. 30 ml. The tubes were rotated in an air thermostat at $25^{\circ} \pm 1^{\circ}\text{C}$ for periods of time varying from one day to two weeks. For the Na - Ca and Na - Sr exchanges on chabazite, the thermostat was held at $50^{\circ} \pm 1^{\circ}\text{C}$. The suspensions were separated by centrifuging and the extent of exchange measured.

4.4.6. Measurement of the extent of ion exchange

In all experiments radioactive tracers were used to measure the extent of exchange. This was governed by the weight of zeolite and the concentration of the solution used. Two methods of labelling were used (a) solid initially labelled (b) solution initially labelled.

(a) Solid initially labelled. In exchanges involving Na^{22} -zeolite the radioactivity of the solution after exchange was measured. The total amount of radioactivity in the solution if all the Na^{22} in the zeolite was exchanged was already known from the equilibration of Na^{22} zeolite with inactive sodium chloride solution. Hence the extent of exchange occurring was readily obtained by direct proportion. In exchanges involving K Cl and Rb Cl solutions allowance had to be made for the small

amount of radioactivity due to the naturally occurring radioisotopes K^{40} and Rb^{86} . However this correction was only necessary for strong solutions of these electrolytes.

(b) Solution initially labelled. In exchanges involving labelled solutions the radioactivity of the solution before and after exchange was measured, and from the decrease in solution activity the extent of exchange was calculated.

4.4.7. Counting Equipment and Technique

The radioactivity existing in the solution phase was measured using the Geiger-Muller tubes discussed below, in conjunction with an Ekco probe unit type N558 and an Ekco N530E scalar. The solutions were measured using a Mullard MX/124 G-M tube operating at an E.H.T. of 400 volts and discriminator bias of 5V. In certain cases radioactive solutions were measured by evaporating them down on aluminium planchettes and counting the residual solid activity using a Mullard MX/123 end window G.M. tube operating at 600V with a discriminator bias of 5V. Background counts obtained from both tubes were of the order of 20 counts/minute. Solution (and solid) activity were of the order of 20 - 50 counts/sec, and the samples were generally counted for 1 Ksec.

In certain instances it was found that the activity

of the exchanged solution was of the order of 30 - 60 counts/minute, a rate comparable to that of background. In these instances the residual activity was measured using a Panex low background counter. This consisted of a Geiger-Muller tube type MX157, which is essentially two counters, one a large gamma sensitive guard counter, and the other a small mica-window beta sensitive counter. The background count from a normal counter is due largely to cosmic particles of high energy. The anticoincidence unit is designed to reject counts caused by these particles which penetrate the sensitive volumes of both the beta and guard counters. Any count from the beta tube which coincides with a count from the guard tube is automatically rejected. Consequently the background counting rate is reduced to about 2.5 counts/min. Using this counting system the samples were counted overnight so as to accumulate a sufficient number of counts to render the statistical error of counting small.

In all cases the counting rates were corrected for the dead time of the tube by

$$N_o = \frac{N}{1 - \tau N}$$

where N is the observed number of counts/second, N_o is the true number of counts/second and τ is the dead time of the tube in seconds.

The radioactive isotopes used in this work were all obtained from the Radiochemical Centre, Amersham and were of guaranteed radiochemical purity.

The transferring of radioactive solutions on to the planchettes was found to be more reliable if a weighing procedure was adopted rather than a volumetric procedure. The radioactive solution after exchange was separated from the zeolite by centrifuging, and transferred to a narrow-necked polythene ampoule of 7 ml capacity. This was weighed before and after transferring solution to the planchette, thus enabling the weight of solution on the planchette to be measured. The solution was then evaporated to dryness, and its activity measured.

Where the activity on the planchette was due to the weak β emitter, Ca^{45} , the procedure was slightly modified. Ca^{45} was supplied as its chloride which is very deliquescent and readily takes up moisture from the air. A varying layer of moisture is thus obtained on the planchette when a sample of the chloride is being counted. This introduces self-absorption factors. To overcome this difficulty a slight excess of a solution containing ammonium oxalate was pipetted on to the planchette to precipitate the calcium as its oxalate. The solution was then evaporated to dryness and its radioactivity measured. Calcium oxalate is not deliquescent and therefore no absorption factors due to moisture are present.

4.4.8. Additional Experimental Methods

X-ray powder photographs of some of the different exchanged forms of chabazite and NaY were taken using $\text{Cu}_{K\alpha}$ radiation. The 'd' spacings were calculated using Bragg's law, $2d \sin \theta = \lambda$, where θ is the Bragg angle and λ is the wavelength of the radiation. The unit cell dimensions were determined from the formula

$$a = d\sqrt{h^2 + k^2 + l^2} \quad \text{for the cubic NaY}$$

$$\text{and } \frac{1}{d} = \sqrt{\frac{4}{3a^2} (h^2 + hk + k^2) + \frac{l^2}{c^2}} \quad \text{for the hexagonal chabazite}$$

Relative density measurements of some of the zeolite samples were performed using a density bottle. Four weighings were required to determine the density of the zeolites d. Thus

$$d = \frac{(\omega_2 - \omega_1)}{(\omega_4 + \omega_2) - (\omega_3 + \omega_1)} \cdot \rho$$

where ω_1 = weight of bottle alone

ω_2 = weight of bottle and zeolite

ω_3 = weight of bottle + zeolite + water

ω_4 = weight of bottle + water

ρ = density of water at room temperature

In all cases to ensure thermal equilibrium in the above weighings, the bottle and contents were allowed to

stand for fifteen minutes in a thermostat at $25^{\circ} \pm 0.1^{\circ}\text{C}$ before weighing.

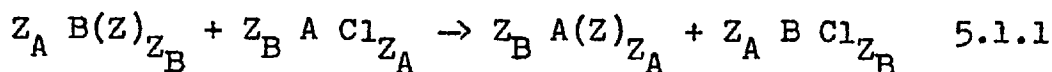
For the investigation of the Na - K exchange on NaY in methanol it was necessary to remove the intracrystalline water and replace it by dry methanol. The zeolite was dehydrated by heating at 360°C for 36 hours at $2 \times 10^{-6}\text{ mm}$ of Hg pressure. The sample was allowed to cool to room temperature and dry methanol sorbed into the zeolite. Finally, to ensure that all the channels and cavities contained methanol, the sample was removed from its evacuation tube and stirred with dry methanol for a few minutes. It was quickly filtered, dried at $\sim 80^{\circ}\text{C}$, and stored over dry methanol in a desiccator at room temperature.

5. Theoretical Treatment of Observations

By means of additional ion exchange measurements, where the solid and solution were continuously rotated with each other for periods of time up to 5 - 6 weeks, ion exchange equilibria were obtained. This enabled the construction of ion exchange isotherms to be made. In many instances the ion exchange isotherms constructed from calorimetric measurements agreed with those of the additional ion exchange measurements. Thus the end points of the calorimeter measurements were true equilibrium points. However, in some cases, mainly in the uni-divalent ion exchanges, the points obtained from the calorimeter measurements were not true equilibrium points, and a subsequent slow process occurred until true equilibrium was obtained.

5.1. The Standard Free Energy of Ion Exchange

The standard free energy of ion exchange is defined as the free energy change for the reaction



where the reactants and products are in their respective standard states.

The free energy for this reaction is given by

$$\Delta G^\circ = - \frac{RT}{Z_A Z_B} \ln K_a \quad 5.1.2$$

where K_a is the thermodynamic equilibrium constant.

The value of K_a can be determined using the thermodynamic treatment of Gaines and Thomas (vide section 3.3). This treatment leads to the expression

$$\ln K_a = (Z_B - Z_A) + \int_0^1 \ln K_c \, dA_Z$$

$$- Z_A Z_B \left[\int_{a_s=1}^{a_s(a)} n_s^A d \ln a_s - \int_{a_s=1}^{a_s(b)} n_s^B d \ln a_s + \int_{a_s(a)}^{a_s(b)} n_s^M d \ln a_s \right]$$

5.1.3

for the thermodynamic equilibrium constant. However, as shown in section 3.3 for crystalline exchangers which undergo ion exchange with virtually no alteration in cell dimensions, this equation can be reduced to

$$\ln K_a = (Z_B - Z_A) + \int_0^1 \ln K_c \, dA_Z \quad 5.1.4$$

and it is this equation that has been used in the evaluation of the thermodynamic equilibrium constant throughout this thesis.

The thermodynamic equilibrium constant K_a is given by the expression

$$K_a = \frac{Z_B^A \cdot f_A^Z \cdot m_{BY}^{Z_B} \cdot \gamma_{+BY}^{Z_A(Z_{B+1})}}{Z_A^B \cdot f_B^Z \cdot m_{AY}^{Z_B} \cdot \gamma_{+AY}^{Z_B(Z_{A+1})}} \quad 5.1.5$$

or

$$K_a = K_c \frac{f_A^Z}{f_B^Z} \quad 5.1.6$$

where $K_c = \frac{Z_B^A}{Z_A^B} \cdot \left[\frac{m_{BY}^{Z_B}}{m_{AY}^{Z_A}} \cdot \frac{\gamma_{+BY}^{Z_A(Z_{B+1})}}{\gamma_{+AY}^{Z_B(Z_{A+1})}} \right] \quad 5.1.7$

The terms inside the square brackets are the contributions made by the mixed electrolyte solution to the value of K_c .

For uni-univalent exchanges i.e. $Z_A = Z_B = 1$, the expression for K_c reduces to

$$K_c = \frac{A_Z}{B_Z} \cdot \left[\frac{m_{BY}}{m_{AY}} \cdot \frac{\gamma_{+BY}^2}{\gamma_{+AY}^2} \right] \quad 5.1.8$$

where γ_{+BY} , γ_{+AY} are the mean molal activity coefficients of the electrolytes in the solution phase. As shown in section 3.3, these should strictly be the activity coefficients of one electrolyte in the presence of a second, and can be estimated using the expressions derived by Glueckauf. Thus for uni-univalent exchanges

$$\gamma_s = \frac{\gamma_{\pm BY}^2}{\gamma_{\pm AY}^2} = \frac{\bar{\gamma}_{\pm BY}}{\bar{\gamma}_{\pm AY}} \quad 5.1.9$$

where $\bar{\gamma}_{\pm BY}$, $\bar{\gamma}_{\pm AY}$ are the activity coefficients of the single electrolytes in a solution at an ionic strength equal to the ionic strength of the mixed electrolytes. The ratio γ_s can be evaluated at various total electrolyte concentrations and is shown to be almost independent of solution strength e.g. for the (NaK)Cl system, $\gamma_s = 1.00$ at 0.01 total molality, 1.01 at 0.1 total molality, and 1.04 at 0.5 total molality.

From equation 5.1.6, for given values of $f_A(Z)$, $f_B(Z)$ i.e. for a given A_Z , there is only one value of K_c since K_a is a constant. Thus on going from one mixed electrolyte solution to another, but keeping the composition of the exchanger fixed, the second solution must have a composition such that the term in the square brackets of equation 5.1.8 is unaltered. However, as has been shown, the ratio $\gamma_{\pm BY}^2 / \gamma_{\pm AY}^2 = \gamma_s$ changes little over a wide range of concentration of the electrolyte solution, so that the corresponding change in m_{BY}/m_{AY} will be negligible. Since for uni-univalent exchanges only

$$\frac{m_{BY}}{m_{AY}} = \frac{B_s}{A_s} = \frac{1-A_s}{A_s} \quad ,$$

where A_s, B_s are the equivalent cationic fractions of the ions A^+, B^+ respectively in solution, the value of A_s , for a given value of A_Z will be practically unaltered as the total strength of the mixed electrolyte solution varies. In other words the shape of the exchange isotherm is almost independent of the strength of the solution used.

For uni-divalent exchanges i.e. $Z_A = 2, Z_B = 1$, the expression for K_c is given by

$$K_c = \frac{A_Z}{B_Z^2} \cdot \left[\frac{m_{BY}^2}{m_{AY_2}} \cdot \frac{\gamma_{+BY}^4}{\gamma_{+AY_2}^3} \right] \quad 5.1.10$$

where, as before, the terms inside the square brackets are the contributions of the electrolyte solution. The ratio $\gamma_{+BY}^4 / \gamma_{+AY_2}^3$ is again estimated from the expression of Glueckauf. Changing the strength of the mixed electrolyte solution will produce a change in this ratio of the activity coefficients. For a constant value of A_Z , K_c has, however, a unique value as already indicated, and therefore the change in the ratio $\gamma_{+BY}^4 / \gamma_{+AY_2}^3$ must be counterbalanced by a corresponding change in the ratio m_{BY}^2 / m_{AY_2} , such that the term in the square brackets of equation 5.1.10 remains unchanged. However, this will result in changes occurring in the values of the cationic fractions in solution i.e. changes in A_s and B_s . This

means that for a given composition of the mixed exchanger, the exchanger can be in equilibrium with solutions of varying ratios of m_{BY}^2/m_{AY_2} and $\gamma_{BY}^4/\gamma_{AY_2}^3$, such that the product of these two ratios is always constant.

Thus the isotherms that have been determined for the uni-divalent exchanges using varying molalities of the electrolyte solutions represent the average isotherms in the range of concentrations used. However, the values of K_c derived from the ion exchange equilibrium data are the unique values corresponding to particular values of A_Z .

5.2. Evaluation of the activity coefficients of the components of the mixed exchanger

The thermodynamic treatment of Gaines and Thomas leads to the following expressions for the activity coefficients of the components $A(Z)_{Z_A}$, $B(Z)_{Z_B}$ forming the mixed exchanger.

$$\ln f_{A(Z)}^{Z_B} = -(Z_A - Z_B)B_Z - \int_{K_c}^{K_c} B_Z d \ln K_c$$

$$-Z_A Z_B \left[\int_{a_s=1}^{a_s(a)} n_s^A d \ln a_s + \int_{a_s(a)}^{a_s'} n_s^A d \ln a_s \right] \quad 5.2.1$$

$$\text{and} \\ \ln f_{B(Z)}^{Z_A} = (Z_A - Z_B)A_Z + \int_{K_c^0}^{K_c} A_Z d \ln K_c \\ - Z_A Z_B \left[\int_{a_{s=1}}^{a_{s(b)}} n_s^B d \ln a_s - \int_{a_{s(b)}}^{a_s'} n_s^B d \ln a_s \right] \quad 5.2.2$$

where a_s' is the activity of the water in the mixed exchanger phase; $K_c = K_c^0$ when $A_Z = 0$; and $K_c = K_c'$ when $A_Z = 1$. As explained previously in the evaluation of the standard free energy of exchange (vide section 3.3), the terms inside the square brackets can be neglected in comparison with the error involved in the graphical determination of the integrals. Thus the expressions for the activity coefficients of the components of the mixed exchanger reduce to

$$\ln f_{A(Z)}^{Z_B} = -(Z_A - Z_B)B_Z - \int_{K_c^0}^{K_c} B_Z d \ln K_c \quad 5.2.3$$

$$\text{and} \\ \ln f_{B(Z)}^{Z_A} = (Z_A - Z_B)A_Z + \int_{K_c^0}^{K_c} A_Z d \ln K_c \quad 5.2.4$$

If the equilibrium measurements had been made with solutions of infinite dilution, then the exchangers would always be in their standard states. In this case

the activity of the water, a_s , would be unity. The expressions for the activity coefficient of the components of the mixed exchanger would therefore be

$$Z_B \ln f_A^0(Z) = -(Z_A - Z_B)B_Z - \int_{K_c}^{K_c} B_Z d \ln K_c \quad 5.2.5$$

$$Z_A \ln f_B^0(Z) = (Z_A - Z_B)A_Z + \int_{K_c}^{K_c} A_Z d \ln K_c \quad 5.2.6$$

In several exchanges involving univalent ions only, a plot of $\log K_c$ against A_Z has been found to be linear, and can be represented by the equation

$$\log K_c = \log K_c^0 + 2C A_Z \quad 5.2.7$$

where, as before, $K_c = K_c^0$ when $A_Z = 0$ and $2C$ is the slope of the graph.

Hence $d \log_{10} K_c = 2C d A_Z$ since K_c^0 is constant. Substituting this in equations 5.2.5 and 5.2.6

$$\begin{aligned} \log_{10} f_A^0(Z) &= - \int_{A_Z=1}^{A_Z} (1-A_Z)2C d A_Z = -2C \left[A_Z - \frac{A_Z^2}{2} \right]_1^{A_Z} \\ &= C [1-2A_Z + A_Z^2] = C [1-A_Z]^2 = C B_Z^2 \end{aligned} \quad 5.2.8$$

$$\text{and } \log_{10} f_B^0(Z) = \int_0^{A_Z} A_Z 2C d A_Z = C \left[A_Z^2 \right]_0^{A_Z} = C A_Z^2 \quad 5.2.9$$

The thermodynamic equilibrium constant K_a is obtained from

$$\log K_a = \int_0^1 \log K_c \, dA_Z \quad 5.2.10$$

by substitution of eq. 5.2.7.

Thus

$$\begin{aligned} \log K_a &= \int_0^1 dA_Z \cdot \log K_c^0 + \int_0^1 2C A_Z \, dA_Z \\ &= \left[A_Z \log K_c^0 \right]_0^1 + C \left[A_Z^2 \right]_0^1 \\ &= \log K_c^0 + C \end{aligned} \quad 5.2.11$$

$$= \log K_{c(A_Z = 0.5)} \quad 5.2.12$$

where $K_{c_{A_Z=0.5}}$ is the value of K_c when $A_Z = 0.5$. Substituting eq. 5.2.11 in eq. 5.2.7 the equation of the straight line becomes

$$\log K_a = \log K_c + C(1 - 2A_Z) \quad 5.2.13$$

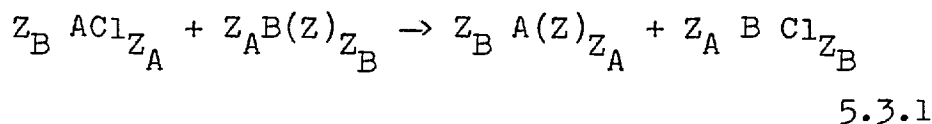
The expressions derived for the activity coefficients of the components of the mixed exchanger on a thermodynamic basis (equations 5.2.8 and 5.2.9) are similar to those obtained by Kielland (82) on a semi-empirical basis (equations 3.3.10). Also eq. 5.2.13 is the same as that obtained by substituting Kielland's relationships in the expression for the thermodynamic equilibrium constant

quotient. Thus for uni-univalent exchanges where a graph of $\log K_c$ against A_Z is linear, the activity coefficients of the components of the mixed exchanger may be represented by Kielland's equations, and the value of the thermodynamic equilibrium constant is the value of K_c when $A_Z = 0.5$.

For the uni-univalent exchanges where the graph of $\log K_c$ against A_Z is not linear, the activity coefficients of the components in the mixed exchanger and the thermodynamic equilibrium constants must be determined using equations 5.2.3, 5.2.4 and 5.1.4. For all uni-divalent exchanges these quantities can only be determined using these equations.

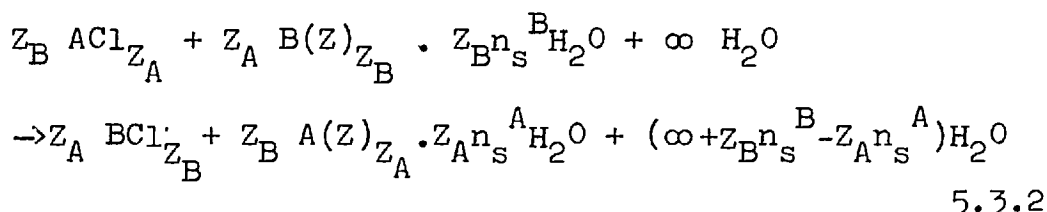
5.3. The Standard Heat of Ion Exchange

The standard heat of ion exchange ΔH° is defined as the heat of the reaction



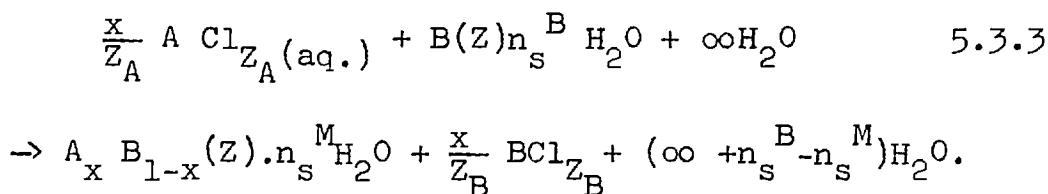
involving one equivalent of each reactant and product in their respective standard states. The standard state of the exchanger is the same as that defined by Cruickshank and Meares (52) i.e. pure exchanger $A(Z)_{Z_A}$ or $B(Z)_{Z_B}$ in equilibrium with an infinitely dilute solution of $A Cl_{Z_A}$ or $B Cl_{Z_B}$ respectively at atmospheric pressure

and temperature of the experiment. The standard state of the solution phase is infinite dilution. In order that the change in water content on exchange may be shown, equation 5.3.1. may be rewritten



where n_s^A , n_s^B are the number of moles of water in one equivalent of the exchangers $A(Z)_{Z_A}$, $B(Z)_{Z_B}$ respectively, in their standard states. The standard state chosen for the exchanger is the same as that chosen by Gaines and Thomas in their treatment of ion exchange equilibria.

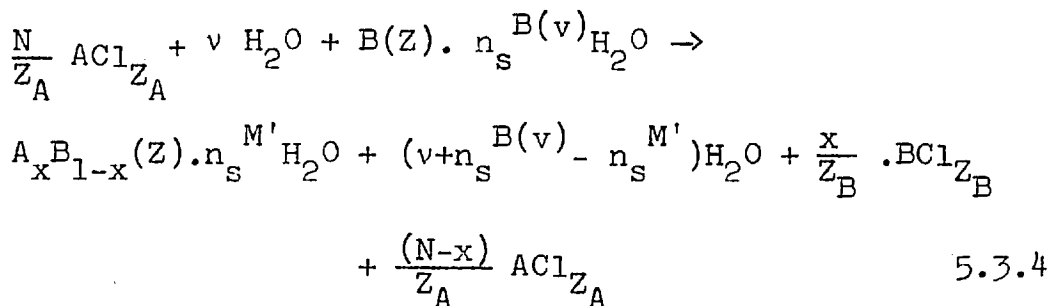
The standard heat of partial ion exchange, ΔH_x^0 , where x is the number of equivalents exchanged in 1 equivalent of pure exchanger $B(Z)_{Z_B}$, may be defined as the heat of the reaction



where $A_x B_{1-x} (Z)$ represents 1 equivalent of the partially exchanged exchanger. All reactants and products are in their respective standard states.

The Experimental Heat of Ion Exchange

The experimentally measured heat of ion exchange does not correspond to either ΔH^0 or ΔH_x^0 , since the reactants and products involved are not in their standard states. The calorimeter contains initially an electrolyte solution at a finite concentration, and a pure cationic form of the zeolite equilibrated with water vapour over pure water at 25°C. The product consists of a mixed exchanger in equilibrium with an electrolyte solution of finite concentration and of a particular ratio of the exchanging cations. The reaction occurring in the calorimeter can be represented as the exchange between 1 equivalent of the exchanger $B(Z)_{Z_B}$, in a non-standard state and containing $n_s^{B(v)}$ moles of water, and N equivalents of ACl_{Z_A} contained in v moles of water. This, when corrected to a reaction involving 1 equivalent of exchanger, may be written as



In order to obtain an expression for the change in heat content of the system during the exchange reaction, and also so that the heat of ion exchange may be derived,

the heat contents of the various components in the calorimeter, both as reactants and products, must be defined. These can be derived in terms of the apparent molar and apparent equivalent heat contents of the components in the aqueous and exchanger phases respectively.

For a two component system, of which one is water, the apparent molar heat content of the second, ϕ_2 is given by

$$\phi_2 = \frac{H - n_1 H_s^0}{n_2} \quad 5.3.5$$

where n_1 is the number of moles of water, n_2 is the number of moles of component 2, and H, H_s^0 are the total heat contents of the system and pure water respectively. This may be rewritten

$$H = n_2 \phi_2 + n_1 H_s^0 \quad 5.3.6$$

The heat contents of the reactant and product solutions

Applying eq. 5.3.6 to the reactant solution consisting of $\frac{N}{Z_A}$ moles of ACl_{Z_A} contained in v moles of water, the heat content of the reactant solution $H_{\text{ACl}}^{m_A}$ is given by

$$H_{\text{ACl}}^{m_A} = \frac{N}{Z_A} \phi_{\text{ACl}}^{m_A} + v H_s^0 \quad 5.3.7$$

where $\phi_{\text{ACl}}^{m_A}$ is the apparent molar heat content of ACl_{Z_A} at a molality m_A^0 . The molality of the solution m_A^0 is related to the number of equivalents N , or the number of

moles $\frac{N}{Z_A}$, by

$$m_A^o = \frac{N}{Z_A} \cdot \frac{1000}{18 \nu} \quad 5.3.8$$

The solution in the calorimeter after the exchange has taken place consists of two electrolytes ACl_{Z_A} , BCl_{Z_B} , and water. Its heat content can be considered as the sum of the heat contents of two solutions, one of each pure component electrolyte and an associated heat of mixing ΔH_M . The proportions and concentrations of the two solutions of the pure electrolytes must be consistent with the composition of the product solution. The heat content of the product solution is therefore given by

$$H_M = \frac{(N-x)}{Z_A} \cdot \phi_{ACl}^{m_A} + \frac{x}{Z_B} \phi_{BCl}^{m_B} + (v+n_s^{B(v)} - n_s^{M'}) H_s^o + \Delta H_M \quad 5.3.9$$

where m_A , m_B are the molalities of the constituent pure electrolyte solutions. The values of the terms $\phi_{ACl}^{m_A}$, $\phi_{BCl}^{m_B}$ and ΔH_M are dependent on the choice of the molalities. The heats of mixing of solutions of equal ionic strength have been investigated by Young and Smith (97). They have found the heat of mixing to be small, and satisfactorily represented by

$$\Delta H_M = k I X_{ACl} (1 - X_{ACl}) \quad 5.3.10$$

where k is an empirical constant dependent on the two

electrolytes in the system, and X_{ACl} is the mole fraction of ACl_{Z_A} in the final solution. If it is assumed that k is independent of ionic strength, the heats of mixing in a particular system can be determined at any ionic strength using eq. 5.3.10. The values of the constant k have been determined for various ion pairs by Young, Wu and Krawetz (98) and are summarized in Table 5.

Table 5

<u>System</u>	<u>cals/mole</u>
Na - Li, Cl	84.5
Na - K, Cl	-38.2
Na - Rb, Cl	-50.0
Na - Cs, Cl	-35.2

The molalities of the constituent electrolytes in the product solution are related to the ionic strength of the product solution by

$$m_A = \frac{2I}{Z_A(Z_A+1)} \quad ; \quad m_B = \frac{2I}{Z_B(Z_B+1)} \quad 5.3.11$$

where

$$I = \frac{m_A^0 Z_A}{N} \left[\frac{1}{2}(Z_A+1)(N-x) + \frac{1}{2}(Z_B+1)x \right] \quad 5.3.12$$

provided that there is no change in the number of water molecules in solution. This will be the case for the zeolite exchangers since the change in water content $(n_s^{B(v)} - n_s^{M'})$ will be small and negligible in comparison

to the total number of water molecules in the solution phase, provided the solutions are dilute.

In the calorimeter experiments the solutions used were dilute, generally less than 0.1M, and therefore the value of the heat of mixing term is small and becomes negligible as the solutions become more dilute. Table 6 summarizes the largest values of the heats of mixing used in the product solutions of the ion exchanges studied.

<u>Table 6</u>		
<u>System</u>	$\Delta H_M(I = 1.0)$ cals/mole	$\Delta H_M(I = 0.1)$
Na - Li, Cl	+42.1	+2.1
Na - K, Cl	-34.1	-1.2
Na - Rb, Cl	-47.2	-1.3
Na - Cs, Cl	-31.1	-1.2

More recently, a revised form of equation 5.3.10 has been put forward by Wu, Smith and Young (99). The heat of mixing at constant ionic strength of one is given by the power series

$$\frac{\Delta H_M}{x_2 x_3} = \alpha + \beta(x_2 - x_3) + \dots \quad 5.3.13$$

where x_2, x_3 are the solute mole fractions of the electrolytes and α and β are constants. Typical values of the constants α and β are given in Table 7.

Table 7

<u>System</u>	<u>α</u>	<u>β</u>
Na - Li, Cl	84.6	6.6
Na - K, Cl	-38.3	0.5
Na - Rb, Cl	-49.5	3.3
Na - Cs, Cl	-34.8	-0.2

As before, these heats become negligible for molalities of 0.1 M or less. For the other uni-univalent systems studied, i.e. Na - Ag, Na - Tl, and Na - NH_4 , no data are available for the heats of mixing of aqueous electrolytes of these ions. However the molalities used in these exchanges were of the order of 0.1 or less so that it can be assumed that the heats of mixing for these solutions are zero. Similarly, no data are available for the heats of mixing of NaCl and CaCl_2 , BaCl_2 and SrCl_2 , and NaNO_3 and $\text{Pb}(\text{NO}_3)_2$; and the heat of mixing of these solutions was accordingly neglected.

The Heat Contents of the Reactant and Product Exchanger Phases

The heat content H_{BZ}^{V} , of 1 equivalent of the pure exchanger $\text{B}(\text{Z})_{\text{Z}_\text{B}}$ in its non-standard state, in equilibrium with water vapour over pure water at 25°C and containing $n_{\text{S}}^{\text{B}(\text{v})}$ moles of water is

$$H_{BZ}^v = \phi_{BZ}^v + n_s^B(v) \cdot H_s^o \quad 5.3.14$$

In its standard state the heat content of 1 equivalent of the pure exchanger $B(Z)_{Z_B}$, containing n_s^B moles of water is

$$H_{BZ}^o = \phi_{BZ}^o + n_s^B H_s^o \quad 5.3.15$$

The pure exchanger in its non-standard state of equilibrium with water vapour over pure water can be converted to its standard state i.e. pure exchanger in equilibrium with an infinitely dilute solution of BCl_Z , by immersing it in water and allowing it to come to equilibrium, with the accompanying liberation of the heat of wetting. Thus the heat of wetting is given by

$$\Delta H_{B(Z)}^w = \phi_{B(Z)}^o - \phi_{B(Z)}^v \quad 5.3.16$$

Since the pure exchangers in their non-standard states are fully equilibrated with water vapour over pure water, the intracrystalline channels and the cages of the exchangers will be fully saturated. The heat of wetting therefore represents the heat associated with the wetting of the surfaces of the exchangers with water.

The heat content of the pure exchanger in its non-standard state H_{BZ}^v can be expressed in terms of its apparent equivalent heat content in its standard state from equations 5.3.14 and 5.3.16, thus

$$H_{BZ}^V = \phi_{BZ}^O - \Delta H_{BZ}^W + n_s^{B(v)} H_s^O \quad 5.3.17$$

Similarly for one equivalent of the mixed exchanger, the heat of wetting is given by

$$\Delta H_{(A,B)Z}^W = \phi_{(A,B)Z}^O - \phi_{(A,B)Z}^V \quad 5.3.18$$

The heat content of the product exchanger $A_x B_{1-x}(Z)$ containing $n_s^{M'}$ moles of water, in its non-standard state, in equilibrium with a solution of the exchanging ions at a finite concentration is, by analogy with eq. 5.3.14

$$H'_{(A,B)Z} = \phi'_{(A,B)Z} + n_s^{M'} \cdot H_s^O \quad 5.3.19$$

In its standard state the heat content of 1 equivalent of the mixed exchanger, $A_x B_{1-x}(Z)$, containing n_s^M moles of water is

$$H_{(A,B)Z}^O = \phi_{(A,B)Z}^O + n_s^M H_s^O \quad 5.3.20$$

If the product exchanger, equilibrated with water vapour over pure water at 25°C , is immersed in the product solution, the exchanger will be converted to the non-standard state obtained in the calorimeter measurements. The accompanying heat change is the heat of equilibration $\Delta H_{(A,B)Z}^E$.

The heat content of the mixed exchanger and the product solution before being added to one another is

$$H_c = \left[\phi^v(A,B)Z + n_s^{M(v)} H_s^o \right] + \left[\left(\frac{N-x}{Z_A} \right) \cdot \phi_{ACl}^m + \frac{x}{Z_B} \phi_{BCl}^m + (v + n_s^{B(v)} - n_s^{M'}) H_s^o + \Delta H_M \right] \quad 5.3.21$$

The immersion of the exchanger in the product solution produces a transfer of water between the exchanger and the solution. The heat content of the system will be

$$H_d = \phi'(A,B)Z + n_s^{M'} H_s^o + \frac{(N-x)}{Z_A} \phi_{ACl}^m + \frac{x}{Z_B} \phi_{BCl}^m + (v + n_s^{B(v)} + n_s^{M(v)} - 2n_s^{M'}) H_s^o + \Delta H_M \quad 5.3.22$$

The terms $n_s^{B(v)} + n_s^{M(v)} - 2n_s^{M'}$ are small compared with the total number of moles of water in solution, i.e. v and therefore the values of ϕ_{ACl}^m , ϕ_{BCl}^m and ΔH_M will be unaltered by the addition of the exchanger to the solution. The change in heat content $H_d - H_c$ is given by

$$H_d - H_c = \phi'(A,B)Z - \phi^v(A,B)Z = \Delta H^E(A,B)Z \quad 5.3.23$$

This represents the heat of equilibration of the product exchanger between two non-standard states.

The heat content $H'(A,B)Z$ of the product exchanger in its non-standard state, in equilibrium with a solution of the exchanging ions at a finite concentration, is given by

$$H'(A,B)Z = \phi(A,B)Z + n_s^{M'} H_s^O \quad 5.3.24$$

By combining eq. 5.3.24 with equations 5.3.18 and 5.3.23 one obtains

$$H'(A,B)Z = \phi^O(A,B)Z - \Delta H^W(A,B)Z + \Delta H^E(A,B)Z + n_s^{M'} H_s^O \quad 5.3.25$$

In all cases where $\Delta H^W(A,B)Z$ and $\Delta H^E(A,B)Z$ were measured it was found that the difference was small, and since the difference was less than the error involved in the measurement of these quantities, the heats of wetting and equilibration of the mixed exchangers were assumed to be the same. (vide Table 14, section 6.4).

The Experimental Heat of Ion Exchange

The ion exchange reaction occurring in the calorimeter may be represented by eq. 5.3.3. If H_R and H_p are the total heat contents of the reactants and products respectively, then the calorimetrically determined heat of ion exchange ΔH_x , corrected to a reaction involving one equivalent of exchanger is

$$\Delta H_x = H_p - H_R \quad 5.3.26$$

From equations 5.3.9 and 5.3.25, the total heat content of the products H_p is

$$H_p = \phi^O(A,B)Z^- \Delta H^W(A,B)Z^+ \Delta H^E(A,B)Z^+ n_s^{M'} H_s^O$$

$$+ \frac{(N-x)}{Z_A} \phi_{ACl}^m A + \frac{x}{Z_B} \phi_{BCl}^m B + (v+n_s^{B(v)} - n_s^{M'}) H_s^O + \Delta H_M \quad 5.3.27$$

Similarly, from equations 5.3.7 and 5.3.17, the total heat content of the reactants H_R is

$$H_R = \left[\phi^O_B(Z) - \Delta H^W_B(Z) + n_s^{B(v)} H_s^O \right] + \left[\frac{N}{Z_A} \phi_{ACl}^m A + v H_s^O \right] \quad 5.3.28$$

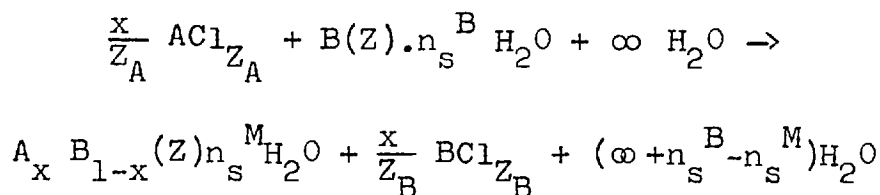
The heat of ion-exchange ΔH_x is given by the difference between equations 5.3.27 and 5.3.28. Thus

$$\Delta H_x = \phi^O(A,B)Z^- \phi^O_B(Z) - \Delta H^W(A,B)Z^+ \Delta H^E(A,B)Z$$

$$+ \Delta H^W_B(Z) + \frac{(N-x)}{Z_A} \phi_{ACl}^m A + \frac{x}{Z_B} \phi_{BCl}^m B - \frac{N}{Z_A} \phi_{ACl}^m A + \Delta H_M \quad 5.3.29$$

The Standard Heat of Partial Ion Exchange

The standard heat of partial ion exchange is defined as the heat involved in the reaction



where all the reactants and products are in their defined standard states. The change in heat content in this reaction i.e. ΔH_x^O is given by

$$\Delta H_x^\circ = \left[\phi_{(A,B)Z}^\circ + n_s^M H_s^\circ \right] + \left[\frac{x}{Z_B} \phi_{BCl}^\circ + (\infty + n_s^B - n_s^M) H_s^\circ \right] \\ - \left[\phi_{BZ}^\circ + n_s^B H_s^\circ \right] - \left[\frac{x}{Z_A} \phi_{ACl}^\circ + \infty H_s^\circ \right] \quad 5.3.30$$

$$= \phi_{(A,B)Z}^\circ - \phi_{BZ}^\circ + \frac{x}{Z_B} \phi_{BCl}^\circ - \frac{x}{Z_A} \phi_{ACl}^\circ \quad 5.3.31$$

where ϕ_{ACl}° is the apparent molar heat content of ACl_{Z_A} at infinite dilution, and at the temperature and pressure of the experiment.

Thus from equations 5.3.29 and 5.3.31

$$\Delta H_x - \Delta H_x^\circ = \Delta H_{BZ}^W - \Delta H_{(A,B)Z}^W + \Delta H_{(A,B)Z}^E + \Delta H_M \\ + \frac{x}{Z_B} \left[\phi_{BCl}^{m_B} - \phi_{BCl}^\circ \right] - \frac{x}{Z_A} \left[\phi_{ACl}^{m_A} - \phi_{ACl}^\circ \right] \\ + \frac{N}{Z_A} \left[\phi_{ACl}^{m_A} - \phi_{ACl}^\circ \right] \quad 5.3.32$$

But the function $\phi_{ACl}^{m_A} - \phi_{ACl}^\circ$ represents the relative apparent molal heat content $\phi_{ACl}^{m_A}$ of the electrolyte ACl_{Z_A} at a molality m_A and at atmospheric pressure and the temperature of the experiment. Similarly $\phi_{BCl}^{m_B} - \phi_{BCl}^\circ$ represents the relative apparent molal heat content $\phi_{BCl}^{m_B}$ of BCl_{Z_B}

$$\text{Thus } \phi_{ACl}^{m_A} = \phi_{ACl}^{m_A} - \phi_{ACl}^\circ \quad 5.3.33$$

$$\text{and } \phi_{BCl}^{m_B} = \phi_{BCl}^{m_B} - \phi_{BCl}^o \quad 5.3.34$$

These functions can be derived experimentally since they are numerically equal to but of opposite sign to the heats of dilution to infinite dilution. Values of the relative apparent molal heat contents for many electrolytes have been tabulated by Harned and Owen (100); and values of the heats of dilution of many electrolytes have been tabulated by Rossini et al. (96) and Parker (101).

If one inserts equations 5.3.33 and 5.3.34 in equation 5.3.32 one obtains

$$\begin{aligned} \Delta H_x = & \Delta H_x^o - \Delta H^W_{(A,B)Z^+} + \Delta H^E_{(A,B)Z^+} + \Delta H^W_{BZ^+} + \Delta H_M \\ & + x \left[\frac{\phi_{BCl}^{m_B}}{Z_B} - \frac{\phi_{ACl}^{m_A}}{Z_A} \right] + \frac{N}{Z_A} \left[\phi_{ACl}^{m_A} - \phi_{ACl}^o \right] \end{aligned} \quad 5.3.35$$

Thus the standard heats of partial ion exchange may be derived from the experimentally determined heats of partial ion exchange from the relation

$$\begin{aligned} \Delta H_x^o = & \Delta H_x - \Delta H^W_{BZ^+} + \Delta H^W_{(A,B)Z^-} - \Delta H^E_{(A,B)Z^-} - \Delta H_M \\ & - x \left[\frac{\phi_{BCl}^{m_B}}{Z_B} - \frac{\phi_{ACl}^{m_A}}{Z_A} \right] - \frac{N}{Z_A} \left[\phi_{ACl}^{m_A} - \phi_{ACl}^o \right] \end{aligned} \quad 5.3.36$$

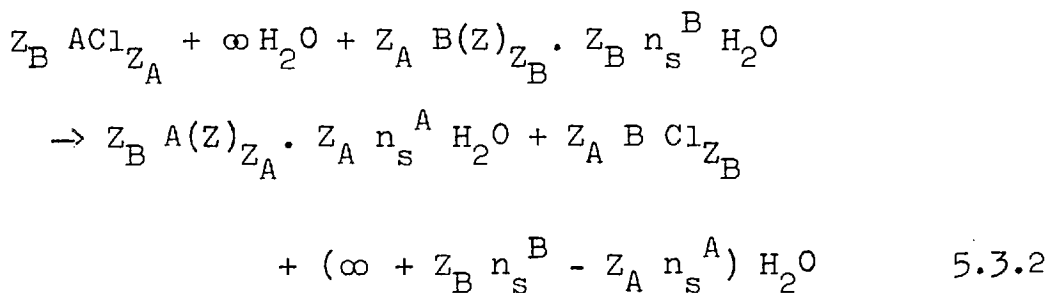
When the exchanging ions are both univalent $Z_A = Z_B$ then $m_A = m_A^o$ and therefore $\phi_{ACl}^{m_A} = \phi_{ACl}^o$. Consequently

the last term in equation 5.3.36 reduces to zero.

All the terms on the right hand side of equation 5.3.36 can be determined experimentally or can be derived from tabulated data. However no accurate data exist for the heats of dilution of thallous acetate and lead nitrate solutions, so the heats of exchange involving these ions have not been corrected for the heat contents of the solutions. The experimental heats of partial ion exchange were determined for solutions of 0.1 molality or less and consequently these corrections will be small. Thus the accuracy of the values of the standard heats of partial ion exchange, ΔH_x^0 depends almost entirely on the accuracy of the calorimetrically measured heats of partial ion exchange, heats of wetting and heats of equilibration. The error in the value of ΔH_x^0 is therefore in the region of $\pm 25 - 30$ cal per gram equivalent of exchanger.

The Standard Heat of Ion Exchange

The standard heat of ion exchange, ΔH^0 was defined as the heat of the reaction represented by



involving all the reactants and products in their defined standard states. However, this quantity cannot be determined experimentally since complete exchange is not attained in the calorimeter. It can be determined from a graph of ΔH_x° against A_x by extrapolation of the graph to $A_x = 1$. The accuracy of this method of evaluating ΔH° depends on the length of the extrapolation required. If, however, a heat of ion exchange ΔH_a is measured in the calorimeter for the exchange from pure $B(Z)_{Z_B}$ to some intermediate composition, and ΔH_b is measured for the exchange from pure $A(Z)_{Z_A}$ to the same intermediate composition, then the standard heat of ion exchange can be derived by an algebraic combination of ΔH_a and ΔH_b taking into consideration corrections due to the heat contents of the solutions.

If equivalent amounts of electrolyte solution ACl_{Z_A} at a molality m_A° and pure exchanger $B(Z)_{Z_B}$, equilibrated with water vapour over pure water at 25°C , are mixed in a calorimeter, a reaction occurs with an accompanying heat of ion exchange ΔH_a , when corrected to a reaction involving 1 equivalent of electrolyte and exchanger. The same equilibrium state can also be attained, if the ion exchange is reversible, by reacting the same equivalent amounts of electrolyte solution BCl_{Z_B} and pure exchanger $A(Z)_{Z_A}$, again equilibrated with water vapour

over pure water at 25°C. This reaction will have an accompanying heat of exchange ΔH_b . If the same equilibrium is attained in both reactions, the difference between the values of the measured heats of ion exchange $\Delta H_a - \Delta H_b$ is given by

$$\begin{aligned} \Delta H_a - \Delta H_b = & \left[\phi_{AZ}^{\circ} - \Delta H_{AZ}^W + n_s^{A(v)} H_s^{\circ} \right] \\ & + \left[\frac{1}{Z_B} \phi_{BCl}^{m^{\circ}B} + (v + n_s^{B(v)} - n_s^{A(v)}) H_s^{\circ} \right] \\ & - \left[\phi_{B(Z)}^{\circ} - \Delta H_{B(Z)}^W + n_s^{B(v)} H_s^{\circ} \right] - \left[\frac{1}{Z_A} \phi_{ACl}^{m^{\circ}A} + v H_s^{\circ} \right] \end{aligned} \quad 5.3.37$$

which reduces to

$$\Delta H_a - \Delta H_b = \phi_{AZ}^{\circ} - \phi_{BZ}^{\circ} - \Delta H_{AZ}^W + \Delta H_{BZ}^W + \frac{1}{Z_B} \phi_{BCl}^{m^{\circ}B} - \frac{1}{Z_A} \phi_{ACl}^{m^{\circ}A} \quad 5.3.38$$

The standard heat of ion exchange of the reaction represented in equation 5.3.2 involving all the reactants and products in their standard states is

$$\begin{aligned} \Delta H^{\circ} = & \left[\phi_{AZ}^{\circ} + n_s^{A} H_s^{\circ} \right] + \left[\frac{1}{Z_B} \phi_{BCl}^{\circ} + (\infty + n_s^{B} - n_s^{A}) H_s^{\circ} \right] \\ & - \left[\phi_{BZ}^{\circ} + n_s^{B} H_s^{\circ} \right] - \left[\frac{1}{Z_A} \phi_{ACl}^{\circ} + \infty H_s^{\circ} \right] \end{aligned} \quad 5.3.39$$

which reduces to

$$\Delta H^{\circ} = \phi_{AZ}^{\circ} - \phi_{BZ}^{\circ} + \frac{1}{Z_B} \phi_{BCl}^{\circ} - \frac{1}{Z_A} \phi_{ACl}^{\circ} \quad 5.3.40$$

From equations 5.3.38 and 5.3.40

$$\Delta H_a - \Delta H_b = \Delta H^O - \Delta H_{AZ}^W + \Delta H_{BZ}^W + \frac{1}{Z_B} \left[\phi_{BCl}^{m_B} - \phi_{BCl}^O \right] - \frac{1}{Z_A} \left[\phi_{ACl}^{m_A} - \phi_{ACl}^O \right] \quad 5.3.41$$

But the terms $\phi_{BCl}^{m_B} - \phi_{BCl}^O$ and $\phi_{ACl}^{m_A} - \phi_{ACl}^O$ represent the relative apparent molal heat contents $'\phi_{BCl}^{m_B}$ and $'\phi_{ACl}^{m_A}$ respectively. Thus

$$\Delta H^O = \Delta H_a - \Delta H_b + \Delta H_{AZ}^W - \Delta H_{BZ}^W - \frac{1}{Z_B} '\phi_{BCl}^{m_B} + \frac{1}{Z_A} '\phi_{ACl}^{m_A} \quad 5.3.42$$

All the functions appearing on the right hand side of equation 5.3.42 can be determined experimentally, or can be derived from tabulated data. Thus the standard heat of ion exchange can be evaluated. For exchanges involving thalious acetate and lead nitrate solutions, no data are available for the relative apparent molal heat contents of these solutions. However, provided that the solutions are dilute, as is generally the case, these quantities are small compared with the experimental heats ΔH_a and ΔH_b .

The standard state chosen for the electrolyte in the solution in the above treatment of the calorimetric determination of the standard heat of ion exchange, i.e. infinite dilution, is not the same as that chosen by Gaines and Thomas in their thermodynamic treatment of the ion exchange equilibria, i.e. 'the hypothetical

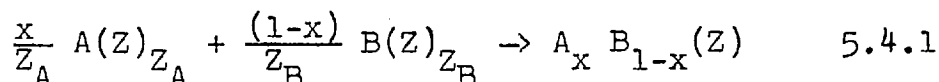
ideal 1 molal solution' (vide section 3.3). However, it has been shown by Ward (90) that the heats of ion exchange corresponding to the two standard states are identical. Therefore even though different standard states are chosen for the electrolyte in the solution phase in the definitions of the standard heat of ion exchange, ΔH° , and the standard free energy of exchange ΔG° , the values of ΔG° and ΔH° , which are determined experimentally can be used to determine the standard entropy of exchange using the relation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

provided that the calorimetric determined isotherm agrees with the equilibrium isotherm, i.e. there is no slow process occurring in the calorimeter experiments.

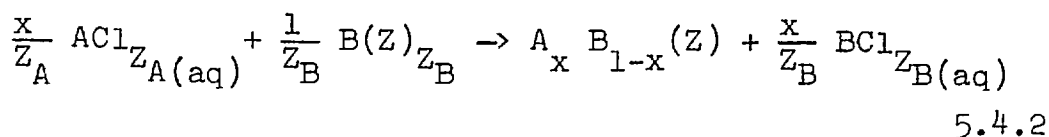
5.4. Thermodynamic functions for the formation of the mixed exchanger

One equivalent of the mixed exchanger, $A_x B_{1-x}(Z)$ can be considered to be formed from $\frac{x}{Z_A}$ equivalents of the pure exchanger $A(Z)_{Z_A}$ and $\frac{(1-x)}{Z_B}$ equivalents of the pure exchanger $B(Z)_{Z_B}$, the reactants and products being in their respective standard states. Thus

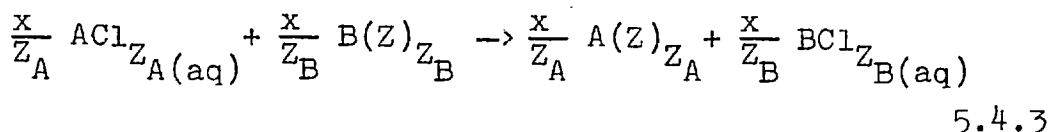


This reaction can be considered as the algebraic

difference between the two reactions



and



involving all the reactants and products in their standard states.

The heat of ion exchange for the reaction represented by equation 5.4.2. is the standard heat of partial ion exchange ΔH_x^0 . If ΔH^0 is the standard heat of complete ion exchange, defined by equation 5.3.1, then the heat involved in the reaction represented by equation 5.4.3 is $x\Delta H^0$. The heat content change ΔH_x^M for the reaction represented by equation 5.4.1 is therefore

$$\Delta H_x^M = \Delta H_x^0 - x\Delta H^0 \quad 5.4.4$$

For the formation of an ideal solution from its components $\Delta H_x^M = 0$.

The change in free energy ΔG_x^0 occurring for the reaction represented by equation 5.4.2 is given by

$$\Delta G_x^0 = \mu^0_{(\text{A,B})Z} + \frac{x}{Z_B} \mu^0_{\text{B}_s} - \frac{1}{Z_B} \mu^0_{\text{B(Z)}_{Z_B}} - \frac{x}{Z_A} \mu^0_{\text{A}_s} \quad 5.4.5$$

where $\mu^0_{(\text{A,B})Z}$ is the chemical potential of 1 equivalent of the mixed exchanger, $\text{A}_x \text{B}_{1-x}(\text{Z})$ in its standard state.

If ΔG° is the standard free energy of complete exchange, then the free energy change for the reaction represented by eq. 5.4.3 is $x \Delta G^\circ$.

Thus the free energy change ΔG_x^M for the reaction represented by equation 5.4.1 is given by

$$\Delta G_x^M = \Delta G_x^\circ - x \Delta G^\circ \quad 5.4.6$$

The free energy of complete exchange ΔG° is given by

$$\Delta G^\circ = \frac{1}{Z_A} \mu^\circ_{A(Z)_{Z_A}} + \frac{1}{Z_B} \mu^\circ_{B_S} - \frac{1}{Z_B} \mu^\circ_{B(Z)_{Z_B}} - \frac{1}{Z_A} \mu^\circ_{A_S} \quad 5.4.7$$

Thus substituting equations 5.4.5 and 5.4.7 in equation 5.4.6.

$$\Delta G_x^M = \mu^\circ_{(A,B)Z} - \frac{x}{Z_A} \mu^\circ_{A(Z)_{Z_A}} - \frac{(1-x)}{Z_B} \mu^\circ_{B(Z)_{Z_B}} \quad 5.4.8$$

The chemical potential, $\mu^\circ_{(A,B)Z}$ of 1 equivalent of the mixed exchanger $A_x B_{1-x}(Z)$ in its standard state can be represented as the sum of the chemical potentials of the appropriate quantities of the two components in the mixed exchanger. Thus

$$\begin{aligned} \mu^\circ_{(A,B)Z} = & \frac{x}{Z_A} \left[\mu^\circ_{A(Z)_{Z_A}} + RT \ln A_Z f^\circ_{A_Z} \right] \\ & + \frac{(1-x)}{Z_B} \left[\mu^\circ_{B(Z)_{Z_B}} + RT \ln B_Z f^\circ_{B_Z} \right] \quad 5.4.9 \end{aligned}$$

Thus the free energy change for the formation of 1

equivalent of mixed exchanger from its components is given by

$$\Delta G_x^M = \frac{x}{Z_A} RT \ln A_Z f_{A_Z}^{\circ} + \frac{(1-x)}{Z_B} RT \ln B_Z f_{B_Z}^{\circ} \quad 5.4.10$$

For ideal behaviour, the activity coefficients $f_{A_Z}^{\circ}$, $f_{B_Z}^{\circ}$ are unity. Consequently equation 5.4.10 reduces to

$$\Delta G_x^{M(1d)} = \frac{x}{Z_A} RT \ln A_Z + \frac{(1-x)}{Z_B} RT \ln B_Z \quad 5.4.11$$

For nonideal behaviour the activity coefficients can be calculated from ion exchange equilibrium data using equations 5.2.5 and 5.2.6.

The entropy change ΔS_x^M associated with the reaction represented by equation 5.4.1 is obtained from

$$\Delta G_x^M = \Delta H_x^M - T\Delta S_x^M \quad 5.4.12$$

Although different standard states have been chosen for the electrolyte in the solution phase in the definitions of the standard heats of ion exchange $x\Delta H^{\circ}$ and ΔH_x° and the standard free energies of exchange, $x\Delta G^{\circ}$ and ΔG_x° , for the reactions represented by equations 5.4.2 and 5.4.3, this does not produce any complications when the respective functions ΔH_x^M and ΔG_x^M for the reaction represented by equation 5.4.1, since the terms referring to the electrolytes in the solution phase cancel out.

6. Results

6.1. Calibration

The heat, ΔH , involved in a reaction taking place in the calorimeter is related to the area under the heat curve by

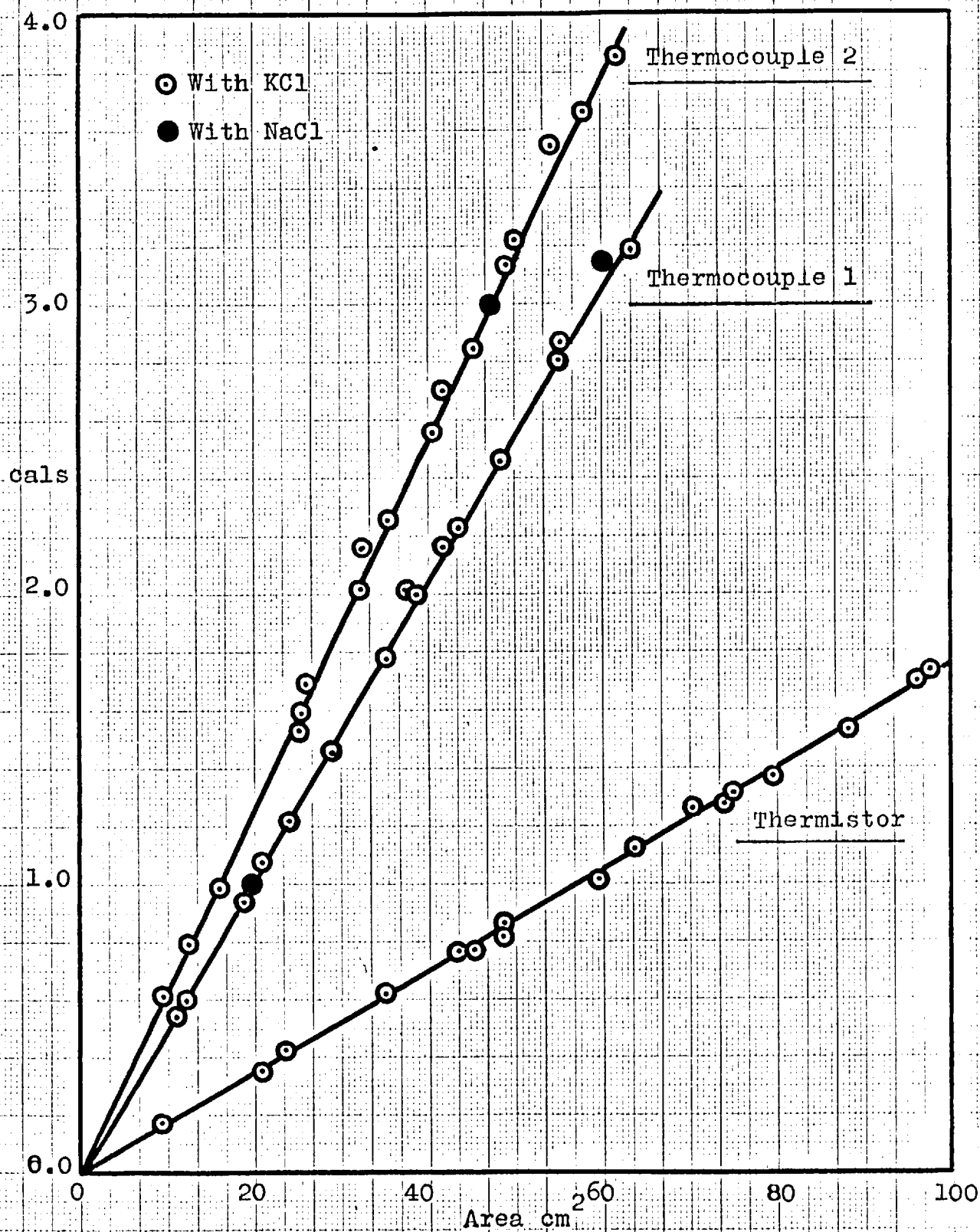
$$\Delta H = k_r A$$

where k_r is a constant characteristic of the reactant cell. The integral heats of solution of KCl and NaCl were used to evaluate k_r . Data for the heats of solution of these salts are available in tables compiled by Rossini et al. (96). The results for the calibration of the two thermocouple systems and the thermistor system are shown in Fig. 5. The values of the calibration constants are -0.0176, -0.0518 and -0.0636 cal/sq. cm. for the thermistor, thermocouple 1 and thermocouple 2 respectively. The system involving the thermistor is the most sensitive, although the increased sensitivity is counterbalanced by a slight decrease in base line stability on the strip chart for the steady state condition.

6.2. Analysis

6.2.1. Analysis of the Chabazite Zeolites

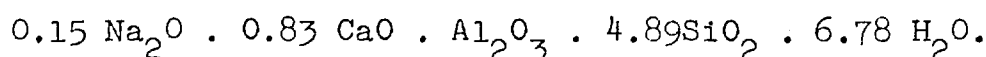
Four analyses of the sample of natural chabazite of Nova Scotian origin, equilibrated with water vapour



over saturated ammonium chloride solution at room temperature, were made. The mean values (°/o by weight) of the components were found to be

°/o Na ₂ O	°/o CaO	°/o Al ₂ O ₃	°/o SiO ₂	°/o H ₂ O
1.61	8.07	17.64	50.75	21.13

These values enable the oxide formula of this sample to be calculated:-



X-ray powder photographs were taken of the natural chabazite from which the hexagonal unit cell parameters, $a = 13.77 \text{ \AA}$ $c = 14.98 \text{ \AA}$ were calculated. The unit cell content was therefore represented by



a value of 2.08 gm/cm^3 being used for the density in the derivation of this formula.

Several samples of sodium chabazite were prepared from the natural form by repeated treatment with aqueous sodium chloride solutions for several weeks. The analyses of these samples are summarized in table 8. In all cases the zeolites have been equilibrated with water vapour over saturated ammonium chloride solutions.

The value of the sodium oxide content is that obtained using the radiochemical technique outlined in section 4.2. Values derived by this method are more

Table 8

Analyses of Sodium Chabazite

Sample	%Na ₂ O	%CaO	%Al ₂ O ₃	%SiO ₂	%H ₂ O
I	10.00	0.25	17.29	51.85	20.04
II	9.84	0.24	17.20	51.95	20.05
III	10.36	0.33	17.75	51.83	19.51
IV	10.62	-	17.51	52.36	19.29

reliable than those obtained by a gravimetric method since the sodium content of silicates by estimation as the sulphate is known to be inaccurate. The data of Table 8 lead to the following oxide formulae for the samples:-

Sample I 0.95 Na₂O. 0.03 CaO. Al₂O₃. 5.10SiO₂. 6.57 H₂O
 Sample II 0.94 Na₂O. 0.03 CaO. Al₂O₃. 5.14 SiO₂. 6.61 H₂O
 Sample III 0.96 Na₂O. 0.03 CaO. Al₂O₃. 4.97 SiO₂. 6.23 H₂O
 Sample IV 1.00 Na₂O. Al₂O₃. 5.08 SiO₂. 6.24 H₂O

X-ray powder photographs of the samples were taken, and were found to exhibit the lines characteristic of the chabazite structure. The unit cell dimensions of sample IV were determined, $a = 13.74 \text{ \AA}$, $c = 15.00 \text{ \AA}$ from which the formula of the unit cell was determined i.e.

10.6 Na 10.6 Al 26.8 Si 74.8 O 33.0 H₂O

Several ion exchanged forms of chabazite were prepared by the methods outlined in section 4.1. The analytical results are shown in Tables 9 and 10 as percentage composition by weight, and also as moles on the basis of $\text{Al}_2\text{O}_3 = 1.0$. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of the samples fluctuate around a value of 5.0 characteristic of chabazite of Nova Scotian origin. The difference in the ratio total cation/aluminium from unity might be due in part to the experimental accuracy of the chemical analysis, especially for the residual Na content of the cation exchanged zeolite.

The water contents of the alkali metal forms of chabazite decrease with increasing crystallographic radius. A similar trend is observed with the alkaline earth metals. This is to be expected since the unit cell dimensions change little on ion exchange.

The analysis of lead chabazite shows that the lead enters the chabazite framework as the divalent ion. This is in contrast to the results of Barrer and Hinds (47) who concluded from their analytical data that the lead enters the analcite structure as the univalent complex ion $\text{Pb}(\text{OH}^+)$.

Although pure cationic forms of chabazite have not been prepared, the data of Tables 9 and 10 show that in most cases more than 90% exchange can be obtained.

Table 9

Analysis of Monovalent Forms of Chabazite

Exchanged			<u>SiO₂</u>	<u>Al₂O₃</u>	<u>H₂O</u>	<u>Na₂O</u>	<u>M₂O</u>	<u>CaO</u>
Forms								
Li	(	°/oWt.	52.32	17.37	22.05	-	4.62	0.70
	)	Moles	5.12	1.00	7.19	-	0.90	0.07
K	(	°/oWt.	50.99	16.86	17.32	-	13.71	0.43
	)	Moles	5.15	1.00	5.84	-	0.89	0.04
Rb	(	°/oWt.	44.43	15.27	13.92	-	25.37	0.90
	)	Moles	4.97	1.00	5.17	-	0.91	0.11
Cs	(	°/oWt.	44.07	14.83	10.36	-	32.97	0.71
	)	Moles	5.05	1.00	3.96	-	0.80	0.09
NH ₄	(	°/oWt.	53.68	17.80	20.17	-	8.64	0.08
	)	Moles	5.13	1.00	6.42	-	0.95	0.01
Ag	(	°/oWt.	40.74	13.50	14.97	-	31.04	-
	)	Moles	5.13	1.00	6.28	-	1.01	-
Tl	(	°/oWt.	35.47	11.71	5.92	0.003	47.66	-
	)	Moles	5.15	1.00	2.86	-	0.98	-

Table 10

Analysis of Divalent Forms of Chabazite

Exchanged

Forms		<u>SiO₂</u>	<u>Al₂O₃</u>	<u>H₂O</u>	<u>Na₂O</u>	<u>MO</u>	<u>CaO</u>
Ca	(%/oWt.	50.64	17.35	22.15	0.36	-	8.95
	Moles	4.99	1.00	7.23	0.03	-	0.94
Sr	(%/oWt.	48.50	16.46	19.68	0.20	15.36	-
	Moles	5.01	1.00	6.77	0.02	0.92	-
Ba	(%/oWt.	46.83	15.48	15.25	0.22	24.14	-
	Moles	5.14	1.00	5.58	0.02	1.03	-
Pb	(%/oWt.	40.79	14.07	15.82	-	29.99	-
	Moles	4.93	1.00	6.37	-	0.97	-

The analysis of Cs-Chabazite does show that complete exchange is not possible, thus confirming an earlier result of Barrer (46).

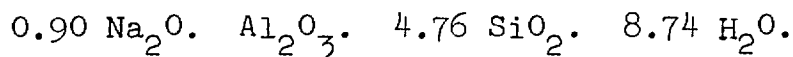
6.2.2. Analyses of the Y type zeolites

Analyses were made of NaY equilibrated with water vapour over saturated ammonium chloride at room temperature. The following values of the percentage by weight of the components are the mean of three determinations

% Na ₂ O	% Al ₂ O ₃	% SiO ₂	% H ₂ O
9.33	17.02	47.65	26.24

The figure derived for the sodium oxide content is

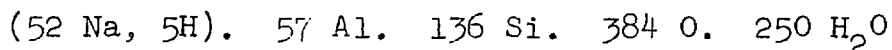
that obtained by the radiochemical technique outlined in section 4.2. The above figures lead to the oxide formula for NaY of



(exchange capacity 3.01 meq/gm)

For electroneutrality within the exchanger the ratio cation/aluminium should be unity. However, in the sample of NaY used in this work this ratio is less than one. In order to preserve electroneutrality within the exchanger, the appropriate quantity of hydronium ions H_3O^+ is believed to be present in NaY, although infra-red spectroscopy has not revealed the existence of this ion in similar cation deficient zeolites (112).

The cubic unit cell parameter, $a = 24.67 \text{ \AA}$, was determined from X-ray powder photographs. Thus the unit cell composition of NaY was represented by



Several ion exchanged forms of NaY have been prepared by the methods outlined in section 4.1. The analytical results are shown in Tables 11 and 12, as percentage composition by weight and as moles on the basis of $\text{Al}_2\text{O}_3 = 1.00$.

The water contents of the alkali metal forms decreased with increasing crystallographic radius. The

Table 11

Analysis of Monovalent Forms of NaY

Exchanged

Forms		<u>SiO₂</u>	<u>Al₂O₃</u>	<u>H₂O</u>	<u>Na₂O</u>	<u>M₂O</u>
Li	(°/oWt.	49.06	17.22	27.80	0.003	4.90
	Moles	4.84	1.00	9.15	0.026	0.97
K	(°/oWt.	45.52	16.36	22.63	0.05	14.95
	Moles	4.73	1.00	7.83	0.003	0.99
Rb	(°/oWt.	43.79	15.49	19.06	1.61	19.85
	Moles	4.81	1.00	6.97	0.17	0.70
Cs	(°/oWt.	40.48	14.37	16.24	2.00	27.95
	Moles	4.79	1.00	6.40	0.23	0.70
Ag	(°/oWt.	37.23	13.24	19.62	0.3	29.24
	Moles	4.78	1.00	8.46	0.04	0.97
Tl	(°/oWt.	34.33	12.19	16.58	2.00	34.98
	Moles	4.79	1.00	7.80	0.27	0.69

Table 12

Analysis of Divalent Forms of NaY

Exchanged

Forms		<u>SiO₂</u>	<u>Al₂O₃</u>	<u>H₂O</u>	<u>Na₂O</u>	<u>MO</u>
Ca	(°/oWt.	47.49	17.32	26.24	1.74	6.85
	Moles	4.66	1.00	8.59	0.17	0.72
Ba	(°/oWt.	43.20	15.85	23.77	2.36	16.71
	Moles	4.64	1.00	8.50	0.24	0.70

number of moles of water (on the basis of $\text{Al}_2\text{O}_3 = 1.00$) is greater for a given cationic form of the Y zeolite than for the same cationic form of chabazite. This is to be expected since the structure of Y is more open than that of chabazite.

For zeolites with the same framework structure but different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, the more hydrated zeolite is the one with the greater $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. This is to be expected since increasing the silica content decreases the number of cations per unit cell volume, and hence increases the intracrystalline volume for sorbed species. Thus comparing the analytical results of Tables 11 and 12 for the Y zeolite with the analytical results for NaX (15), there is an increase of $\sim 40\%$ in the water content of the Y zeolite (on the basis of $\text{Al}_2\text{O}_3 = 1.00$) for any given cationic form.

Complete exchange of Na^+ in NaY by other monovalent ions is possible only for Li^+ , K^+ and Ag^+ . For the Na - Rb, Na - Cs and Na - Tl exchanges the limit of exchange corresponded to approximately 70% replacement of sodium. The same limit of exchange was observed when the Na^+ ion was replaced by the divalent ions Ca^{2+} , Sr^{2+} and Ba^{2+} . Thus approximately 30% of the Na^+ ions are in sites in the crystal that are not accessible to the larger monovalent ions and to the divalent ions at 25°C .

6.3. Ion exchange equilibrium data

The ion exchange equilibrium data were used to construct exchange isotherms and to evaluate the standard free energy of exchange ΔG^0 , and the activity coefficients of the components of the mixed exchanger phases. Unless otherwise stated the standard free energy of exchange refers to the exchange reaction at 25°C. In order to apply equations 5.2.3 and 5.2.4 to the ion exchange equilibrium data, Kielland plots, i.e. plots showing the variation of $\log K_c$ with A_Z were constructed. The mean molal activity coefficients of the aqueous electrolyte solutions used to calculate K_c were derived from the tabulated data of Harned and Owen (100) and from various papers available in the literature (104).

6.3.1. Uni-univalent exchanges in chabazite

The exchange isotherms and the corresponding Kielland plots for the exchanges Na - Li, Na - K, Na - Rb, Na - Cs, Na - NH₄, Na - Ag, and Na - Tl are shown in Figs. 6 - 19 inclusive.

Na - Li exchange

The Na - Li exchange isotherm is concave to the Li_Z axis indicating that Na⁺ is the preferred ion in this exchange. Exchanges using a Li - zeolite and NaCl solution show that the reaction is reversible. The plot of

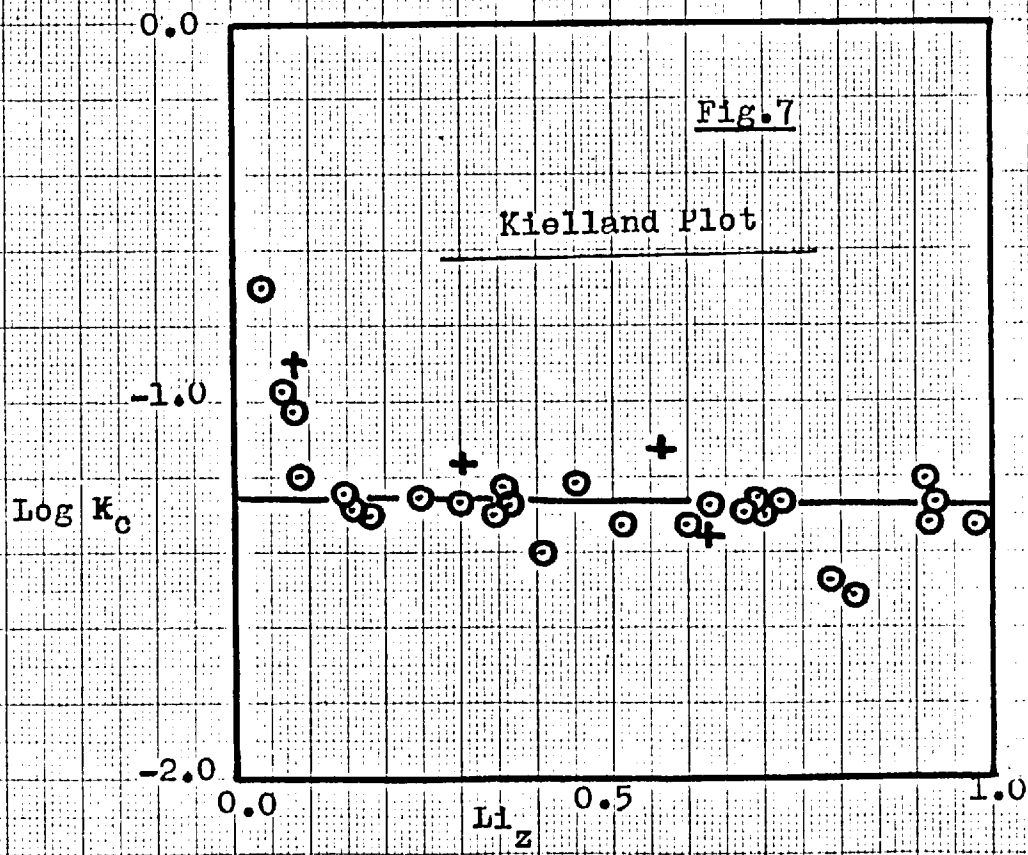
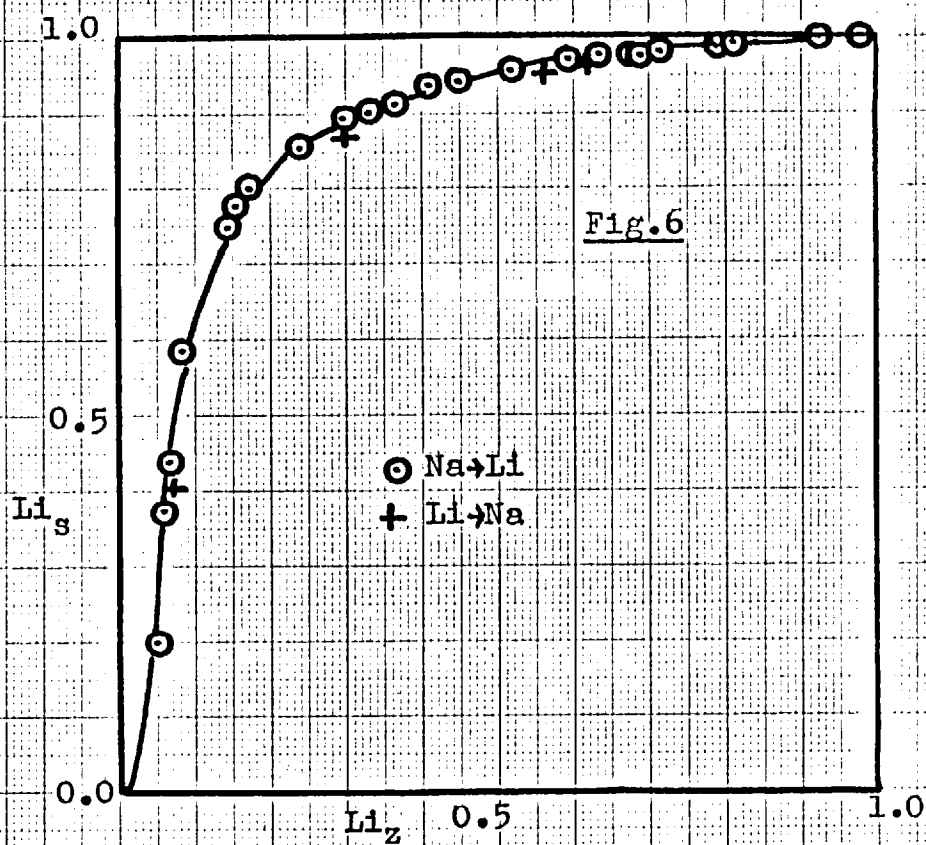
$\log K_c$ vs Li_Z is best represented by a straight line of zero slope i.e. K_c is constant for all values of Li_Z . The standard free energy of exchange, ΔG° is given by $\Delta G^\circ = -RT \ln K_a$. Thus

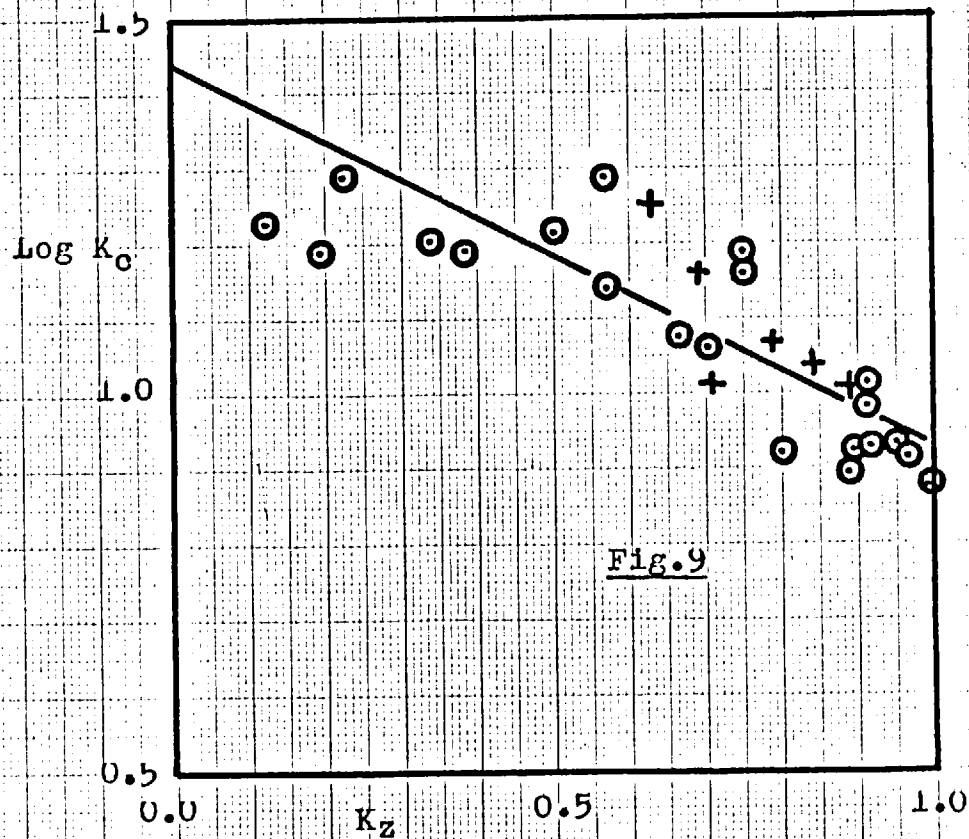
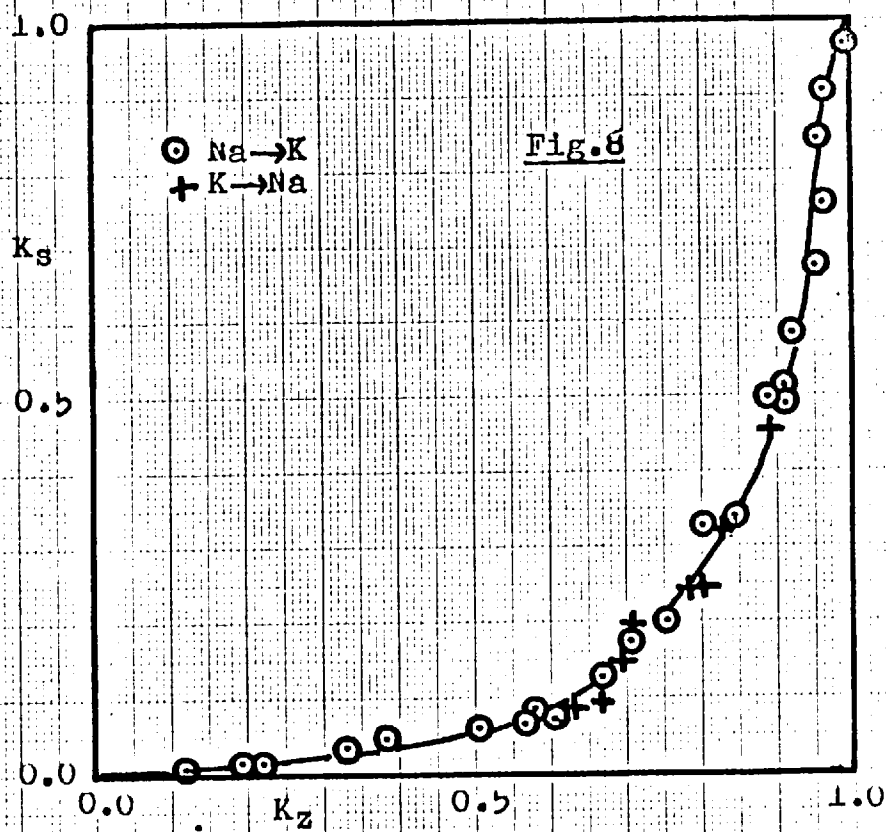
$$\log K_a = -1.26; \quad \Delta G^\circ = 1.72 \text{ kcal/gm. eq.}$$

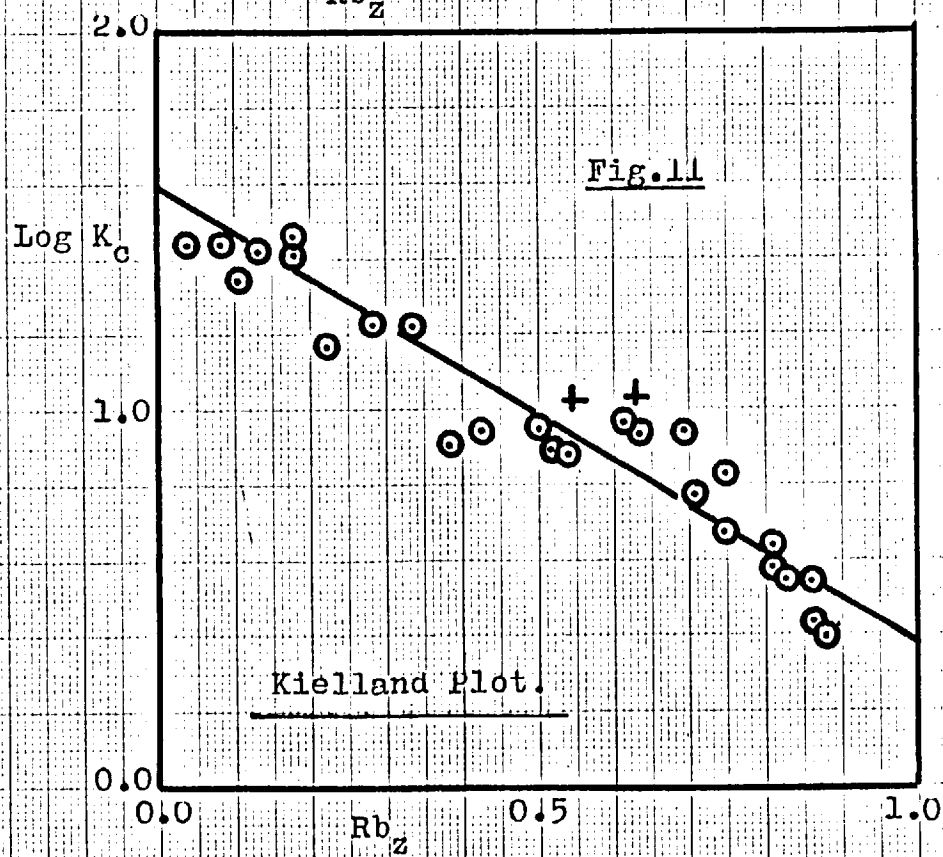
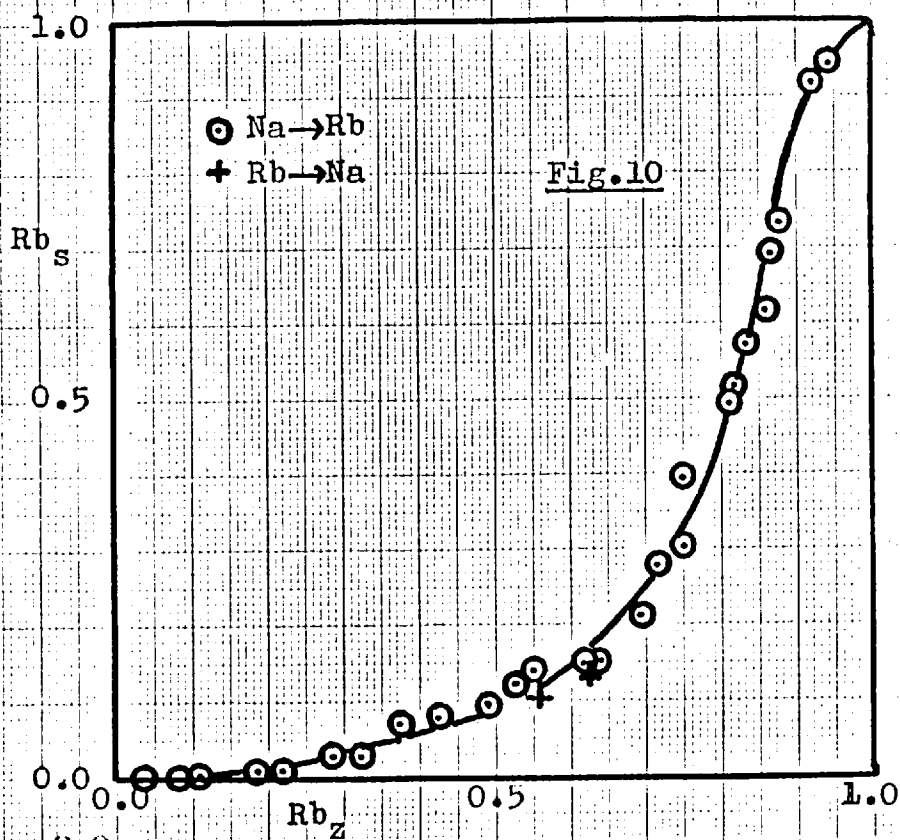
The activity coefficients of the components in the exchanger are given by Kielland's relation (equation 3.3.10). However, the zero slope of the Kielland plot indicates ideal behaviour in the solid solution, i.e. the activity coefficients of both components are unity at all cationic compositions of the exchanger.

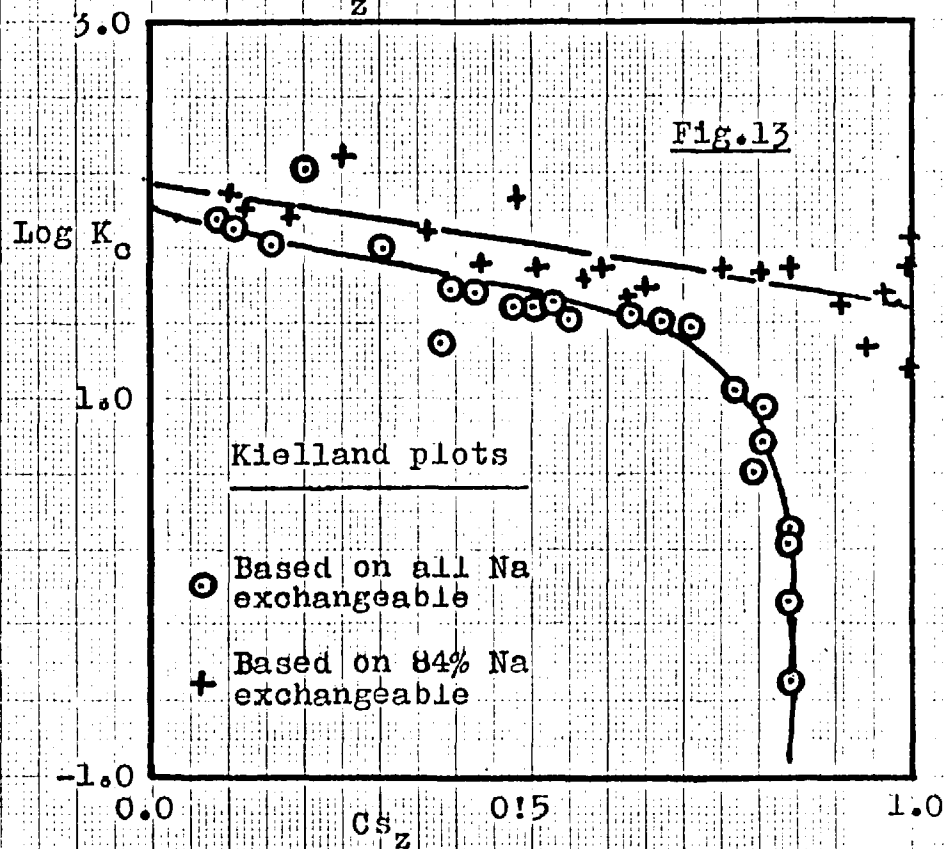
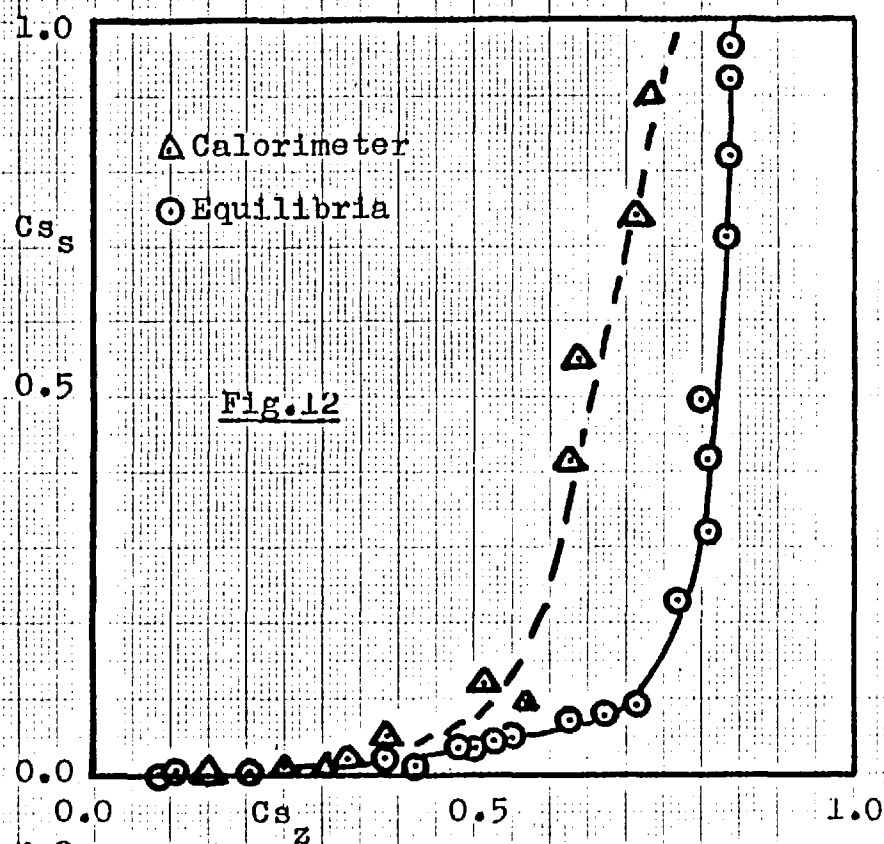
Na - K, Na - Rb, Na - NH_4 and Na - Ag exchanges

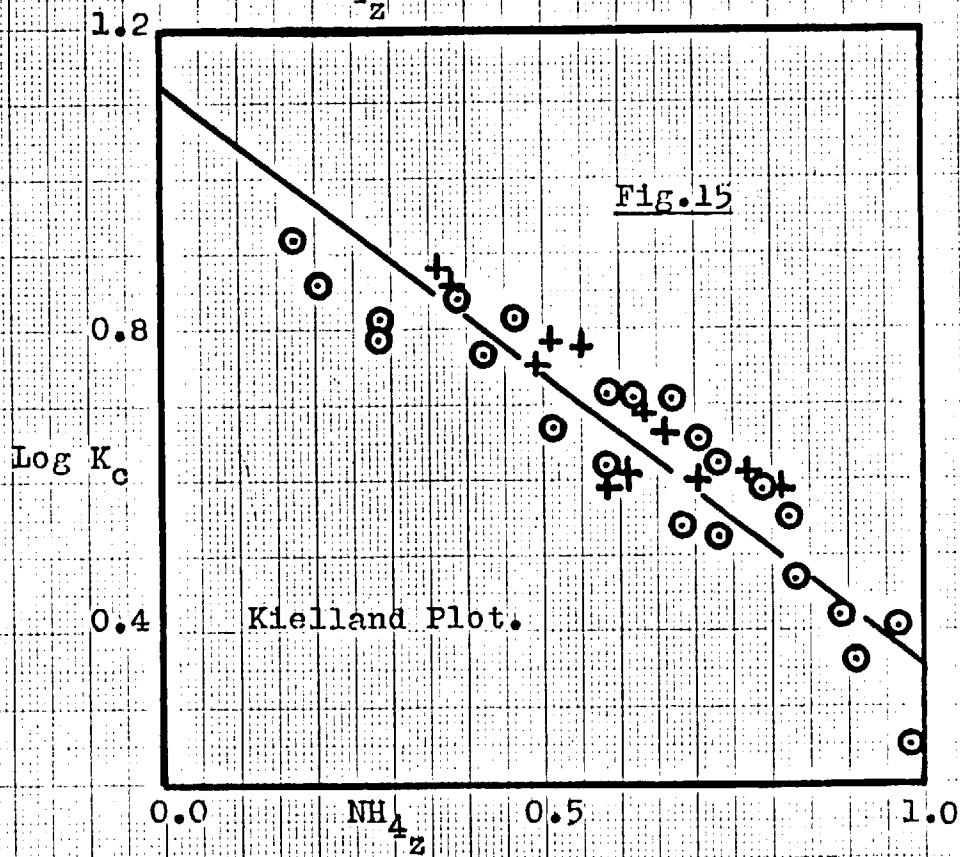
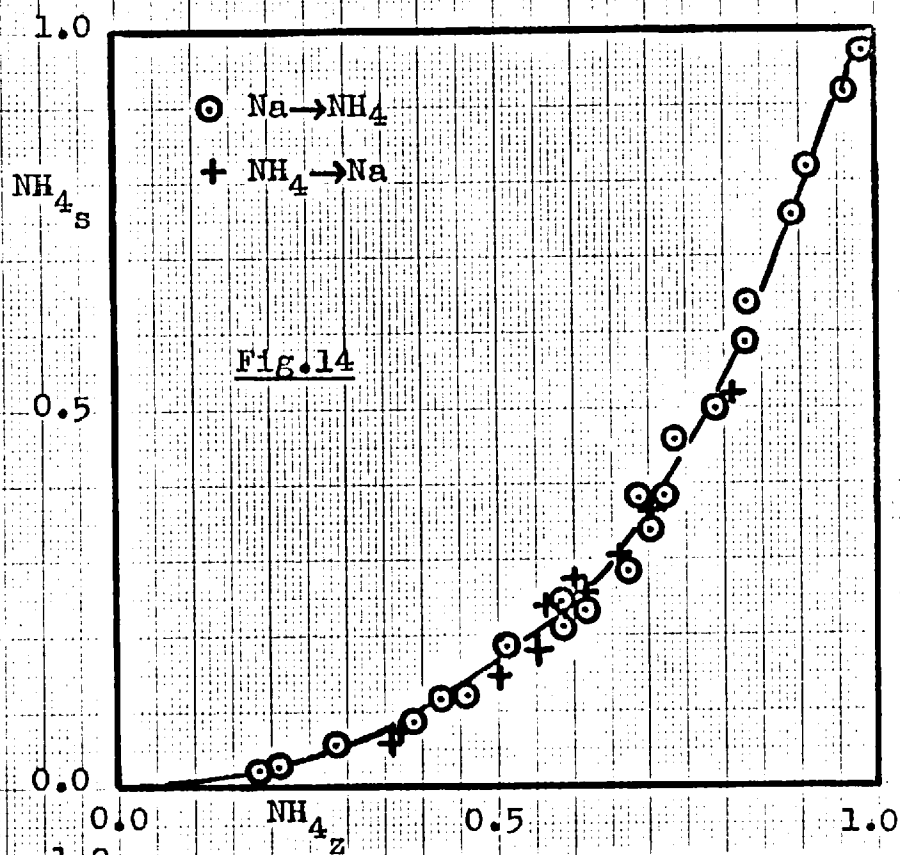
These exchanges were found to proceed to 100% replacement of the Na^+ and to be reversible. The exchange isotherms were convex to the A_Z axis (where A_Z is the cationic fraction of the in-going ion) indicating that Na^+ is the least preferred ion in all these exchanges. Plots of $\log K_c$ against A_Z were best represented by straight lines, thus enabling the thermodynamic equilibrium constants to be evaluated from the value of K_c at $A_Z = 0.5$. The standard free energies of exchange were, $\Delta G^\circ_{Na-K} = -1.60 \text{ kcal/gm.eq.}$; $\Delta G^\circ_{Na-Rb} = -1.34 \text{ kcal/gm.eq.}$ $\Delta G^\circ_{Na-NH_4} = -0.99 \text{ kcal/gm.eq.}$; $\Delta G^\circ_{Na-Ag} = -1.44 \text{ kcal/gm.eq.}$

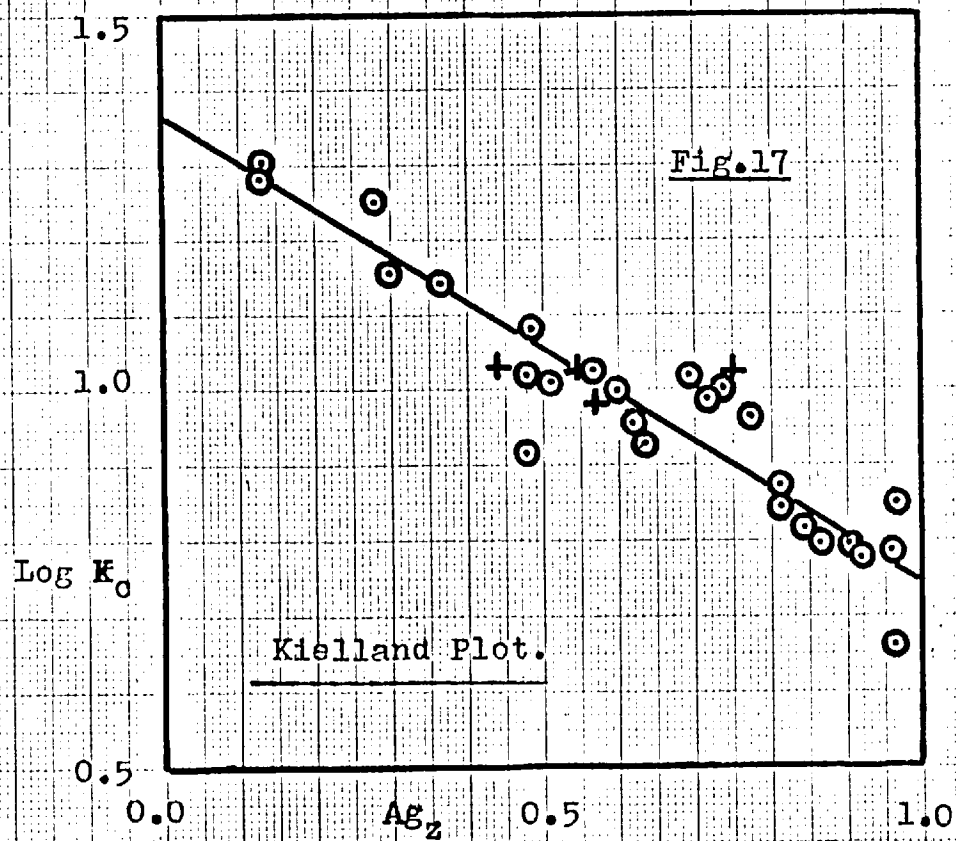
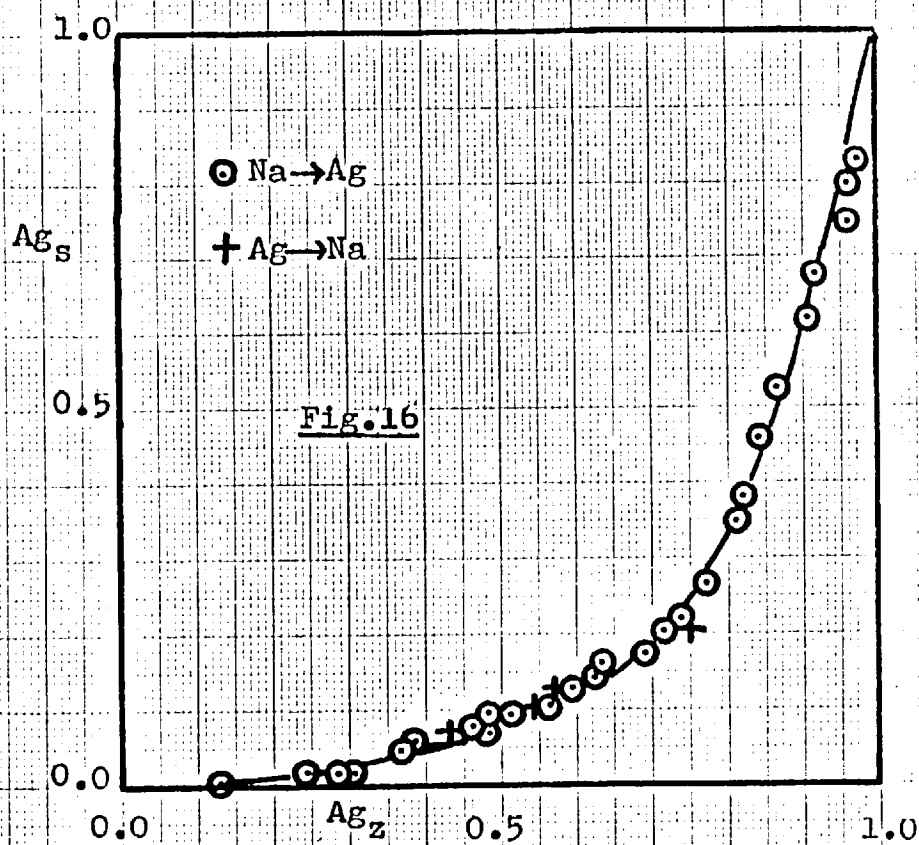


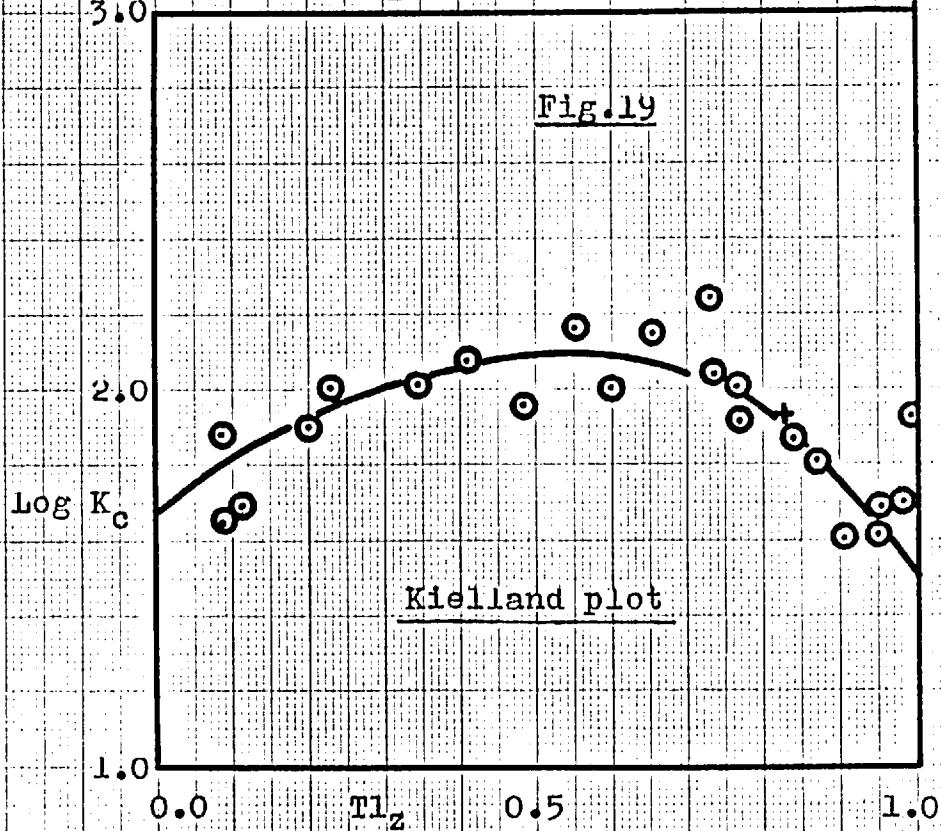
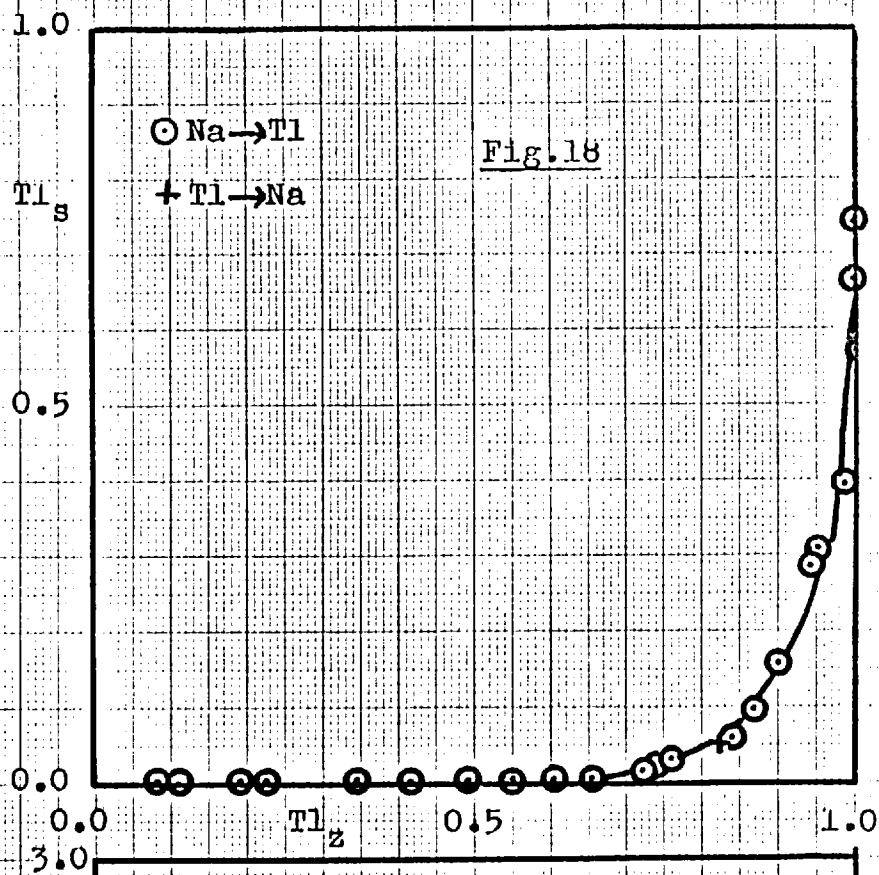












The slopes of the Kielland plots for these exchanges are not zero. Hence the activity coefficients of the components of the mixed exchangers are given by Kielland's relationships

$$\log f_A = C B_Z^2 ; \quad \log f_B = C A_Z^2$$

where $2C$ is the slope of the graph. Thus

$$\log f_{\text{NaCh}} = -0.23 K_Z^2 ; \quad \log f_{\text{KCh}} = -0.23 \text{Na}_Z^2$$

$$\log f_{\text{NaCh}} = -0.64 \text{Rb}_Z^2 ; \quad \log f_{\text{RbCh}} = -0.64 \text{Na}_Z^2$$

$$\log f_{\text{NH}_4\text{Ch}} = -0.38 \text{Na}_Z^2 ; \quad \log f_{\text{NaCh}} = -0.38 (\text{NH}_4)_Z^2$$

$$\log f_{\text{AgCh}} = -0.29 \text{Na}_Z^2 ; \quad \log f_{\text{NaCh}} = -0.29 \text{Ag}_Z^2$$

Values of the selectivity coefficient K_c were greater than 1 for all values of A_Z . Thus no selectivity reversals occurred and Na^+ was the least preferred ion by all the sites in chabazite.

Na - Cs exchange

Complete exchange of Na^+ for Cs^+ in chabazite at 25°C was not obtained, the limit being 84% replacement. The isotherms and corresponding Kielland plots are shown in Figs. 12 and 13 respectively. On the basis of all the Na^+ being potentially exchangeable the Kielland plot is not linear and approaches minus infinity as $\text{Cs}_Z \rightarrow 0.84$. However, the Kielland plot, calculated on the basis of

only 84% of the Na^+ being exchangeable, is linear of slope -0.58. The thermodynamic equilibrium constant is given by the value of K_c when $\text{Cs}_Z = 0.5$ (based on the reduced exchange capacity). Thus $\log K_{0.5} = 1.8$, and the corresponding standard free energy of exchange is

$$\Delta G^\circ_{\text{Na-Cs}} = -2.50 \text{ k cal/gm. eq.}$$

The activity coefficients of the components in the mixed exchanger are given by

$$\log f_{\text{NaCh}} = -0.29 \text{ Cs}_Z^2; \quad \log f_{\text{CsCh}} = -0.29 \text{ Na}_Z^2$$

As opposed to all other uni-univalent exchanges on chabazite the Na-Cs exchange has an associated slow process since the calorimetrically determined isotherm does not agree with that determined by rotating the exchanger and solution in sealed tubes for four days.

Na - Tl exchange

Complete exchange of Na^+ for Tl^+ was observed in the Na - Tl exchange, this exchange exhibiting a very high selectivity for thallium. The exchange isotherm and the corresponding Kielland plot are shown in figs. 18 and 19. The variation of $\log K_c$ against Tl_Z is non-linear the curve exhibiting a maximum at $\text{Tl}_Z = 0.55$. The thermodynamic equilibrium constant is therefore calculated from equation 5.1.4 i.e.

$$\ln K_a = (Z_B - Z_A) + \int_0^1 \ln K_c \, dA_Z \quad 5.1.4$$

which reduces for a uni-univalent exchange to

$$\ln K_a = \int_0^1 \ln K_c d A_Z \quad 6.3.1$$

The integral in this equation represents the area under the curve of the Kielland plot and can be evaluated by graphical integration. A value of 96.5 is thus obtained for K_a , from which a standard free energy of exchange of -2.62 kcals/gm. eq. is obtained.

The activity coefficients of the components of the mixed exchanger are calculated from the Kielland plot using equations 5.2.3 and 5.2.4. The variation of the activity coefficients with cationic composition of the exchanger is shown in Fig. 34. The maximum and minimum of f_{NaCh} and f_{TlCh} respectively occur at the same value of Tl_Z at which the Kielland plot has a maximum i.e. at $Tl_Z \approx 0.55$.

6.3.2. Uni-univalent ion exchange in NaY

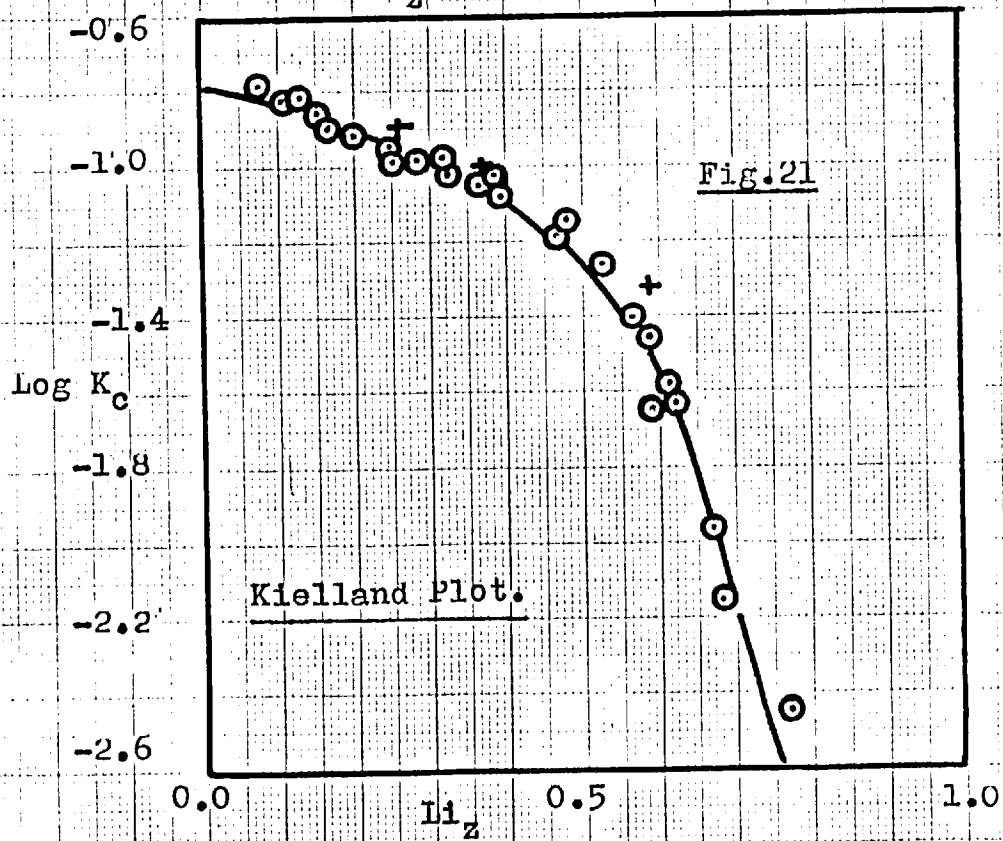
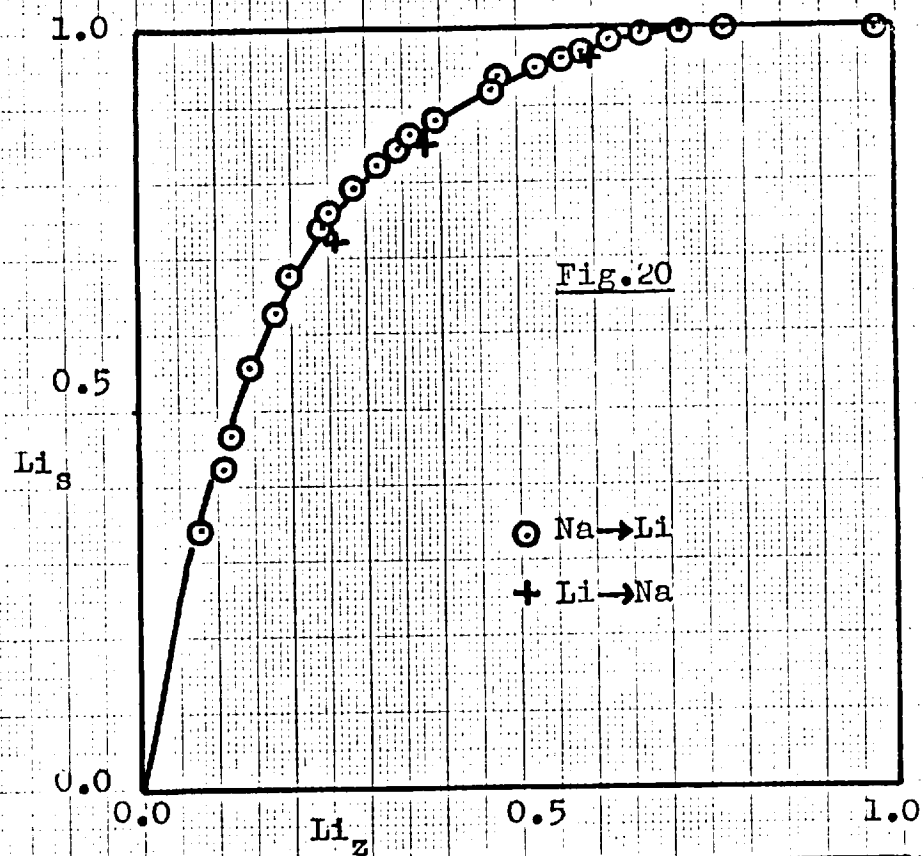
The exchange isotherms and the corresponding Kielland plots for the Na-Li, Na-K, Na-Rb, Na-Cs, Na-Ag and Na-Tl exchanges on NaY are shown in Figs. 20 - 31 inclusive. Chemical analysis has revealed that only the smaller univalent ions Li^+ , K^+ , and Ag^+ can completely replace the Na^+ in this zeolite.

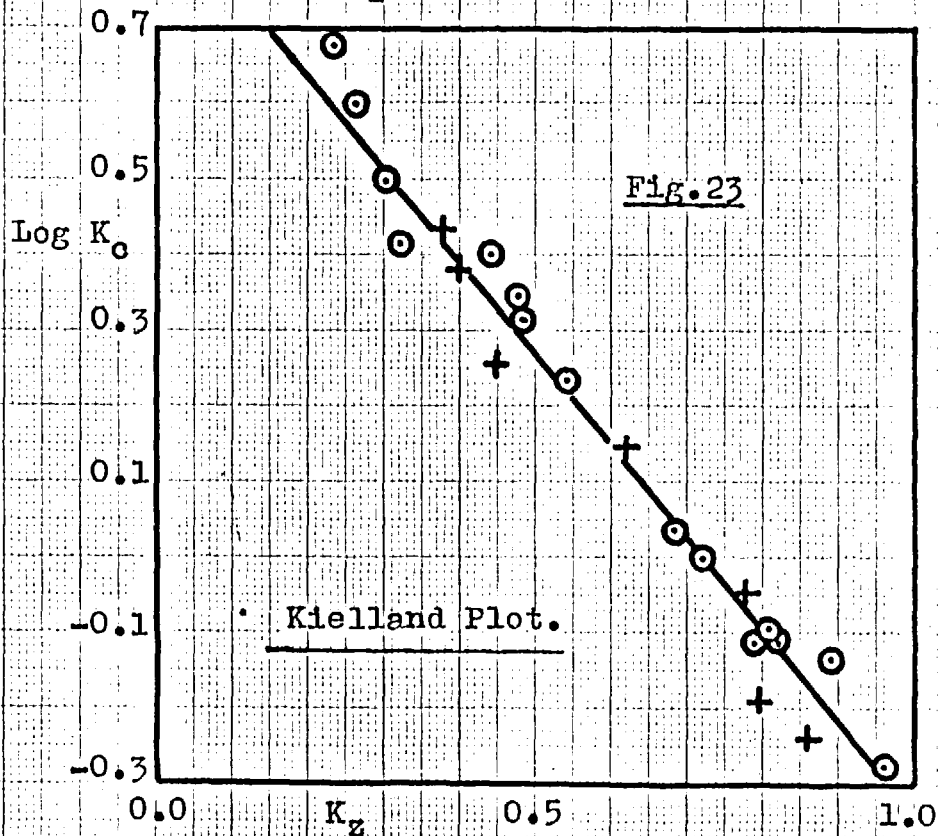
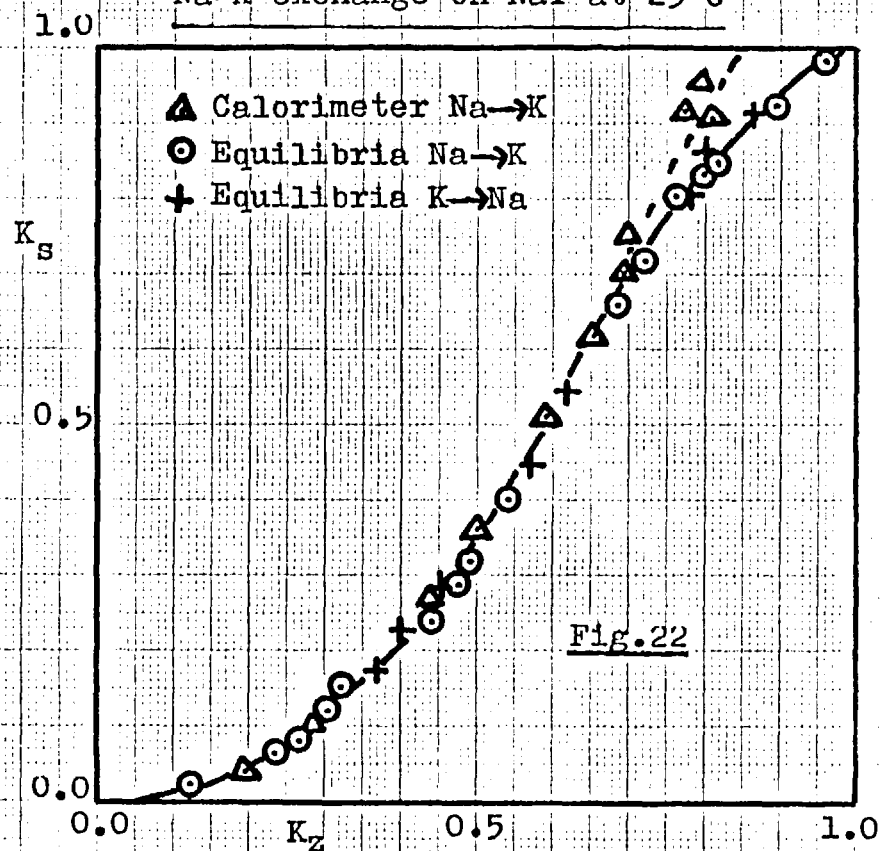
Na - Li exchange

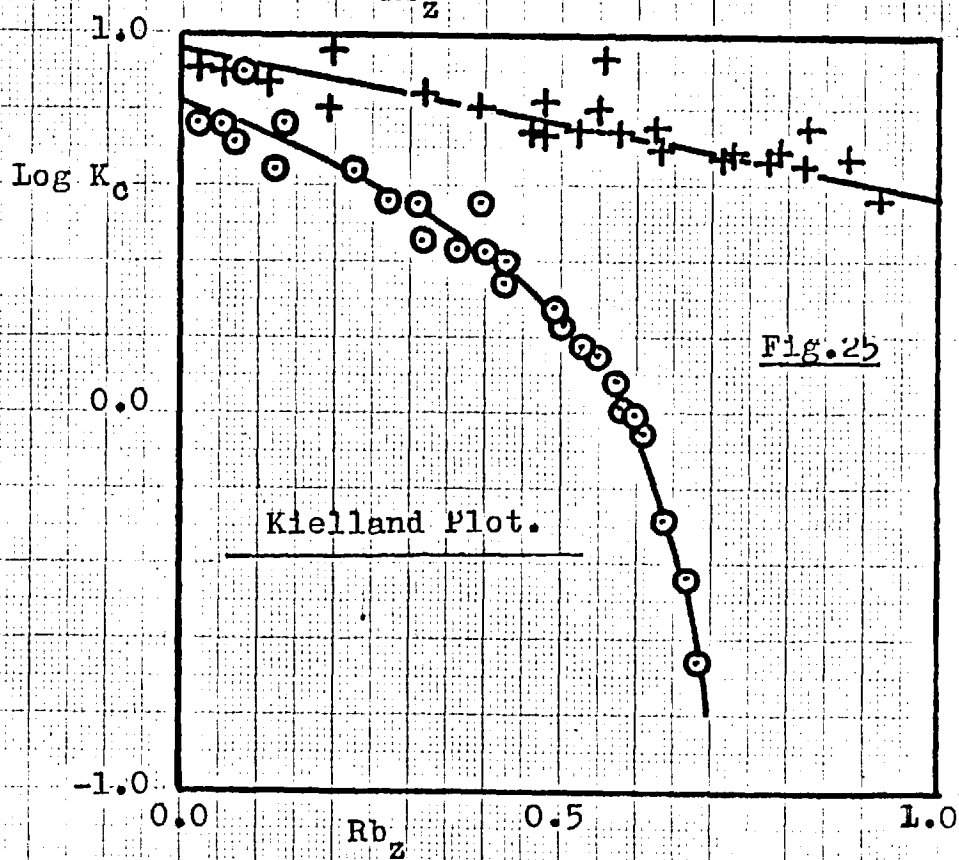
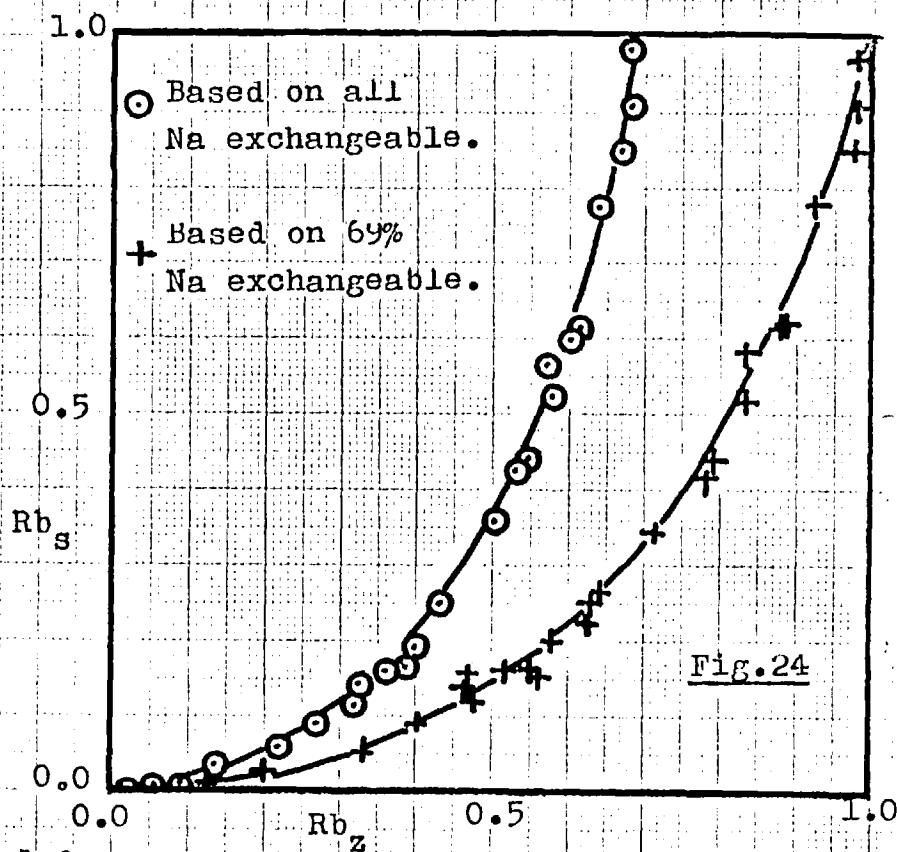
The Na - Li exchange isotherm is found to be reversible and concave to the Li_Z axis indicating that Na^+ is the preferred ion in this exchange (Fig. 20). The variation of $\log K_c$ with Li_Z is non-linear and continuously decreases with increasing Li_Z . Thus the thermodynamic equilibrium constant K_a must be obtained from the Kielland plot by graphical integration and equation 6.3.1. However, the integration requires the extrapolation of the Kielland plot from $Li_Z = 0.77$ to $Li_Z = 1.0$. Consequently the value of K_a depends on the accuracy of the extrapolation. The value of the standard free energy of exchange thus calculated is $\Delta G^\circ = 2.86 \pm 0.11$ kcal/gm. eq. The activity coefficients of the components in the mixed exchanger are determined from the Kielland plot using equations 5.2.3 and 5.2.4. The variation of these functions with cationic composition of the exchanger is shown in Fig. 35.

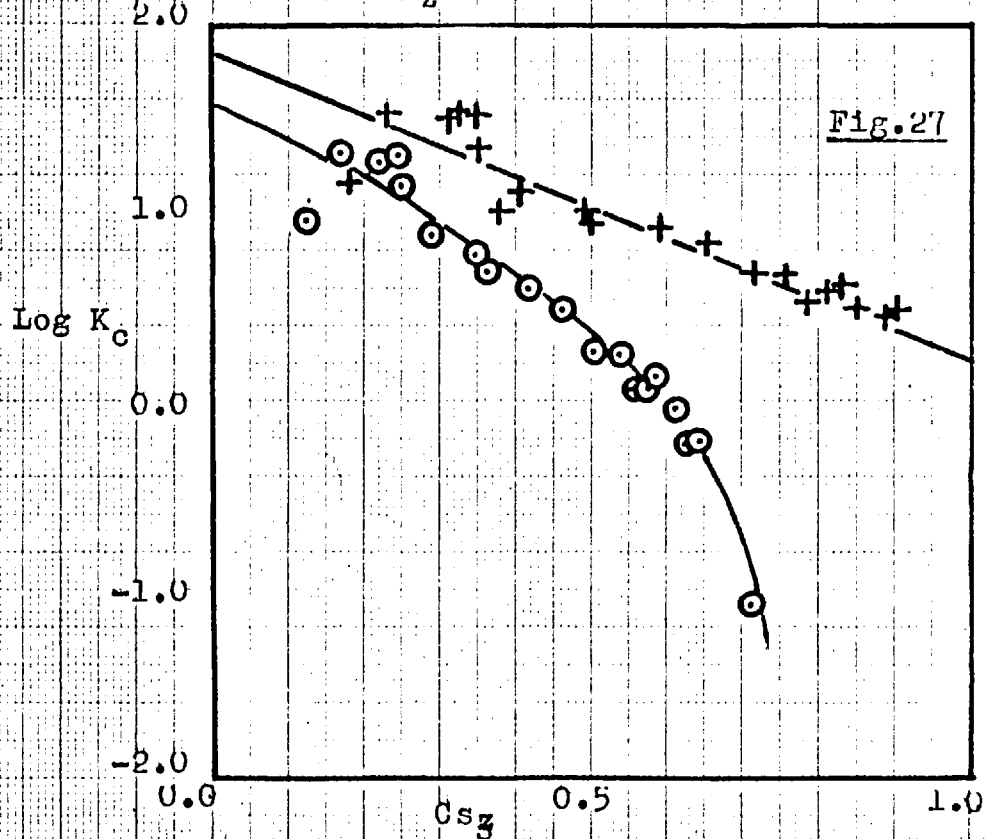
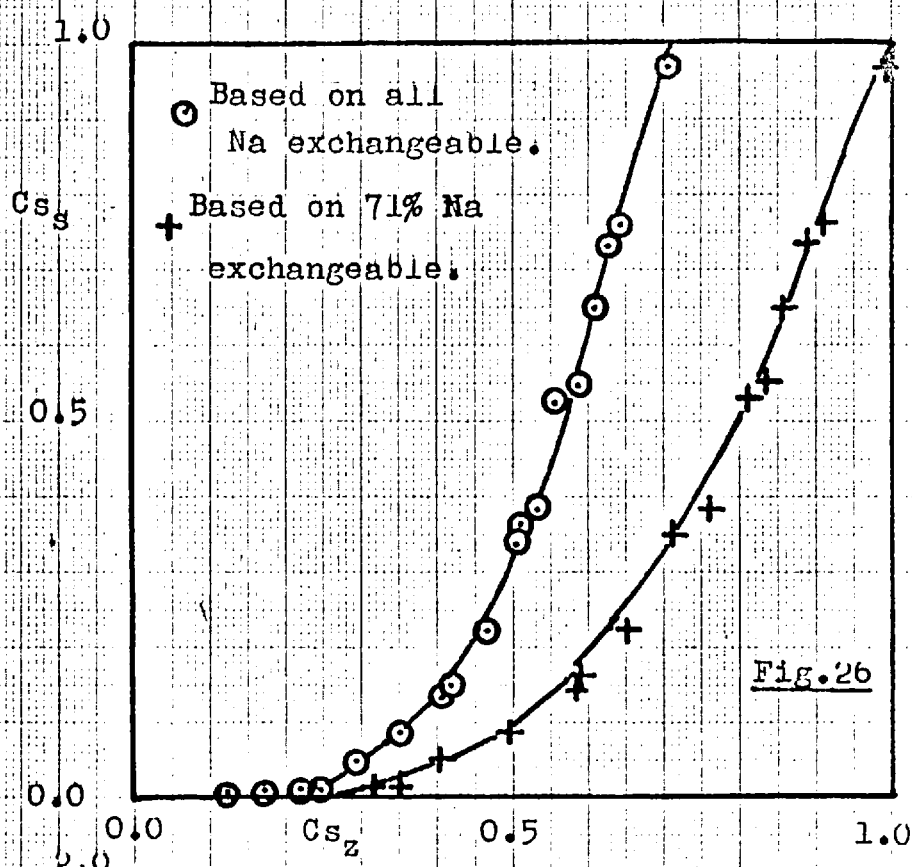
Na - K and Na - Ag exchanges

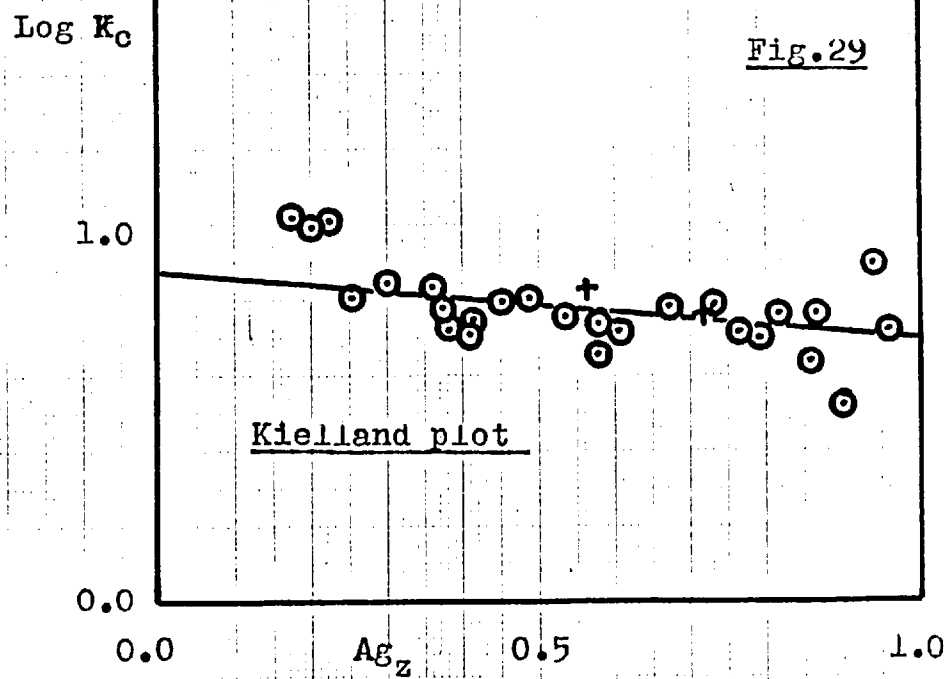
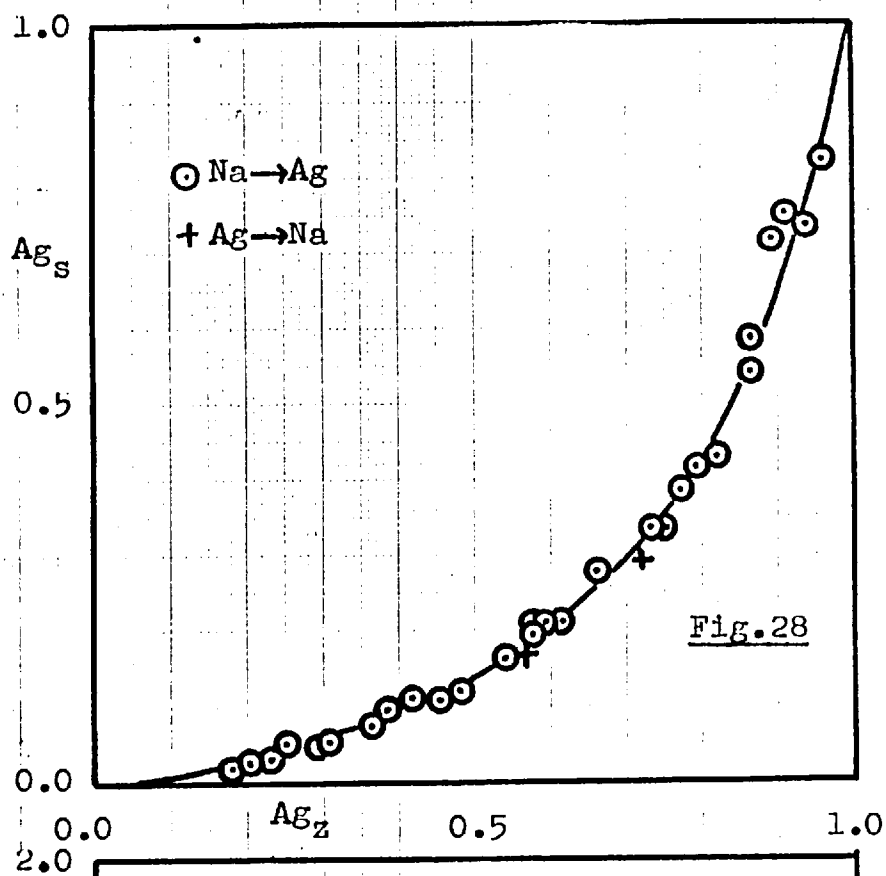
These exchanges were also found to proceed to 100% exchange and to be reversible. The exchange isotherms and corresponding Kielland plots are shown in Figs. 22, 23, 28 and 29. The Na - K exchange isotherm is sigmoidal with a reversal of selectivity at $K_Z = 0.70$. Initially

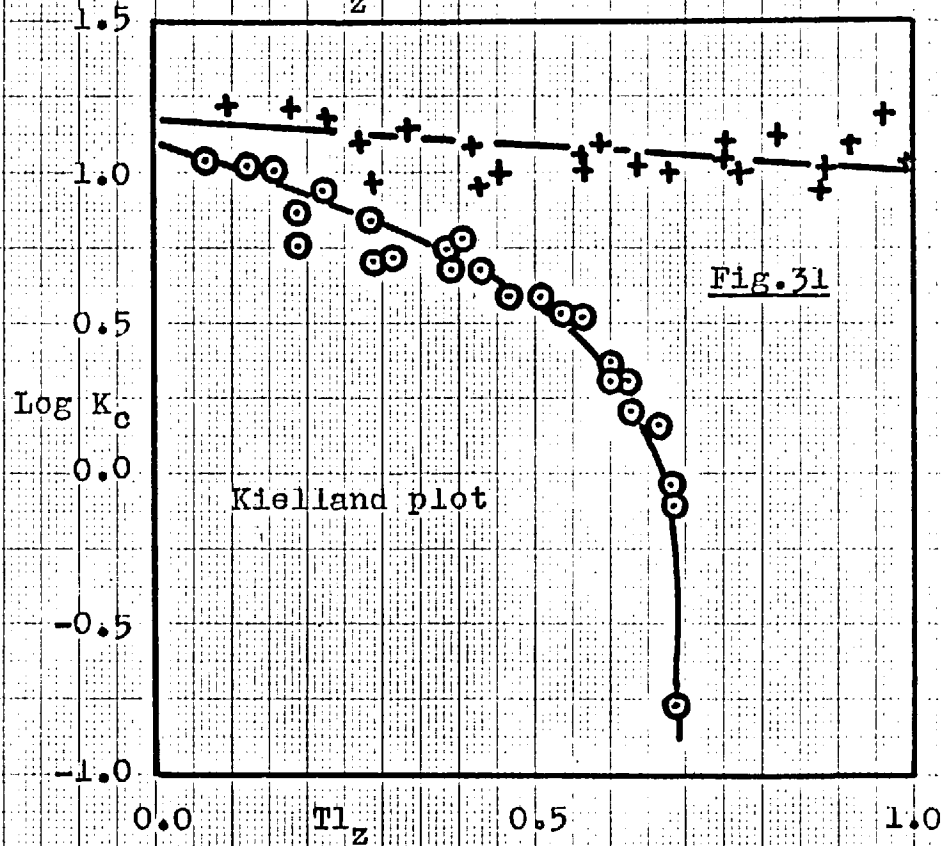
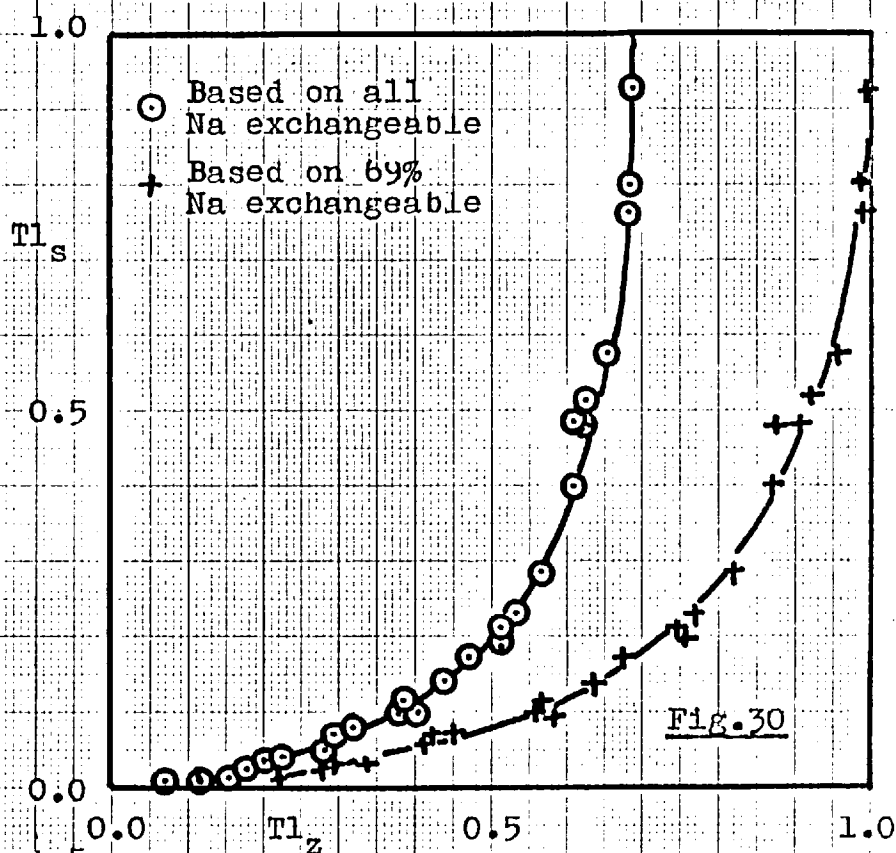




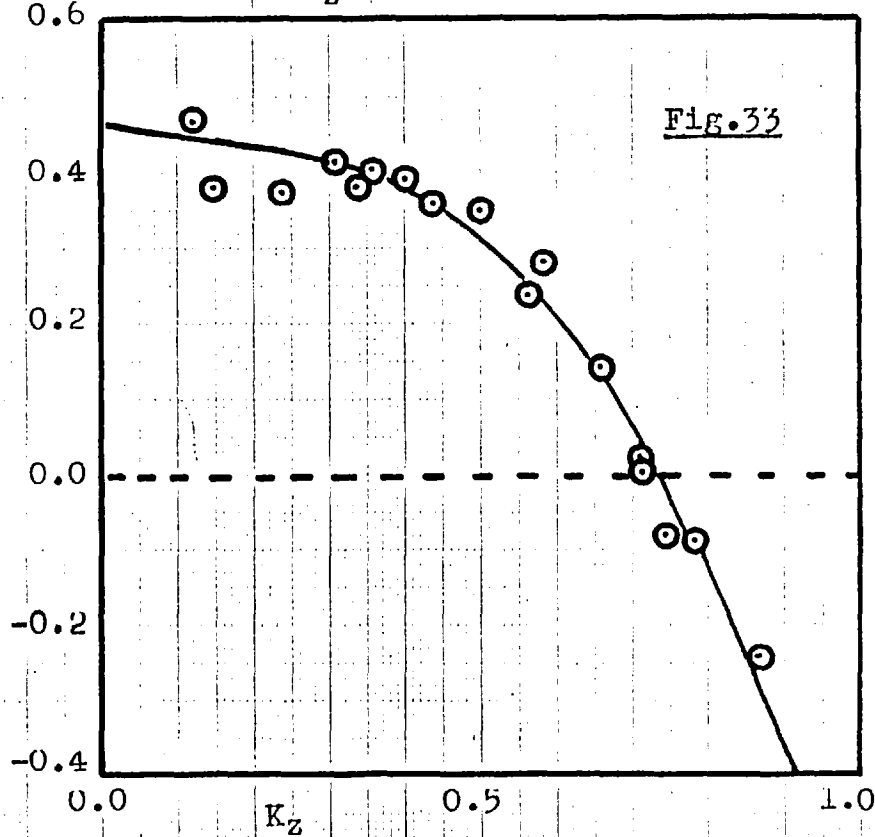
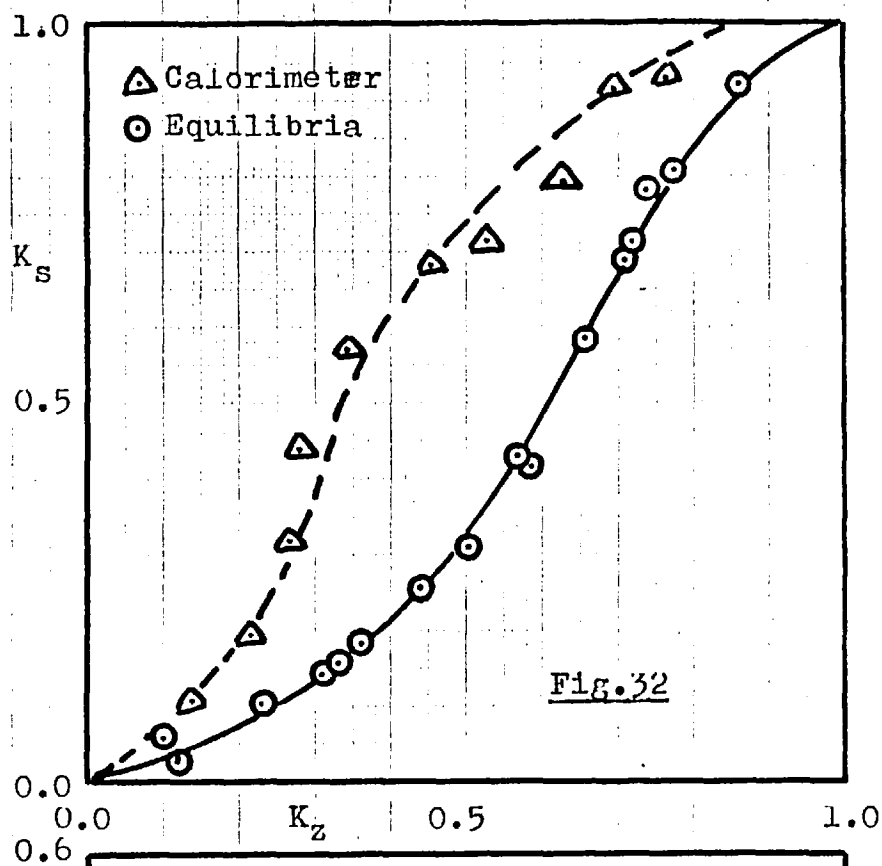








(Methanol as solvent)



the isotherm is convex to the K_Z axis indicating that K^+ is the preferred ion, but $\text{from } K_Z = 0.70 \text{ to } K_Z = 1.00$ the isotherm is concave to this axis thus showing Na^+ to be the preferred ion in this range of exchange. This sigmoidal character is not observed in the Na - Ag exchange where Ag^+ is the preferred ion at all compositions of the exchanger. The Kielland plots are linear so that the value of the thermodynamic equilibrium constant K_a is the value of K_c at $A_Z = 0.5$.

Thus $\log K_{a_{Na \rightarrow K}} = 0.27$; and $\log K_{a_{Na \rightarrow Ag}} = 0.79$.

The corresponding standard free energies of exchange are

$$\Delta G^{\circ}_{Na \rightarrow K} = -0.37 \text{ kcal/gm.eq.}; \quad \Delta G^{\circ}_{Na \rightarrow Ag} = -1.08 \text{ kcal/gm.eq.}$$

The activity coefficients of the components in the mixed exchangers are given by Kielland's relations:-

$$\log f_{NaY} = -0.65 K_Z^2; \quad \log f_{KY} = -0.65 Na_Z^2$$

$$\log f_{NaY} = -0.07_5 Ag_Z^2; \quad \log f_{AgY} = -0.07_5 Na_Z^2$$

Na - Rb, Na - Cs and Na - Tl exchanges

For the exchanges involving these ions complete replacement of the Na^+ in the zeolite was not possible under the conditions used, the maximum limits being 69%, 71% and 69% for the ions Rb^+ , Cs^+ and Tl^+ respectively.

The exchange isotherms and corresponding Kielland plots are shown in Figs. 24 - 27, 30 - 31 inclusive. These have been based on all the Na^+ ions being potentially exchangeable, and also on the reduced exchange capacities corresponding to the maximum extent of exchange. The Kielland plots on the basis of all the Na^+ ions being exchangeable are not linear but approach minus infinity as Rb_Z , Cs_Z and Tl_Z approach 0.69, 0.71 and 0.69 respectively. Recalculation of K_c on the reduced exchange capacities leads to linear Kielland plots. The thermodynamic equilibrium constants are then equal to the values of K_c at $A_Z = 0.5$, and the standard free energies of exchange are given by $\Delta G^\circ = -RT \ln K_a$. Thus

Na $\rightarrow$ Rb $\log K_a = 0.78$; $\Delta G^\circ = -1.06$ kcals/gm. eq.

Na $\rightarrow$ Cs $\log K_a = 1.04$; $\Delta G^\circ = -1.42$ kcals/gm. eq.

Na $\rightarrow$ Tl $\log K_a = 1.09$; $\Delta G^\circ = -1.49$ kcals/gm. eq.

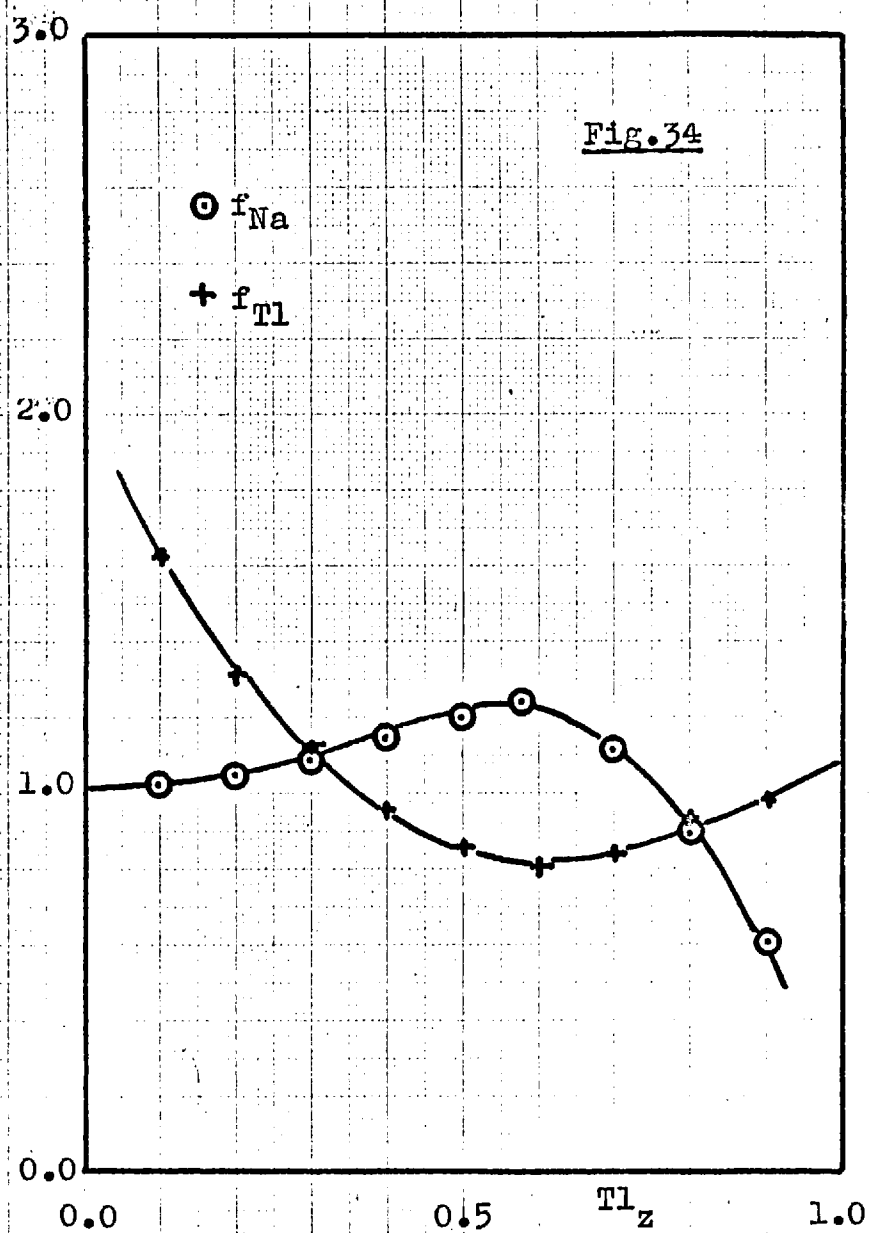
The activity coefficients of the components in the mixed exchanger are given by Kielland's relations:-

$$\log f_{\text{NaY}} = -0.14 \text{Rb}_Z^2 ; \quad \log f_{\text{RbY}} = -0.14 \text{Na}_Z^2$$

$$\log f_{\text{NaY}} = -0.79 \text{Cs}_Z^2 ; \quad \log f_{\text{CsY}} = -0.79 \text{Na}_Z^2$$

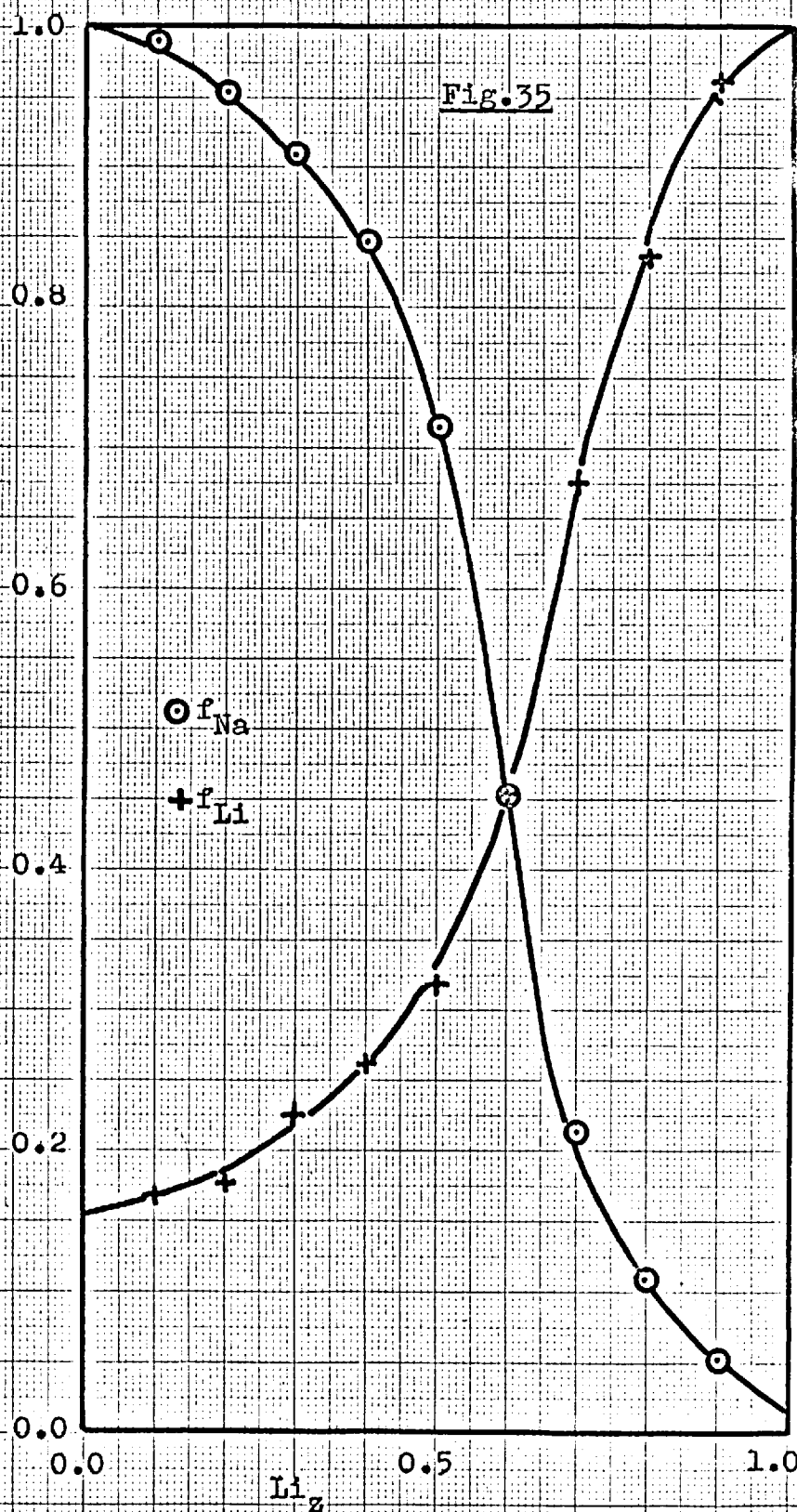
$$\log f_{\text{NaY}} = -0.06 \text{Tl}_Z^2 ; \quad \log f_{\text{TlY}} = -0.06 \text{Na}_Z^2$$

Variation of the activity coefficients of
the components of the mixed (Na-Tl) Chabazite
exchanger



Variation of the activity coefficient of
the components of the mixed (Na-Li)Y exchanger.

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Na - K exchange in NaY with methanol as solvent

The Na - K exchange in NaY has also been studied in a non-aqueous solvent, methanol. The exchange isotherm, shown in Fig. 32, is sigmoidal in shape showing a reversal of selectivity at $K_Z = 0.72$. The isotherm is very similar to that for the corresponding exchange in aqueous solution (Fig. 22). The curve of Fig. 33 does not represent a Kielland plot since no correction has been made for the mean activity coefficients of the electrolytes in solution. The ordinate in this figure is $\log\left(\frac{K_Z}{1-K_Z} \cdot \frac{m_{\text{NaI}}}{m_{\text{KI}}}\right)$, where K_Z is the equivalent cationic fraction of potassium in the exchanger. For dilute aqueous solutions the ratio of the mean activity coefficients of the electrolytes in solution, γ_s , is almost unity. Thus plots of $\log\left(\frac{K_Z}{1-K_Z} \cdot \frac{m_{\text{NaI}}}{m_{\text{KI}}}\right)$ against K_Z will almost coincide with the Kielland plots. If the same assumption occurs for non-aqueous solvents then Fig. 33 represents the Kielland plot. The free energy of exchange is determined by graphical integration and equation 5.1.4, and is -0.25 kcals/gm. eq.

6.3.3. Uni-divalent exchanges in chabazite

The isotherms for the Na - Ca, Na-Sr, Na - Ba and Na - Pb exchanges and the corresponding Kielland plots are shown in Figs. 36 - 43 inclusive. The isotherms are all similar in shape and exhibit reversal of selectivity

over the latter part of exchange. Initially, however, the divalent ions show the greater affinity for the exchanger. The Kielland plots are not linear, as in the case in several uni-univalent exchanges. Consequently the thermodynamic equilibrium constant K_a and the activity coefficients of the components of the solid solution are calculated using equations 5.1.4, 5.2.3, and 5.2.4. The values of K_a obtained by graphical integration are

$$\log K_{a_{Na \rightarrow Ca}} = -0.120 ; \quad \log K_{a_{Na \rightarrow Sr}} = -0.058.$$

$$\log K_{a_{Na \rightarrow Ba}} = 0.00 ; \quad \log K_{a_{Na \rightarrow Pb}} = 0.248.$$

The standard free energies of exchange ΔG° , are given by $\Delta G^\circ = -\frac{RT}{2} \ln K_a$. Therefore

$$\Delta G^\circ_{Na \rightarrow Ca} = 0.089 \text{ kcal/gm.eq.}; \quad \Delta G^\circ_{Na \rightarrow Sr} = 0.043 \text{ kcal/gm.eq.}$$

$$\Delta G^\circ_{Na \rightarrow Ba} = 0.00 \text{ kcal/gm.eq.}; \quad \Delta G^\circ_{Na \rightarrow Pb} = -0.165 \text{ kcal/gm.eq.}$$

The thermodynamic equilibrium constants and the standard free energies for the Na $\rightarrow$ Ca and Na $\rightarrow$ Sr exchanges refer to the reaction at 50°C, whereas for all the other exchanges these quantities refer to the reaction at 25°C.

For the exchanges involving the alkaline earth metal ions, the maxima in the Kielland plots occur at

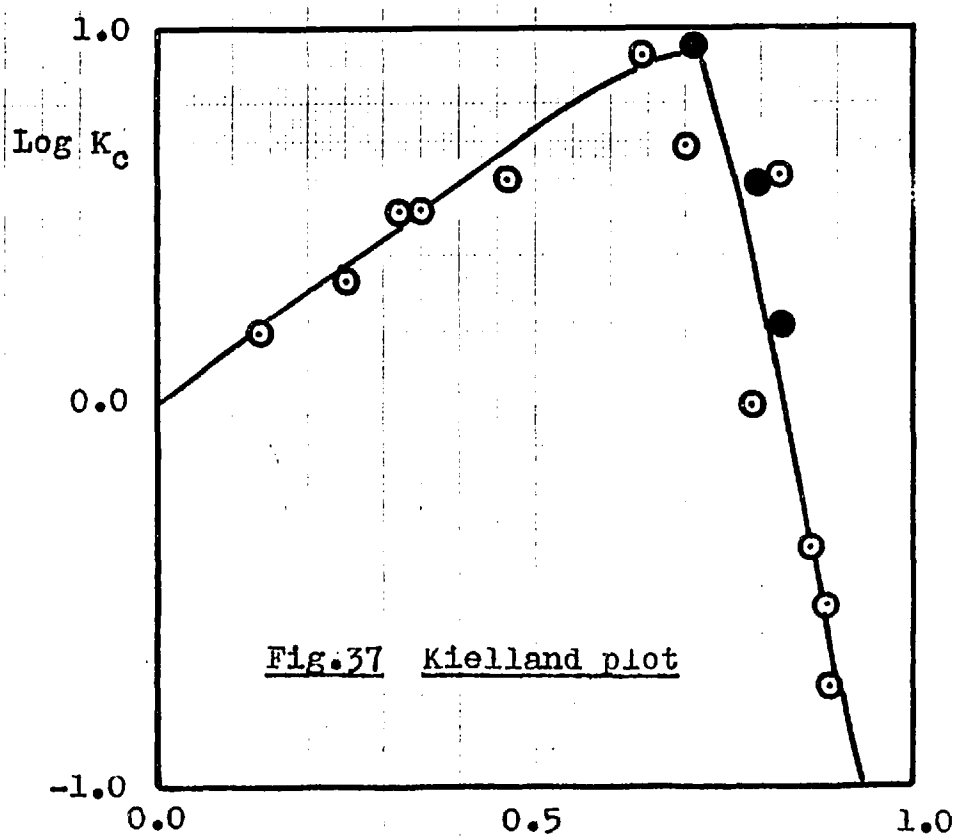
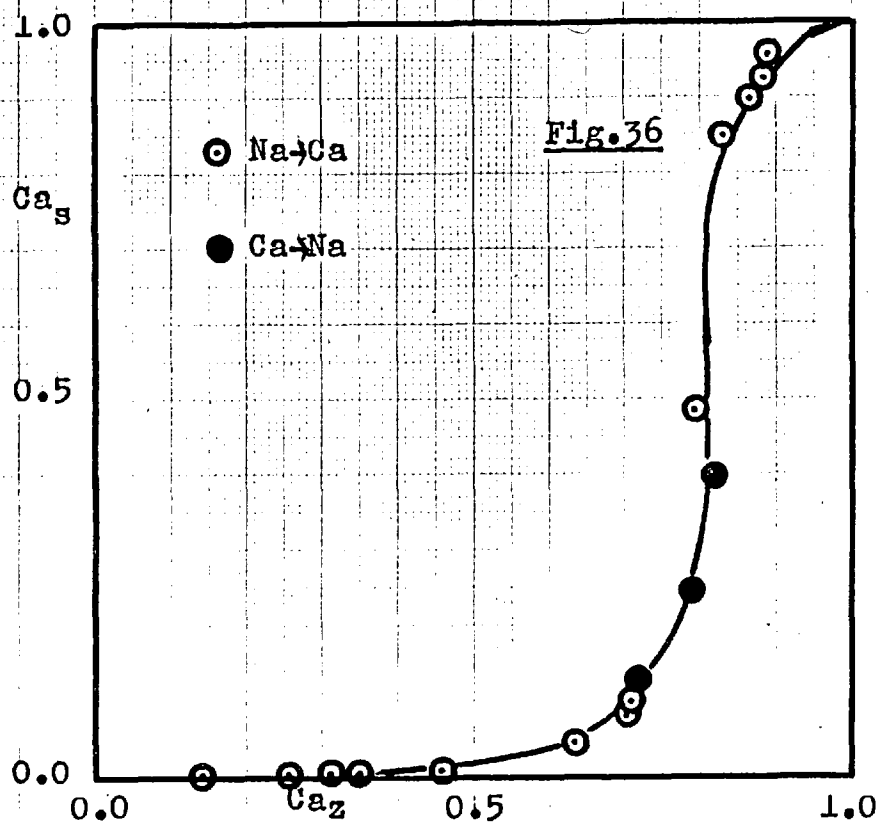
approximately the same position i.e. at an equivalent cationic fraction in the exchanges of 0.7 - 0.75.

The activity coefficients of the components in the mixed exchanger phase were calculated using equations 5.2.3 and 5.2.4 and are shown in Figs. 50 - 53 inclusive.

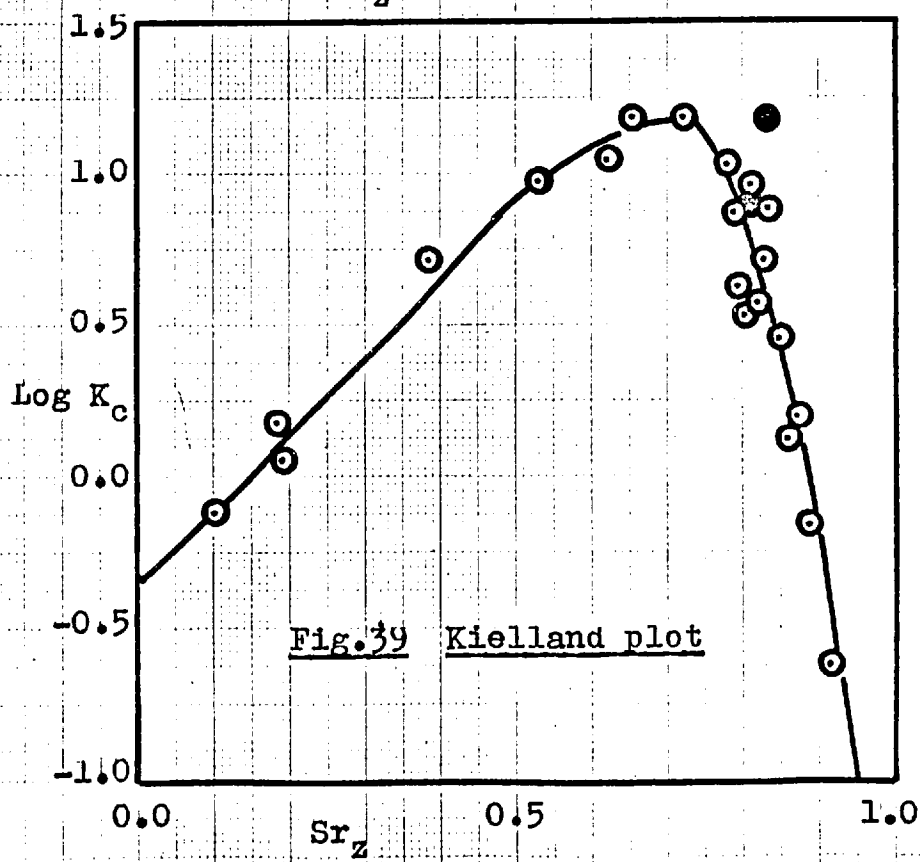
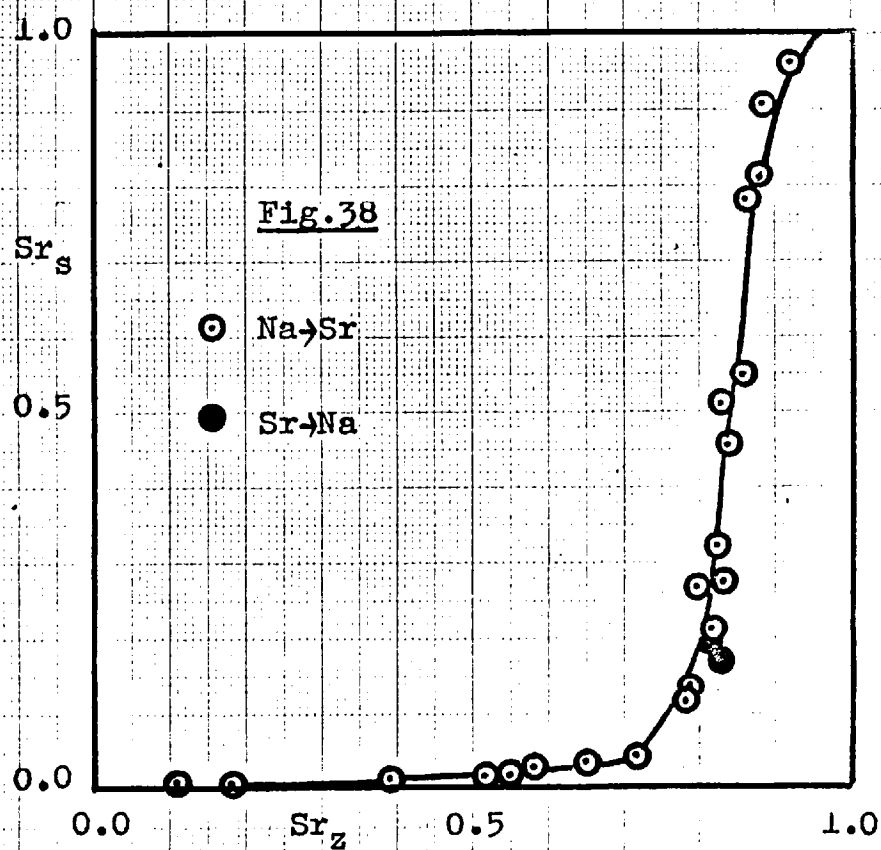
6.3.4. Uni-divalent exchanges in NaY

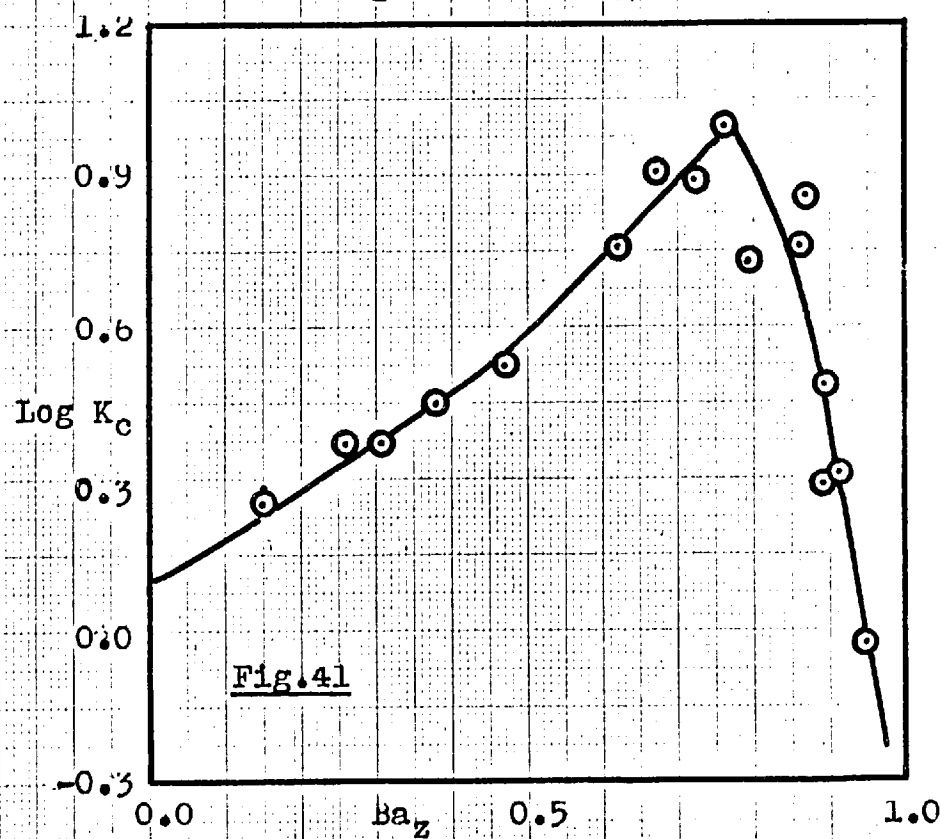
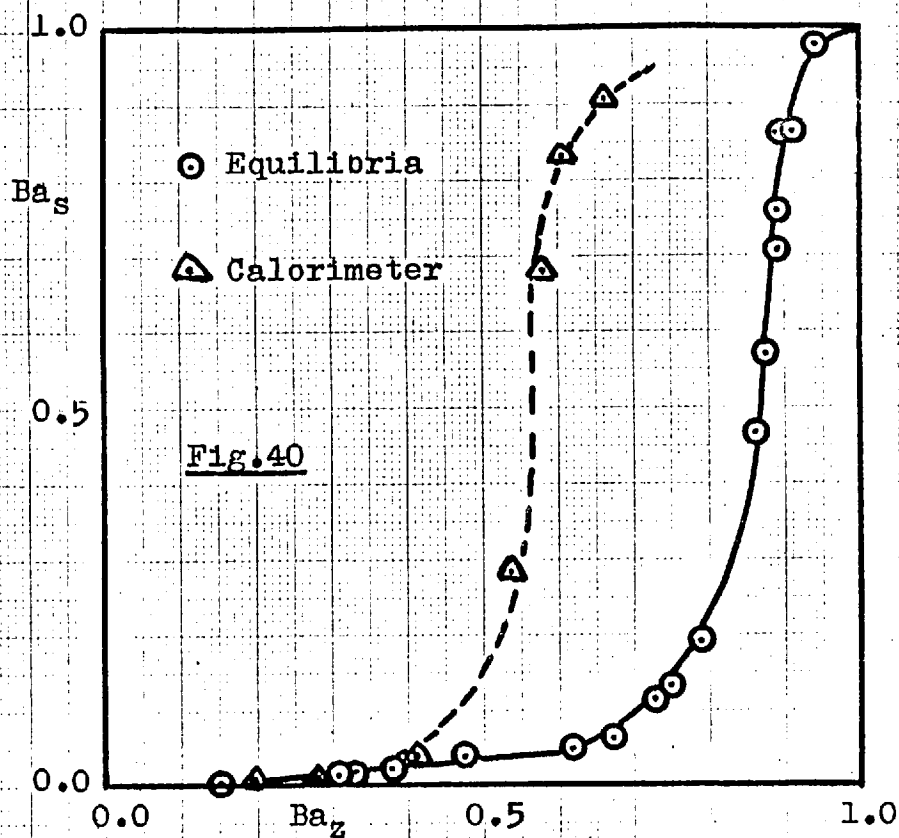
Chemical analyses of some divalent ion exchanged samples of the Y zeolite have shown that complete replacement of the Na^+ ion by the divalent ions is not possible under the conditions employed in this work. The values of A_Z used in the calculation of K_c are those based on the reduced exchange capacities of the zeolite. The exchange isotherms and the corresponding Kielland plots for the Na - Ca, Na - Sr and Na - Ba exchanges on NaY are shown in Figs. 44 - 49 inclusive. As in the case of the uni-divalent exchanges on chabazite, the plots of $\log K_c$ against A_Z (where A = Ca, Sr or Ba) are not linear, but are smooth curves exhibiting maxima. The thermodynamic equilibrium constant K_a and the activity coefficients of the components forming the solid solution are calculated using equations 5.1.4, 5.2.3, 5.2.4. The corresponding standard free energies of exchange are given by $\Delta G^\circ = - \frac{RT}{2} \ln K_a$. Thus

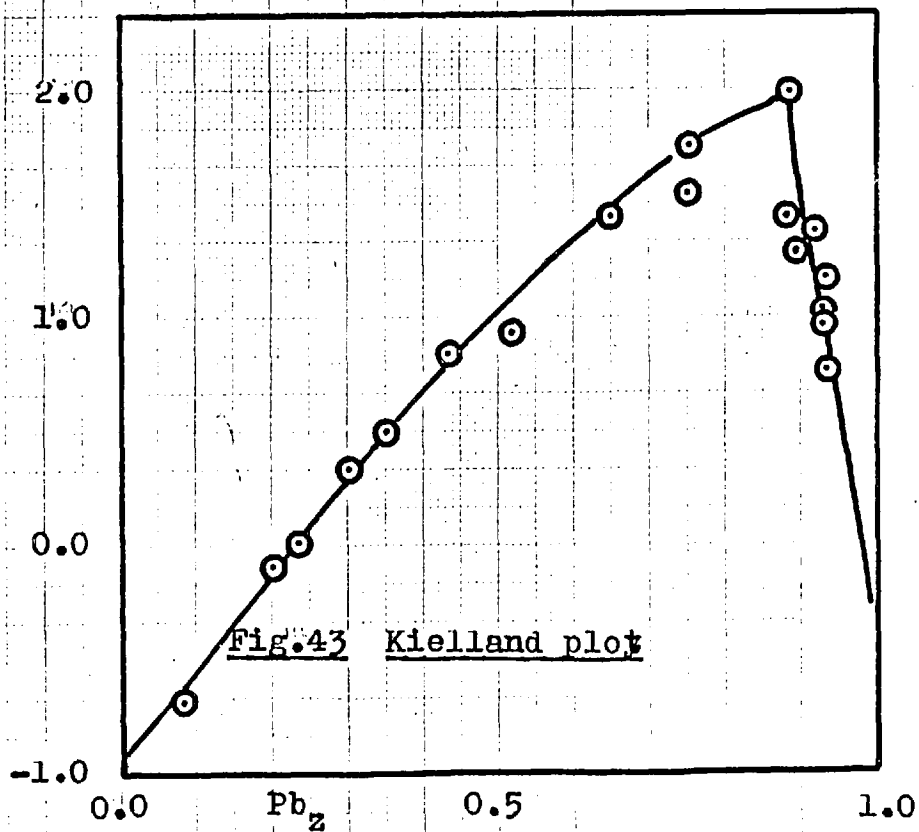
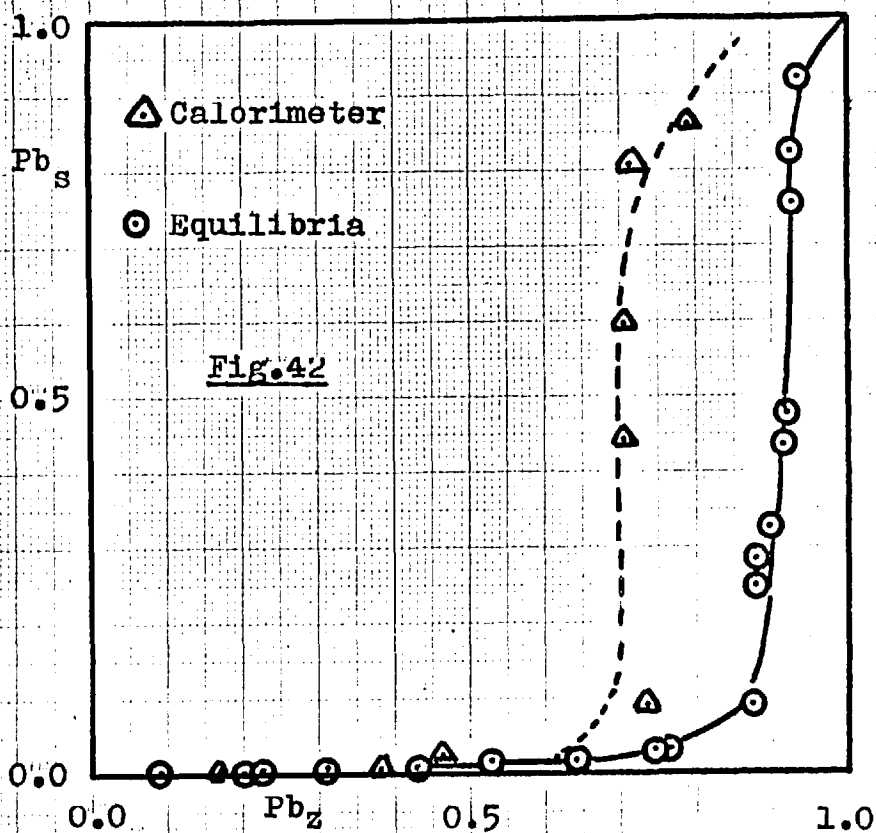
$$\log K_{a_{\text{Na} \rightarrow \text{Ca}}} = -0.25 ; \quad \Delta G^\circ_{\text{Na} \rightarrow \text{Ca}} = 0.168 \text{ kcal/gm.eq.}$$

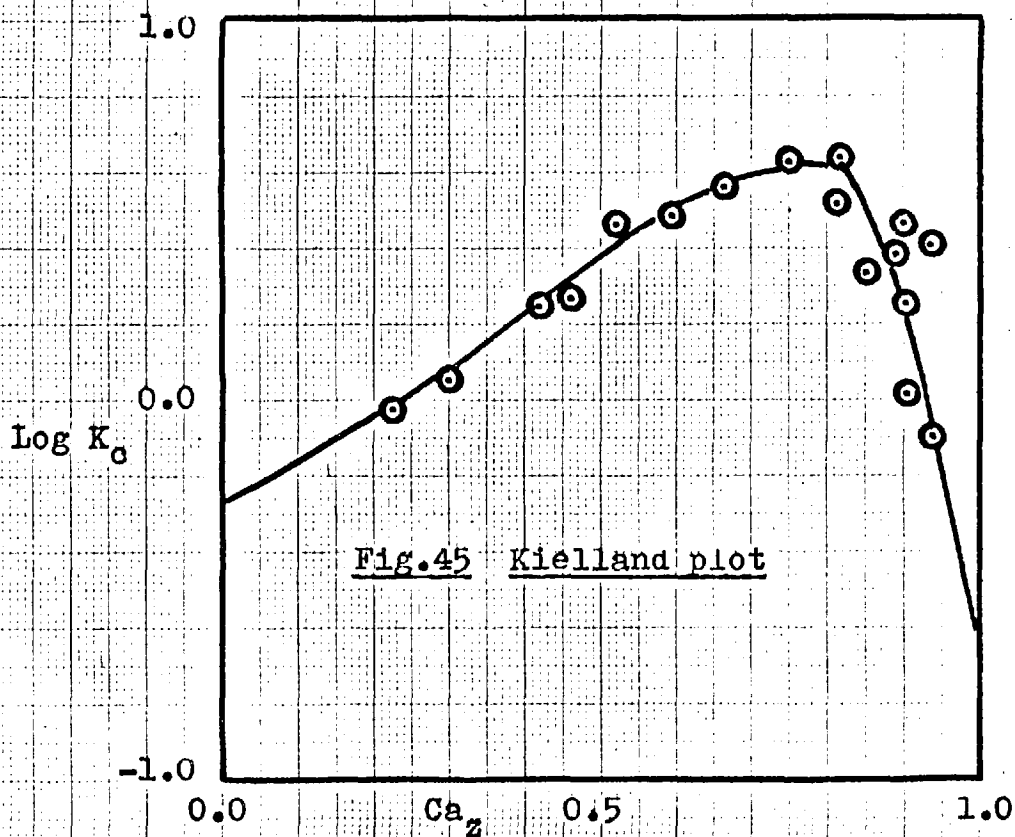
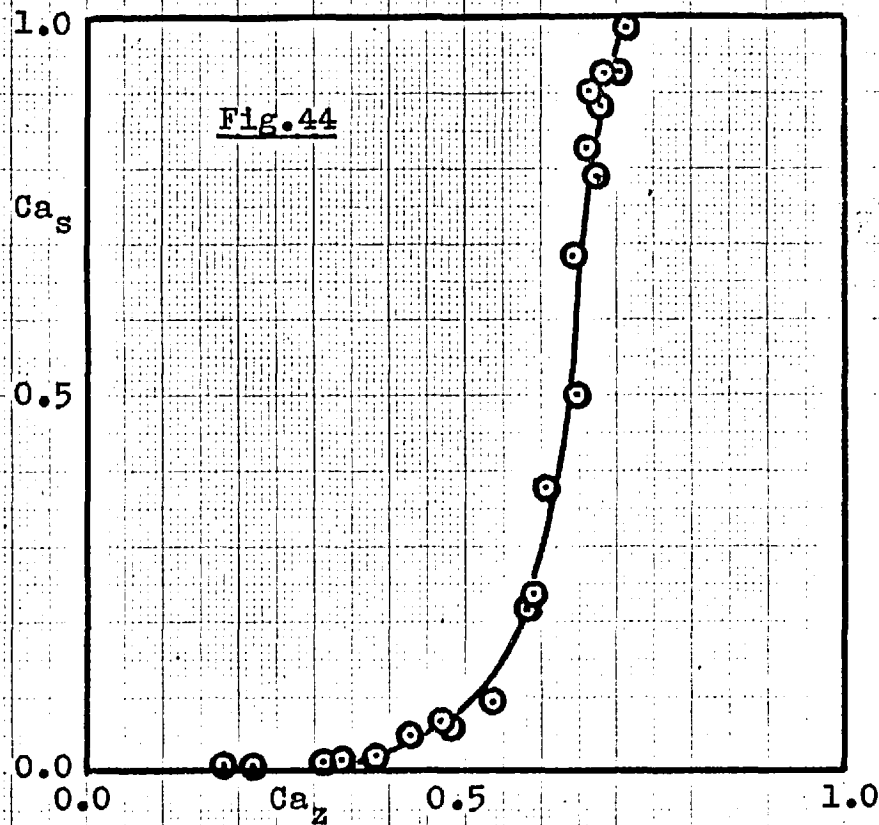


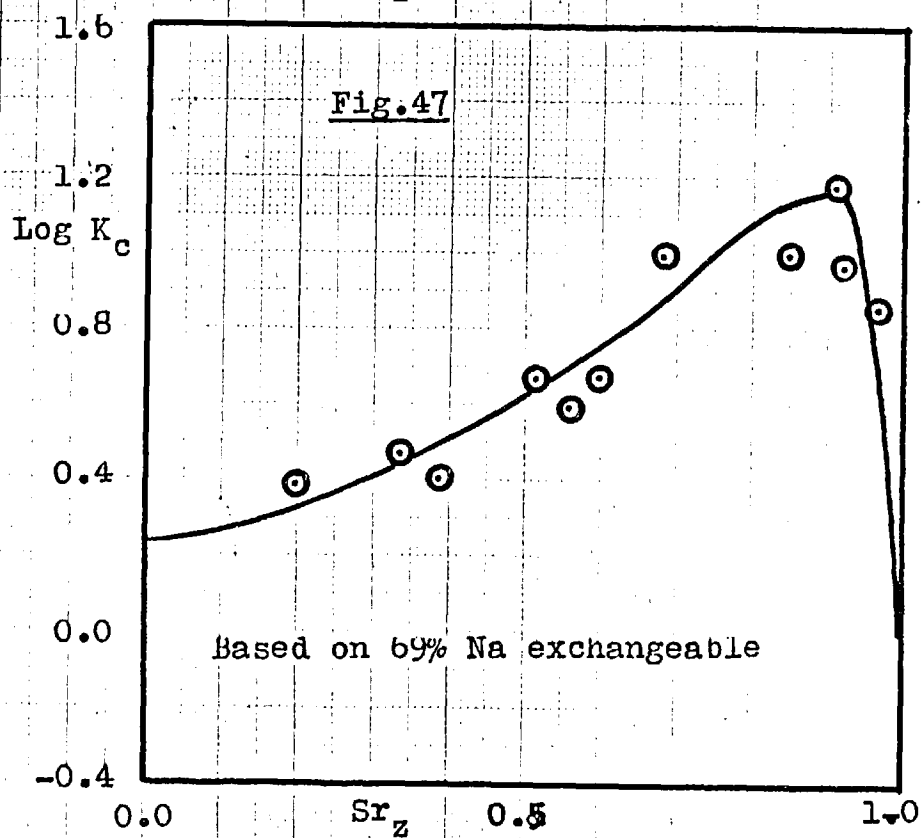
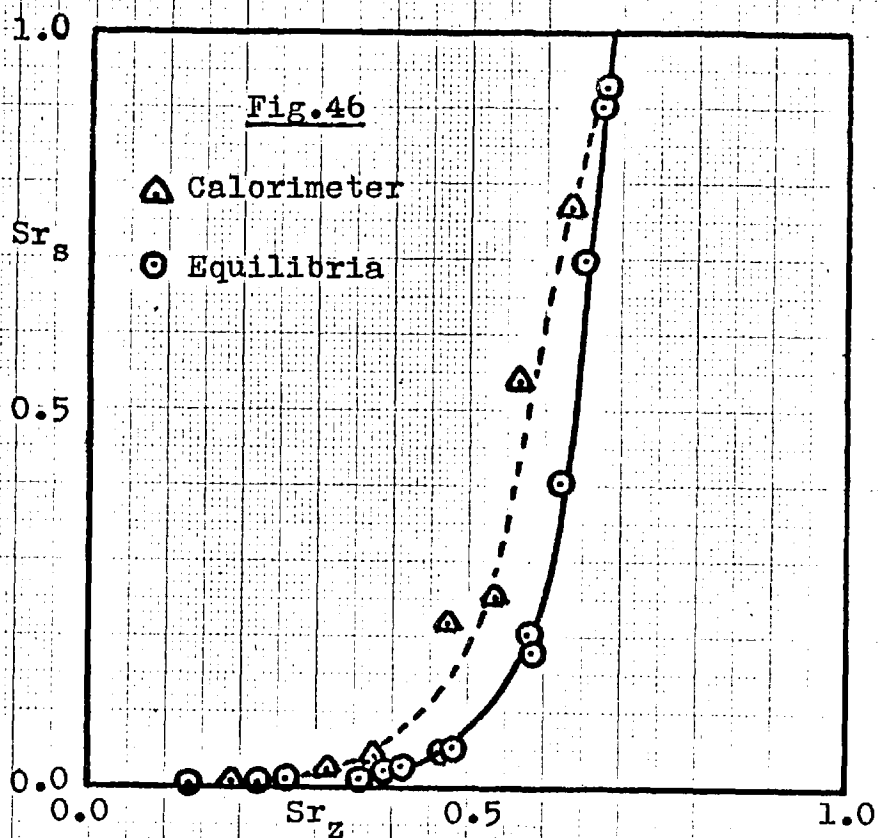
Na-Sr exchange on Chabazite at 50°C

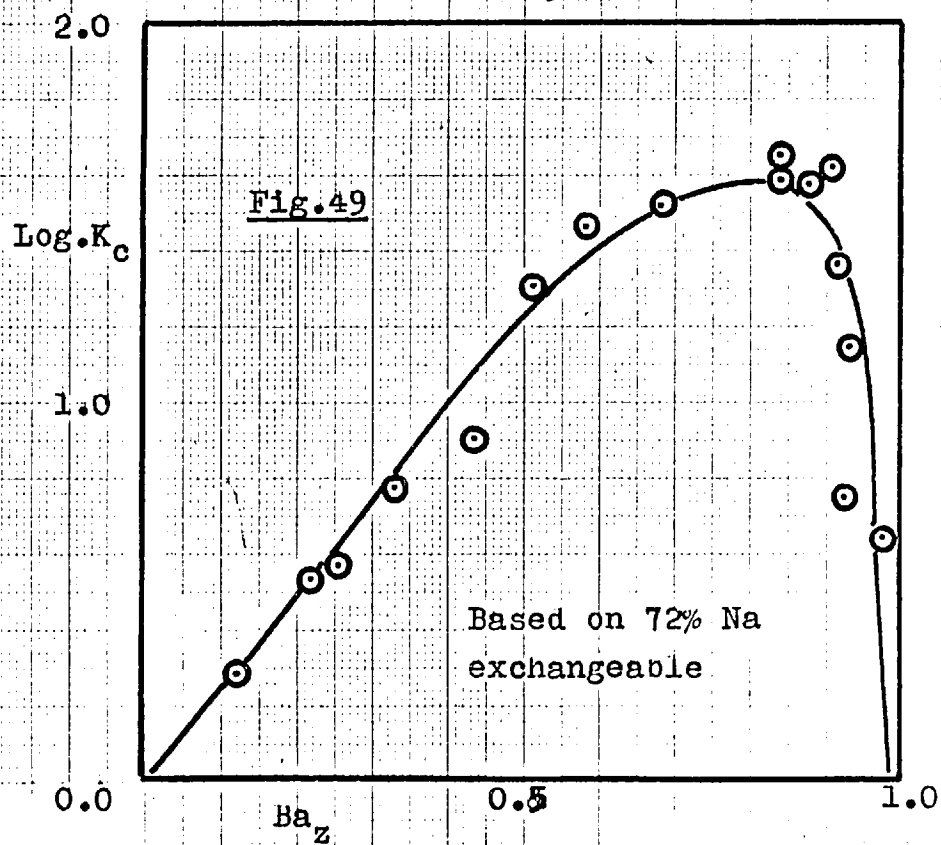
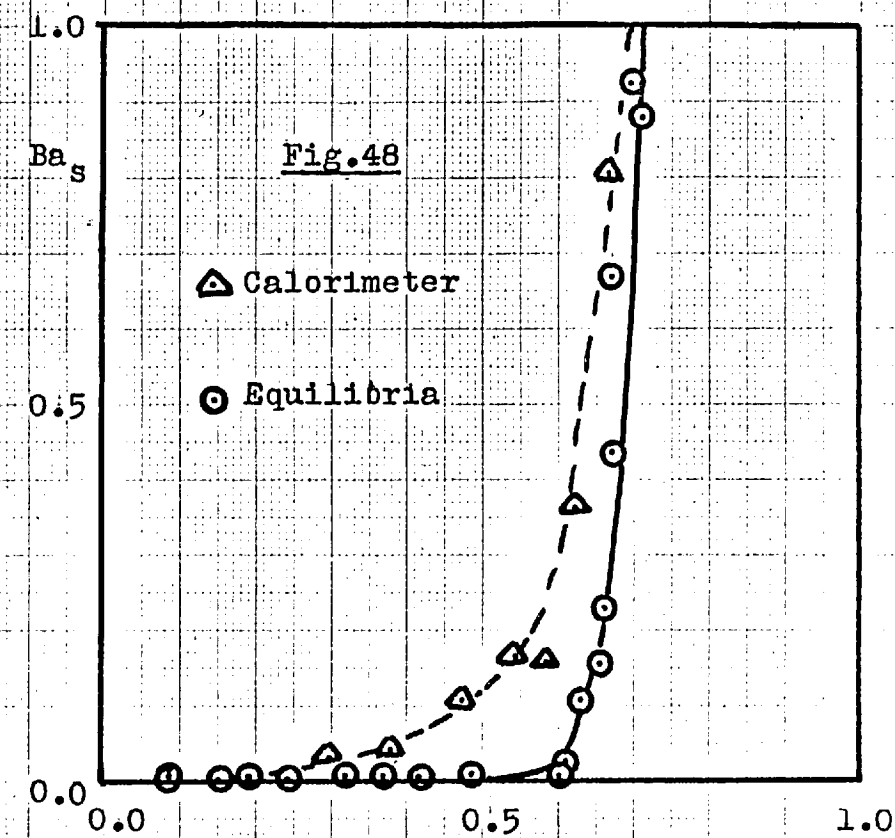




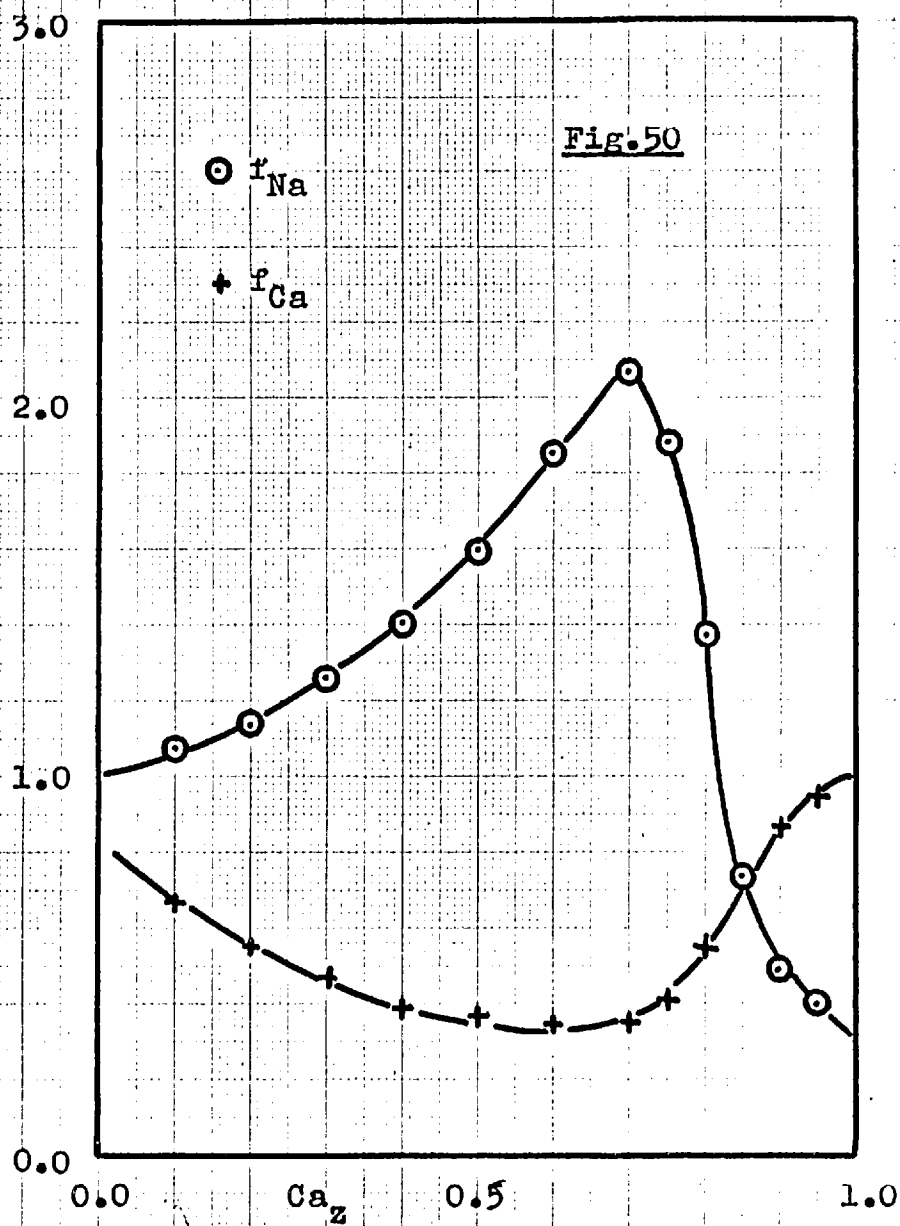




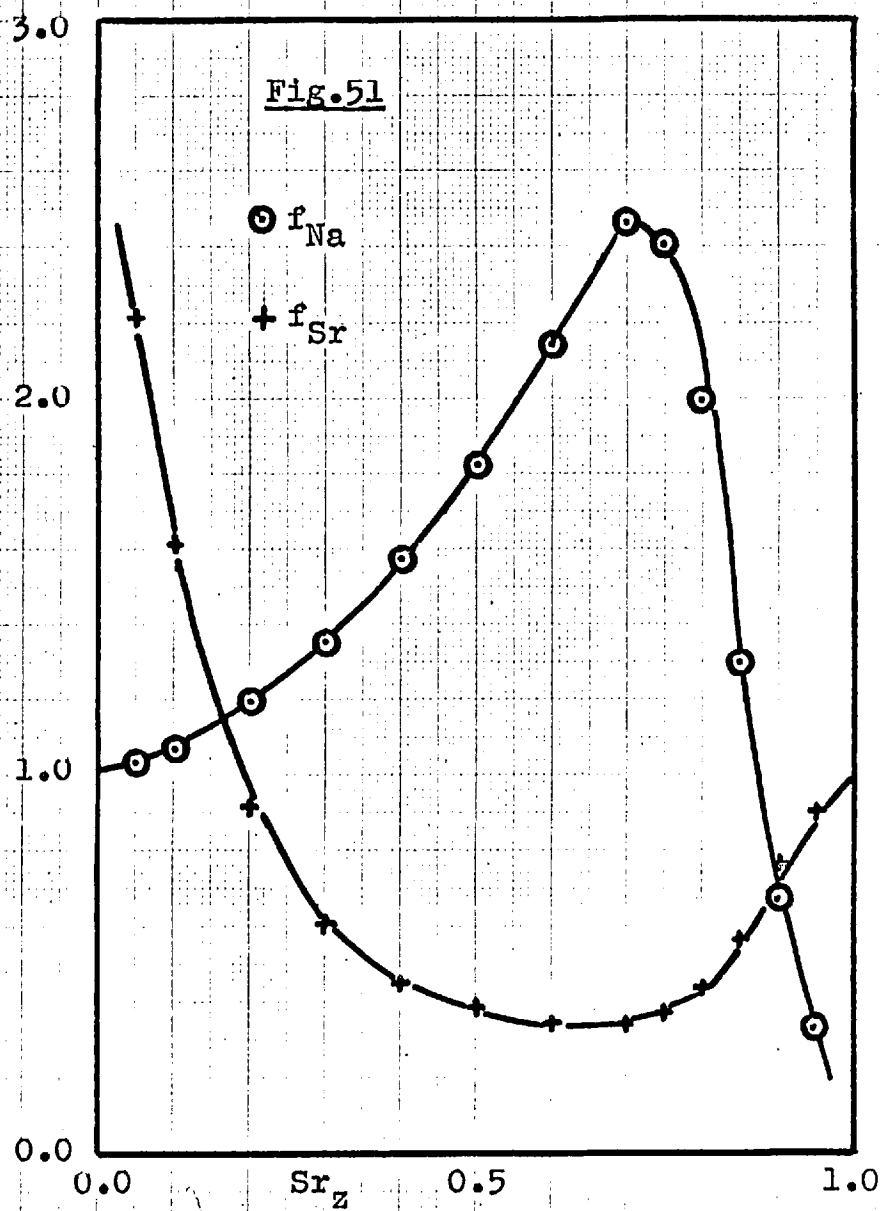




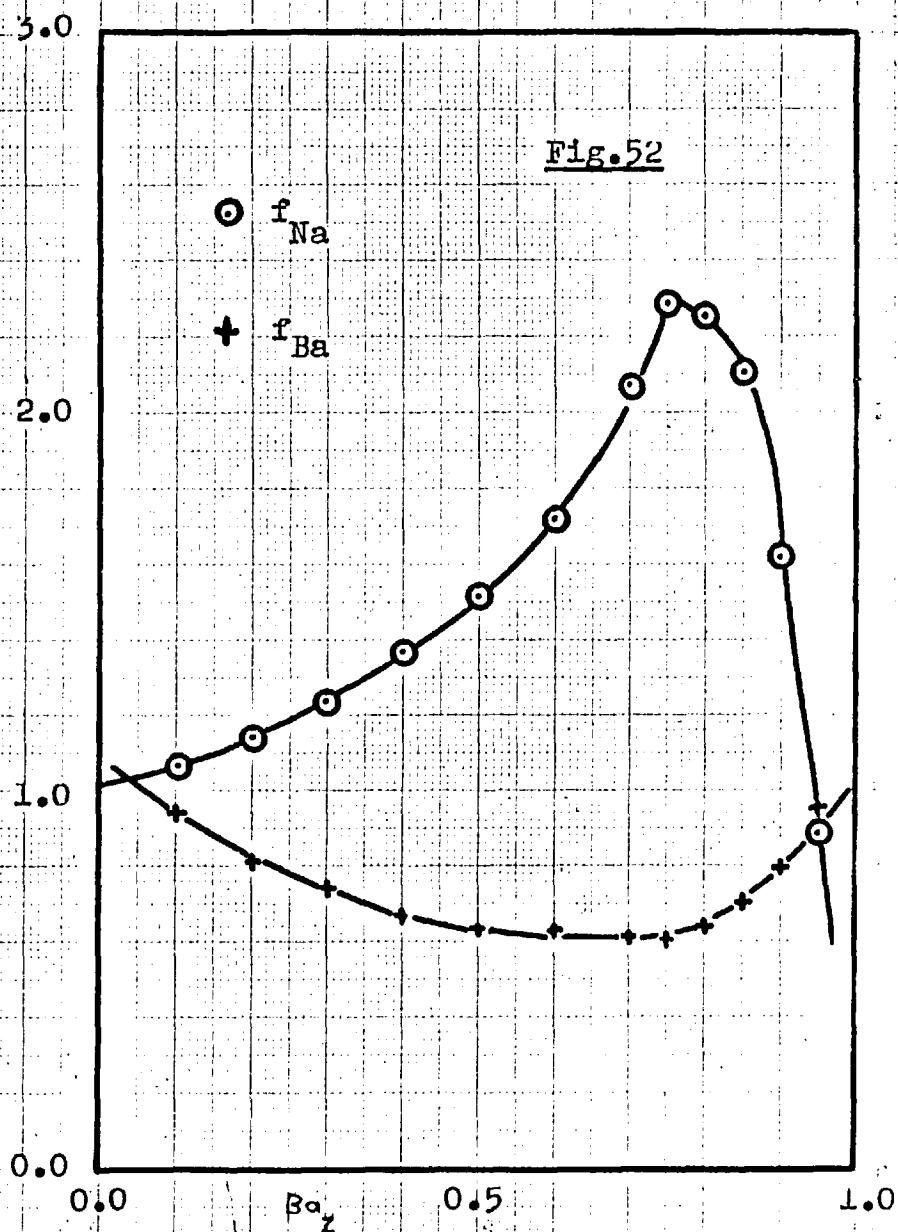
Variation of the activity coefficients in
the mixed (Na-Ca) Chabazite exchanger

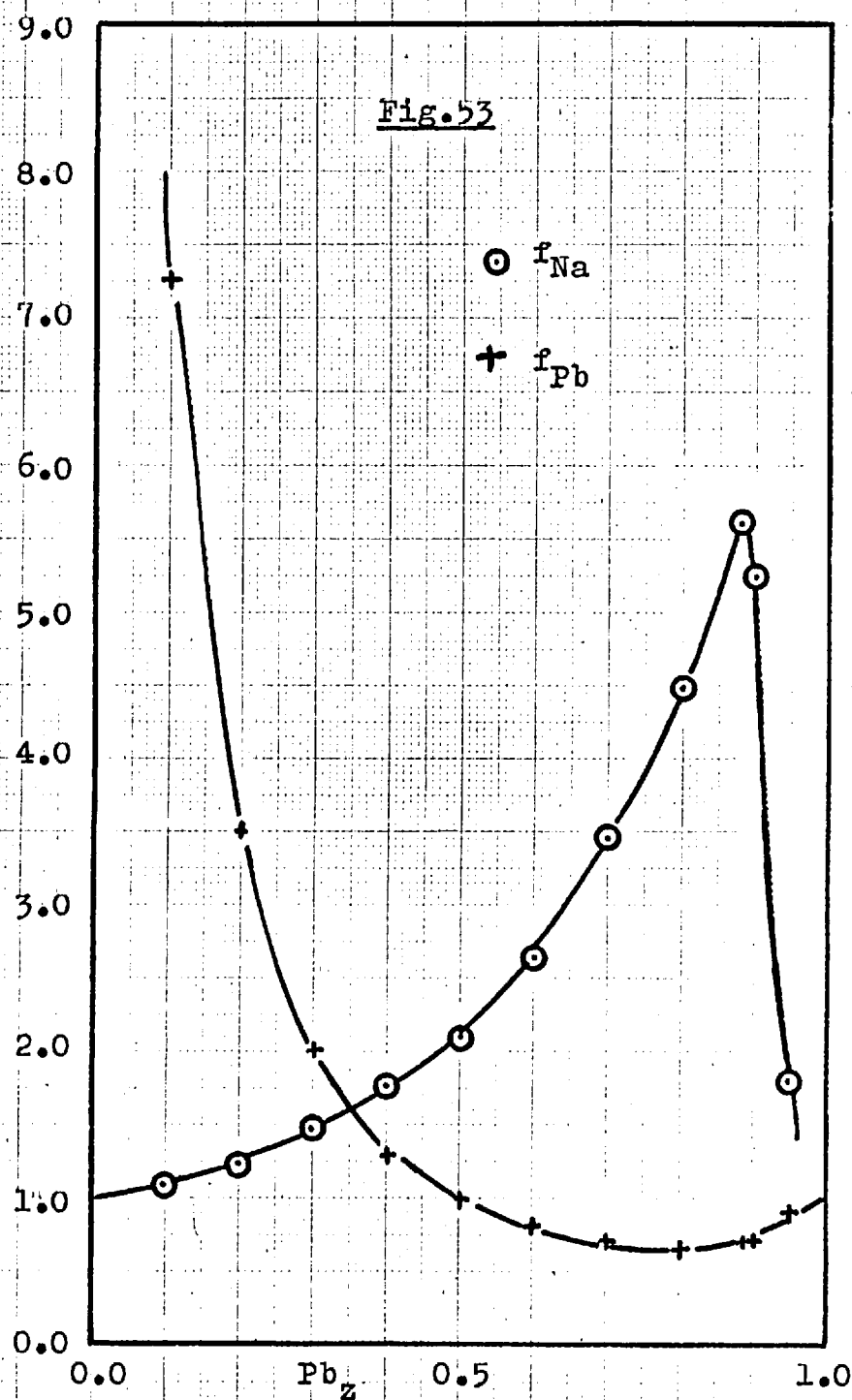


Variation of the activity coefficients in
the mixed (Na-Sr) Chabazite exchanger



Variation of the activity coefficients in
the mixed (Na-Ba) Chabazite exchanger





Variation of the activity coefficients
of the components in the mixed (Na-Ca) exchange

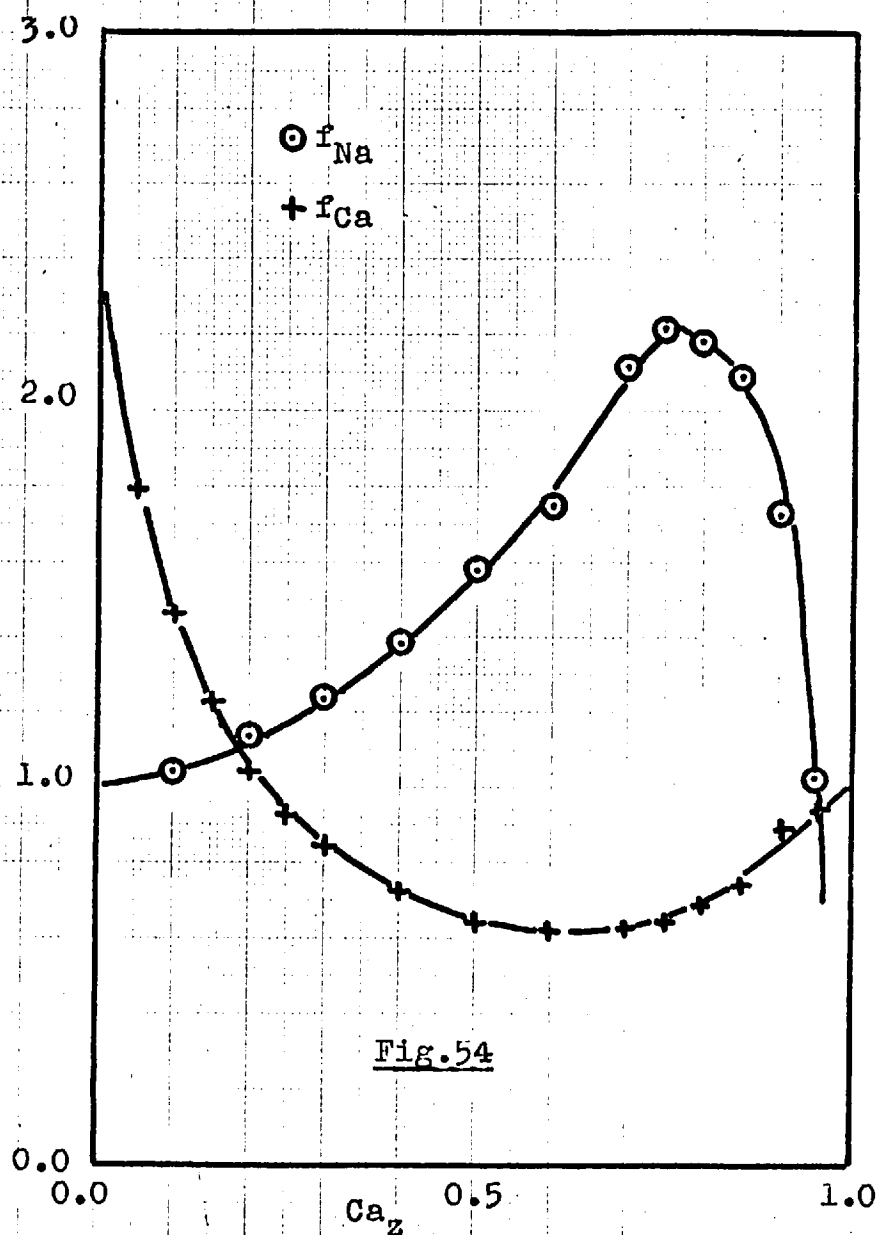
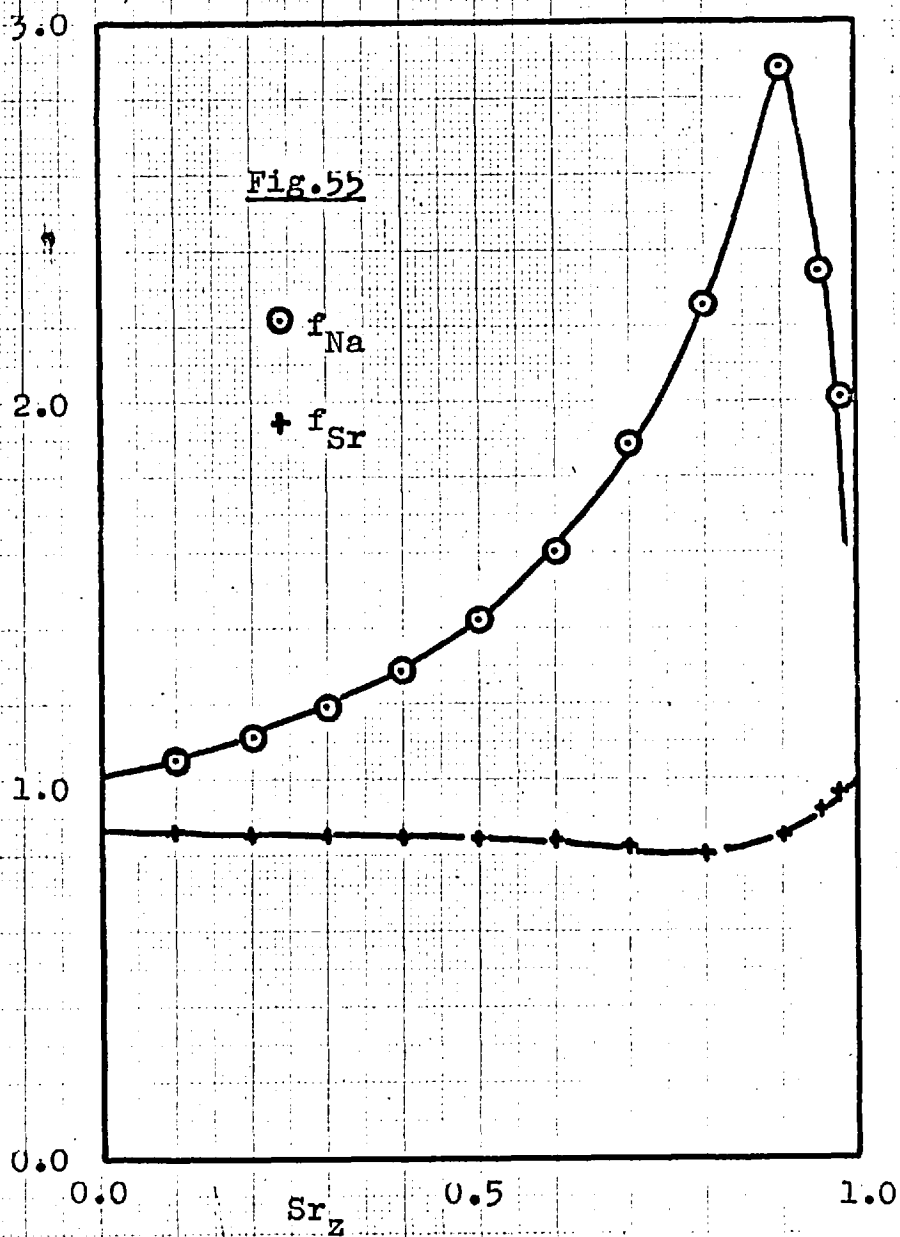
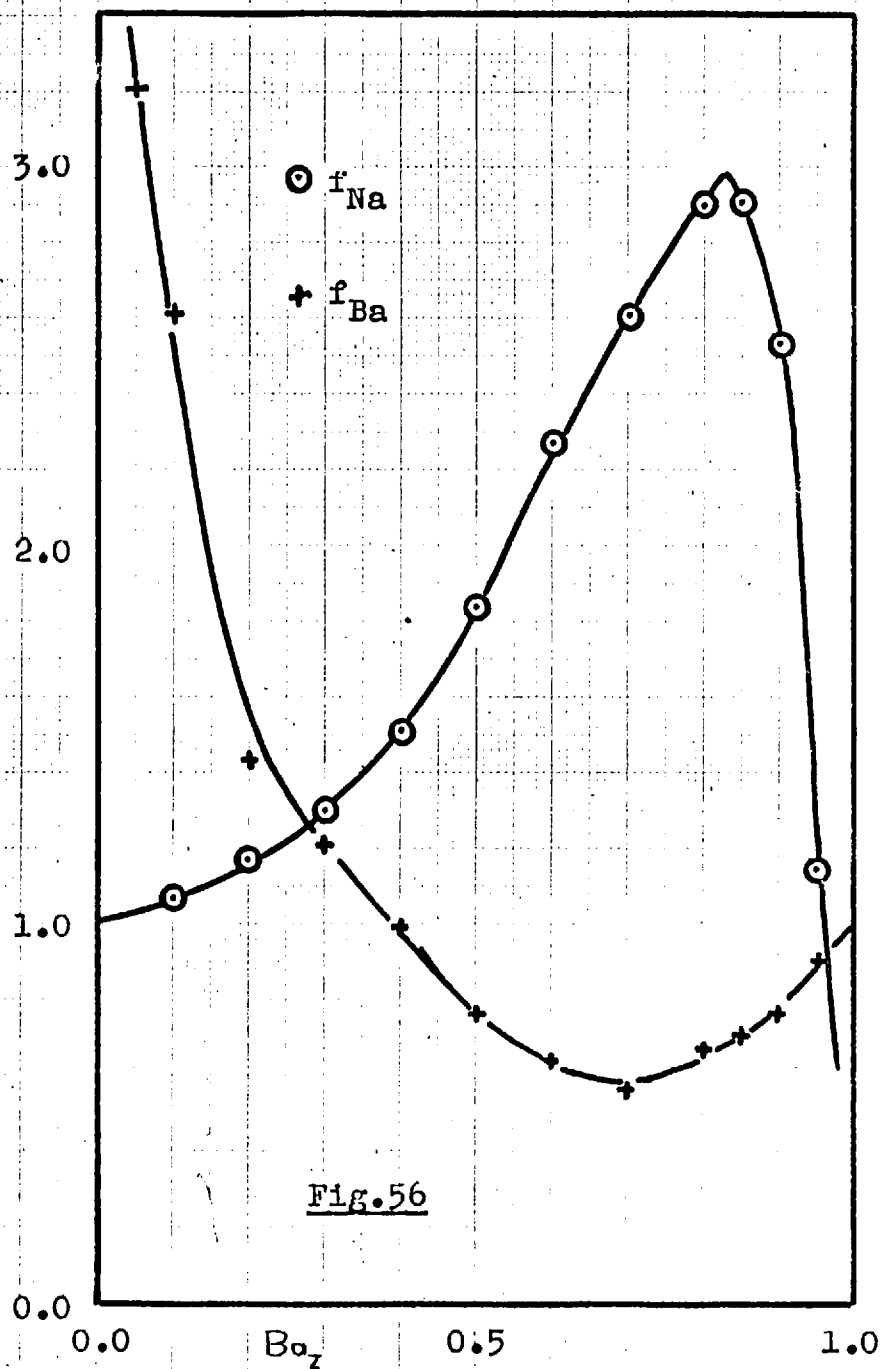


Fig.54

Variation of the activity coefficients
in the mixed (Na-Sr)Y exchanger



Variation of the activity coefficients
in the mixed (Na-Ba)Y exchanger



$$\log K_{a_{Na \rightarrow Sr}} = 0.197; \quad \Delta G^{\circ}_{Na \rightarrow Sr} = -0.134 \text{ kcals/gm.eq.}$$

$$\log K_{a_{Na \rightarrow Ba}} = 0.566; \quad \Delta G^{\circ}_{Na \rightarrow Ba} = -0.386 \text{ kcals/gm.eq.}$$

The activity coefficients of the components in the mixed exchangers are shown in Figs. 54-56 inclusive.

6.4. The heats of wetting and heats of equilibration of zeolites

The heats of wetting, ΔH^W_{BZ} of the almost pure cationic forms of chabazite and Linde Sieve Y are shown in Table 13. The heats of wetting measured in the calorimeter are of the order of the smallest heats (0.03 - 0.05 cal) which could be measured. They are therefore accurate to only ± 0.02 kcals/gm. eq. of exchanger.

Although the zeolites are not in their standard states before immersing in water to determine the heat of wetting, the intracrystalline channels and cavities will be saturated, since the exchangers have been equilibrated with water vapour over pure water for 2 - 3 days. Thus the heat of wetting that is measured is that associated with the wetting of the surface of the exchanger with water.

The heats of wetting $\Delta H^W_{(A,B)Z}$ and heats of equilibration $\Delta H^E_{(A,B)Z}$ of the mixed exchangers were

Table 13

Heats of wetting of pure cationic forms of chabazite
and NaY

Cationic Form	ΔH_{BZ}^W kcal/gm.eq.		Cationic Form	ΔH_{BZ}^W kcal/gm.eq.	
	Chabazite	NaY		Chabazite	NaY
Li	-0.07	-0.09	Ag	-0.06	-0.05
Na	-0.08	-0.09	Tl	-0.100	-0.05
K	-0.13	-0.03	Ca	-0.09	-
Rb	-0.05	-0.045	Sr	-0.09	-
Cs	-0.055	-0.05	Ba	-0.08	-
NH ₄	-0.03	-	Pb	-0.09	-

also measured. The heat of equilibration represents the heat involved when the mixed exchanger is immersed in a solution containing the appropriate ratio of the exchangeable cations such that no further exchange can take place. Values of the heats of wetting and heats of equilibration are shown in Table 14.

In view of the experimental error associated with these values i.e. ± 0.02 kcal/gm. eq. of exchanger, the difference between $\Delta H_{(A,B)Z}^E$ and $\Delta H_{(A,B)Z}^W$ is considered to be negligible.

Table 14

Heats of Wetting and Equilibration of Mixed Exchangers

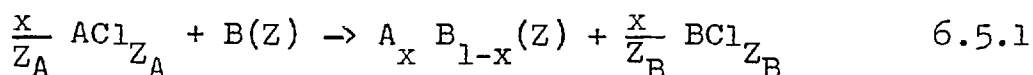
Exchange System	Concentration of exchanging solution	$\Delta H^W_{(A,B)Z}$	$\Delta H^E_{(A,B)Z}$
		kcal/gm.eq.	
Mixed chabazite exchangers			
Na-Li	0.5M	-0.07	-0.07
Na-K	0.1M	-0.09	-0.08
Na-Rb	0.1M	-0.06	-0.06
Na-Cs	0.1M	-0.05	-0.055
Na-NH ₄	0.1M	-0.04	-0.04
Na-Ag	0.1M	-0.09	-0.065
Na-Tl	0.1M	-0.08	-0.08
Na-Ca	-	-	-
Na-Sr	-	-	-
Na-Ba	0.1M	-0.07	-0.075

Exchange System	Concentration of exchanging solution	$\Delta H^W_{(A,B)Z}$	$\Delta H^E_{(A,B)Z}$
	mixed (Na,A)Y exchangers		
Na-Li	0.5M	-0.06	-0.06
Na-K	0.1M	-0.07	-0.07
Na-Rb	0.1M	-0.06	-0.06
Na-Cs	0.1M	-0.05	-0.05
Na-NH ₄	-	-	-
Na-Ag	0.1M	-0.06	-0.065
Na-Tl	0.1M	-0.09	-0.09
Na-Ca	0.1M	-0.08	-0.08
Na-Sr	0.1M	-0.085	-0.08
Na-Ba	0.1M	-0.07	-0.07

(B = Na⁺ is the ion originally in the exchanger)

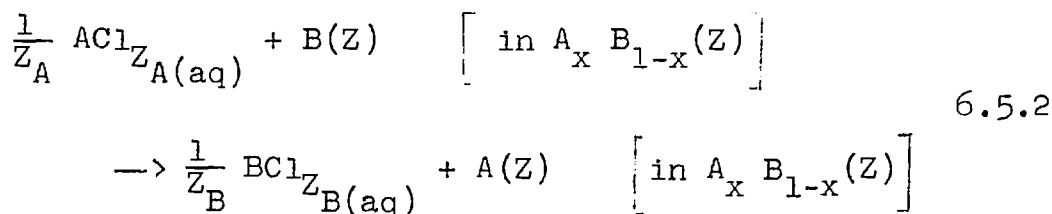
6.5. The Standard Heat of Partial Ion Exchange and the Standard Heat of Exchange

The standard heat of partial ion exchange ΔH_x° is the heat of the reaction



where all the reactants and products are in their defined standard states. The standard heat of partial ion exchange thus measured is an integral heat since it is the heat associated with the replacement of x equivalents of B^{Z_B+} , in 1 equivalent of pure exchanger B(Z)_{Z_B} , by x equivalent of the entering ion A^{Z_A+} , thus forming the mixed exchanger $\text{A}_x \text{B}_{1-x}(\text{Z})$. The variation of the standard heat of partial ion exchange with cationic composition of the exchanger (i.e. x or A_Z) is shown by the differential heat of exchange

$\frac{\partial \Delta H_x^\circ}{\partial x}$, which is the heat of reaction for 1 equivalent of exchange in the reaction



where the composition of the exchanger phase, $\text{A}_x \text{B}_{1-x}(\text{Z})$, is unchanged during the reaction. All the reactants and products in equation 6.5.2 are in their defined

standard states.

The standard heat of partial ion exchange, ΔH_x° has been measured for the Na - Li, Na - K, Na - Rb, Na - Cs, Na - Ag, Na - Ca, Na - Sr and Na-Ba exchanges in both chabazite and NaY. The Na - NH_4 exchange has been studied only in chabazite. Heats of partial ion exchange of the Na - Tl exchange in both NaY and chabazite, and also the Na - Pb exchange in chabazite have been obtained, but these have not been corrected for the heat contents of the solutions owing to the unavailability of the required data.

The differential heats of ion exchange $\frac{\partial \Delta H_x^\circ}{\partial x}$ were derived by drawing tangents to the smoothed curves of ΔH_x° against A_Z at various values of A_Z . Although the accuracy of the values of $\frac{\partial \Delta H_x^\circ}{\partial x}$ is only in the region of ± 0.1 kcal/gm. eq. of exchanger, the graphs of the differential heat of exchange against cationic composition do illustrate the main features of the variation of ΔH_x° with A_Z .

The standard heat of exchange, ΔH° , was obtained by the appropriate combination of the experimental data (equation 5.3.41) or by extrapolation of the graph of ΔH_x° against A_x to $A_x = 1.0$.

6.5.1. Uni-univalent exchanges in chabazite

Na - Li exchange

The variation of the standard heat of partial ion exchange, ΔH_x^0 against Li_Z is shown in Fig. 57, and the corresponding graph of $\frac{\partial \Delta H_x^0}{\partial x}$ in Fig. 58. The standard heat of ion exchange, ΔH^0 , obtained by extrapolation to $Li_Z = 1.0$, is 3.06 kcals/gm. eq. as compared with the experimentally determined value of 3.04 kcals/gm. eq. (equation 5.3.41). Thus the mean value of the standard heat of exchange is

$$\Delta H^0 = 3.05 \text{ kcals/gm. eq.}$$

The differential heat $\frac{\partial \Delta H_x^0}{\partial x}$ is approximately constant (~ 1.4 kcals/gm. eq.) during the initial part of the exchange but rises sharply in the range $Li_Z = 0.7$ to $Li_Z = 1.0$.

Na - K exchange

The variation of the standard heat of partial ion exchange, ΔH_x^0 with K_Z is shown in Fig. 59, and the corresponding graph of the differential heat in Fig. 60. The extrapolated value of ΔH_x^0 at $K_Z = 1.0$ is -2.62 kcals/gm. eq. as compared with the experimentally determined values of -2.59 and -2.61 kcals/gm. eq. Thus the mean value of the standard heat of ion exchange is given by

$$\Delta H^0 = -2.61 \text{ kcals/gm. eq.}$$

The differential heat of ion exchange rises almost linearly from $K_Z = 0$ to $K_Z = 0.7$ at which $\frac{\partial \Delta H^\circ}{\partial x} = -3.0$ kcal/gm. eq. In the range $K_Z = 0.7$ to 1.0, $\frac{\partial \Delta H^\circ}{\partial x}$ decreases rapidly reaching a value of -0.7 kcal/gm. eq. at $K_Z = 1.0$.

Na - Rb Exchange

The variation of the standard heat of partial ion exchange against Rb_Z is shown in Fig. 61, and the corresponding graph of $\frac{\partial \Delta H^\circ}{\partial x}$ is shown in Fig. 62. The standard heat of partial ion exchange is negative and varies linearly with Rb_Z , reaching a value of -2.24 kcal/gm. eq. at $Rb_Z = 1.0$.

The standard heat of exchange ΔH° is
 $\Delta H^\circ = -2.24$ kcal/gm. eq.

The differential heat of ion exchange is constant at all values of Rb_Z , and is

$$\frac{\partial \Delta H^\circ}{\partial x} = -2.24 \text{ kcal/gm. eq.}$$

Na - Cs exchange

The maximum amount of exchange observed in the equilibrium measurements was 84% and in the shorter calorimeter measurements was 72%. The isotherm obtained from the calorimetrically determined measurements did not agree with that obtained from equilibrium measurements, so that the end points from the calorimeter

measurements were not true equilibrium points.

Fig. 63 shows the variation of the standard heats of partial ion exchange with cationic composition of the exchanger. The upper graph is based on the assumption that all the Na ions are potentially exchangeable, whereas the lower graph is based on a reduced exchange capacity corresponding to only 84% of the Na⁺ ions being exchangeable. The standard heat of partial ion exchange varies linearly with Cs_Z reaching a value of -2.89 kcal/gm. eq. at Cs_Z = 1.0 (based on 84% Na⁺ exchangeable).

The variation of the differential heats of ion exchange with cationic composition of the exchanger are shown in Fig. 64. The differential heats are constant for all values of Cs_Z and are equal to

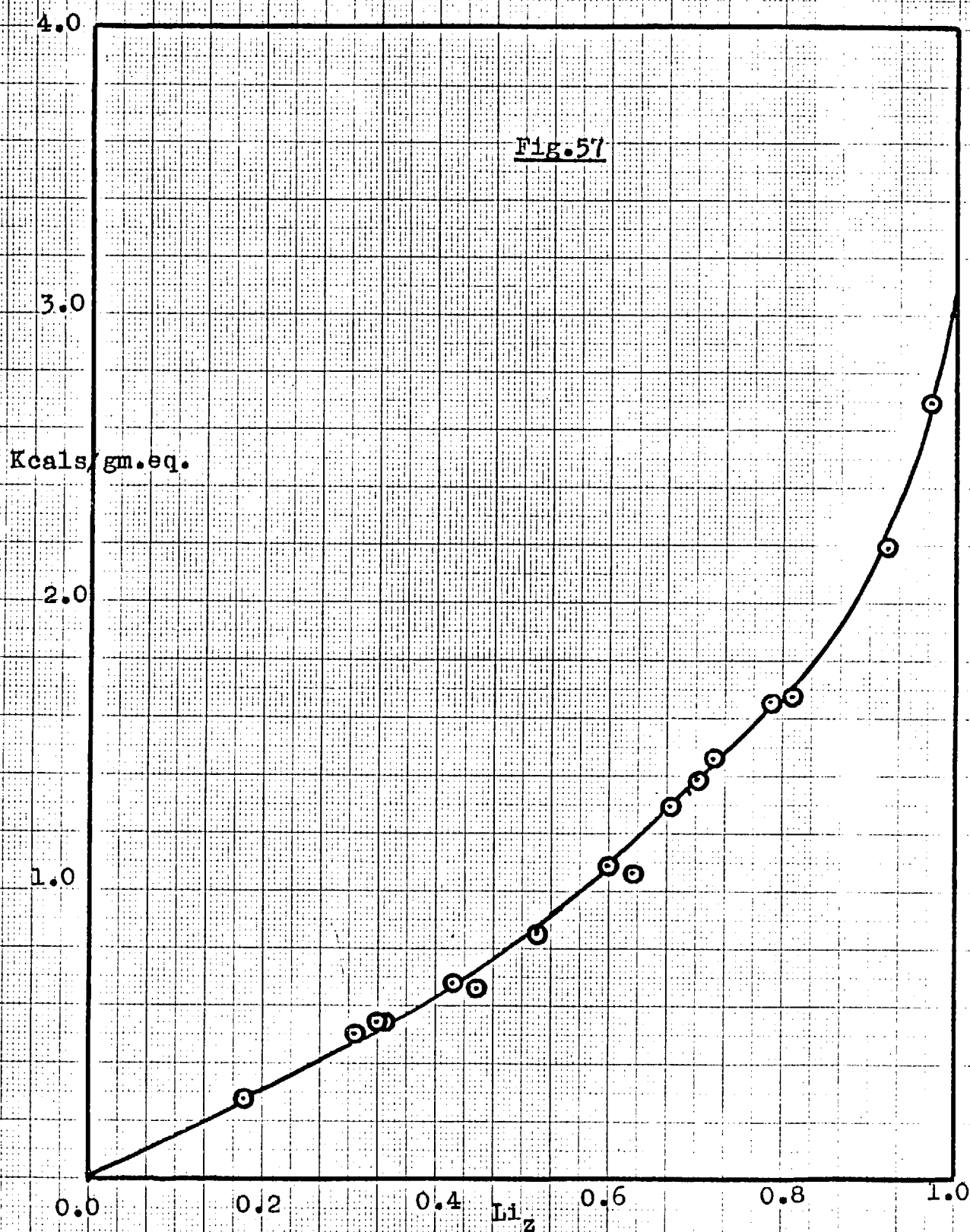
$$\frac{\partial \Delta H^{\circ}_x}{\partial x} = -3.44 \text{ kcal/gm. eq. (based on all Na}^+ \text{ exchangeable)}$$

$$\frac{\partial \Delta H^{\circ}_x}{\partial x} = -2.89 \text{ kcal/gm. eq. (based on 84\% Na}^+ \text{ exchangeable)}$$

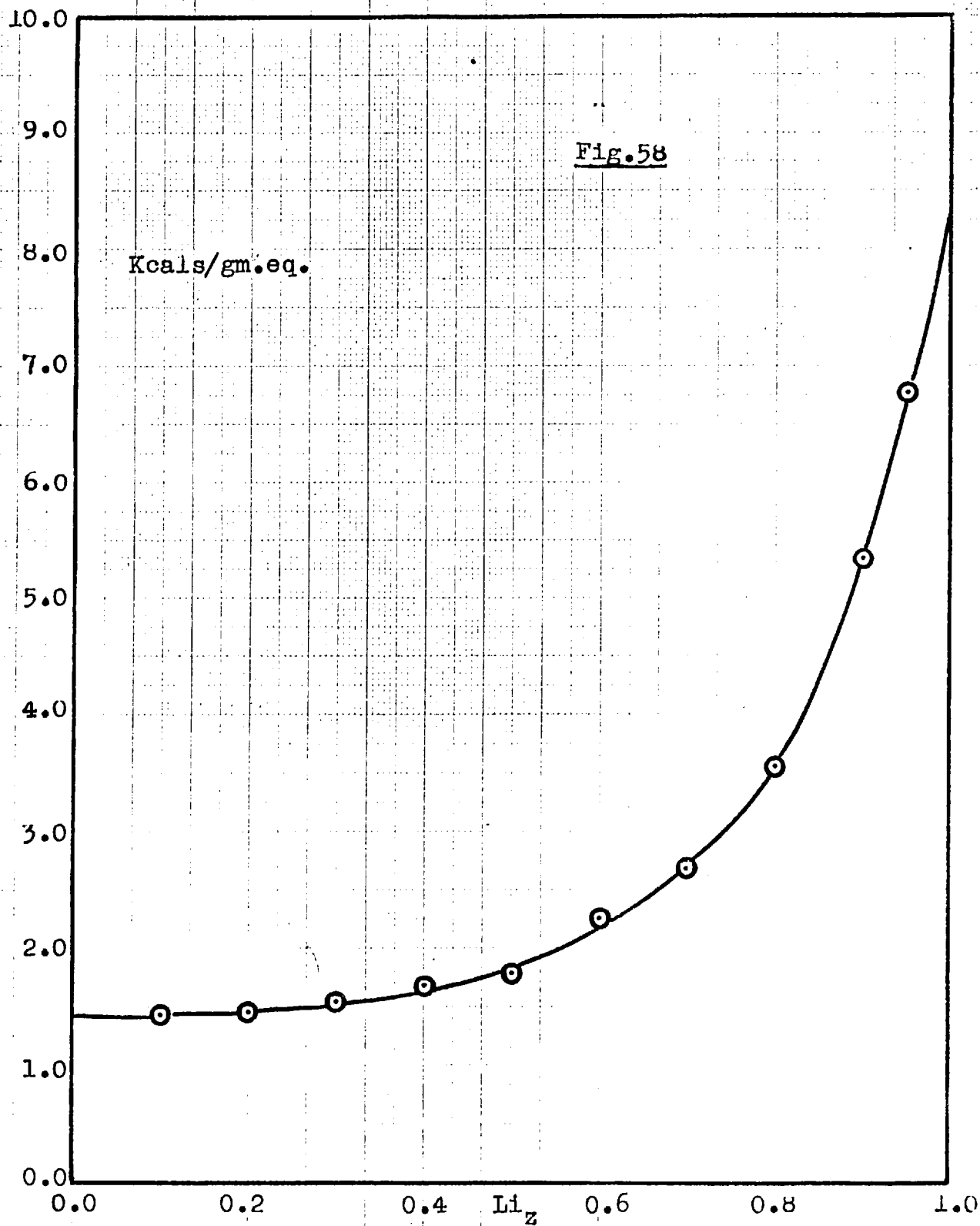
Na-NH₄ exchange

The variation of the standard heat of partial ion exchange with cationic composition, (NH₄)_Z of the exchanger is shown in Fig. 65, and the corresponding graph of the differential heat in Fig. 66. The standard heat

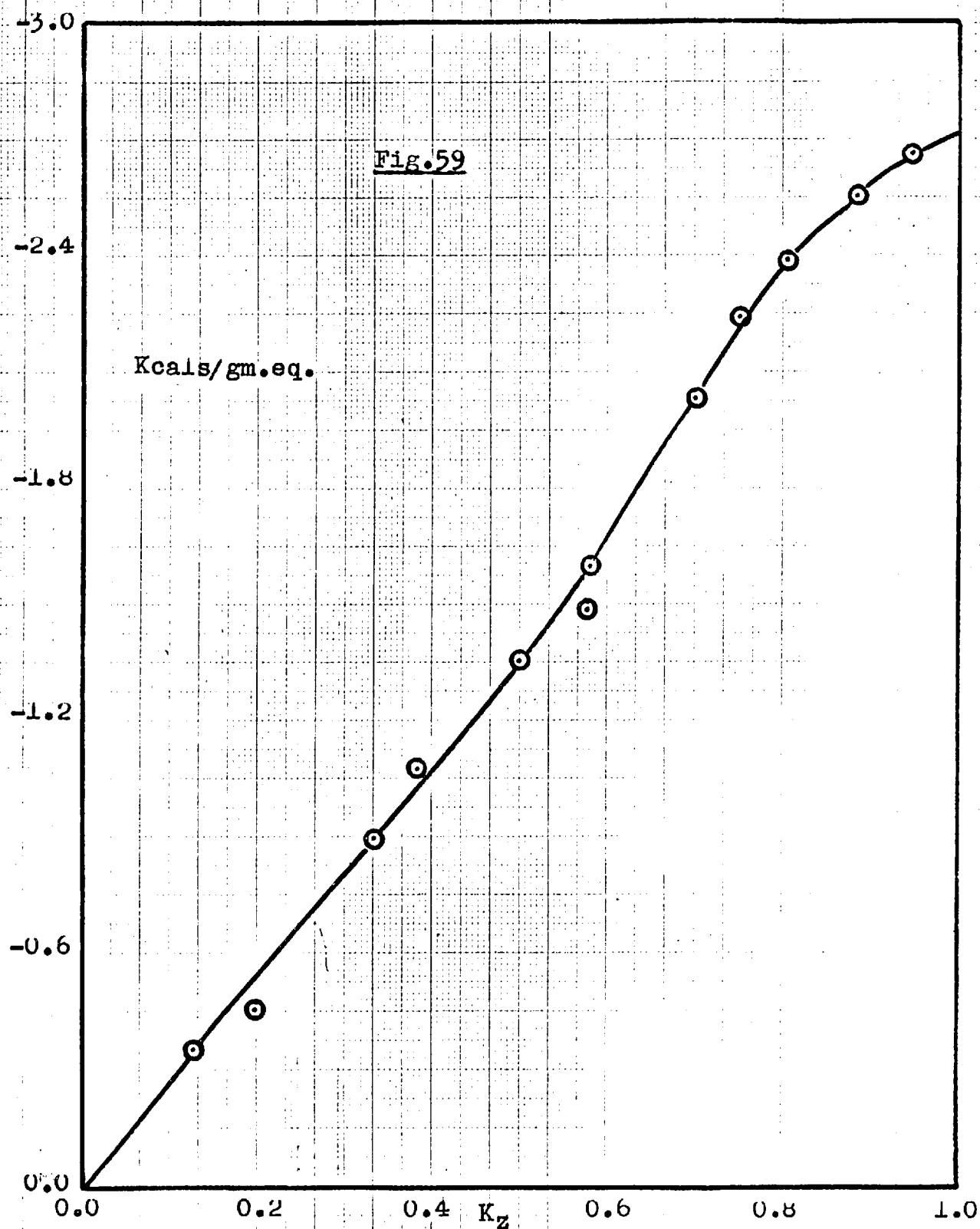
Standard heat of partial ion exchange

Fig. 57

Differential heat of ion exchange

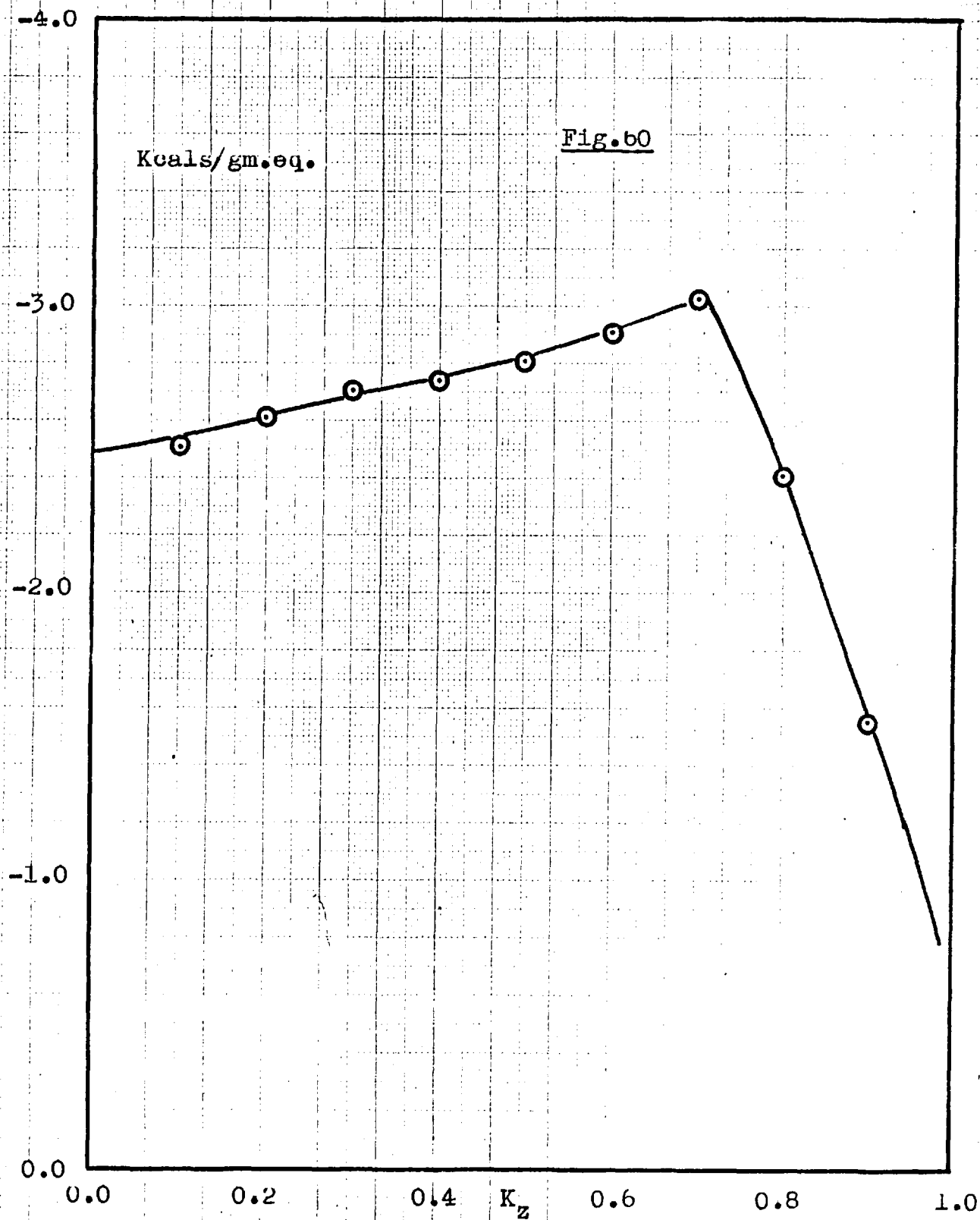


Standard heat of partial ion exchange

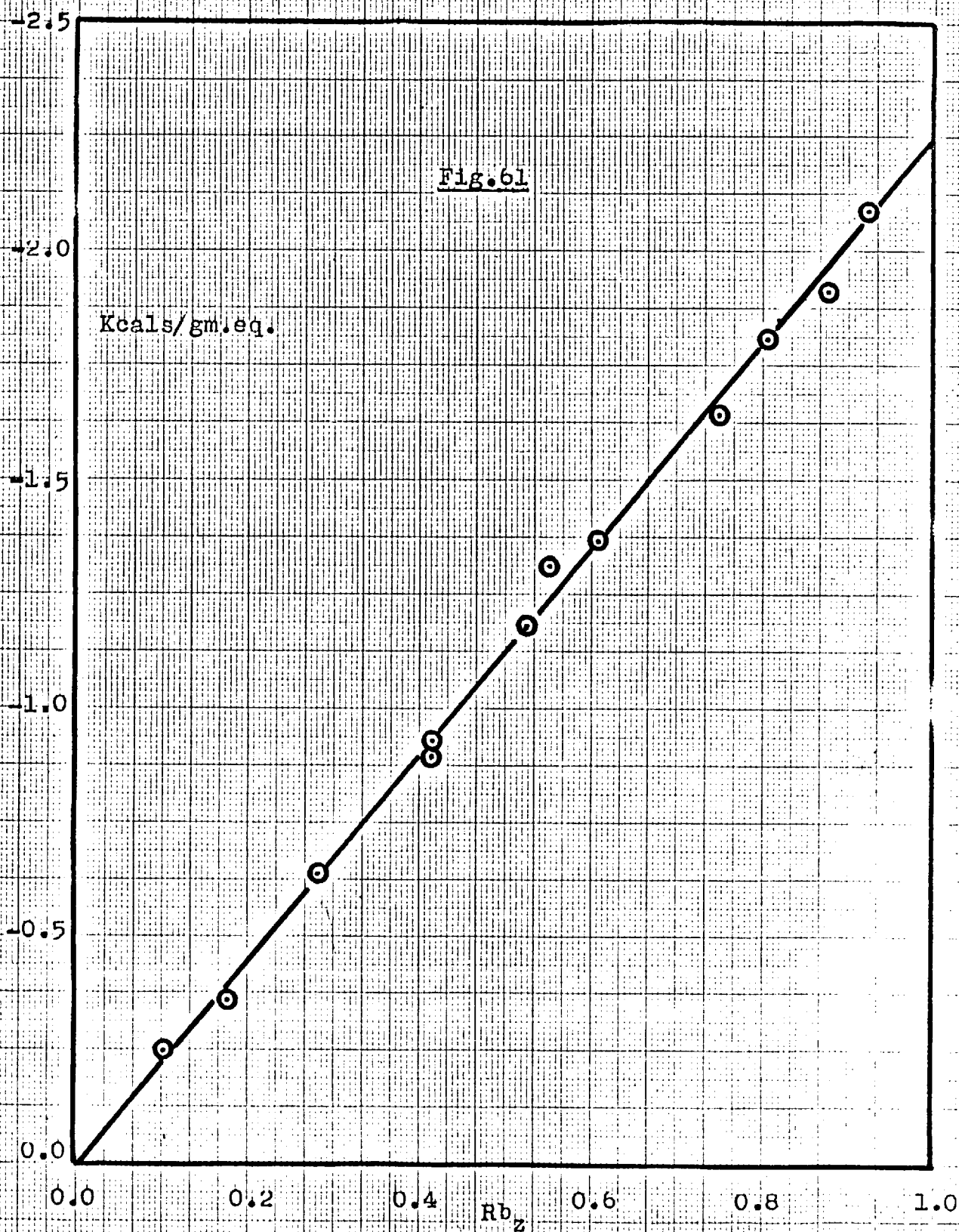


Na-K exchange on Chabazite

Differential heat of ion exchange



Standard heat of partial ion exchange



Differential heat of ion exchange

-4.0

Fig.62

Kcals/gm.eq.

-3.0

-2.0

-1.0

0.0

0.0

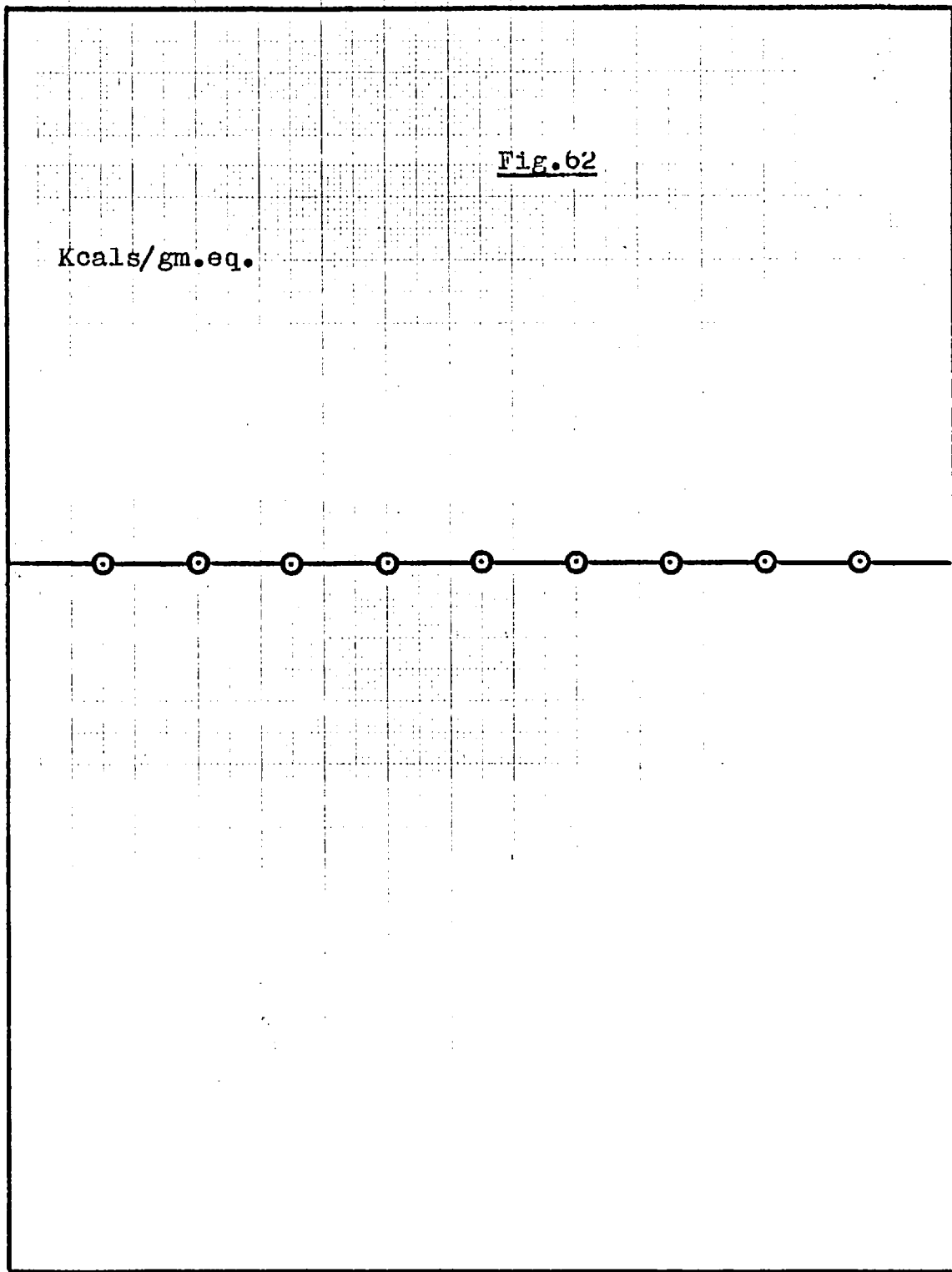
0.2

0.4

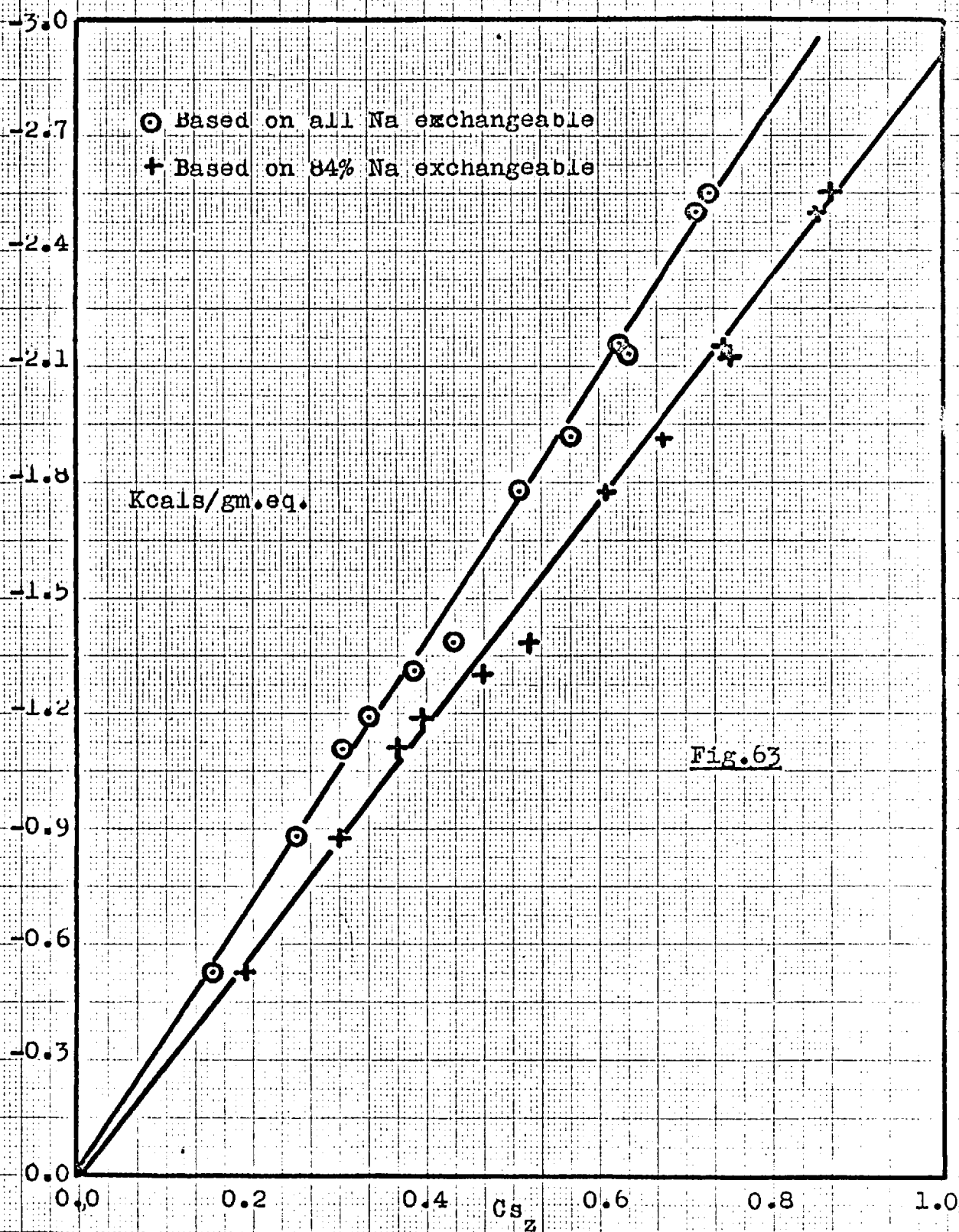
Rb_Z 0.6

0.8

1.0



Standard heats of partial ion-exchange



Differential heats of ion exchange

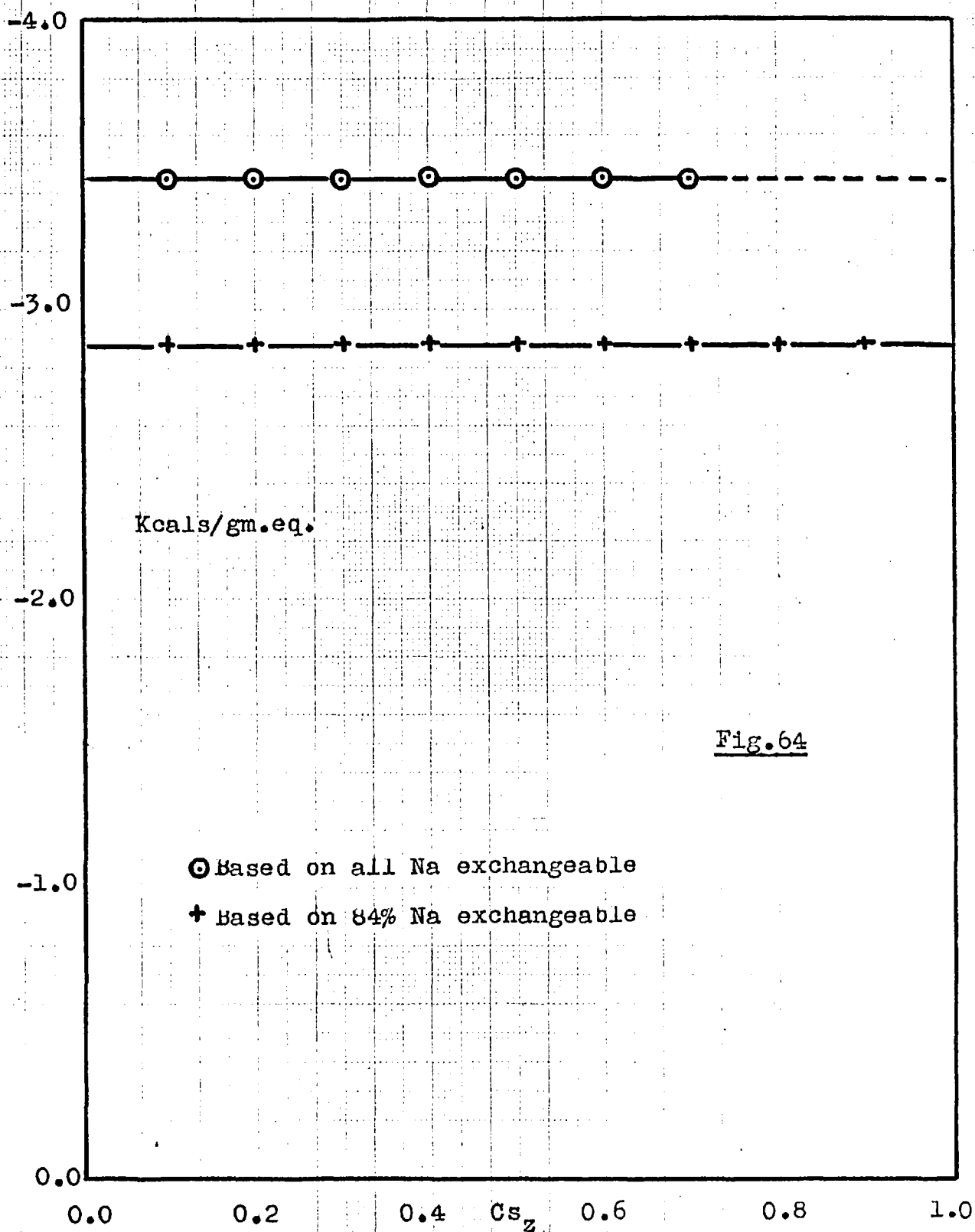
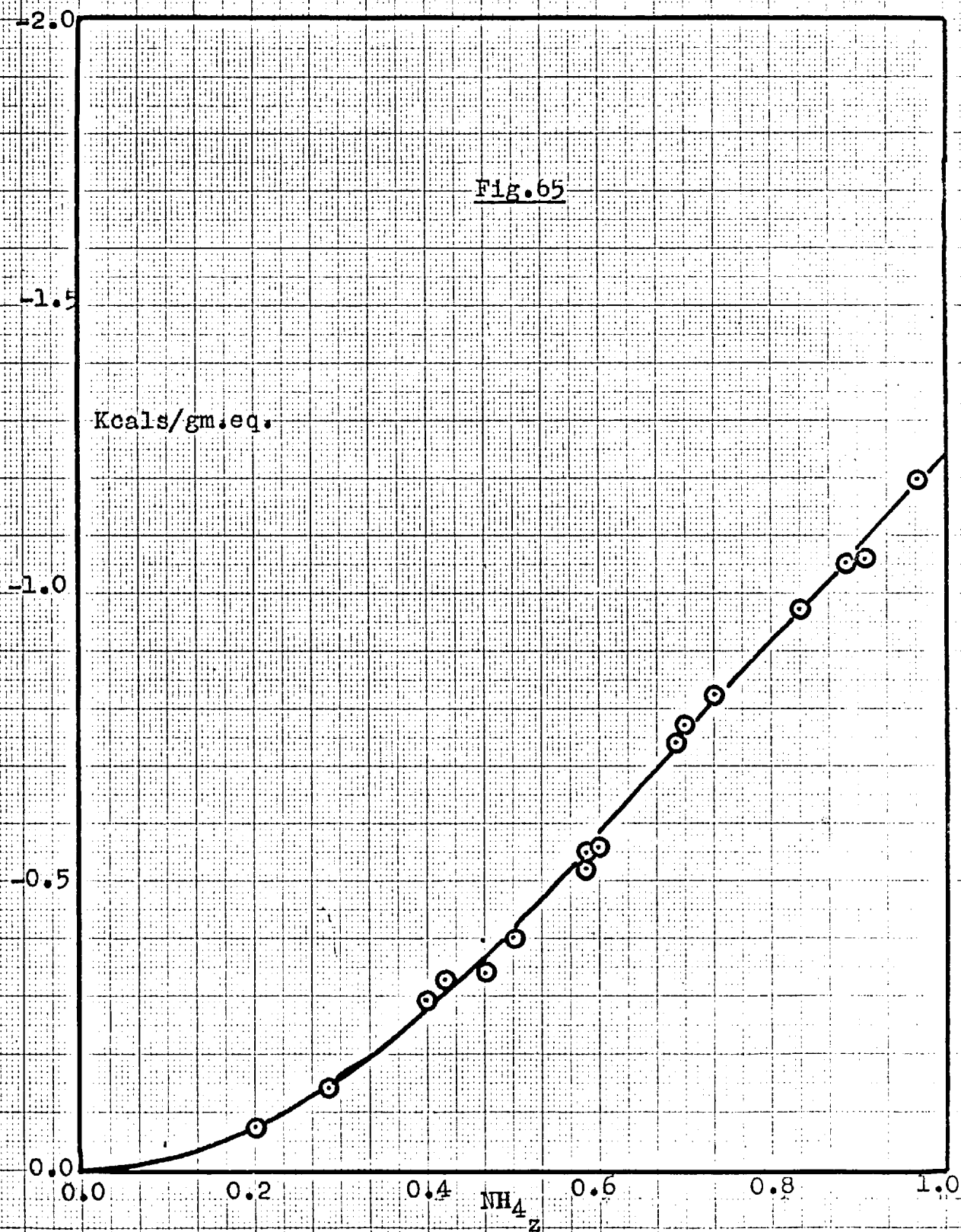


Fig. 64

Standard heat of partial ion exchange



Differential heat of ion exchange

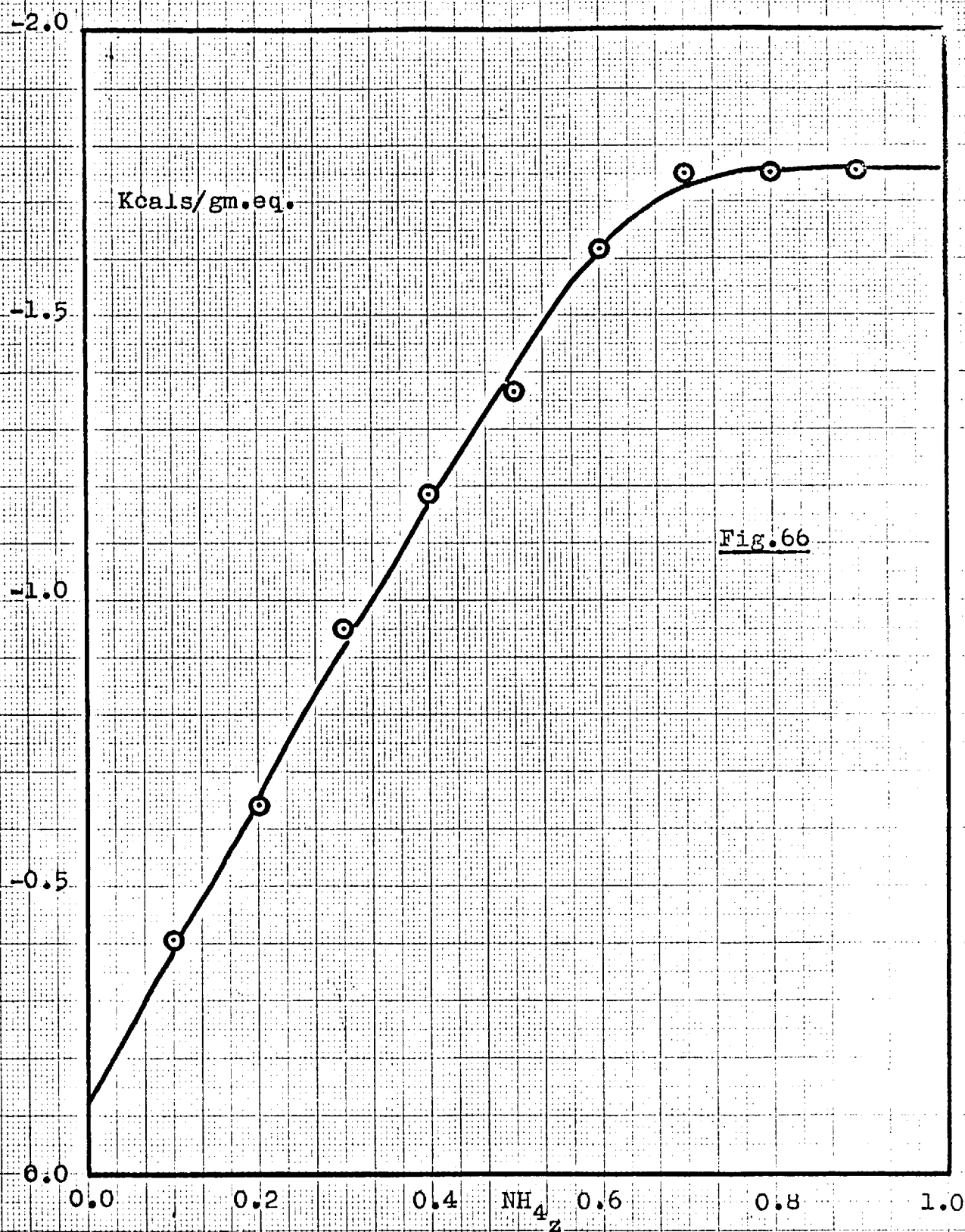
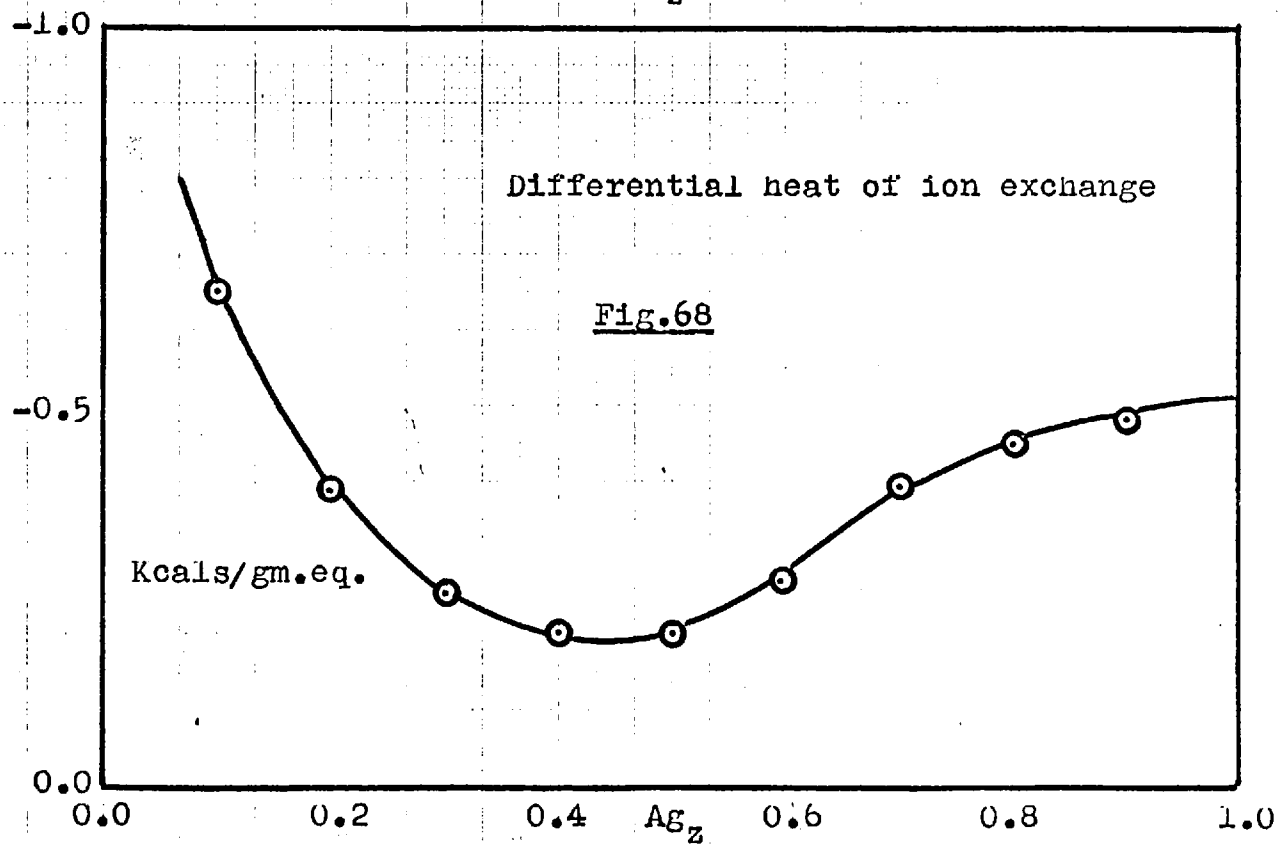
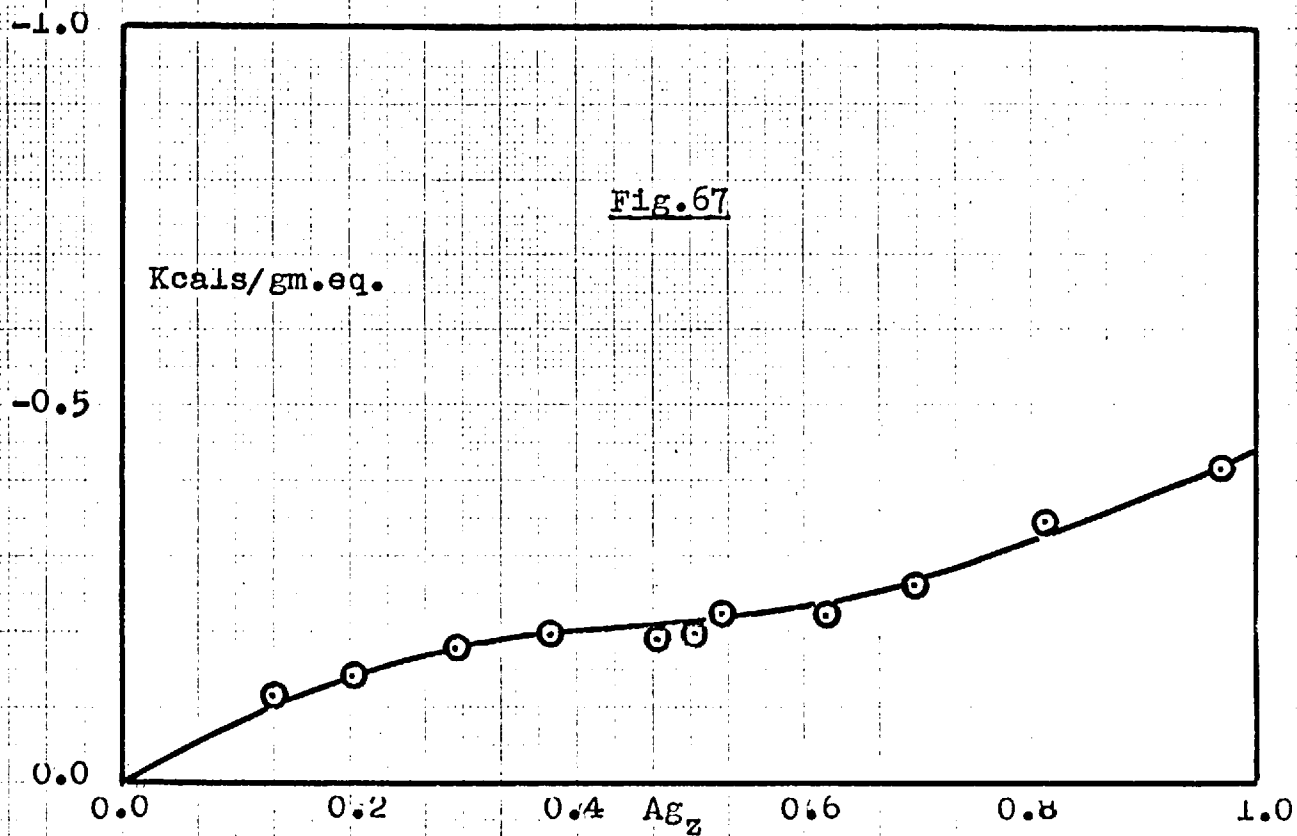
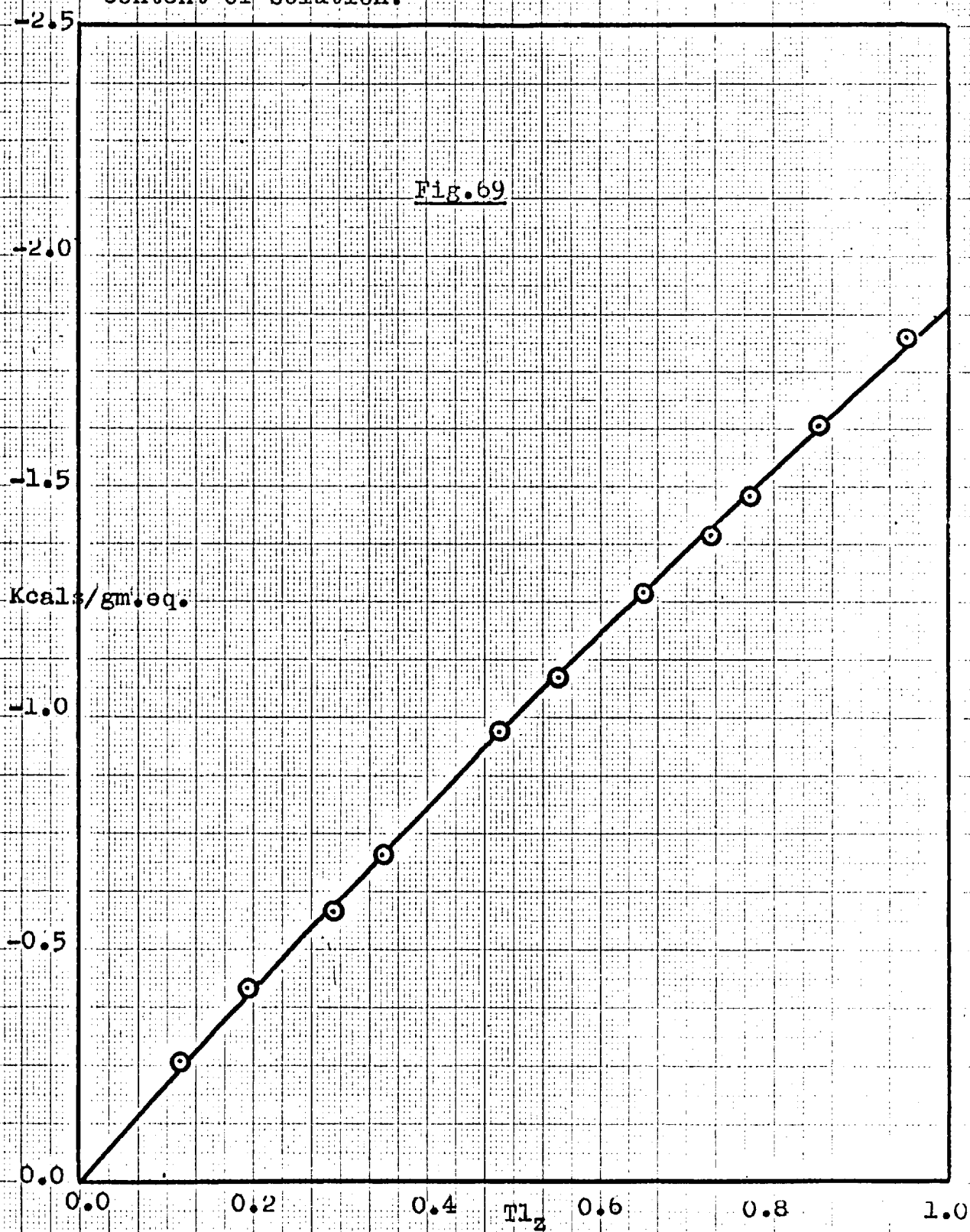


Fig.66

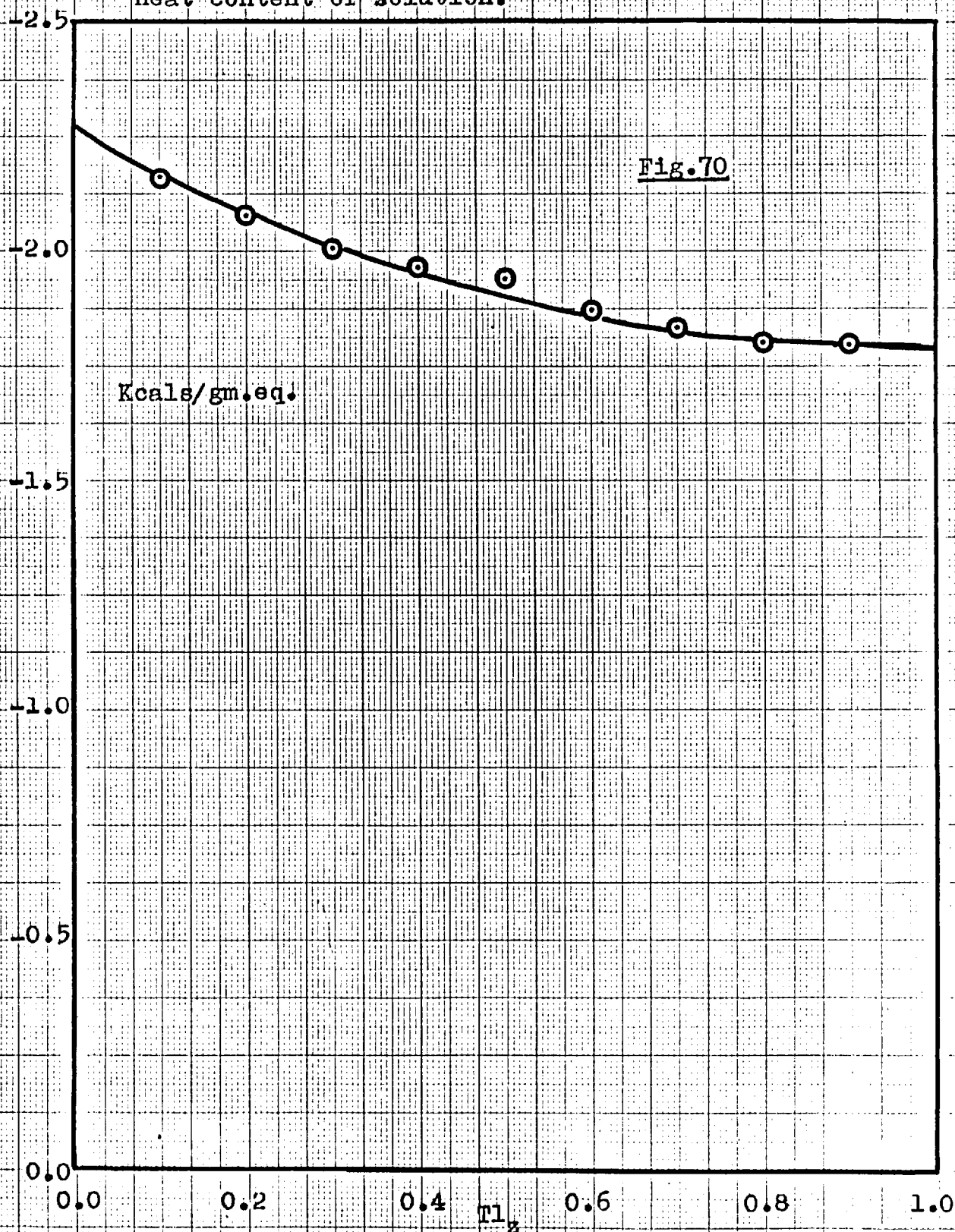
Standard heat of partial ion exchange.



Heat of partial ion exchange, uncorrected for heat content of solution.



Differential heat of ion exchange, uncorrected for
heat content of solution.



of partial ion exchange is negative i.e. exothermic from $(\text{NH}_4)_Z = 0$ to $(\text{NH}_4)_Z = 1.0$. The standard heat of partial exchange is small in the range $(\text{NH}_4)_Z = 0$ to $(\text{NH}_4)_Z = 0.4$, but rises sharply from $(\text{NH}_4)_Z = 0.4$ to $(\text{NH}_4)_Z = 1.0$. The value of the standard heat of exchange obtained by extrapolation to $(\text{NH}_4)_Z = 1.0$ is -1.24 kcals/gm. eq., as compared with the experimentally determined value of -1.21 kcals/gm. eq. The mean value of the standard heat of exchange is thus

$$\Delta H^\circ = -1.22_5 \text{ kcals/gm. eq.}$$

The differential heat of ion exchange $\frac{\partial \Delta H^\circ_x}{\partial x}$

is negative from $(\text{NH}_4)_Z = 0$ to $(\text{NH}_4)_Z = 1.0$. Initially the value of $\frac{\partial \Delta H^\circ_x}{\partial x}$ is small, but rises almost linearly to $(\text{NH}_4)_Z = 0.7$. From $(\text{NH}_4)_Z = 0.7$ to $(\text{NH}_4)_Z = 1.0$, $\frac{\partial \Delta H^\circ_x}{\partial x}$ is constant.

Na - Ag exchange

The variation of the standard heat of partial ion exchange with Ag_Z is shown in Fig. 67, and the corresponding graph of the differential heat in Fig. 68. The standard heats of partial ion exchange are negative from $\text{Ag}_Z = 0$ to $\text{Ag}_Z = 1.0$, and are small. The extrapolated value of ΔH° at $\text{Ag}_Z = 1.0$ is -0.44 kcals/gm. eq.

Thus the standard heat of ion exchange for the Na - Ag exchange in chabazite is

$$\Delta H^{\circ} = -0.44 \text{ kcal/gm. eq.}$$

The differential heat $\frac{\partial \Delta H^{\circ}}{\partial x}$, which is negative in the range $Ag_Z = 0$ to $Ag_Z = 1.0$, passes through a minimum in the range $Ag_Z = 0.4$ to 0.5 . The initial value of the differential heat is larger than the standard heat of ion exchange, but decreases to this minimum at which the value of $\frac{\partial \Delta H^{\circ}}{\partial x}$ is $-0.19 \text{ kcal/gm. eq.}$ From $Ag_Z = 0.5$ to $Ag_Z = 1.0$, $\frac{\partial \Delta H^{\circ}}{\partial x}$ rises slowly to a value of $-0.5 \text{ kcal/gm. eq.}$ at $Ag_Z = 1.0$.

Na - Tl exchange

The variation of the heat of partial ion exchange with cationic composition of the exchanger is shown in Fig. 69, and the corresponding differential heat in Fig. 70. The heats represented by the ordinates in these figures are not the standard heats and corresponding differential heat respectively, since the experimental heats have not been corrected for the relative apparent molal heat contents of the solutions owing to the unavailability of the required data. The heat of partial ion exchange is that derived from equation 5.3.35 ignoring the last two terms in this equation. However, the experimental heats were determined using solutions of 0.1M

thallous acetate or less, so that the corrections necessary are small. Thus, to a good approximation Fig. 69 represents the variation of the standard heat of partial ion exchange with cationic composition of the exchanger. This is negative i.e. exothermic in the range $Tl_Z = 0$ to $Tl_Z = 1.0$. The extrapolated value of the heat of ion exchange is $\Delta H^0 = -1.90$ kcals/gm. eq.

The differential heat of ion exchange decreases slowly from -2.30 kcals/gm. eq. at $Tl_Z = 0$ to -1.82 kcals/gm. eq. at $Tl_Z = 1.0$.

6.5.2. Uni-univalent exchanges in NaY

Na - Li

The analysis of LiY (vide Table 11) indicates that almost all the Na^+ can be replaced by Li^+ . However, the selectivity coefficient (vide Fig. 21) for the exchange in the range $Li_Z = 0.7$ to $Li_Z = 1.0$ is very small ($\sim 10^{-3}$) so that exchange in this range requires strong solutions of LiCl.

The variation of the standard heat of partial ion exchange with cationic composition of the exchanger is shown in Fig. 71, and the corresponding graph of the differential heat in Fig. 72. The maximum amount of exchange determined in the calorimeter experiments is 63%, consequently the graphs have been extrapolated

from $Li_Z = 0.63$ to $Li_Z = 1.0$. The standard heats of partial ion exchange are positive i.e. the reaction is endothermic over the whole range in which exchange was possible. The standard heats of ion exchange were evaluated experimentally using equation 5.3.41. The standard heats of ion exchange thus determined were 1.33, 1.33 and 1.39 kcals/gm. eq., the mean value being

$$\Delta H^0 = 1.35 \text{ kcals/gm. eq.}$$

The differential heat of ion exchange $\frac{\partial \Delta H^0}{\partial x}$ is positive for all values of Li_Z , rising from $\frac{\partial \Delta H^0}{\partial x} = 0.7 \text{ kcals/gm. eq.}$ at $Li_Z = 0$ to $\frac{\partial \Delta H^0}{\partial x} = 2.0 \text{ kcals/gm. eq.}$ at $Li_Z = 1.0$.

Na - K exchange

Although the analytical data (table 11) and the equilibrium measurements (Fig. 22) indicate that complete exchange of Na for K in the zeolite is possible, the maximum limit to exchange observed in the calorimeter was $\sim 80\%$. The variation of the standard heat of partial ion exchange with K_Z is shown in Fig. 73, and the corresponding graph of the differential heat in Fig. 74. The standard heats of partial ion exchange are negative for all values of K_Z . The graph is not linear but slightly concave to the K_Z axis. The value of the

standard heat of ion exchange obtained by extrapolation of the curve to $K_Z = 1.0$ is -1.44 kcals/gm. eq. as compared with the experimental value of -1.45 kcals/gm. eq. The standard heat of ion exchange is

$$\Delta H^\circ = -1.44_5 \text{ kcals/gm. eq.}$$

The differential heat of ion exchange decreases from $\frac{\partial \Delta H^\circ}{\partial x} = -1.85$ kcals/gm. eq. at $K_Z = 0$ to the extrapolated value of $\frac{\partial \Delta H^\circ}{\partial x} = -1.15$ kcals/gm. eq. at $K_Z = 1.0$.

The exchange isotherm constructed from the calorimetric measurements agrees with that of the equilibrium measurements, where the time of contact is four days, up to $\sim 69\%$ exchange after which a slow process occurs. Thus approximately 69% of the Na^+ ions are in sites readily exchangeable with K^+ ion, while the remaining 31% are in sites which exchange with some difficulty.

Na - Rb, Na - Cs and Na - Tl exchanges

Analytical data (vide table 11) and ion exchange equilibrium measurements indicated that complete replacement of Na^+ by Rb^+ , Cs^+ and Tl^+ is not possible under the conditions used, and the exchange capacity of the zeolite for these ions has been adjusted accordingly. Figs. 75, 77 and 79 show the variation of the heats of

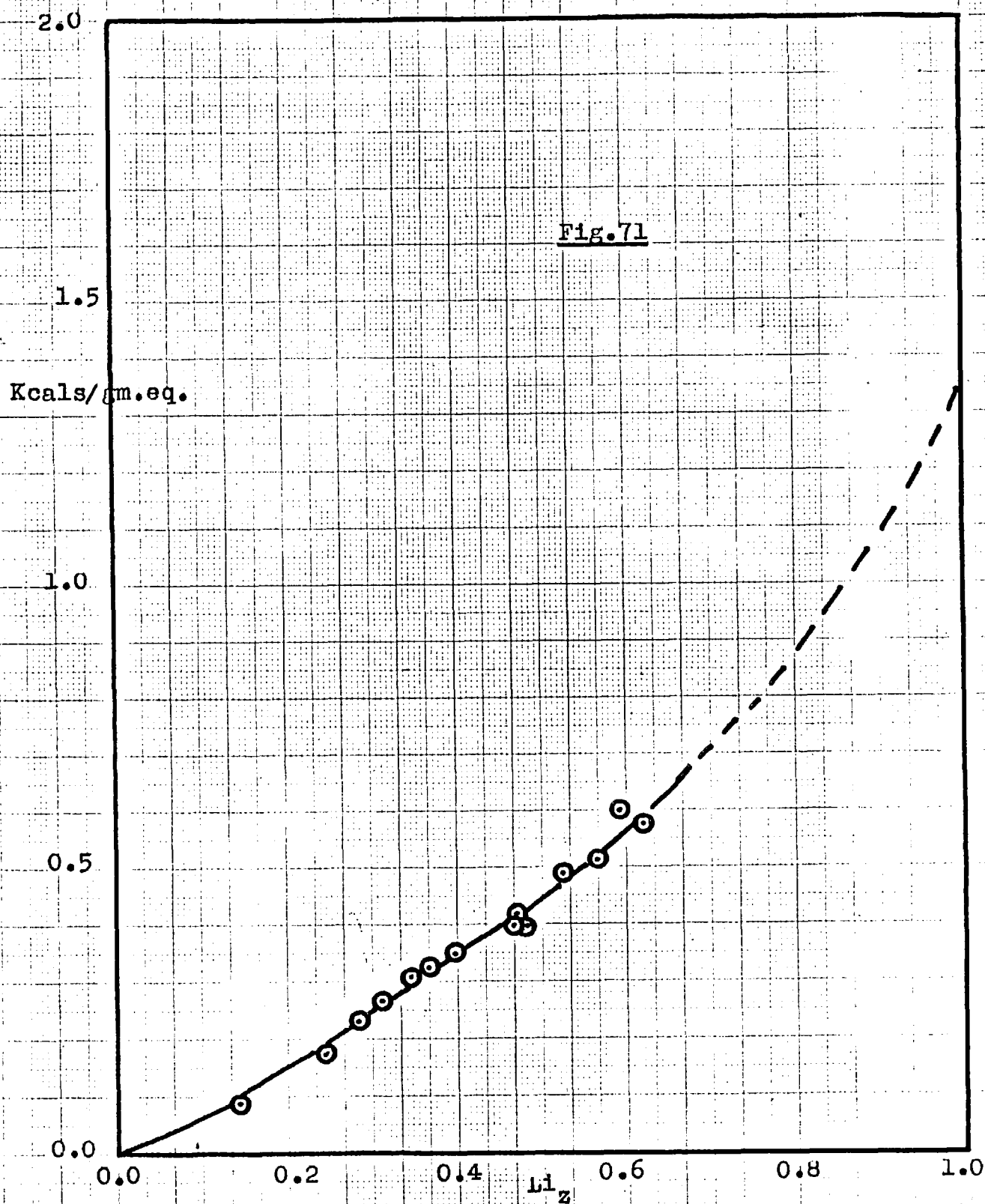
partial ion exchange with cationic composition of the exchanger for the exchanges Na - Rb, Na - Cs and Na - Tl respectively. For the exchanges involving the Rb^+ and Cs^+ ions the ordinates of these graphs represent the standard heats of partial ion exchange, but in the case of the Na - Tl exchange, the ordinate represents an experimental heat to which no correction has been made for the relative apparent molal heat contents of the sodium acetate and thallous acetate solutions. However, as explained previously this correction is small. The corresponding graphs of the differential heats are shown in Figs. 76, 78, 80. In all cases the graphs are based on an exchange capacity of 3.0 meq/gm. (corresponding to all the Na^+ being exchangeable) and on a reduced exchange capacity of ~ 2.1 meq/gm. (corresponding to the limits of 69% and 71% and 69% for the Rb, Cs and Tl exchanges respectively).

For all three exchanges the standard heats of partial ion exchange are negative in the ranges in which exchange was possible. The standard heats of ion exchange are

$$\Delta H_{\text{Na-Rb}}^{\circ} = -1.22 \text{ kcal/gm. eq.}$$

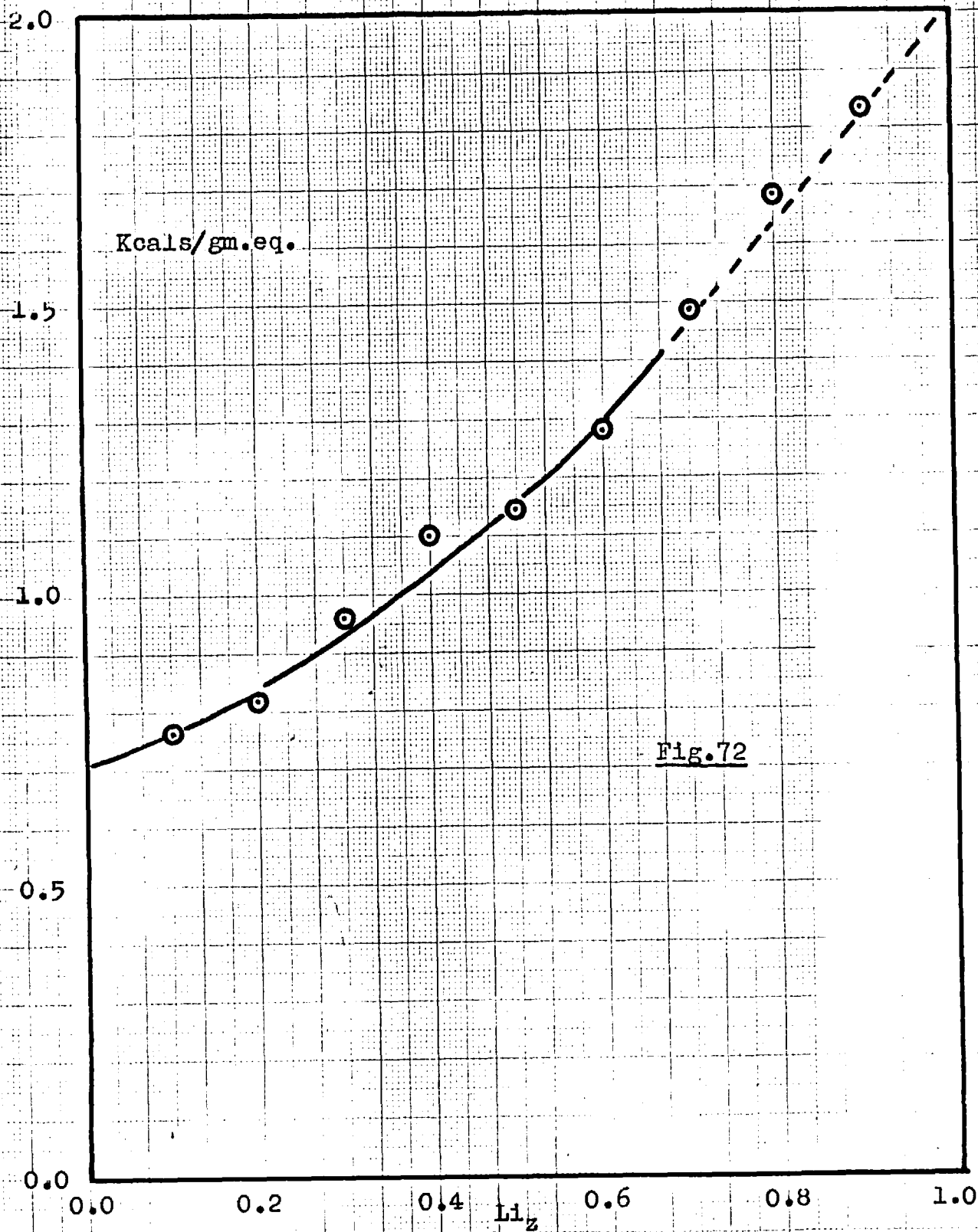
$$\Delta H_{\text{Na-Cs}}^{\circ} = -1.61 \text{ kcal/gm. eq.}$$

$$\Delta H_{\text{Na-Tl}}^{\circ} = -1.38 \text{ kcal/gm. eq.}$$



Na-Li exchange on NaY

Differential heat of ion exchange

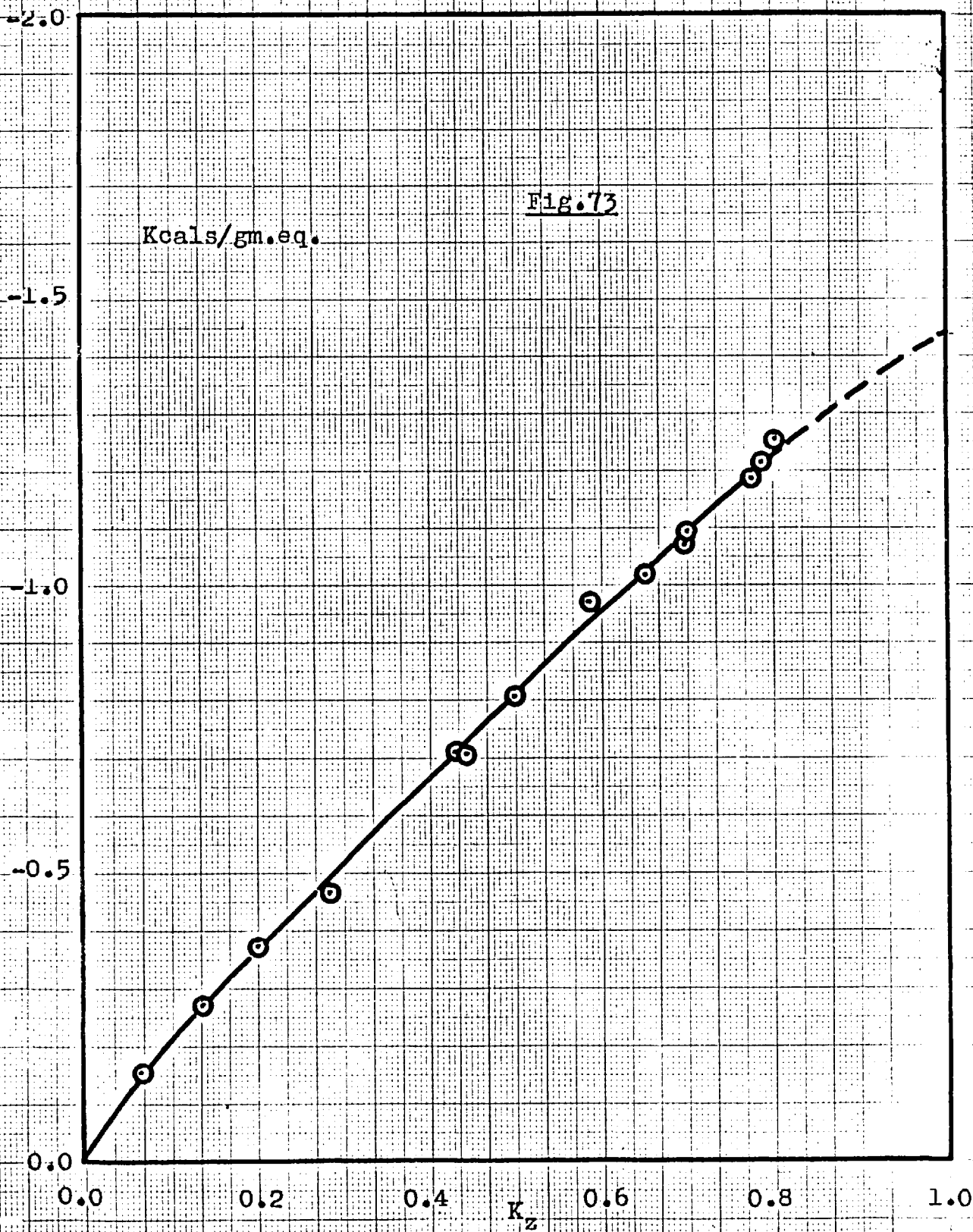
Fig.72

Na-K exchange on NaY

Standard heat of partial ion exchange

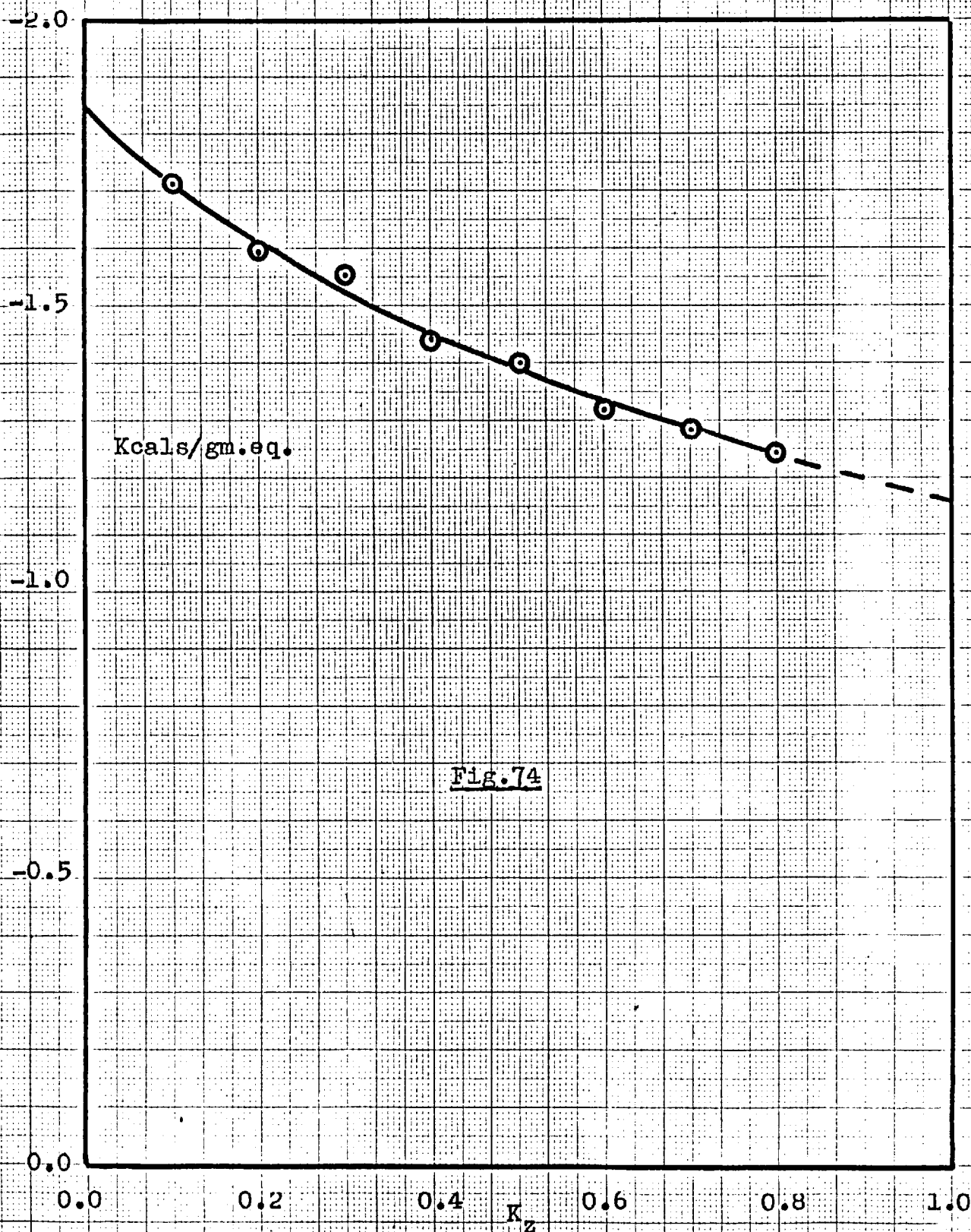
Fig. 73

Kcals/gm.eq.



Na-K exchange on NaY

Differential heat of ion exchange



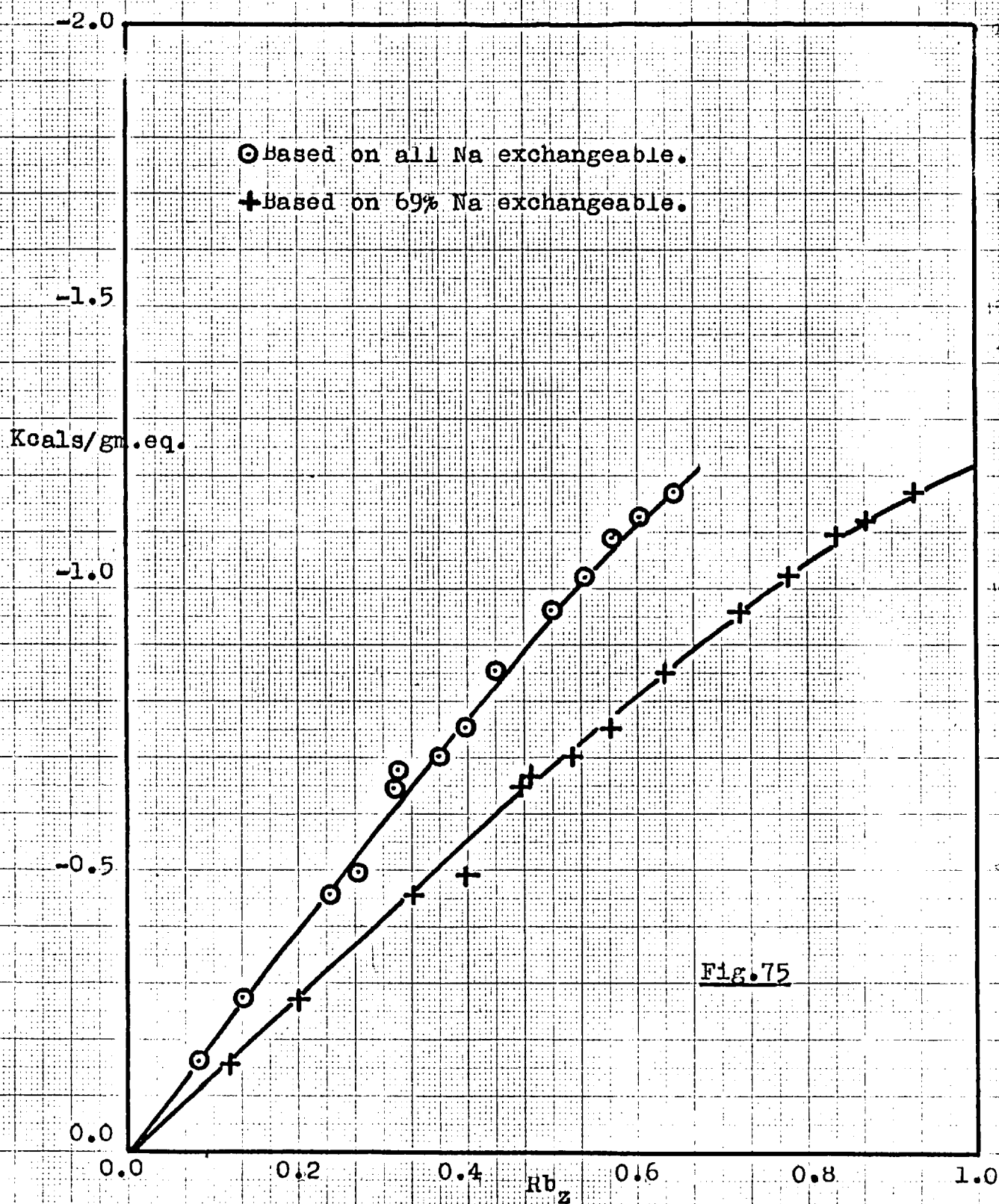
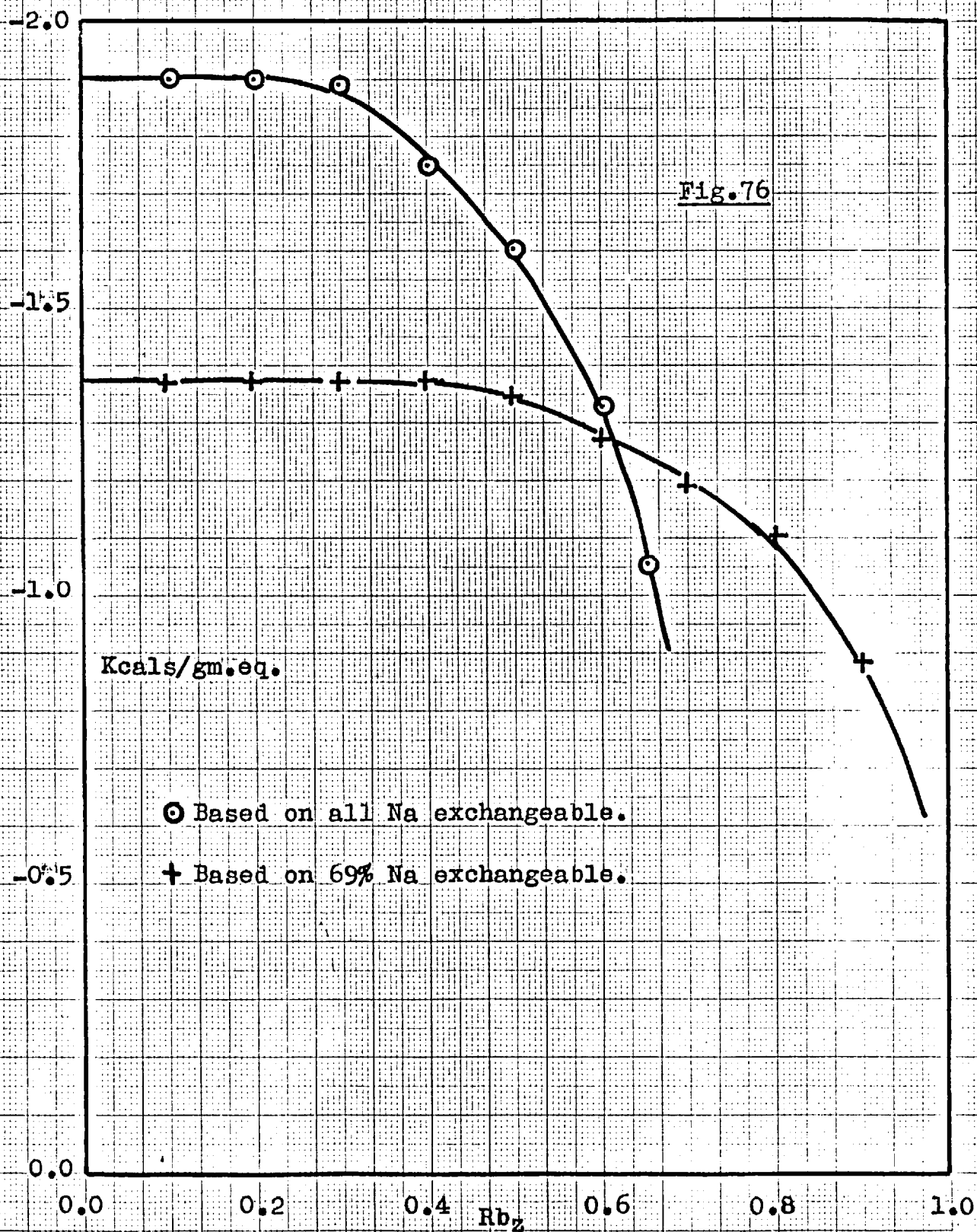
Heat of Na-Rb exchange on NaY

Fig.75

Differential heats of ion exchange



Standard heats of ion exchange

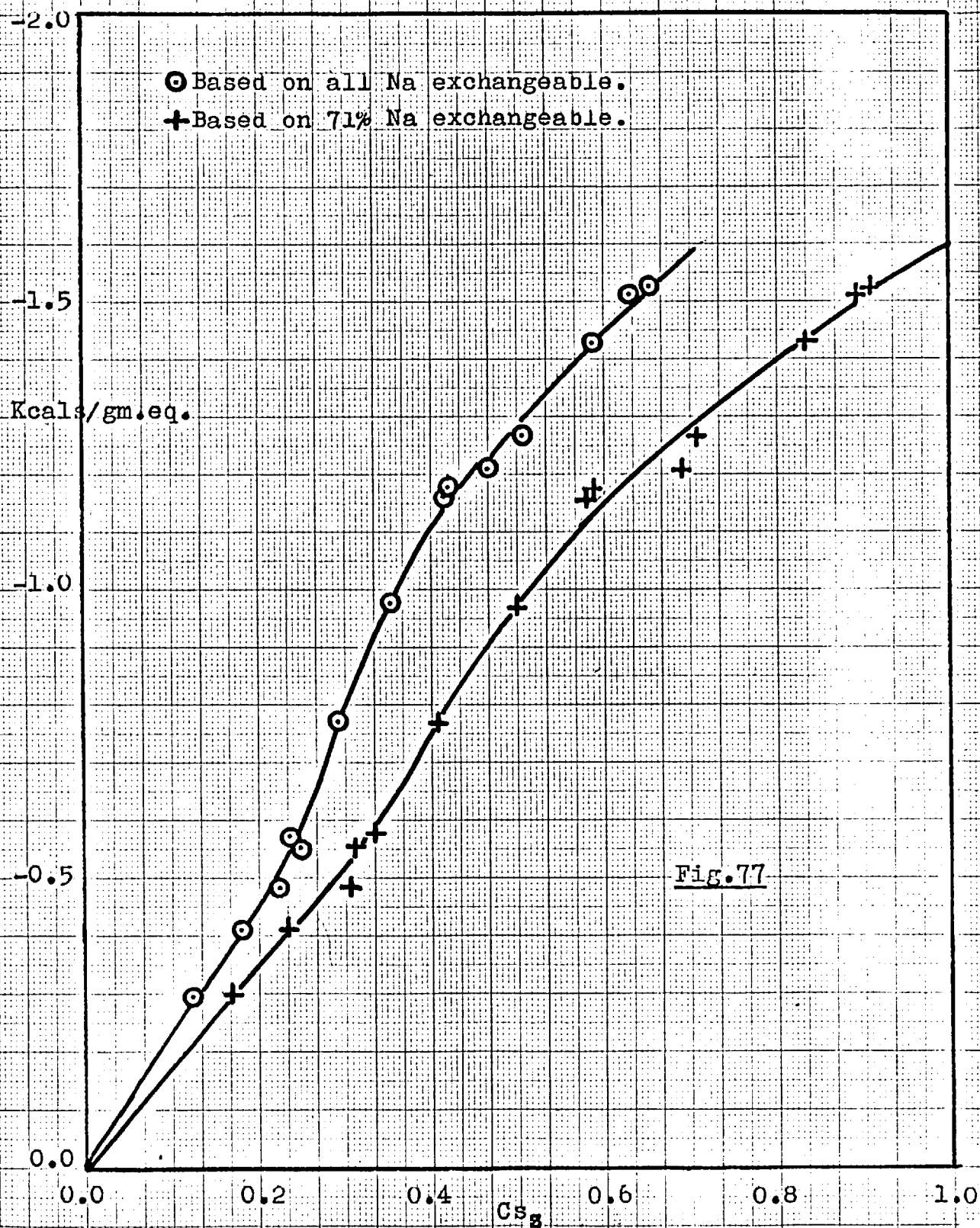
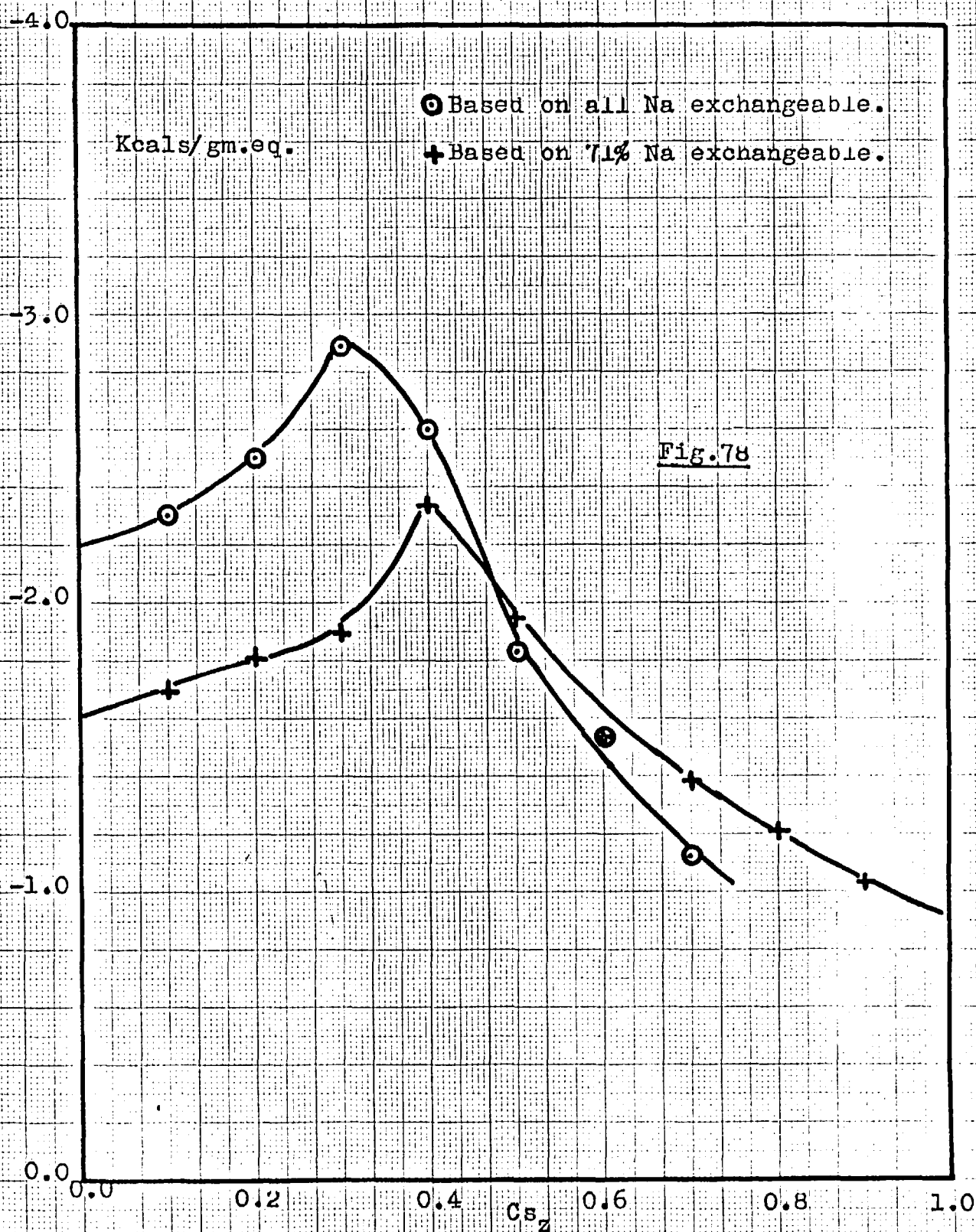


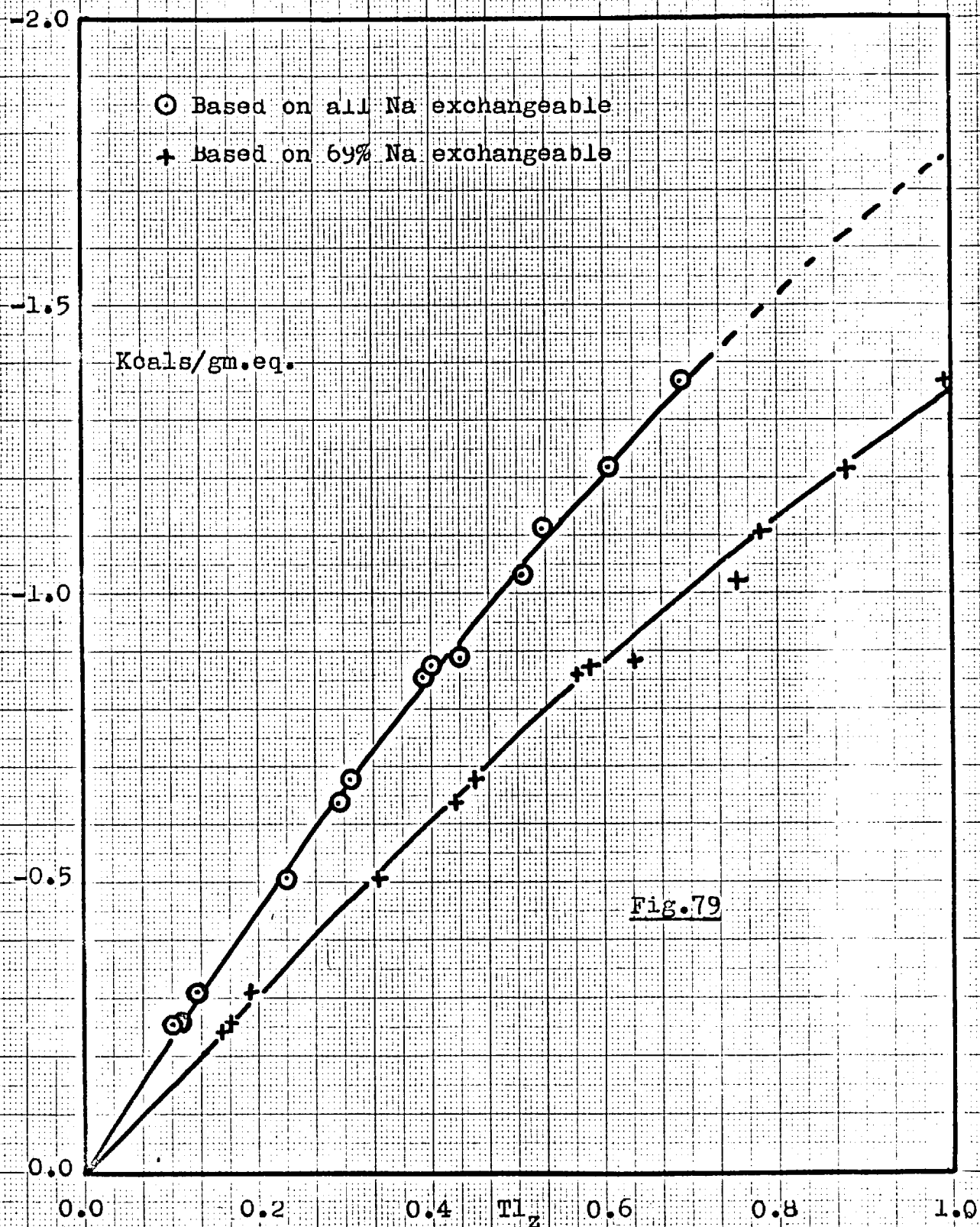
Fig. 77

Na-Cs exchange on NaY

Differential heats of ion exchange

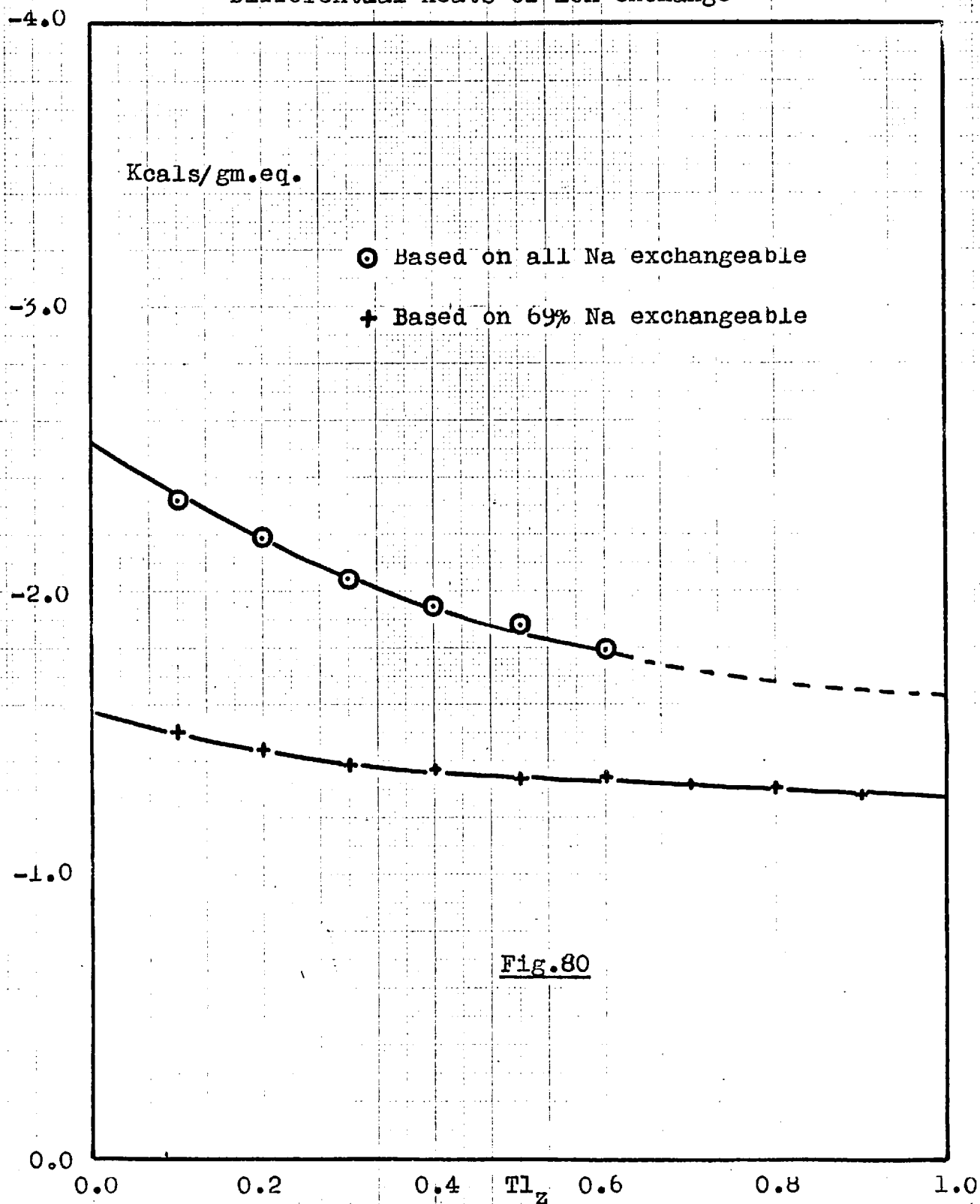


Heats of partial ion exchange, uncorrected for
heat content of solution



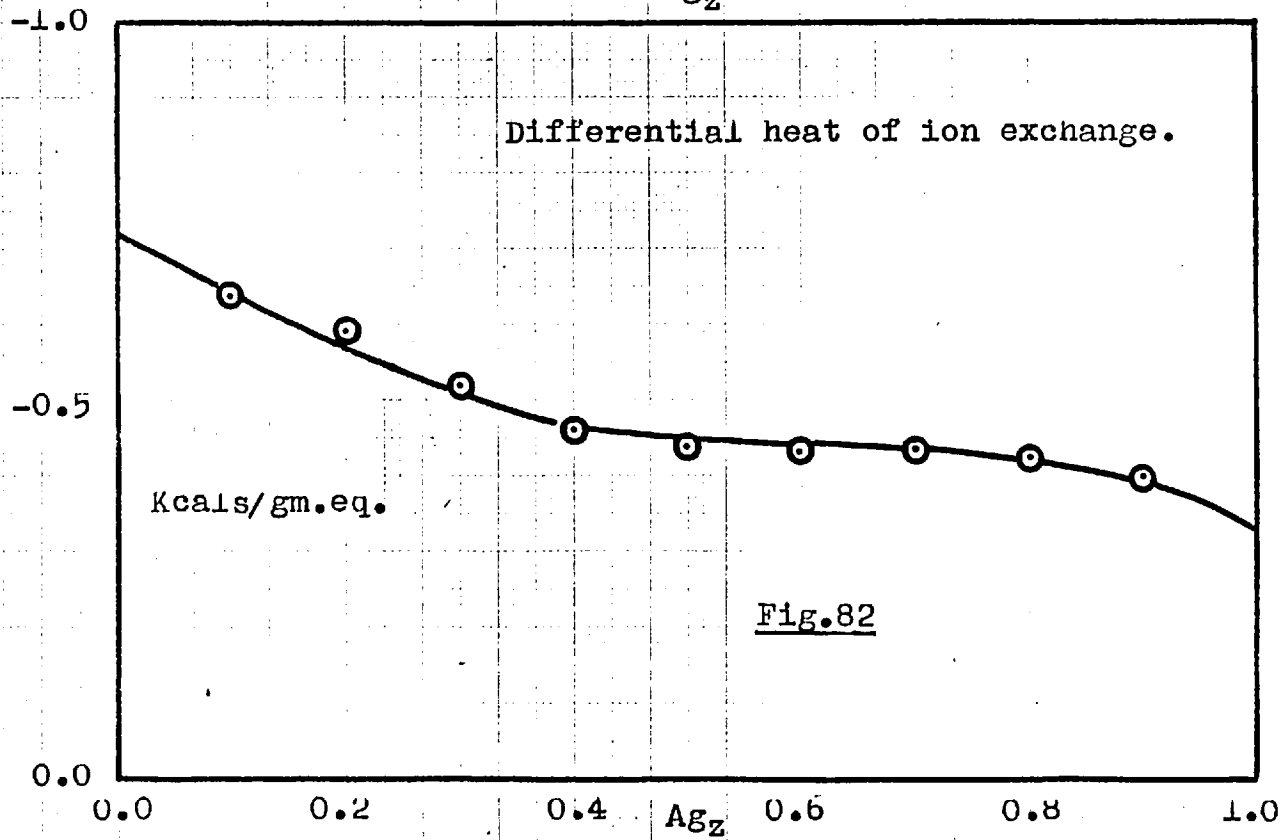
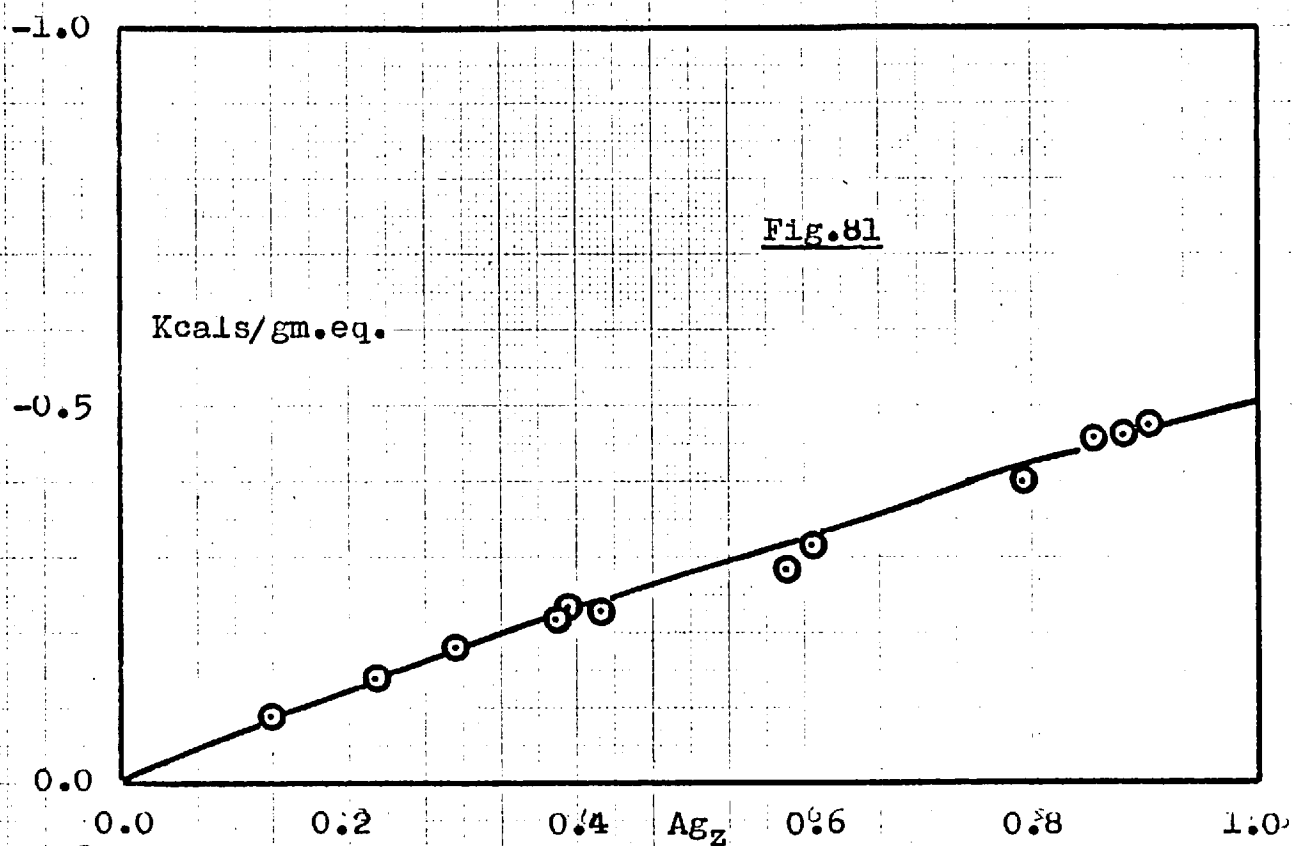
Na-Tl exchange on NaY

Differential heats of ion exchange



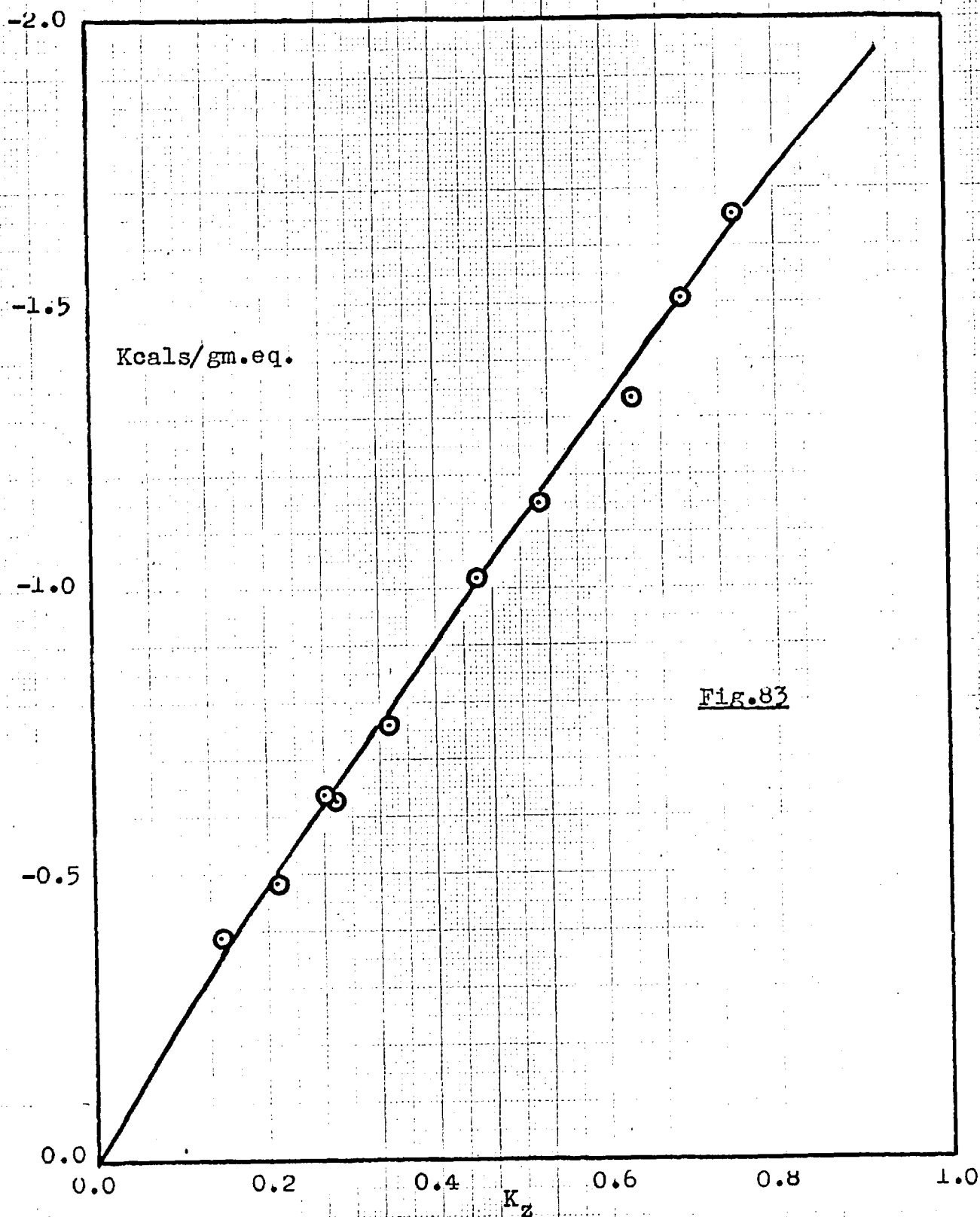
Na-Ag exchange on NaY

Standard heat of partial ion exchange.



Na-K exchange on NaY (Methanol as solvent)

Heat of partial ion exchange, uncorrected for heat content of solution.

Fig.83

The variation of the differential heats of ion exchange with cationic composition decreases continuously for the Na - Rb and Na - Tl exchanges, but exhibits a maximum for the Na - Cs exchange. This maximum occurs at $\text{Cs}_Z = 0.30$ (on an exchange capacity of 3.01 meq./gm.).

The similarity of the graphs of the standard heats of partial ion exchange for the Na - Rb and Na - Tl exchanges might be expected on the basis of the continuous dielectric theory of Barrer and Falconer (9). The only variable parameter this theory considers is the crystallographic radius of the exchanging ions. Since the ionic radii of Rb^+ and Tl^+ are the same i.e. $1.49\text{\AA}$, this theory predicts an energy change of -2.0 kcal/gm.eq. when these ions replace Na^+ in the exchanger. For a simplified picture of ion exchange reasonable agreement is found between the experimental and calculated values.

Na - Ag exchange

The variation of the standard heat of partial ion exchange with Ag_Z and the corresponding graph of $\frac{\partial \Delta H_x^0}{\partial x}$ are shown in Figs. 81 and 82 respectively. The standard heat of partial ion exchange is negative for all values of Ag_Z . The standard heat of ion exchange, obtained by extrapolation of the graph in Fig. 81 from $\text{Ag}_Z = 0.9$

to $Ag_Z = 1.0$, is -0.5 kcals/gm. eq.

Na - K exchange in methanol

The variation of the heat of partial ion exchange with cationic composition of the exchanger is shown in Fig. 83. No corrections have been made for the relative apparent molal heat contents of the methanolic solutions owing to the unavailability of the required data. However, the curve does show that the heat of ion exchange, $\Delta H = -2.05$ kcals/gm. eq. (obtained by extrapolation from $K_Z = 0.75$ to $K_Z = 1.0$) is greater than the standard heat of ion exchange for the same ions in aqueous solution i.e. $\Delta H^0 = -1.44_5$ kcals/gm. eq. A similar trend has been observed by Huang et al. (70) who reported values of $\Delta H = -0.99$ and -1.61 kcals/gm. eq. for the Na - K exchange in NaX in aqueous and methanolic solutions respectively. However, this behaviour is opposite to that predicted by the dielectric theory of Barrer and Falconer (9). Since the dielectric constant of methanol i.e. 31 is less than that of water i.e. 80, the decreasing of the dielectric constant of the solution to a value approaching that of the solid phase (taken to be 20) would reduce the differences in the potential energies of the ions on exchanging from one phase to the other. Thus the energy change associated with the exchange of one ion by another would be less.

6.5.3. Uni-divalent exchanges in chabazite

Na - Ca and Na - Sr exchanges

Exchanges involving the Ca^{2+} and Sr^{2+} ions were found to be so slow, due to the slow rate of diffusion of these ions in chabazite (105), that only 23% and 15% exchange respectively occurred in the calorimeter. Consequently the standard heats of partial ion exchange have only been determined to these limits (Figs. 84 and 85). However, the results are sufficient to show that these exchanges are endothermic although no attempt has been made to evaluate the standard heat of ion exchange.

Na - Ba exchange

The variation of the standard heat of partial ion exchange with cationic composition of the exchanger is shown in Fig. 86. Although chemical analysis has revealed that complete exchange of Na^+ by Ba^{2+} is possible, the maximum amount of exchange observed in the calorimeter measurements is 66%. The reaction is endothermic, and the extrapolated value of the standard heat of ion exchange is

$$\Delta H^{\circ} = 1.76 \text{ kcal/gm. eq.}$$

The variation of the differential heat of ion exchange with cationic composition of the exchanger is shown in Fig. 87. The differential heat, $\frac{\partial \Delta H^{\circ}_x}{\partial x}$ is

positive for all values of Ba_Z in the range $Ba_Z = 0$ to $Ba_Z = 1.0$. Initially, the value of $\frac{\partial \Delta H^\circ}{\partial x}$ is smaller than the standard heat of ion exchange i.e. $\frac{\partial \Delta H^\circ}{\partial x} = 0.7$ kcals/gm. eq. at $Ba_Z = 0$, but rises to a value $\frac{\partial \Delta H^\circ}{\partial x} = 3.48$ kcals/gm. eq. at $Ba_Z = 1$, greater than the standard heat of ion exchange.

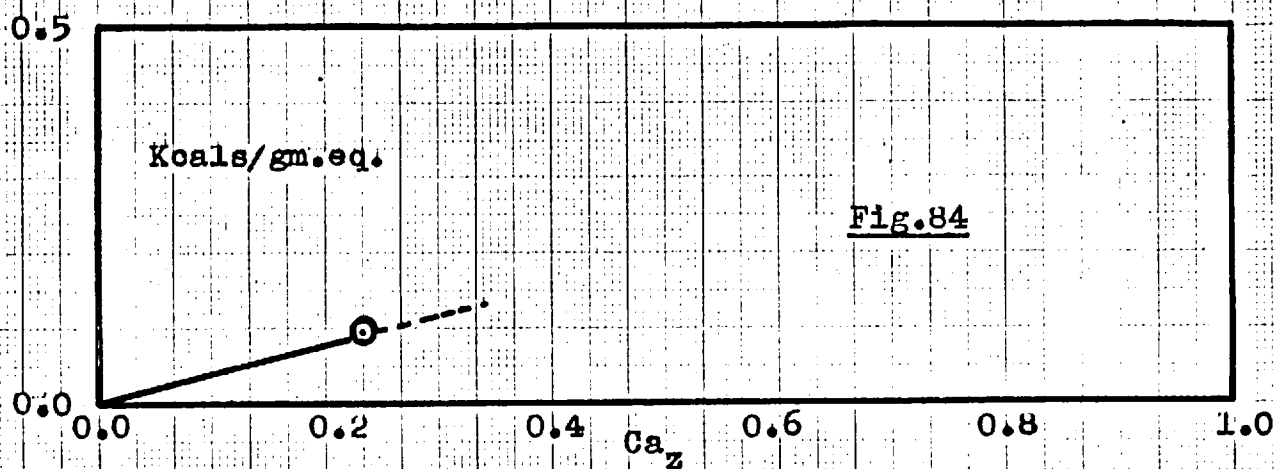
Na - Pb exchange

The variation of the heat of partial ion exchange with cationic composition of the exchanger is shown in Fig. 88, and the corresponding graph of the differential heat in Fig. 89. The ordinates of these graphs do not represent the standard heats of partial ion exchange and corresponding differential heat since no corrections have been made for the relative apparent molal heat contents of the $NaNO_3$ and $Pb(NO_3)_2$ solutions. In the case of the exchanges involving Na - acetate and Tl - acetate solutions, it was assumed that these heat contents were small provided the solutions were dilute ($< 0.1M$). However, for exchanges involving ions of different valencies this assumption cannot be justified. For example, in the Na - Ba exchange in chabazite the correction due to the molal heat contents of the $NaCl$ and $BaCl_2$ at $0.1M$ initial molality was approximately 0.08 kcals/gm. eq.

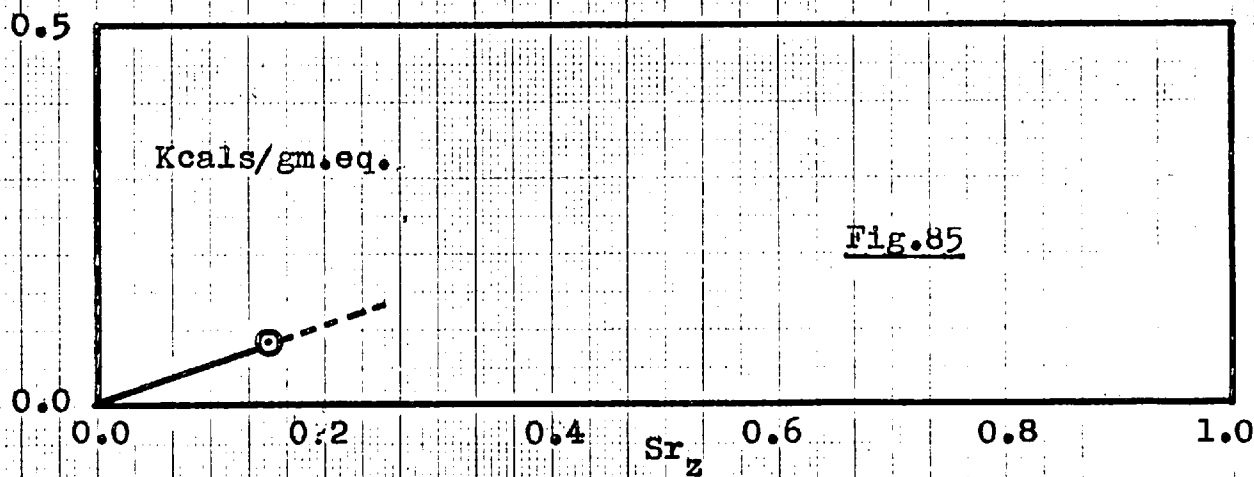
The heat of complete ion exchange for the $Na \rightarrow Pb$

Standard heat of partial ion exchange for the
(Na-Ca) exchange on Chabazite.

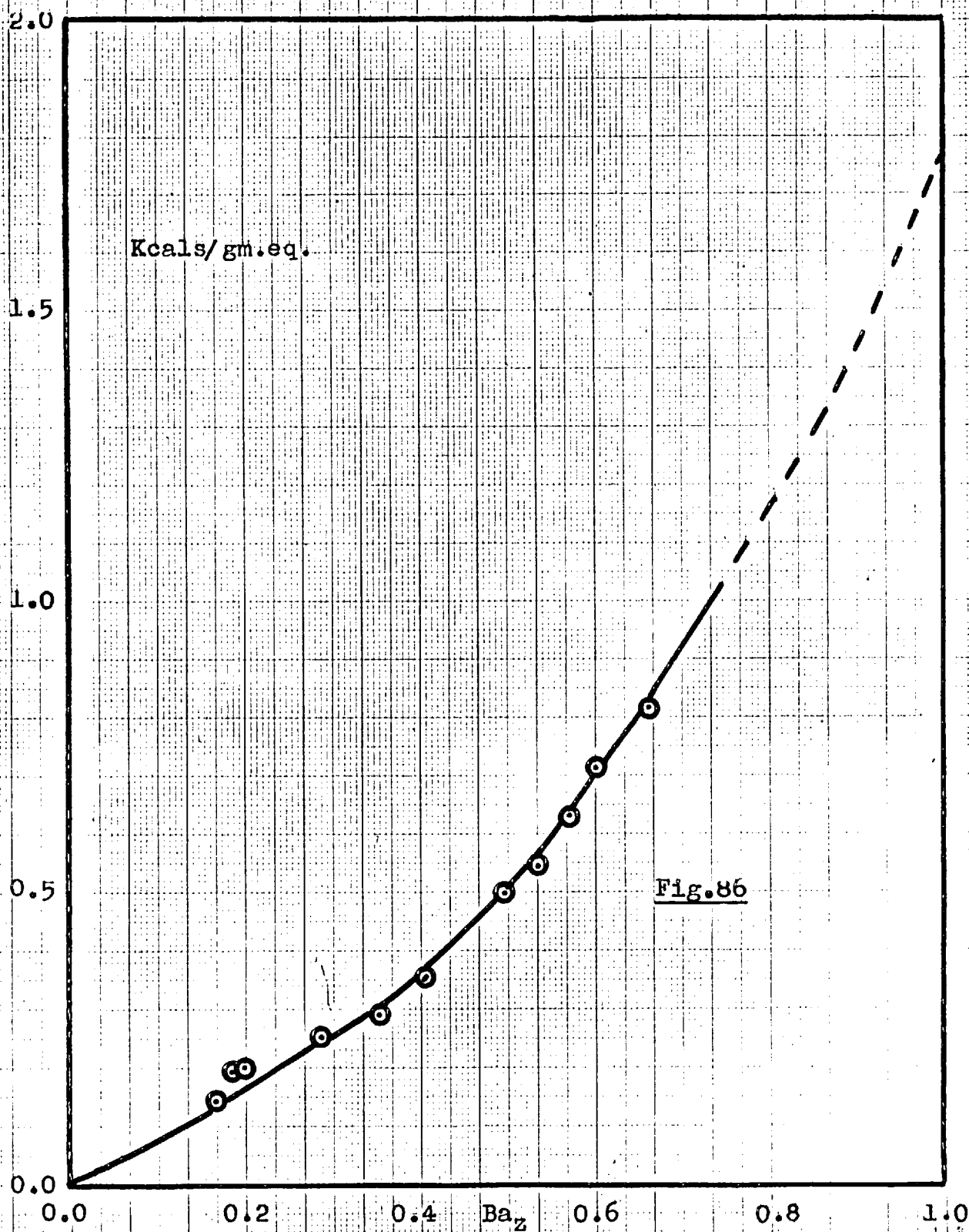
248



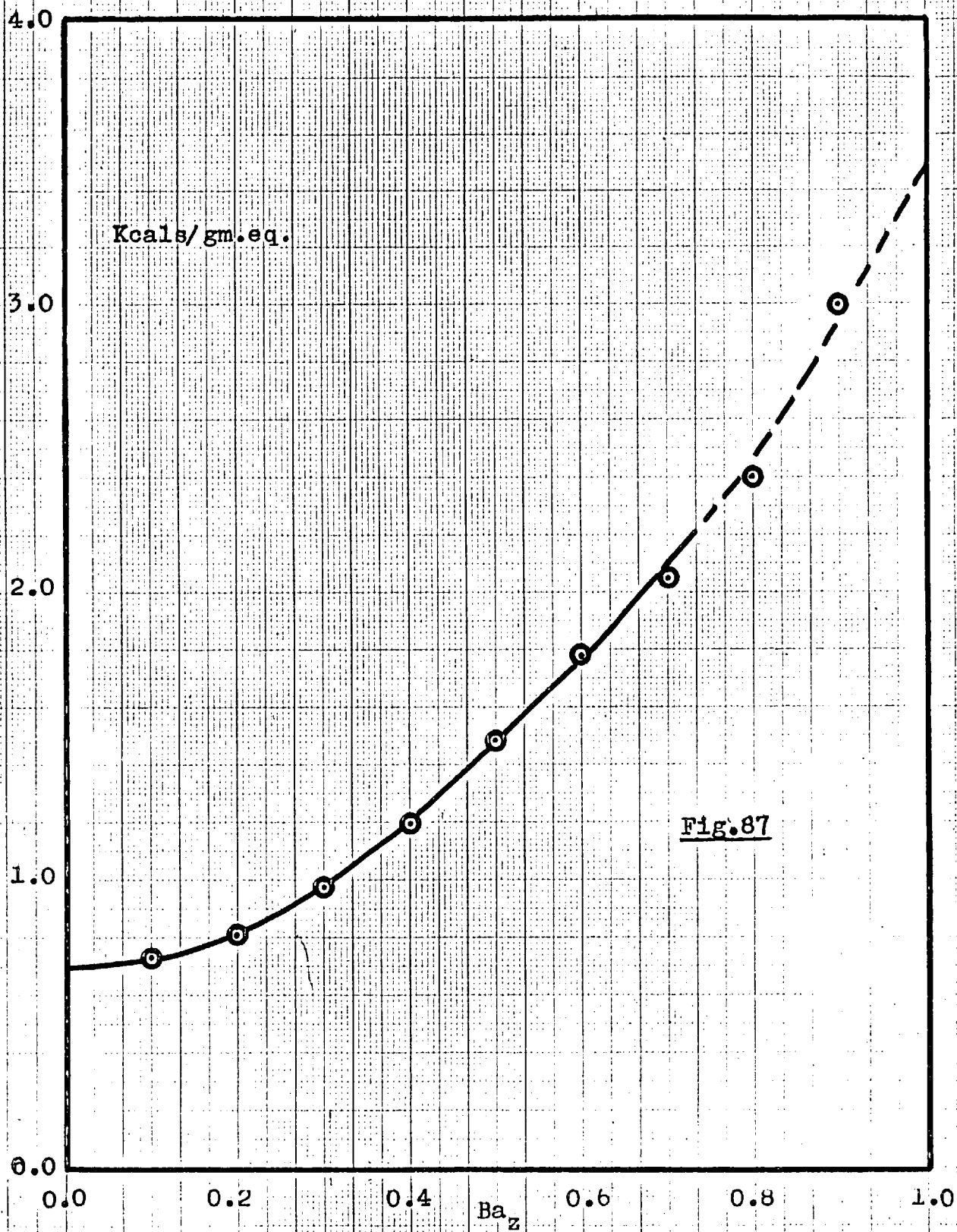
Standard heat of partial ion exchange for the
(Na-Sr) exchange on Chabazite.



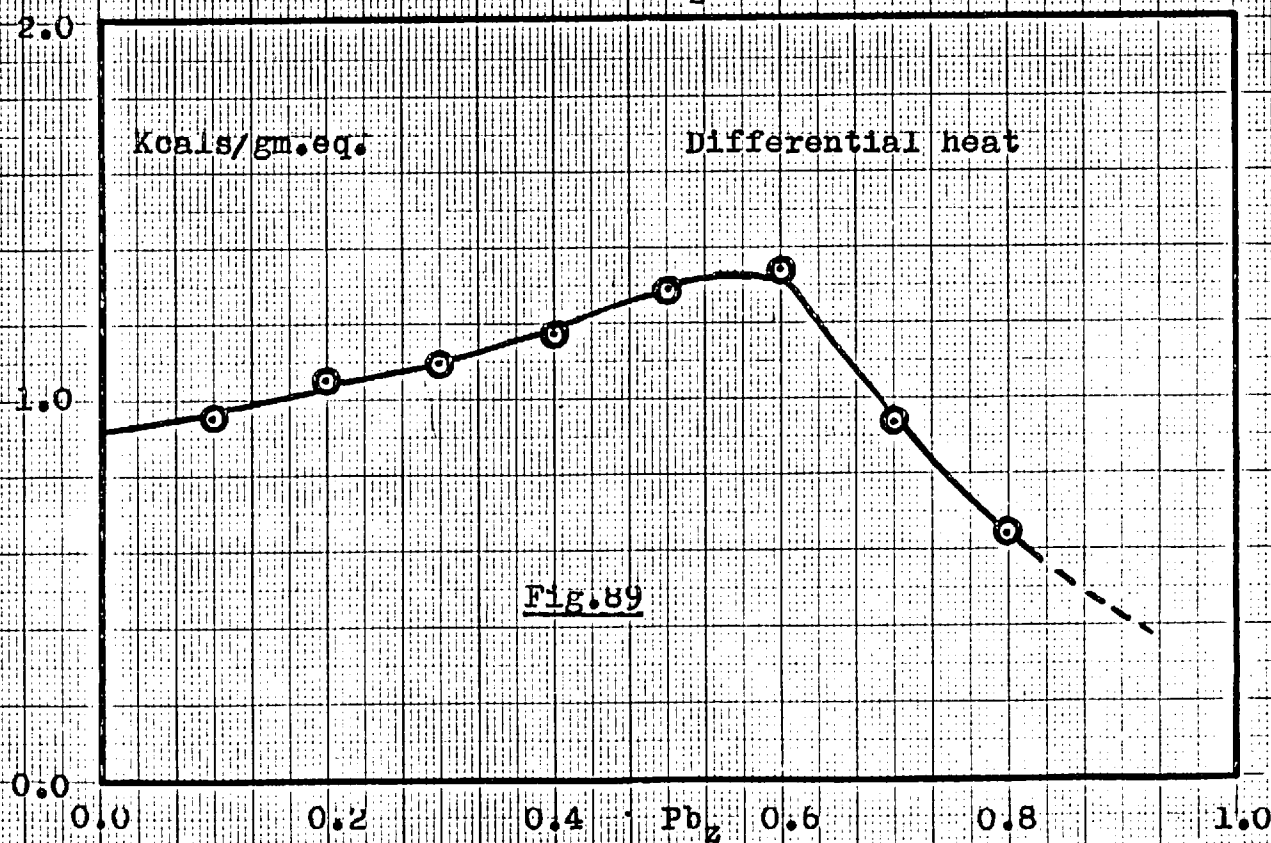
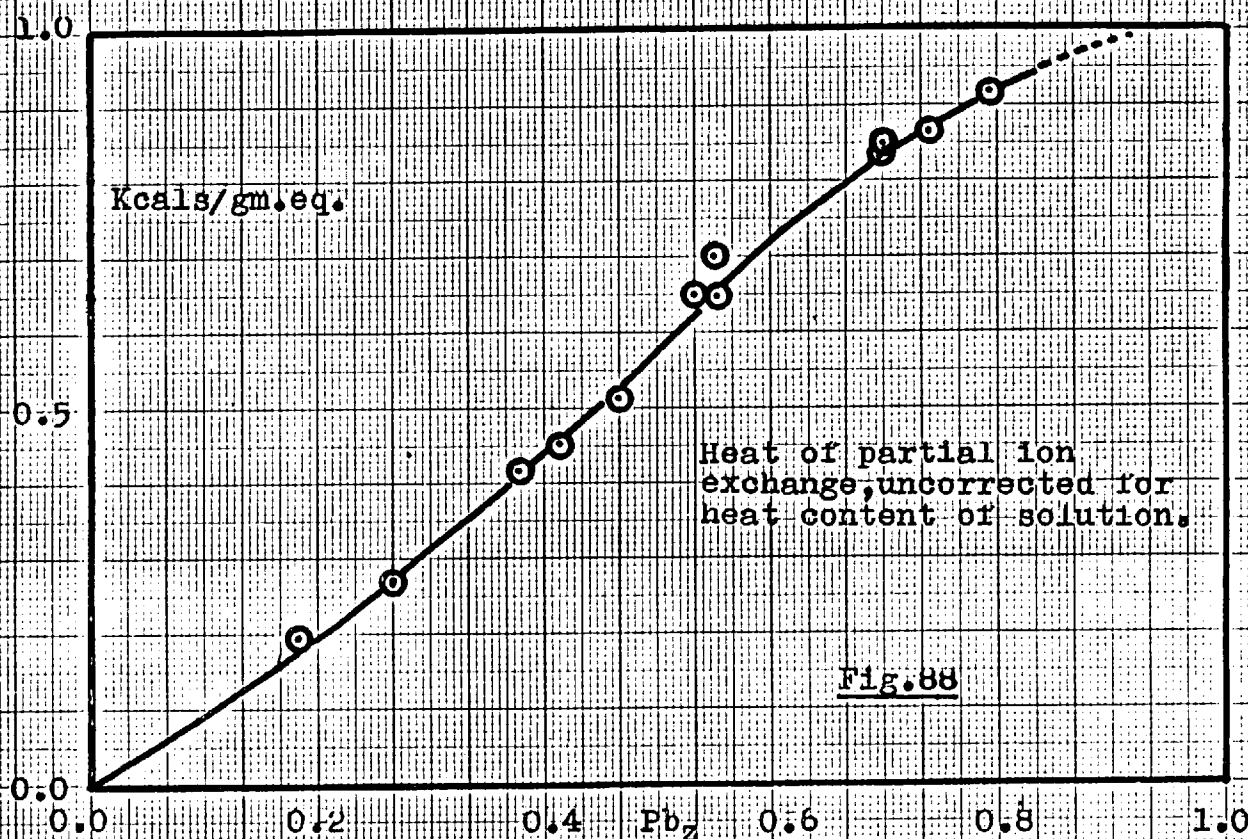
Standard heat of ion exchange



Differential heat of ion exchange



Na-Pb exchange on Chabazite.



exchange can be obtained by extrapolation of the curve from $Pb_Z = 0.80$ to $Pb_Z = 1.0$. Thus

$$\Delta H = 1.03 \text{ kcals/gm. eq.},$$

although this figure might differ from the standard heat of exchange by as much as 10% due to the correction for the heat content necessary.

6.5.4. Uni-divalent exchanges in NaY

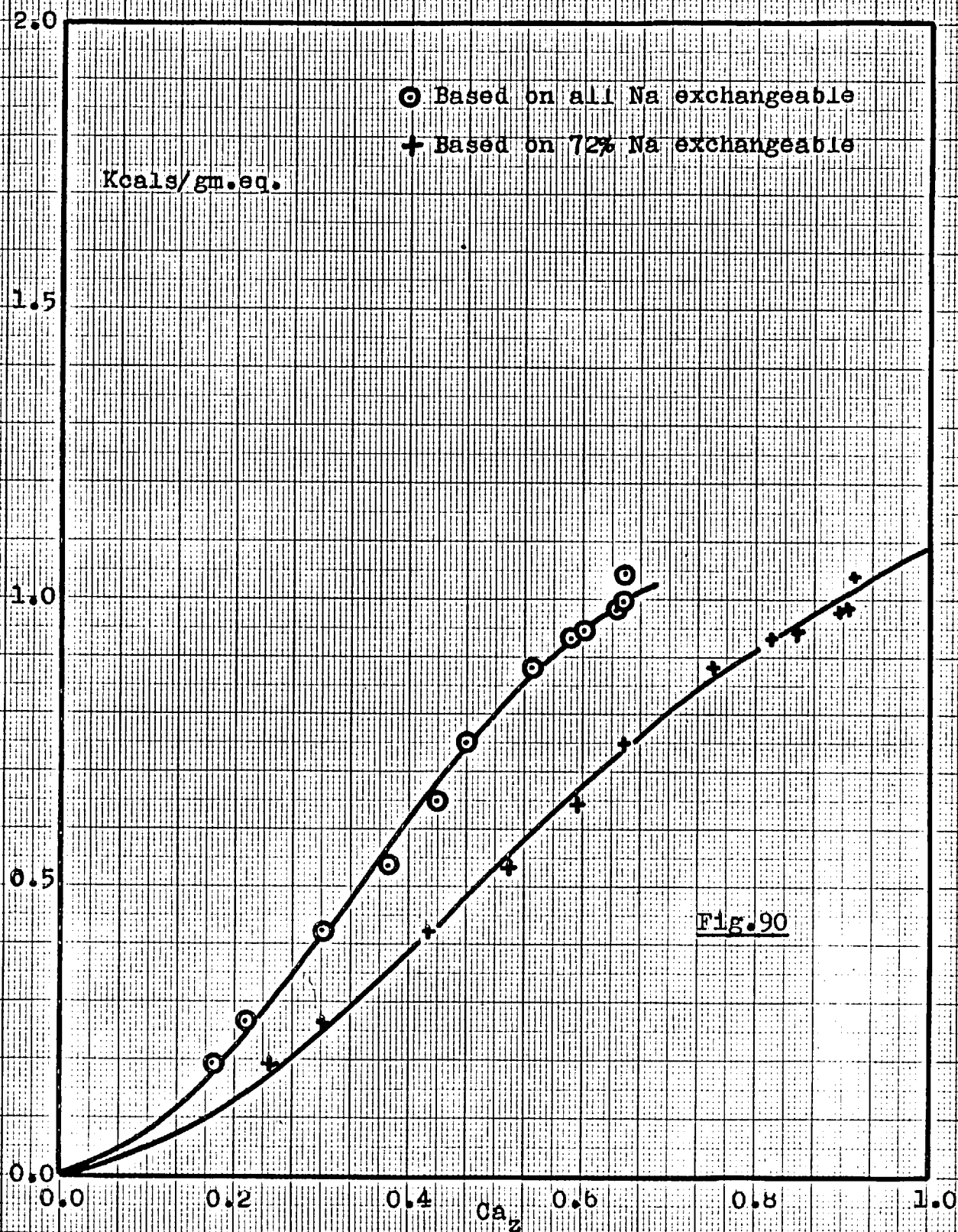
For exchanges involving the ions Ca^{2+} , Sr^{2+} and Ba^{2+} , complete replacement of the Na^+ in NaY by these ions was not possible under the conditions used. The maximum amount of exchange was 72%, 69% and 69% replacement for Ca^{2+} , Sr^{2+} and Ba^{2+} exchanges respectively.

The variation of the standard heat of partial ion exchange for the Na - Ca exchange is shown in Fig. 90 and the corresponding graph of the differential heat in Fig. 91. The standard heat of partial ion exchange is positive for all values of Ca_Z i.e. the reaction is endothermic. The standard heat of ion exchange, ΔH_x is

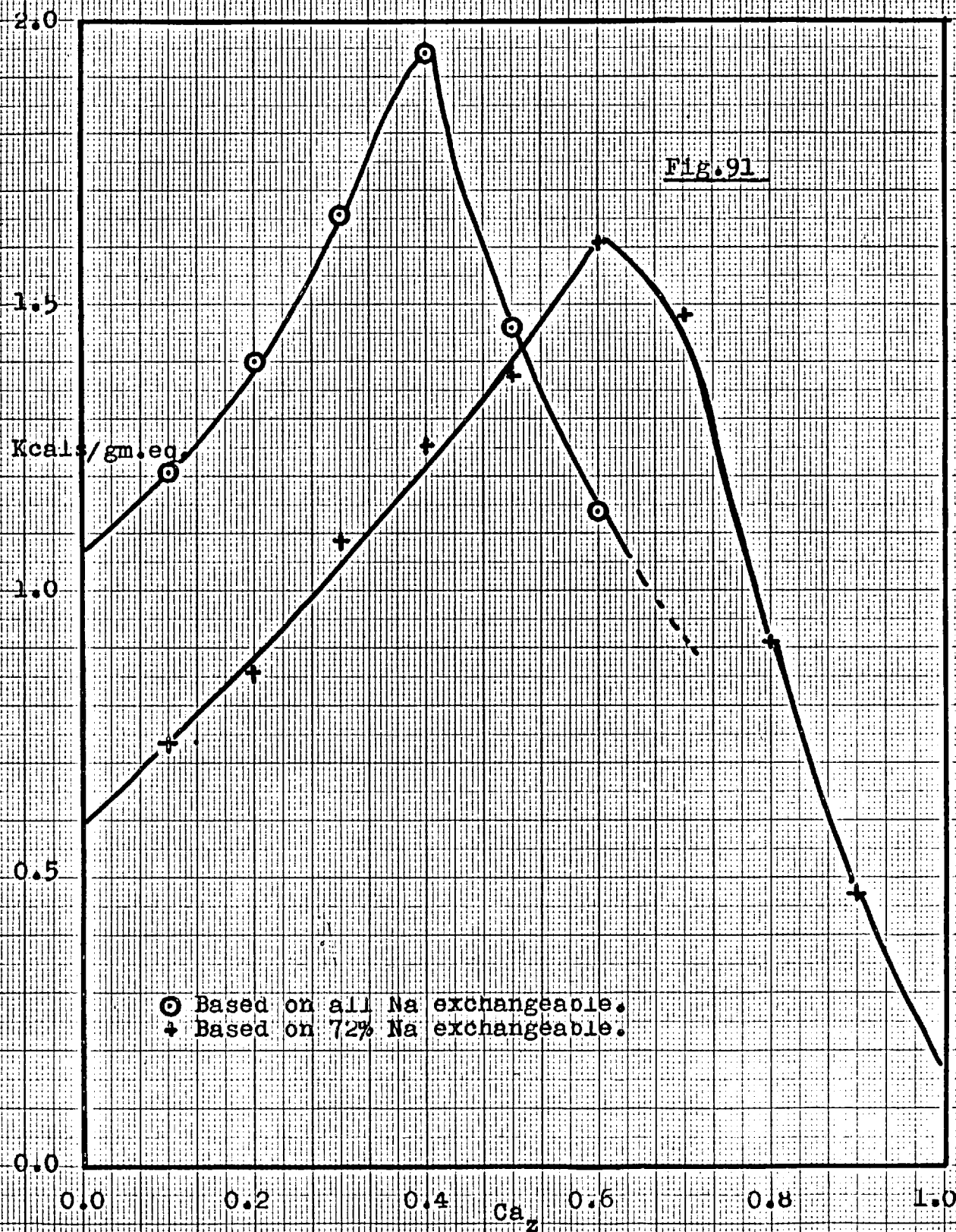
$$\Delta H_x = 1.09 \text{ kcals/gm. eq. (based on 72\% Na exchangeable)}.$$

The differential heat of ion exchange rises from $Ca_Z = 0$ to $Ca_Z = 0.6$ (based on 72% Na^+ exchangeable). From $Ca_Z = 0.6$ to $Ca_Z = 1.0$, $\frac{\partial \Delta H_x}{\partial x}$ decreases rapidly.

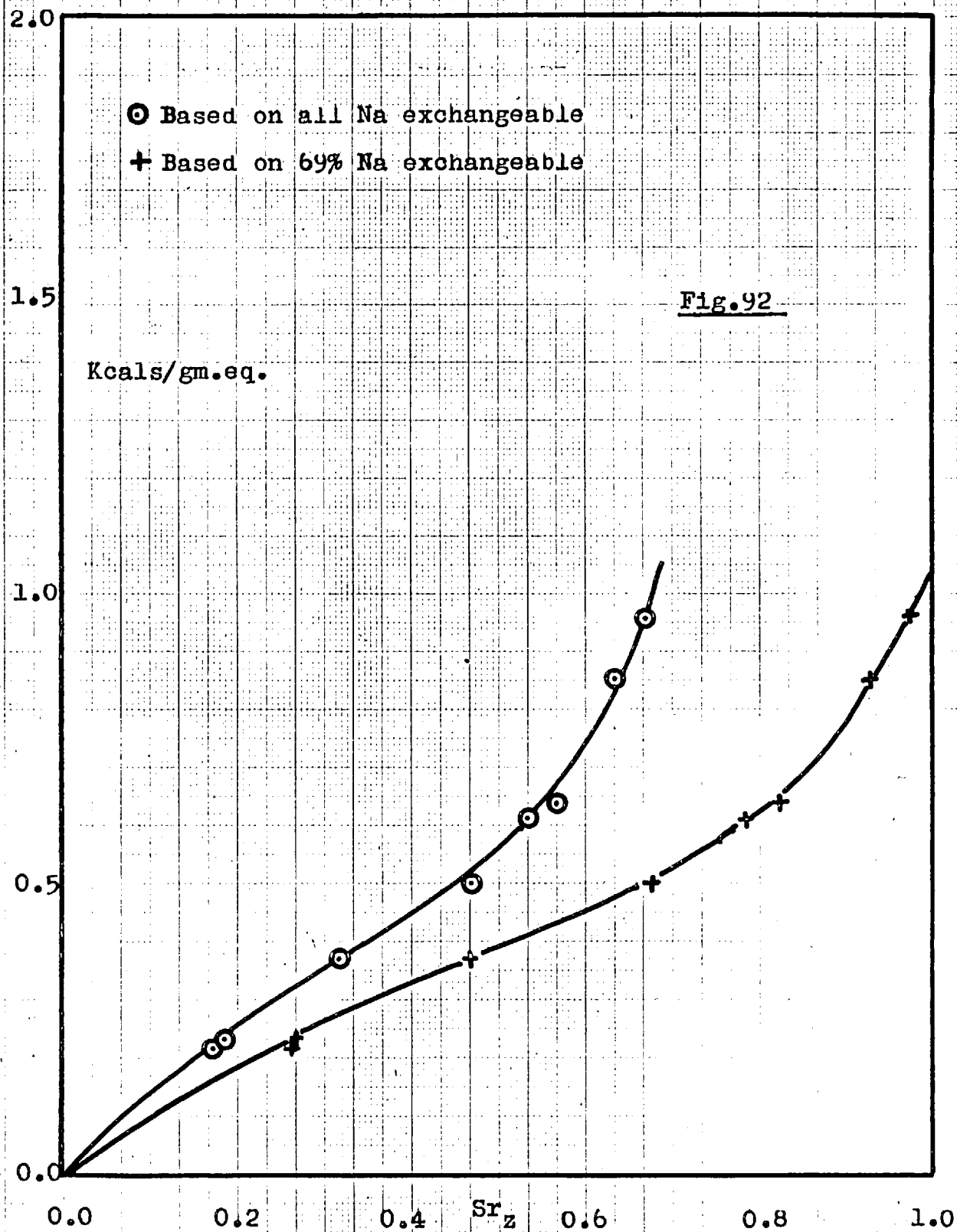
Standard heats of partial ion exchange



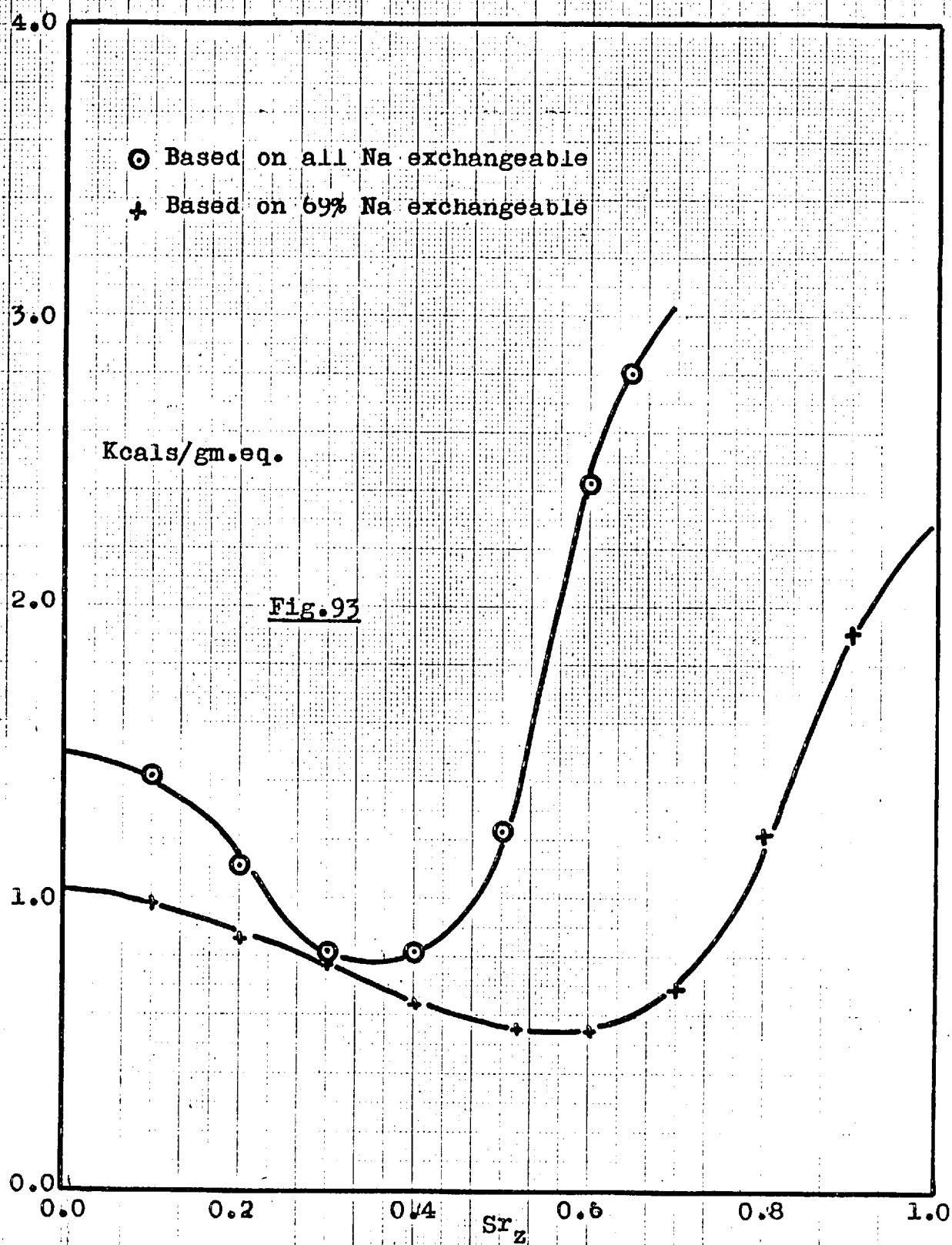
Differential heat of ion exchange

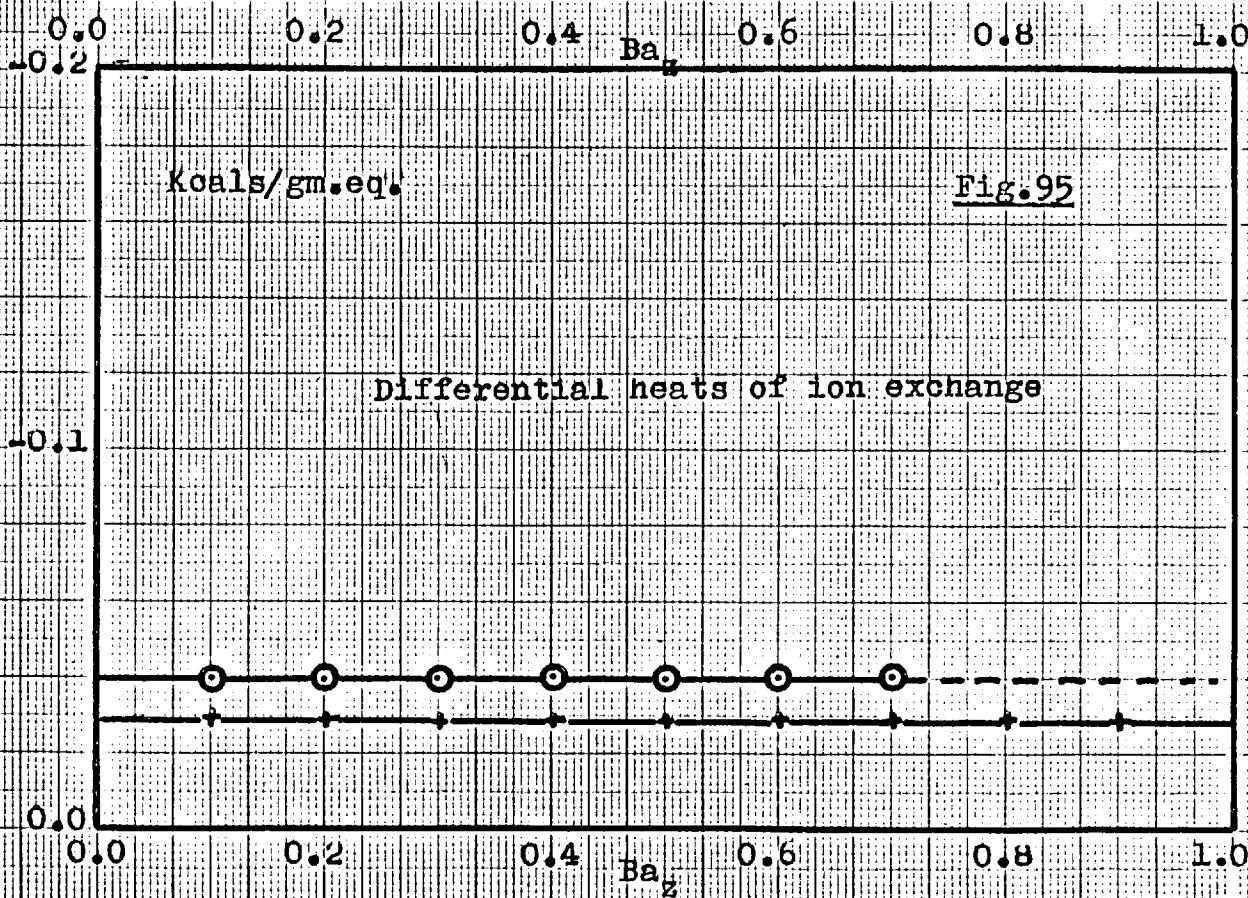
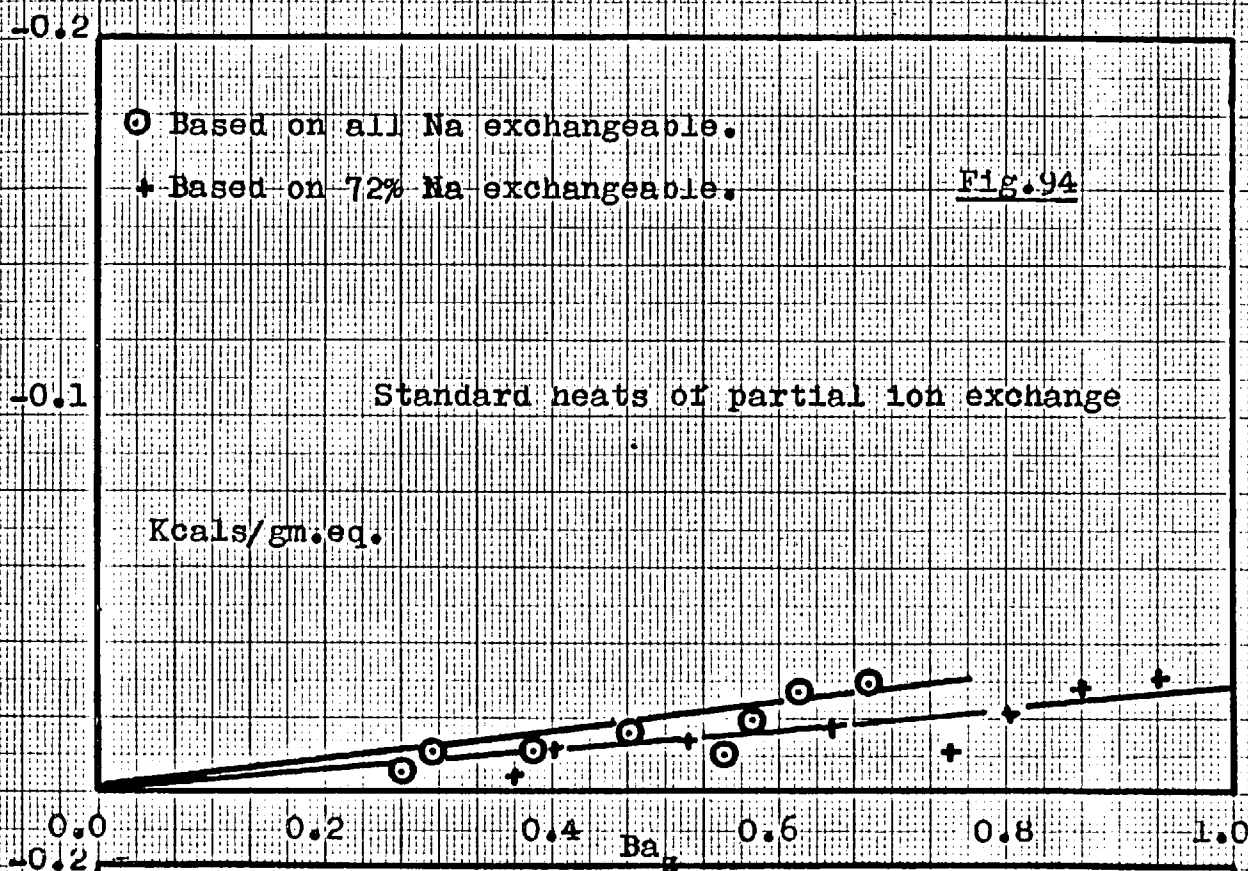


Standard heats of partial ion exchange



Differential heats of ion exchange



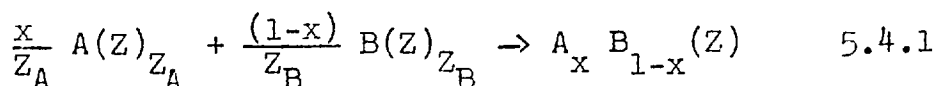


The variation of the standard heat of partial ion exchange for the Na - Sr exchange is shown in Fig. 92 and the corresponding graph of the differential heat in Fig. 93. The standard heat of partial ion exchange is positive for all values of Sr_Z , and the standard heat of ion exchange is $\Delta H^\circ = 1.03$ kcals/gm. eq. of exchanger (based on 69% Na^+ exchangeable). The graph of $\frac{\partial \Delta H^\circ}{\partial x}$ against Sr_Z has a minimum at $Sr_Z \approx 0.55$ (based on 69% Na^+ exchangeable).

The Na - Ba exchange in NaY was found to be slightly exothermic with a standard heat of ion exchange, $\Delta H^\circ = -0.03$ kcals/gm. eq. (on the basis of 69% Na^+ exchangeable). The variation of the standard heat of partial ion exchange and the corresponding differential heat are shown in Figs. 94 and 95 respectively. The standard heat for this exchange is the smallest that has been measured calorimetrically.

6.6. Thermodynamic functions for the formation of the mixed exchanger phase

The formation of 1 equivalent of the mixed exchanger $A_x B_{1-x}(Z)$ in its standard state from its components, both in their standard states, can be represented by the equation



where $A_x \equiv x$ equivalents of pure $A(Z)_{Z_A}$ in the mixed exchanger. The thermodynamic functions, free energy, ΔG_x^M ; the heat change, ΔH_x^M ; and the entropy change ΔS_x^M were obtained from the experimental data using equations 5.4.10, 5.4.4 and 5.4.12 respectively.

If the mixed exchanger is considered as an ideal solution of its components, then the chemical potentials in the mixed exchanger can be related to their mole fractions

$$\mu_{A(Z)_{Z_A}}^{(id)} = \mu_{A(Z)_{Z_A}}^o + RT \ln X_{A(Z)} \quad 6.6.1$$

$$\text{where } X_{A(Z)_{Z_A}} = \frac{Z_B A_Z}{Z_B A_Z + Z_A B_Z} \quad 6.6.2$$

The ideal free energy of mixing of the components of the solid solution is then given by

$$\Delta G_x^{M(id)} = \frac{x}{Z_A} RT \ln X_{A(Z)_{Z_A}} + \frac{(1-x)}{Z_B} RT \ln X_{B(Z)_{Z_B}} \quad 6.6.3$$

For an ideal solution the heat of mixing of the components $\Delta H_x^{M(id)}$ is zero; thus the corresponding ideal entropy change $\Delta S_x^{M(id)}$ is given by

$$\Delta S_x^{M(id)} = -\frac{x}{Z_A} R \ln X_{A(Z)_{Z_A}} - \frac{(1-x)}{Z_B} R \ln X_{B(Z)_{Z_B}} \quad 6.6.4$$

Thus it is possible to compare the functions

ΔG_x^M , ΔH_x^M and $T\Delta S_x^M$ in the exchange systems studied with the corresponding functions when it is assumed that the mixed exchanger is an ideal solution of its components.

The non-ideality of the free energy change of the exchange reaction represented by equation 5.4.1 is given by the difference $\Delta G_x^M - \Delta G_x^{M(id)}$. Thus for uni-univalent exchanges, combining equations 5.4.10 and 6.6.3, one obtains

$$\Delta G_x^M - \Delta G_x^{M(id)} = xRT \ln f_A(Z) + (1-x)RT \ln f_B(Z) \quad 6.6.5$$

since equivalent fractions and mole fractions are the same.

For several uni-univalent exchanges in NaY and chabazite, the activity coefficients of the components were given by Kielland's relationships (82) i.e.

$\log f_A(Z) = C(1-x)^2$ and $\log f_B(Z) = Cx^2$, where $2C$ is the slope of the graph of $\log K_c$ against A_Z . Thus the measure of the non-ideality of the free energy change is given by

$$\Delta G_x^M - \Delta G_x^{M(id)} = 2.303 RT C x(1-x) \quad 6.6.6$$

The statistical approach of Barrer and Falconer (9) has shown that the Kielland constant C can be related to the energy $\frac{2\omega}{Z}$ involved in placing two B^+ ions on adjacent sites in an A^+ rich lattice, relative to

the energy change involved in placing two A^+ ions or an A^+ and a B^+ ion on adjacent sites. They have derived the relation

$$C = \frac{\omega}{2.303} kT \cdot \frac{n_A + n_B}{n} \quad 3.4.10$$

between the energy term ω and the constant C .

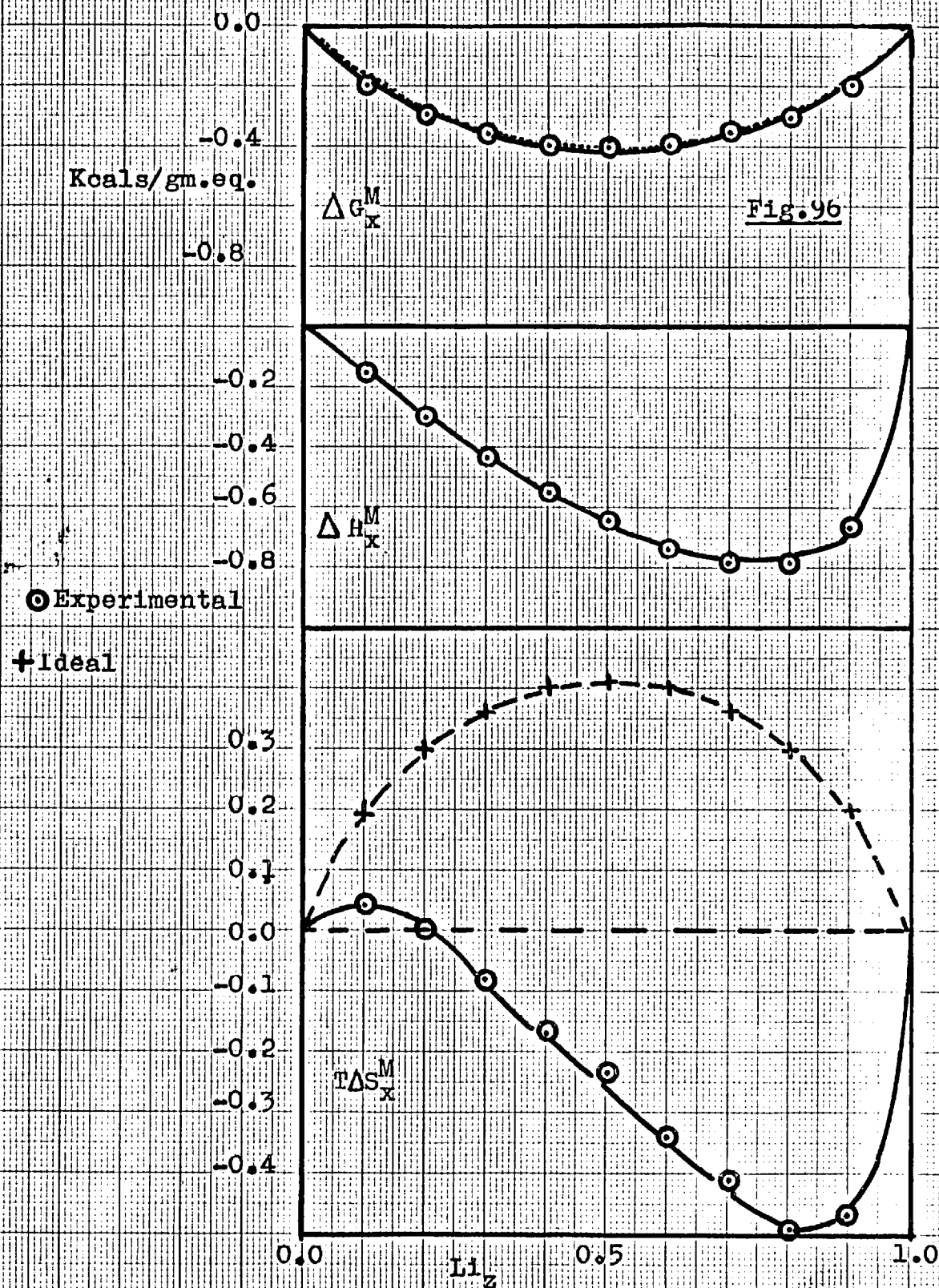
For the uni-univalent exchanges that have been studied the constant C has been found to be negative or zero but never positive. Consequently in terms of the proposed model ω is positive, i.e. there is an increase in energy of the system when two B^+ ions occupy adjacent sites in the A^+ rich lattice. The magnitude of this energy term can be estimated from equation 3.4.10, and the results are shown in Table 15 for several exchanges in chabazite and NaY.

Table 15

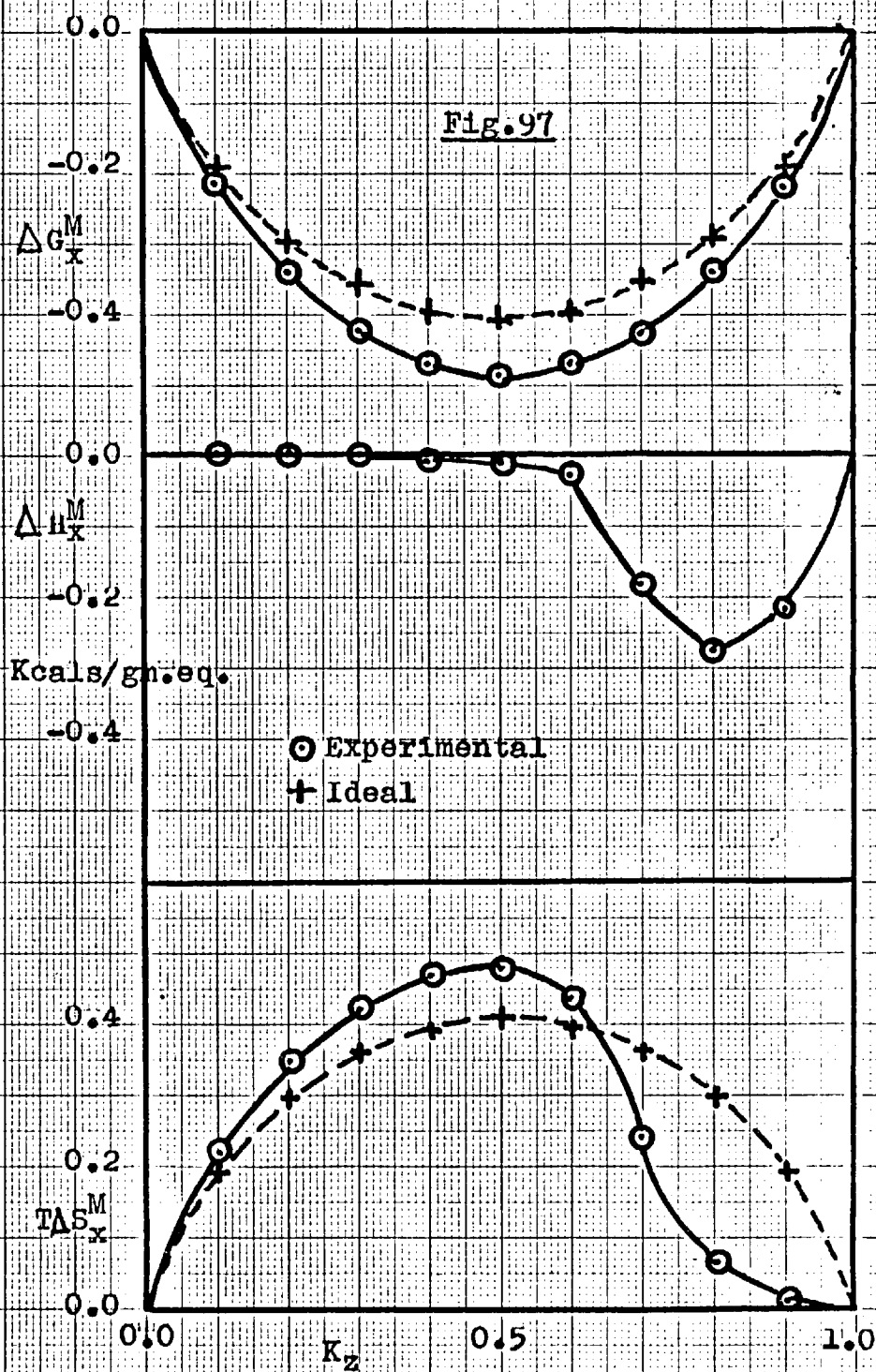
Exchange System	$\omega \cdot \frac{n_A + n_B}{n}$	keals/gm. ion
	<u>Chabazite</u>	<u>NaY</u>
Na - Li	0.000	-
Na - K	0.314	0.887
Na - Rb	0.873	0.191
Na - Cs	0.396	1.078
Na - Ag	0.396	0.102
Na - Tl	-	0.082
Na - NH_4	0.518	-

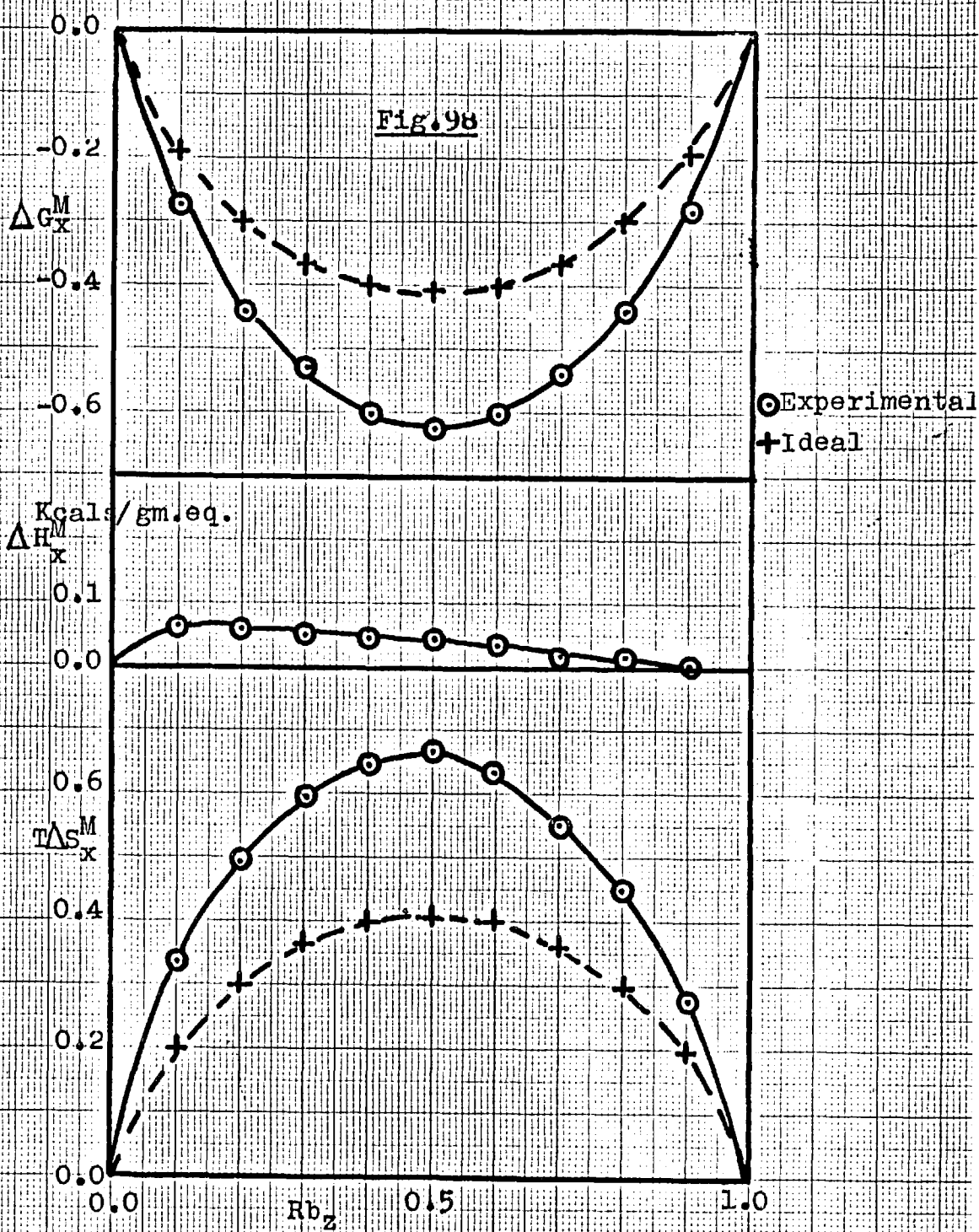
Thermodynamic functions for the formation of the mixed(Na-Li) Chabazite exchanger.

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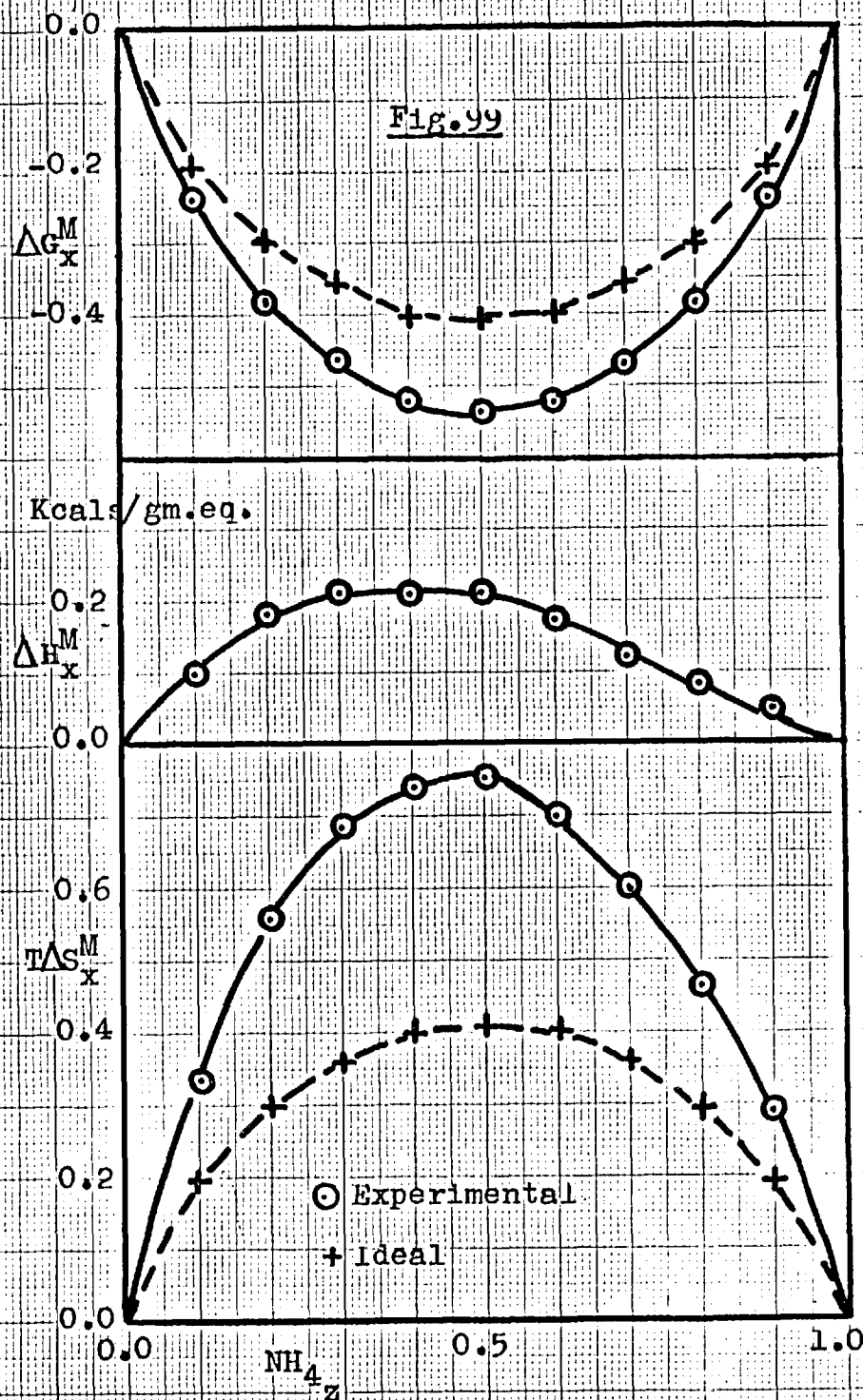
Thermodynamic functions for the formation
of the mixed (Na-K) Chabazite exchanger.

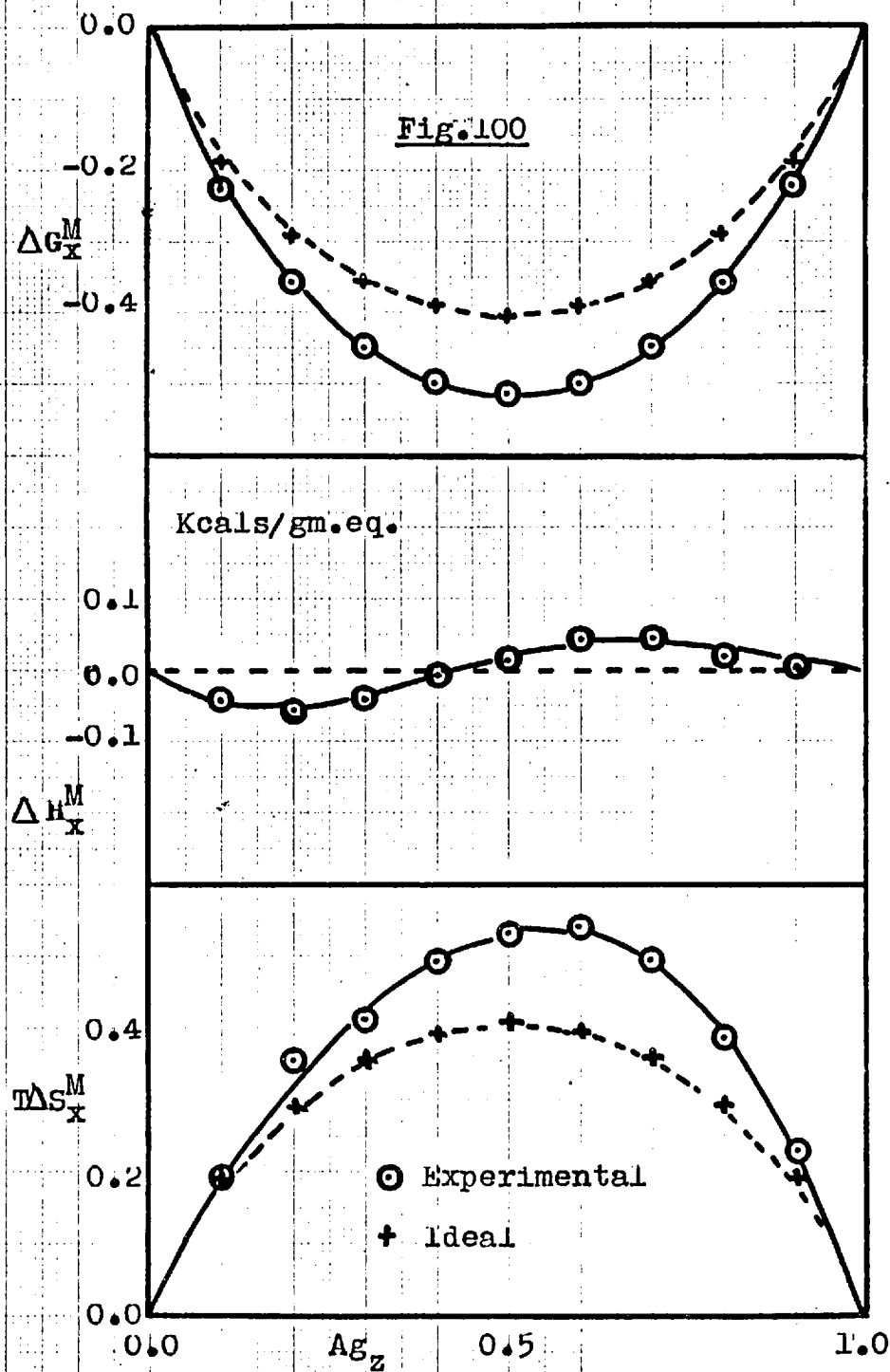


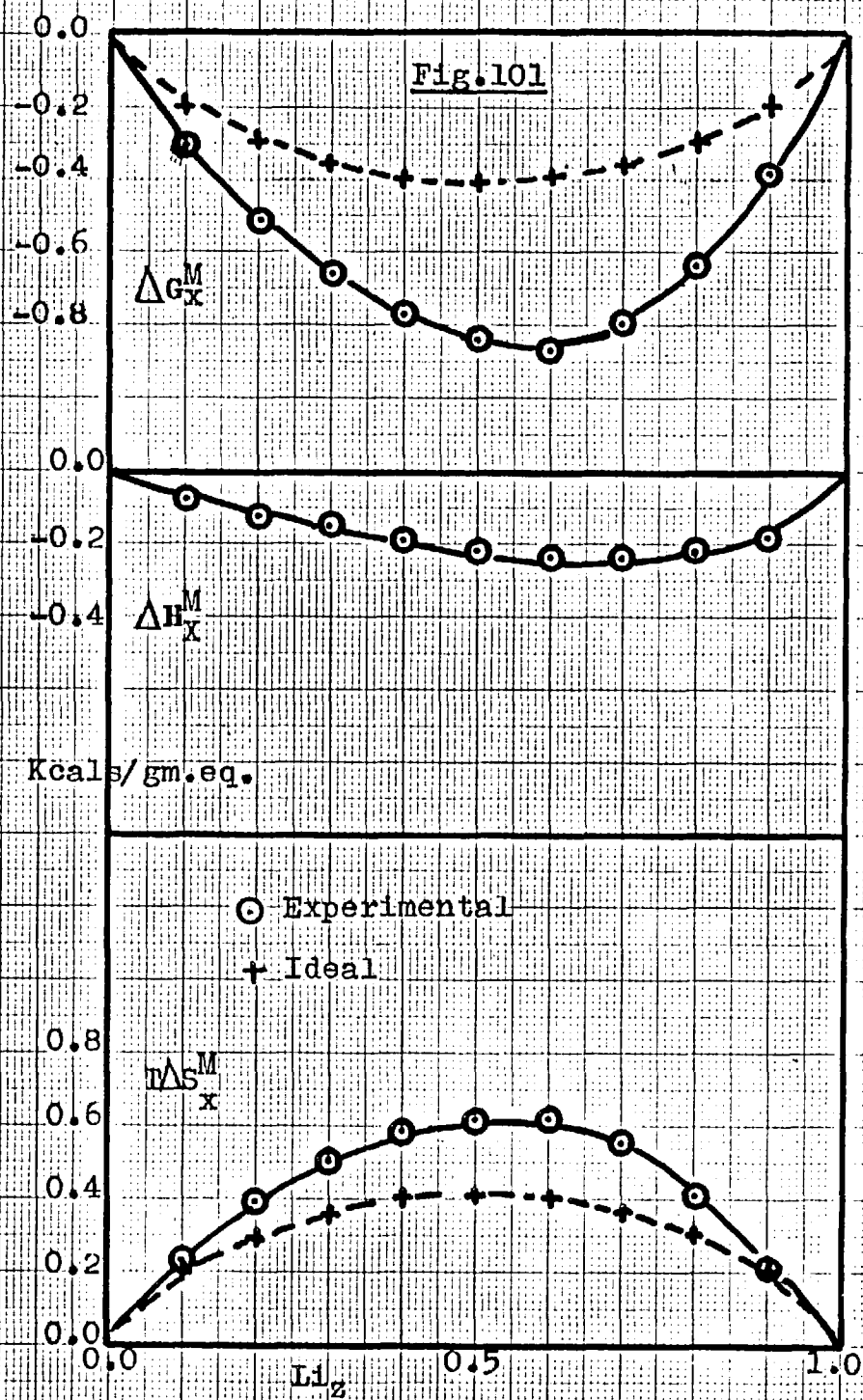


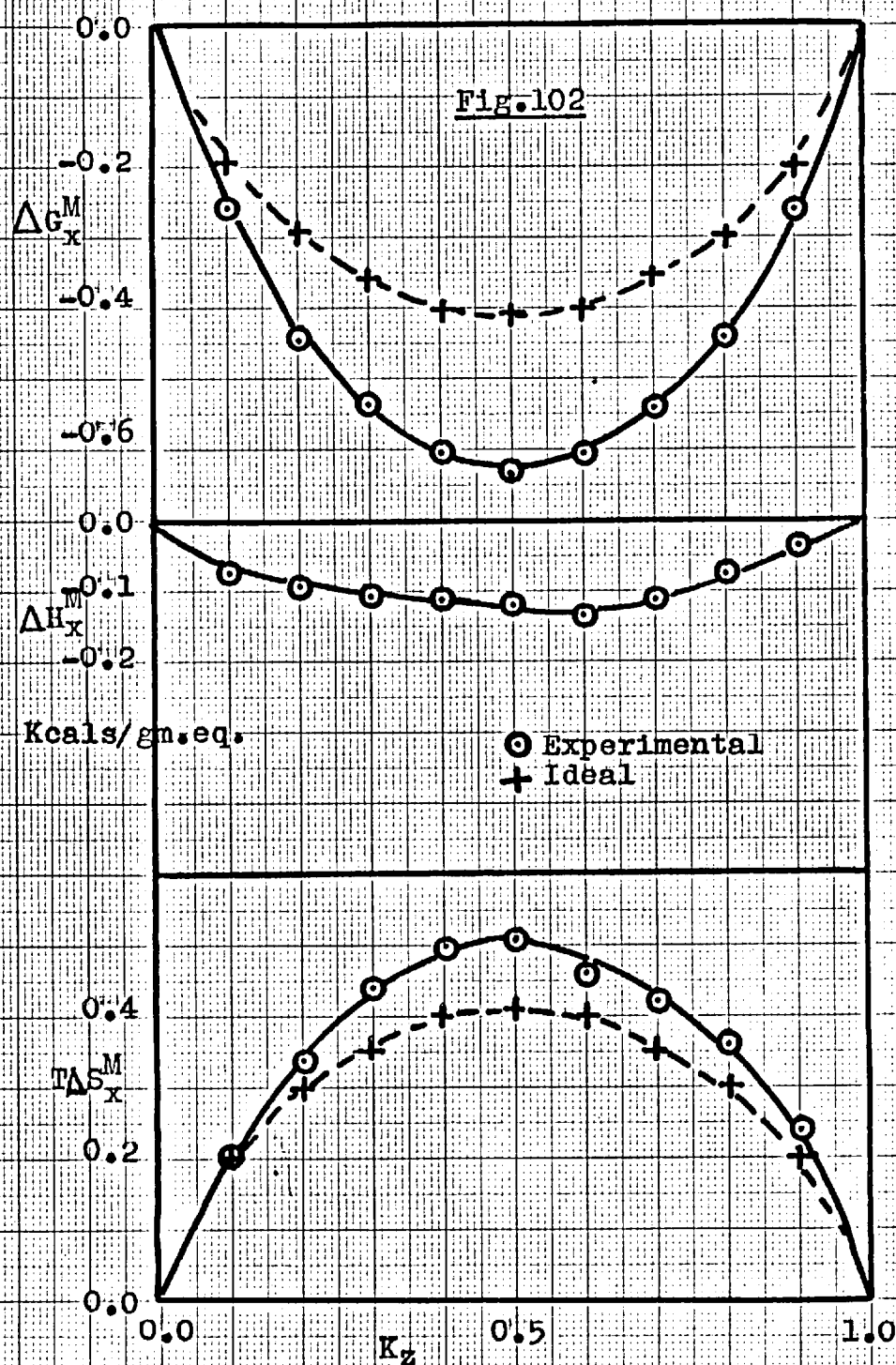
Thermodynamic functions for the formation
of the mixed (Na-NH₄) Chabazite exchanger.

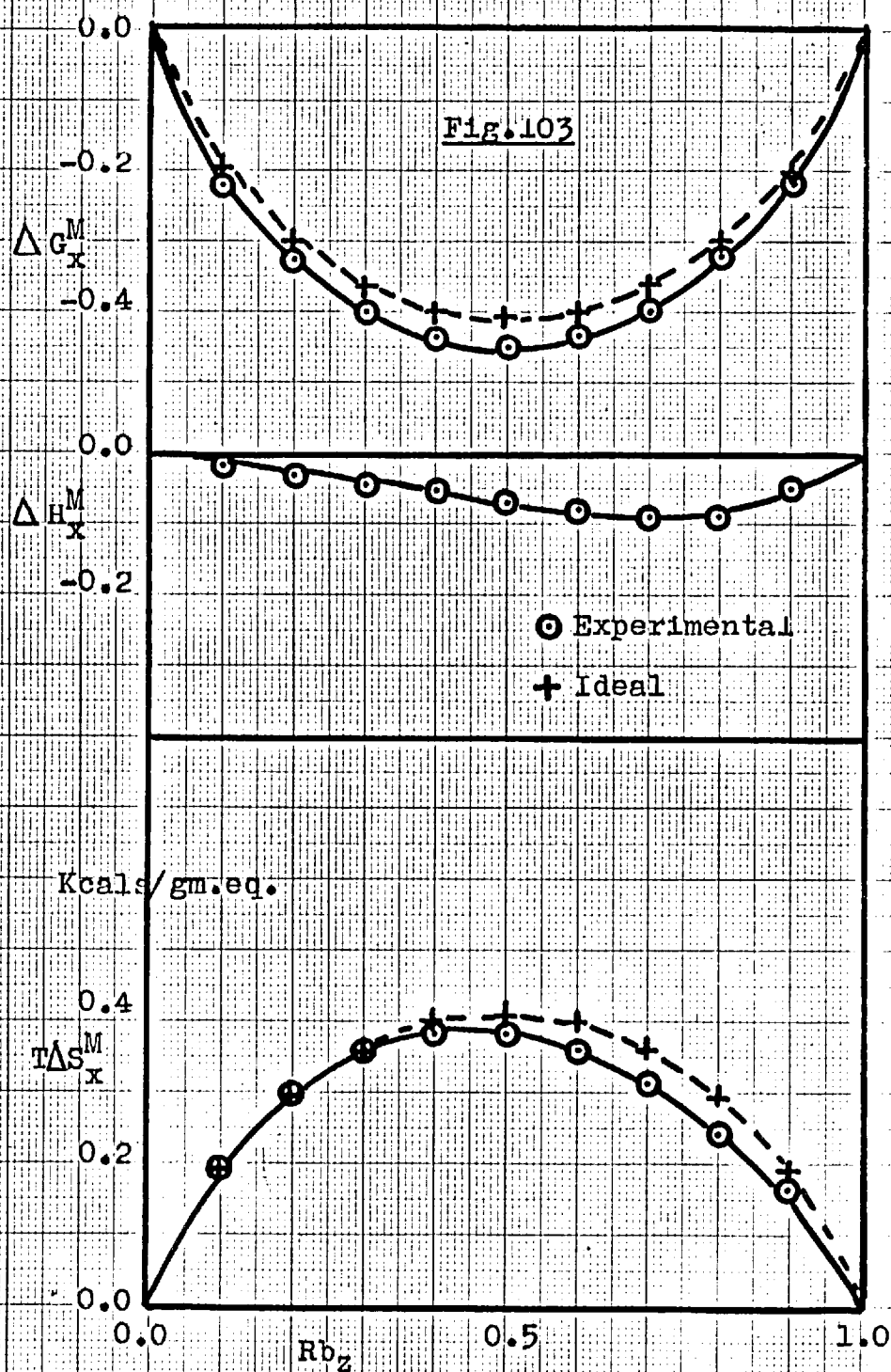
2



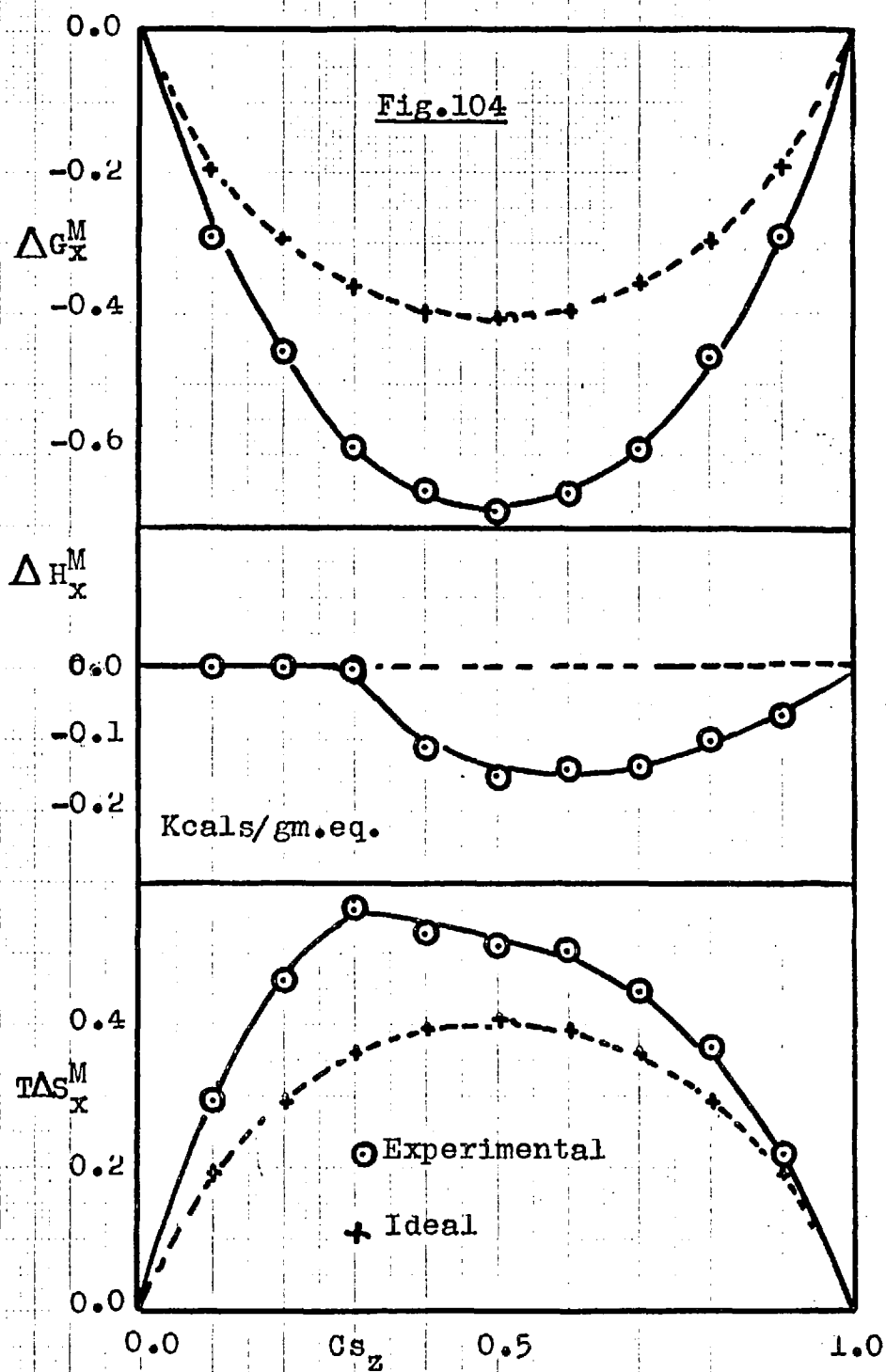


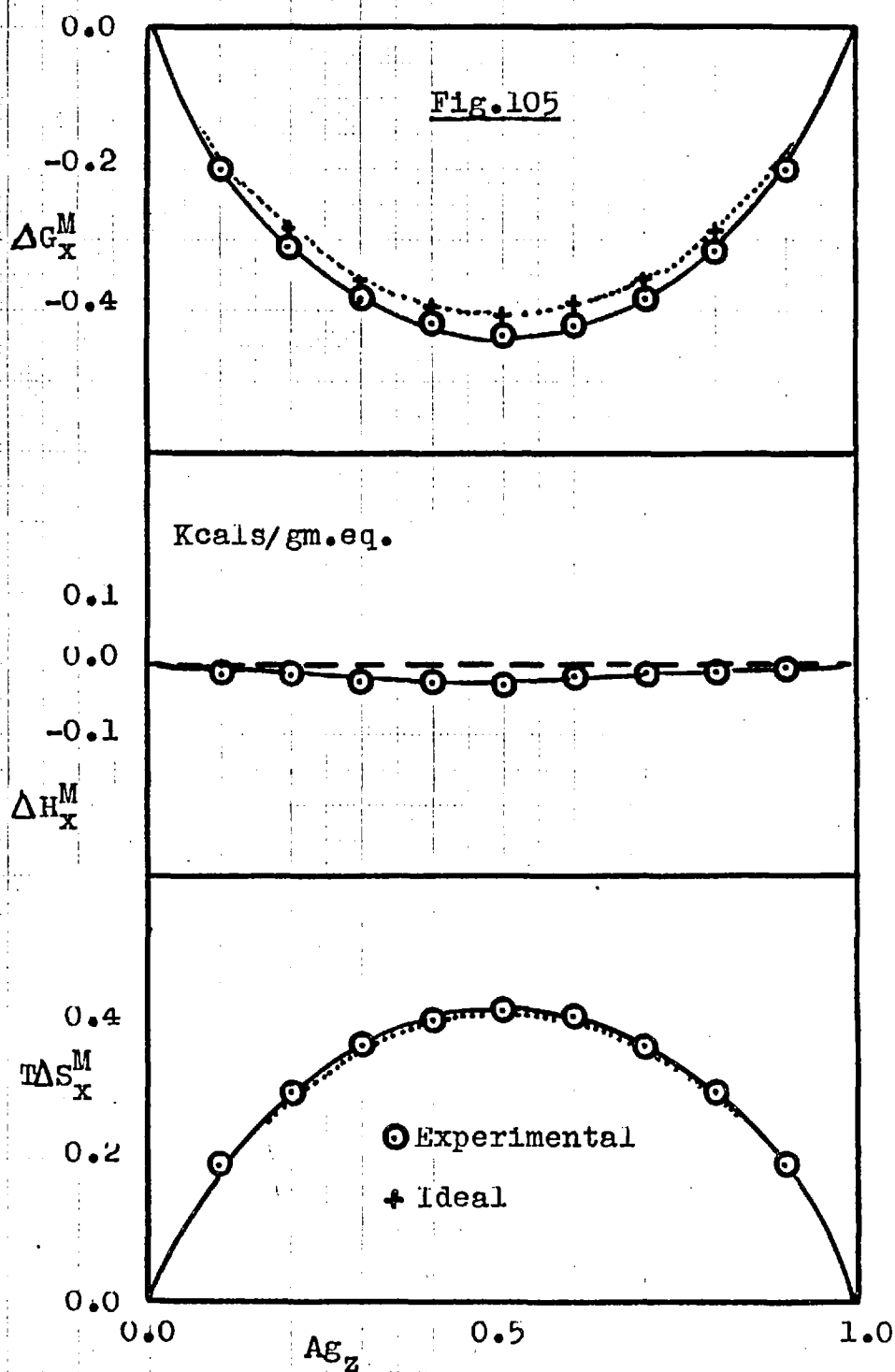




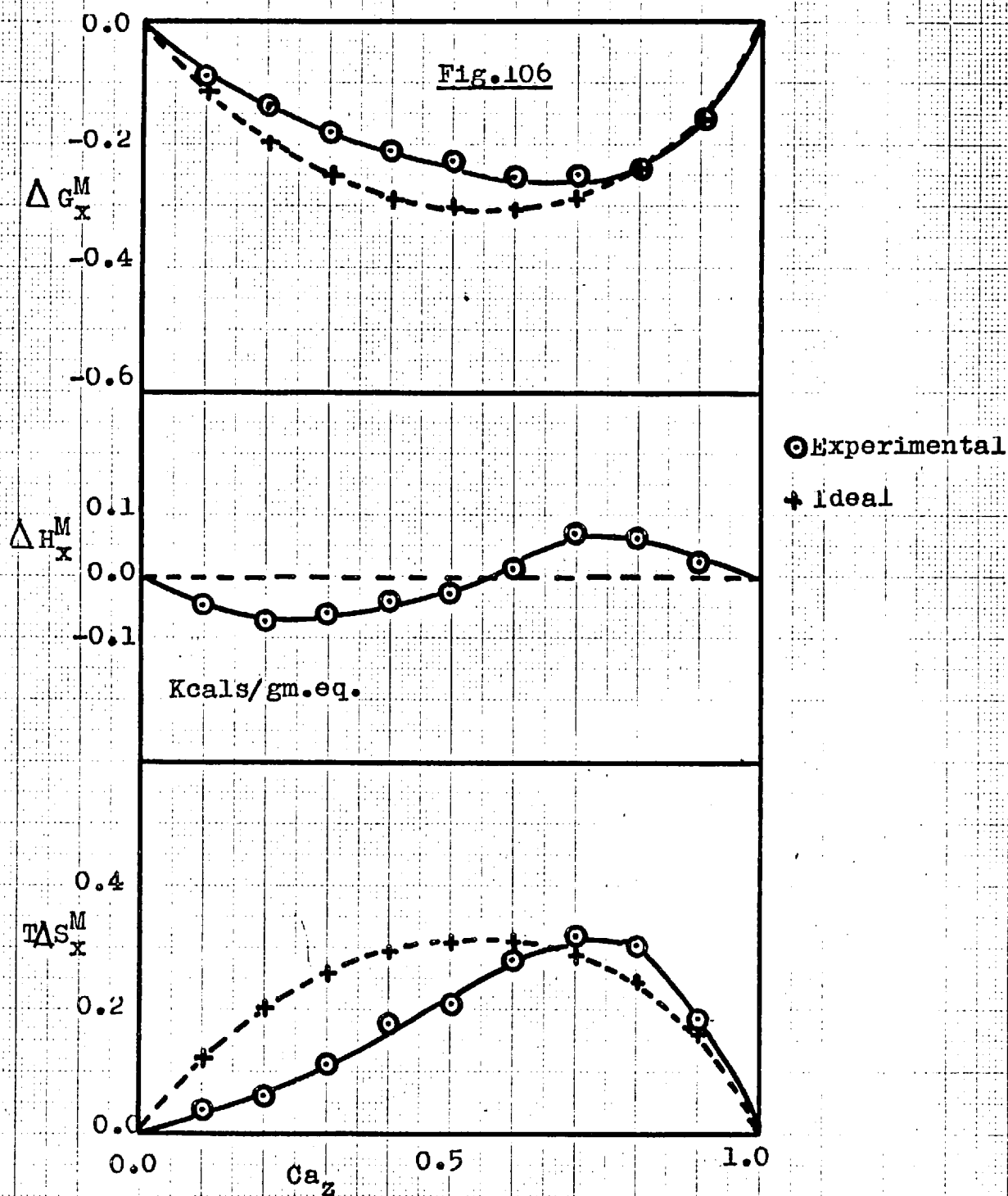


Thermodynamic functions for the formation
of the mixed (Na-Cs)Y exchanger





Thermodynamic functions for the formation
of the mixed (Na-Ca)Y exchanger.



7. DISCUSSION

Cation exclusion effects in ion exchange is a useful method of estimating the distribution of cations among the available sites in the exchangers. If some sites are exchanged with certain ions while others are not, this will exhibit itself in 'cut-offs' when the exchange isotherms are constructed. Systematic variation of the size of the ions participating in exchange and the subsequent determination of the limits to exchange enables the relative number of ions occupying the different sites to be estimated.

7.1. Discussion of the ion exchanges in chabazite in terms of its structure

Almost all the alkali metal ions, also Ag^+ , Tl^+ , NH_4^+ and the alkaline earth metal ions exchange completely with the Na^+ ion in Na - chabazite. Limited exchange is observed only in the Na - Cs exchange, where $\sim 16\%$ of the Na^+ ions are located in sites not exchangeable by the large Cs^+ ion ($r = 1.69\text{\AA}$), but which are readily exchanged by Rb^+ ($r = 1.49\text{\AA}$) and Tl^+ ($r = 1.49\text{\AA}$). Thus a critical diameter of some of the apertures governing ion exchange in Na - chabazite lies between $2.98\text{\AA}$ and $3.38\text{\AA}$.

The cation positions in hydrated Na - chabazite are

not known although certain positions are more likely to be occupied than others. The hexagonal unit cell of chabazite consists of two hexagonal prisms located at opposite ends of a large elliptical cavity, Fig. 1(a), of diameter 6 - 7 Å and about 10 Å in length. Entry of ions or molecules into this cavity can take place either through the six-membered or eight-membered oxygen rings. The eight-membered rings have free diameters of approximately 3.9 Å, thus permitting diffusion of the large ions e.g. Cs^+ , and also monatomic gases such as argon. However, the positioning of cations in or near the centres of the eight-membered rings greatly influences the sorptive properties of dehydrated chabazites. Barrer and Baynham (35) have investigated the sorption of argon and oxygen on almost pure Na - chabazite of the same $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio as that used in this work, i.e. having the same cation density, and have found little sorption of these gases at -183°C . Replacement of the Na^+ ions by Ca^{2+} ions would obviously affect the sorptive properties of the zeolites. If Na^+ ions are believed to be in or near the centres of the eight-membered rings, the exchange of Na^+ ions by Ca^{2+} ions would result in some of the eight-membered rings being unoccupied. This has been found to be the case, a critical composition of the exchanger being approximately 25% exchange.

This point corresponds with the last point at which a sufficient number of the eight-membered rings contain cations to prevent the low temperature sorption of the gases. Thus it appears that the eight-membered rings in dehydrated Na - chabazite are occupied by Na^+ ions. Hydration of the zeolite, however, would alter the position of the ions to some extent, although some of them may be still near to the eight-membered rings.

The unit cell of the Na - chabazite used in this work contains 10.6 Na^+ ions, of which six can be placed in or near the eight-membered rings. The free diameter of these rings is of the order of $3.9 \text{ \AA}$, so that exchange by even the largest monovalent ion used i.e. Cs^+ can take place. The remaining 4.6 monovalent ions per unit cell have not been assigned to any fixed positions inside the exchanger. However, the Na - Cs exchange isotherm has shown that there are 16% of the Na^+ ions in the chabazite structure which are not exchanged by Cs^+ ions, but which exchange freely with the other monovalent ions. This corresponds to 1.7 monovalent ions per unit cell. Other possible sites for the monovalent ions are inside the hexagonal prisms. Access to these hexagonal prism sites is through the six-membered rings of free diameters $2.5 \text{ \AA}$. Thus Cs^+ would not be able to exchange with any Na^+ ions inside these prisms. If

it is assumed that each hexagonal prism contains one Na^+ ion, and that all the other Na^+ ions in the zeolite are exchanged by Cs^+ , then the limit to exchange would be at $\text{Cs}_Z = 8.6/10.6 = 0.81$, as compared with the experimental value of 0.84. On the basis of crystal ionic radii it would be expected that Rb^+ , Tl^+ and possibly K^+ would be excluded from these prisms. However, complete and rapid exchange has been found for these ions. It is known that the oxygen atoms of the framework are vibrating so that it is possible that at one particular instant the diameter of the six-membered ring becomes large enough for these ions to pass through.

Although the exchanges involving the divalent ions do not exhibit limited exchange, the isotherms do show interesting variations which can possibly be interpreted by the positioning of ions in certain sites. The Na - Ca, Na - Sr and Na - Ba exchanges (vide Figs. 36, 38 and 40 respectively) show sharp rises at cationic compositions of 0.80 to 0.85. As explained for the Na - Cs exchange, any sharp variation of the isotherm in this range might involve the ions in the hexagonal prism sites. Thus the reversal of selectivity in this range might correspond with the divalent ion being preferred by the zeolite over the major part of the exchange, but Na^+ being the preferred ion in the hexagonal prisms sites. However,

this is contrary to the conclusions of Rees and Berry (113) who have found that divalent ions prefer sites near six-membered rings to those near the eight-membered rings. Smith et al. (5), using X-ray techniques, have also demonstrated that Ca^{2+} ions exist inside the hexagonal prisms in both the dehydrated and hydrated calcium chabazites.

The ease of ion exchange in chabazite indicates that the majority of the monovalent ions can move relatively easily from one site to another in the crystal. Slow processes, i.e. non-equilibrium isotherms from the calorimetric experiments, have been observed for the Na - Cs exchange, and for the divalent ion exchanges. The calorimetrically determined isotherms for the Na - Cs and Na - Ba exchanges rise sharply at a cationic composition of ≈ 0.60 . It is most likely that the Na^+ ions that are involved in the initial part of the exchanges are those located in the eight-membered rings. The replacement of these ions by other univalent ions or divalent ions would be complete at an equivalent fraction of $6/10.6 = 0.57$, which agrees approximately with that found experimentally for the Na - Cs and Na - Ba exchanges. However, further replacement of Na^+ by these ions can occur, the maximum observed in the calorimeter being 72% and 66% exchange respectively, and 84% and

100% exchange respectively after several days.

The differential heats of ion exchange are not sufficient to establish conclusively the distribution of the cations in Na - chabazite. Although some of the differential heats indicate the near homogeneity of the sites, those that do exhibit a variation in $\frac{\partial \Delta H^{\circ}_x}{\partial x}$ do so at a value of 0.6 - 0.7 for the cationic composition of the exchanger. These measurements seem to indicate that approximately two-thirds of the Na^+ ions are located in one type of site, while the remaining one-third occupy a second type of site.

7.2. Discussion of the limited exchanges in NaY in terms of the structure

The cation positions in the hydrated NaX and NaY zeolites are known (vide section 1.3). Type I sites are those inside the hexagonal prisms, type II are those in the open windows of the sodalite cages, and type III are those in the large supercages. Access to the type I sites is through the six-membered rings of free diameter $\sim 2.5 \text{ \AA}$. The smaller monovalent ions such as Li^+ and Ag^+ would readily exchange with the type I Na^+ ions. K^+ might possibly encounter difficulty in exchanging, while the larger monovalent ions such as Rb^+ , Tl^+ and Cs^+ would not be expected to exchange with the type I

Na^+ ions. If all the type II and type III Na^+ ions are exchanged by these large ions the limit to exchange would be at a cationic fraction of $35/51 = 0.69$, which is in good agreement with the experimental results.

The reversal of selectivity at $K_Z = 0.70$ in the Na - K exchange can be explained by considering the type II and type III sites to be preferred by the K^+ ion, but the type I sites by the Na^+ ion. A similar selectivity reversal for this exchange has also been observed when methanol was used as the solvent and the channels and cavities of the exchanger were filled with methanol.

The calorimetrically determined isotherm for the Na - K exchange agrees with that obtained for the ion equilibrium studies only up to $K_Z = 0.70$. Thereafter a slow process occurs. Thus exchange involving the ions in the sodalite cages and supercages is rapid, whereas that involving the cations in the hexagonal prisms is much slower. This might be due to the entry of an ion of ionic radius slightly greater than that of the 'free diameter' of the six-membered ring leading to the hexagonal prisms site. The same effect has not been observed for this exchange in methanol, a slow process occurring over the whole range of K_Z .

Replacement of two monovalent ions by one divalent ion upsets the local electrostatic charge balance within

the crystal, so that the energetically unfavourable situation of charge separation is produced. Both Ca^{2+} ($r = 0.99 \text{ \AA}$) and Sr^{2+} ($r = 1.13 \text{ \AA}$), from geometrical considerations only should exchange with all the sites in the NaY exchanger. However, the limit has been found to be 72% and 69% for the Na - Ca and Na - Sr exchanges respectively. The Na^+ ions occupying the type III sites are readily exchanged since they are the ones in the supercages. The type II sites are those in the windows of the sodalite cages, four per cage. Replacement of these ions produces no charge separation since the two divalent ions are in the same cage as the original four Na^+ ions. However, replacement of the sixteen type I monovalent ions by eight divalent ions produces charge separation since the hexagonal prisms are separated from each other by the sodalite cages. If the energy of binding of the divalent ions in these cationic sites is not sufficient to overcome the energy produced by charge separation, then the divalent ion will be excluded. In this case the 'cut-off' would be at an equivalent cationic fraction of $35/51 = 0.69$, which agrees reasonably well with the experimental results. Barium, as well as being excluded by this valence effect might also be excluded on account of geometrical considerations since its crystallographic radius is $1.35 \text{ \AA}$.

The limited exchanges in NaY may be compared with those for the corresponding exchanges in NaX. These are summarized in Table 16.

Table 16

Limited exchanges in NaX and NaY

<u>Exchange</u>	<u>Equivalent cationic fraction in exchanger</u>		
	<u>NaY</u>	<u>NaX(15)</u>	<u>NaX(59) (92)</u>
Na - Li,	1.00	1.00	1.00
Na - K,	1.00	1.00	1.00
Na - Rb,	0.69	0.67	0.82 *
Na - Cs,	0.72	0.65	0.82 *
Na - Ag,	1.00	-	1.00
Na - Tl,	0.69	-	1.00
Na - Ca,	0.72	1.00	-
Na - Sr,	0.69	1.00	-
Na - Ba,	0.69	0.74	0.82

* extrapolated value; maximum exchange achieved experimentally was 0.66.

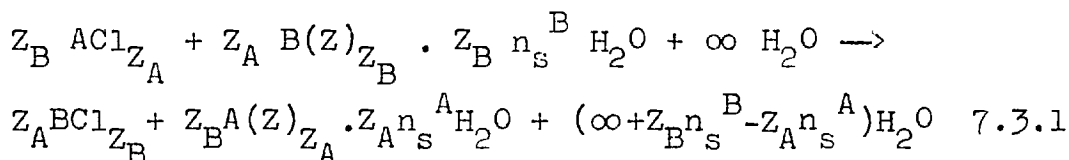
It is of interest to compare the Na - Ca, Na - Sr and Na - Tl exchanges in NaY and NaX. Cation replacement in NaY occurs to the extent of approximately 69^o/o for these ions, whereas complete exchange occurs in NaX. The divalent ions therefore exchange with all the cations in NaX, including those inside the hexagonal prisms. The

non-exchange of the hexagonal prism sites in NaY was attributed to the charge separation that would result from the replacement of two monovalent ions by one divalent ion. The charge on the NaX framework is ~ 1.53 times greater than that of the NaY, so that the energy of binding of the divalent ions with the framework in NaX will be greater than that in NaY. If the increase in the binding energy is sufficient to overcome the energy produced by the charge separation, then exchange involving the hexagonal prism sites will occur.

Similarly, the increased energy of binding of Tl^+ to the anionic framework in NaX is sufficient to overcome the steric resistance of the six-membered oxygen rings, so that the hexagonal prism sites in NaX are exchanged but not in NaY.

7.3. Standard Thermodynamic Functions for the exchanges in chabazite and NaY

The standard free energies ΔG° , standard heats ΔH° and standard entropies $T\Delta S^\circ$ of exchange for the exchanges studied are shown in Tables 17 and 18. The thermodynamic data refer to the reaction



involving one equivalent of the reactants and products in their defined standard states.

In the exchanges where the isotherm constructed from the calorimeter measurements does not agree with that constructed from the equilibrium data, the free energy of exchange has not been correlated with the extrapolated value of the heat of exchange. That is the entropy of exchange is then not evaluated.

X-ray investigations of the various ion exchanged forms of several zeolites (vide Table 1) have shown that the unit cell dimensions are almost unaltered upon exchange. Thus the standard heat of ion exchange can be regarded as a measure of the internal energy change, ΔU , associated with the cation interchanges. The exchanger can then be considered to behave almost ideally. However, the analytical data of tables 9 - 12 indicate that the water contents of the exchangers vary. If this is taken into consideration the behaviour of the exchanger can no longer be regarded as ideal. For the uni-univalent exchanges, when the ion of larger crystallographic radius replaces a smaller one in the crystal there is a decrease in the water content of the exchanger. The replacement of univalent ions by divalent ions, however, is generally accompanied by an increase in the water content of the exchanger.

TABLE 17

Standard thermodynamic functions for exchanges in
chabazite at 25°C

Exchange System	ΔH° (kcal/gm. eq. of exchanger)	ΔG°	$T\Delta S^\circ$	Kielland Coefficient C
Na→ Li	+3.05	+1.72	+1.33	0.00
Na→ K	-2.61	-1.60	-1.01	-0.23
Na→ Rb	-2.24	-1.34	-0.90	-0.64
Na→ Cs	-2.89(b)	-2.50(b)	-	-0.29(b)
Na→ Ag	-0.44	-1.44	+1.00	-0.29
Na→ Tl	-1.90	-2.62	+0.72	-
Na→ NH ₄	-1.23	-0.99	-0.24	-0.38
Na→ $\frac{1}{2}$ Ca	-	+0.09(a)	-	-
Na→ $\frac{1}{2}$ Sr	-	+0.04(a)	-	-
Na→ $\frac{1}{2}$ Ba	+1.76(c)	0.00	-	-
Na→ $\frac{1}{2}$ Pb	+1.03(c)	-0.17	-	-

(a) Equilibrium Data obtained at 50°C

(b) Based on reduced exchange capacity corresponding
to 84% replacement of Na in Na - chabazite

(c) Extrapolated values; extrapolation from Ba_Z = 0.66
to Ba_Z = 1.0, and from Pb_Z = 0.80 to Pb_Z = 1.0.

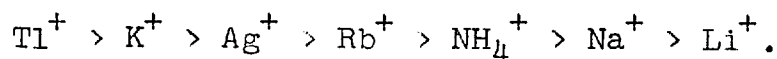
TABLE 18

Standard thermodynamic functions for exchanges in NaY
at 25°C

Exchange System	ΔH° (kcal/gm. eq. of exchanger)	ΔG°	$T\Delta S^\circ$	Kielland Coefficient C
Na→ Li	+1.35	+2.86	-1.51	-
Na→ K	-1.44	-0.37	-	-0.65
Na→ Rb(a)	-1.22	-1.06	-0.16	-0.14
Na→ Cs(a)	-1.61	-1.42	-0.19	-0.79
Na→ Ag	-0.50	-1.08	+0.58	-0.07 ₅
Na→ Tl(a)	-1.38	-1.49	+0.11	-0.06
Na→ $\frac{1}{2}$ Ca(a)	+1.09	+0.17	+0.92	-
Na→ $\frac{1}{2}$ Sr(a)	+1.03	+0.13	-	-
Na→ $\frac{1}{2}$ Ba(a)	-0.03	-0.39	-	-

(a) Based on exchange capacity corresponding to ~70% replacement of Na in NaY.

Among the uni-univalent ion exchanges studied, the preferred ion is the one of larger crystallographic radius. For those ions that exchange completely with Na⁺, the following affinity sequence on the basis of the values of K_a can be derived



With the exception of K^+ and Ag^+ the affinity of the ions for the exchanger increases as the crystallographic radius increases.

Several of the exchanges involving the univalent ions in NaY exhibit limited exchange so that it is necessary to derive two affinity sequences on the basis of K_a ,
(a) on an exchange capacity of 3.01 meq/gm. and
(b) on an exchange capacity of 2.1 meq/gm.

These are

(a) $Ag^+ > K^+ > Na^+ > Li^+$; (b) $Tl^+ > Cs^+ > Rb^+ > Na^+$.

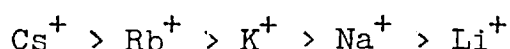
The anomalous positions of Ag^+ and Tl^+ in these sequences might be due in part to their high polarisabilities, and consequently their ability to approach the anionic oxygens of the framework more closely than the other monovalent ions.

Some comparison of the relative selectivity of the exchangers for the ions can be made by comparing the selectivity coefficient K_c at some arbitrary value of A_Z (where A is the ion entering the exchanger). Thus at $A_Z = 0.1$, the following selectivity series were obtained
Chabazite: $Cs^+ \approx Tl^+ > Rb^+ > K^+ \approx Ag^+ > NH_4^+ > Na^+ > Li^+$
NaY: $Cs^+ > Tl^+ > Ag^+ > Rb^+ > K^+ > Na^+ > Li^+$

The values of the selectivity coefficients used in these comparisons have been calculated on the assumption that

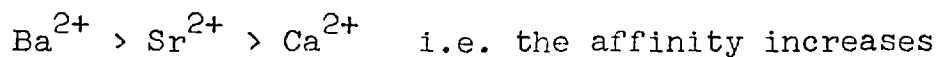
all the Na^+ ions in the exchanges are potentially exchangeable. Selectivity coefficients, however, are not constant but vary with the composition of the exchanger. Even so, the selectivity sequences above are sufficient to compare the relative 'gettering' powers of the exchangers for the univalent ions during the initial part of the exchange.

Affinity sequences have also been determined in other zeolites (vide p.31) and also in the clay mineral exchangers (106)



The variation of the affinity sequences can be explained by the non-homogeneity of cation sites within the zeolite exchangers. Since these exchangers have rigid three-dimensional frameworks, no swelling can occur to accommodate the larger ions such as can occur in the clay minerals and in the organic resins of low degree of crosslinking.

The uni-divalent exchanges studied indicate that for both NaY and chabazite the order of affinity among the divalent ions is



with increasing crystallographic radius. However, the divalent ion does not have a greater affinity than the Na^+ ion in all cases e.g. the Na - Ca exchange in NaY

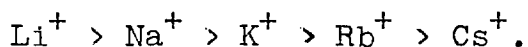
and chabazite and the Na - Sr exchange in chabazite have small positive free energy changes. It might be expected that divalent ions, due to their greater charge density than monovalent ions of comparable radii, would be able to interact more strongly with the anionic sites, leading to a greater preference by the exchanger for the divalent ion.

Uni-divalent exchanges have also been studied in NaX (15) and NaA (107), the order of affinity among the divalent ions again being $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+}$. In all cases the divalent ions are preferred by these zeolites over Na^+ . This might be due to the increased framework charges of these zeolites. A similar affinity sequence has also been observed in the polystyrene sulphonate exchanger (65), where again the divalent ions are preferred to the univalent ions.

However, determination of the overall free energy change alone in these ion exchange processes does not aid the understanding of the mechanism by which exchange occurs. It is therefore advisable to determine the contributions made to the free energy change by the changes in enthalpy and entropy. It might be expected that the entry of the preferred ion into the exchanger would be accompanied by an increase in the interionic binding with the anionic framework, leading to decreases

in internal energy and entropy. Thus in certain cases, ΔG° , ΔU° (measured as ΔH°) and ΔS° would all be negative. Such a behaviour has been found for several uni-univalent exchanges in chabazite and NaY (this work) and NaX (15). Certain exceptions to this generalization are the exchanges involving the ions Ag^+ and Tl^+ . For the Na - Ag and Na - Tl exchanges in NaY and chabazite, ΔG° and ΔU° are both negative, whereas $T\Delta S^\circ$ is positive. A similar behaviour has been observed for the Na - Ag exchange in NaA (107), and in organic resins (71). A factor that must be taken into consideration when discussing entropy changes involved in ion exchange processes is the degree of hydration of the ions in both the solution and exchanger phases; and the changes in hydration when the ions pass from one phase to the other. Obviously, since the molalities of the exchangeable ions in the internal aqueous phase of the exchanger are large (15 - 20M), it is impossible for the ions to be hydrated to the same extent as they are in the external dilute solution. Hydration numbers of ions in aqueous solutions i.e. the number of water molecules associated with ions, depend on the method of their determination. Rosseinsky (110) has tabulated hydration numbers, obtained by different methods, of several monovalent ions. Although the absolute values of the hydration numbers vary, the data

indicate a general trend in the hydration of the alkali metal ions which is



In solution it can be reasonably assumed that the hydration of the ions is in the above sequence. However, in the exchanger phase this is not necessarily the case. Some estimate of the hydration of the ions inside the exchanger can be made by considering the factor, number of water molecules per cation. These have been calculated for several cation exchange forms of the zeolites A, X, Y and chabazite. In all cases the zeolites have been equilibrated with water vapour over saturated ammonium chloride solution in a desiccator at room temperature. The results are shown in Table 19.

However, the data of Table 19 represent the average number of water molecules per cation. Certain cations e.g. those inside the small cavities such as the hexagonal prisms are not hydrated, whereas those in the larger cavities will have a higher number of water molecules per cation. Also it is possible for some of the water molecules inside the exchanger to exist as a continuous fluid, especially in the more open zeolites such as the Linde Sieves X and Y.

A factor that must also be taken into consideration is solvation by the oxygen ions of the anionic framework.

Table 19

Cationic	Number of water molecules per cation			
<u>Form</u>	<u>A</u>	<u>X</u>	<u>Y</u>	<u>Chabazite</u>
Li	2.0	2.7	4.6	3.6
Na	2.1	2.8	4.4	3.2
K	1.9	2.5	3.9	2.9
Rb	1.8*	2.5*	3.5*	2.6
Cs	1.7*	2.5*	3.2*	2.0*
Ag	-	-	4.2	3.1
Ca	2.4	5.6	8.6*	7.2
Sr	-	5.8	-	6.8
Ba	-	5.4	8.5*	5.6

* Partially exchanged forms

For the reaction represented by equation 7.3.1, when an ion A of valence Z_A replaces Na^+ in the zeolite, the heat of exchange, ΔH° , may be written as

$$\Delta H^\circ = (\Delta H^\circ_{\text{Na}} - \frac{1}{Z_A} \Delta H^\circ_A)_{\text{S}} + (\frac{1}{Z_A} \Delta H^\circ_A - \Delta H^\circ_{\text{Na}})_{\text{Z}} \quad 7.3.2$$

where $\Delta H^\circ_{\text{Na}}$ and ΔH°_A are the standard heats of solvation of gaseous Na^+ and ion A^{Z_A+} respectively, and S and Z represent the aqueous and zeolite phases respectively. Similar expressions exist for the standard free energies and entropies of solvation of the ions

in both phases. The first term on the right-hand side of equation 7.3.2 can be evaluated from thermodynamic data (111), and by substituting the experimentally determined heats of exchange in this equation, the second term on the right-hand side can be calculated. Where limited exchange has been obtained, the right-hand side is multiplied by x_{max} . The results for the exchanges studied in chabazite and NaY are shown in Tables 20 and 21 respectively. The differences in the heats of solvation of the gaseous ions in the zeolites are similar to the same differences in aqueous solutions, thus indicating the similarity between hydrated zeolites and aqueous solutions. For all the exchanges in chabazite and NaY, except the Na - Ag exchange, the signs of ΔH° are the same as the signs of the differences in solvation heats of the gaseous ions in aqueous solutions. A similar behaviour is also observed in the signs of the free energy changes, the Na - Ag exchange again being the only exception. This anomalous behaviour of Ag^{+} is not observed in the entropy of exchange and the differences in entropy of hydration of the gaseous Na^{+} and Ag^{+} ions, both functions being positive. For the alkali metal exchanges the signs of the entropies of exchange are also the same as those for the entropies of solvation in the aqueous solutions. The exceptions to this generalization

Table 20

Components of standard heats, entropies and free energies of exchange in chabazite

Cation	Li	K	Rb	Cs	Ag	Tl	NH ₄	Ca	Sr	Ba	Pb
ΔH_s (kcal/s)	+26.1	-20.2	-26.1	-36.0	+16.7	-19.0	-21.2	+93.4	+75.8	+58.9	+80.0
ΔH_z	+23.0	-17.6	-23.9	-32.5	+17.1	-17.1	-20.0	-	-	+57.1	+78.9
ΔG_s (kcal/s)	+23.9	-17.7	-22.7	-30.4	+16.3	-16.2	-	+92.2	-	-	+80.7
ΔG_z	+22.2	-16.1	-21.4	-27.9	+17.7	-13.6	-	+92.1	-	-	+80.9
ΔS_s e.u.	+ 7.5	- 8.5	-11.4	-12.1	+ 1.4	- 9.5	-	-	-	-	-
ΔS_z	+ 3.1	- 5.2	- 8.4	-	- 1.9	-11.9	-	-	-	-	-

where $\Delta H_s = (\Delta H_{Na}^{\circ} - \frac{1}{Z_A} \Delta H_A^{\circ})_s$ and $\Delta H_z = (\Delta H_{Na}^{\circ} - \frac{1}{Z_A} \Delta H_A^{\circ})_z$

Similar expressions exist for ΔG_s , ΔG_z , ΔS_s , ΔS_z .

Table 21

Components of standard heats, entropies and free energies of
exchange in NaY

Cation	Li	K	Rb	Cs	Ag	Tl	Ca	Sr	Ba
ΔH_s (kcal/s)	+26.1	-20.2	-26.1	-36.0	+16.7	-19.0	+93.4	+75.8	+58.9
ΔH_z	+24.7	-18.8	-24.2	-33.7	+17.2	-17.0	+91.9	+74.3	+58.9
ΔG_s (kcal/s)	+23.9	-17.7	-22.7	-30.4	+16.3	-16.2	+92.2	-	-
ΔG_z	+21.0	-17.3	-21.2	-28.4	+17.4	-14.1	+92.0	-	-
ΔS_s e.u.	+ 7.5	- 8.5	-11.4	-12.1	+ 1.4	- 9.5	+ 4.3	-	-
ΔS_z	+12.5	-	-10.6	-11.2	- 0.5	-10.0	- 0.1	-	-

are the Na - Tl exchanges in both chabazite and NaY, where ΔS° is positive but $(\Delta S^\circ_{\text{Na}} - \Delta S^\circ_{\text{Tl}})_S$ is negative; and the Na - Li exchange in NaY where the reverse is found i.e. ΔS° is negative and $(\Delta S^\circ_{\text{Na}} - \Delta S^\circ_{\text{Li}})_S$ is positive.

The negative values for the component $(\Delta S^\circ_{\text{Na}} - \frac{1}{Z_A} \Delta S^\circ_A)_S$ for the ions K^+ , Rb^+ and Cs^+ can be explained by the hydration of these ions in solution. Since there is a greater number of water molecules associated with a Na^+ ion in solution than with the other ions, the decrease in entropy when a gaseous Na^+ ion is immersed in water is greater than that for the same process involving K^+ , Rb^+ or Cs^+ ions. A similar behaviour is noted for the solvation of these ions in the zeolite phase. However, this difference in the zeolite cannot be divided into the component arising from solvation by intracrystalline water, and that from solvation by the anionic oxygen of the framework.

As can be seen from Tables 20 and 21 the differences in the entropies of solvation of the Na^+ and Ag^+ ions in the aqueous solution and in the zeolite phase have opposite signs. These differences in solution are due to the differences in the degree of solvation of the ions. In the exchangers the greater polarisability of the Ag^+ ion enables it to bind strongly with the anionic oxygens

of the framework.

It might be expected that a similar effect would be observed in the Na - Tl exchange since Tl^+ also has a high polarisability. However, the evaluation of the terms on the right-hand side of equation 7.3.2 show that the components of the standard heats, free energies and entropies of exchange in both phases have the same signs and are of similar magnitudes.

The Na - Li exchange in NaY has an overall negative entropy change when Li^+ enters the exchanger from solution, although the components of this entropy change in both phases have the same sign. However, for this exchange in chabazite $\Delta S_s > \Delta S_z$, whereas the reverse is found in NaY. Thus it appears that the factors affecting the entropy of solvation of these ions are different in the chabazite and type Y exchangers. However, as before, it is impossible further to breakdown these solvation entropy changes in the exchangers.

The uni-divalent exchanges studied on NaY and chabazite have been complicated by the slow processes that are involved, so that it has not been possible in many cases to calculate the entropies of exchange. Where it has been possible to calculate the entropy change, as for the Na - Ca exchange in NaY, this function was positive. All the uni-divalent ion exchanges were found to

have positive values of ΔH° , except that of the Na - Ba exchange on NaY which was virtually athermal. Uni-divalent ion exchanges have been studied in several other zeolites eg. NaA (51) (107) and NaX (15); and also in organic resins (65). In almost all these exchanges it was found that the replacement of the monovalent ion by a divalent ion in the exchanger is accompanied by positive values of ΔH° and ΔS° .

The data of tables 20 and 21 show that the standard heats of ion exchange, where it has been possible to determine these values, have the same signs as the differences in the heats of hydration of the ions in the aqueous solutions. Also these differences have the same signs and are of similar magnitudes to those for the solvation of the ions in the zeolite phase. The replacement of two monovalent ions by one divalent ion in the exchanger can produce short range disorder due to the charge separation that is produced. In this case the electrostatic energy will be greater than when all the anionic sites are occupied by monovalent ions. This charge separation can lead to cation exclusion (vide section 2.1).

The difference in the entropies of solvation of the gaseous Na^+ and Ca^{2+} ions in the type Y zeolite is only -0.1 e.u. Thus it appears that for this exchange at

least, the overall entropy of the exchange reaction is determined by the entropy changes due to the different solvation of the ions in the aqueous solutions.

A factor that can contribute to the entropy change in the exchanger is the configurational entropy arising by the replacement of two monovalent ions by one divalent ion. This factor is not present in uni-univalent exchanges where the number of exchanging ions in a given amount of exchanger does not change. Replacement of uni- by divalent ions results in an increase in the number of possible ways of distributing the cations among the available sites. For an ideal exchanger it is assumed that there are N_0 sites per equivalent of exchanger, where N_0 is Avogadro's number. The random distribution of $N_0/2$ divalent ions produces an extra configurational entropy, as compared with the Na form, in which all the available sites are filled, of

$$T\Delta S = k T \ln \frac{N_0!}{\frac{N_0}{2}! \frac{N_0}{2}!} = 0.41 \text{ kcals/gm. eq.}$$

However, this calculated entropy change in the exchanger is of opposite sign to that obtained (vide table 21) for the replacement of Na^+ ions in the Y zeolite by Ca^{2+} ions. The calculation of the configurational entropy term above has assumed random mixing of the ions in the exchanger, but it is known that the cations occupy

preferred sites in the exchanger i.e. there is non-random mixing.

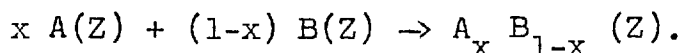
A configurational entropy term also arises when divalent ions in an ideal electrolyte solution are replaced by monovalent ions. Flett and Meares (65) have calculated this configurational term for a solution of concentration 1 equivalent per kilogram of water, and have shown that at 25°C this term contributes 1.29 kcals/gm. eq. Thus the overall contribution to the entropy factor due to configurational changes in both the exchanger and solution is 1.70 kcals/gm. eq.

The experimental heats of ion exchange can also be compared with the predicted energy changes from the structureless dielectric theory of Barrer and Falconer (9), vide section 2.4. This theory predicts that ΔU will be positive when Li^+ enters the Na^+ form of the exchanger and increasingly more negative as K^+ , Rb^+ and Cs^+ enter. For uni-divalent exchanges, the theory predicts a positive ΔU when the divalent ion enters the Na^+ form of the exchanger. This has been found experimentally for several exchanges studied in NaX, NaY, NaA and chabazite. The only exceptions to this are the Na - Ba exchanges in NaX, NaY and NaA which have small negative heats of exchange. Thus considering the simplified picture of ion exchange presented by this model there

appears to be reasonable agreement between the calculated energy changes and the experimentally determined heats of exchange.

7.4. Thermodynamic functions for the formation of the mixed exchanger phase

The thermodynamic functions to be discussed in this section refer to the reaction represented by



The relevant equations for the calculation of the free energies, enthalpies and entropies of mixing for both experimental and ideal behaviour are derived in sections 5.4 and 6.6.

7.4.1. Mixed chabazite exchangers (Figs. 96 - 100)

For all these exchangers the free energy of mixing, ΔG_x^M is negative and either equal to or of greater magnitude than the corresponding function for ideal behaviour. The heat content change, ΔH_x^M , also differs from that of ideal behaviour i.e. $\Delta H_x^{M(id)} = 0$, although the sign of this function varies with the exchange system. The non-ideality of behaviour of the mixed exchangers is also reflected in the entropy change $T\Delta S_x^M$.

The negative values of ΔH_x^M and $T\Delta S_x^M$ in the Na - Li exchanger are indicative of strong interactions present which are therefore accompanied by decreases in

internal energy and entropy. The negative value of $T\Delta S_x^M - T\Delta S_x^{M(id)}$ might also be partly due to the non-random mixing of the cations in the mixed exchanger.

The positive values of ΔH_x^M and $T\Delta S_x^M$ for the Na - Rb and Na - NH_4 mixed exchanges indicate that the interaction of the components is accompanied by increases in internal energy and entropy. These increases might be due in part to the different water contents of the pure components thus producing changes in the degree of hydration of the cations.

The thermodynamic functions for the formation of the mixed Na - Ag exchanger differ only slightly from those of ideal behaviour, particularly the heat content function. Changes in hydration of the cations in the mixed exchangers might be small since the water contents of the pure exchangers are similar (vide Table 9).

7.4.2. Mixed type Y exchangers (Figs. 101 - 106)

As in the case of the mixed chabazite exchangers, the free energies of mixing are negative and generally of greater magnitude than those of ideal behaviour, the only exception being that of the mixed Na - Ca exchanger. The heat content changes also differ from those of ideal behaviour, although the differences are smaller than those for the corresponding mixed chabazite exchangers. The small negative values of ΔH_x^M are indicative of

small interactions which are accompanied by decreases in internal energy. This is not reflected in the entropy changes which are generally greater than those of ideal behaviour.

The entropy function for the mixed (Na - Li)Y exchanger is entirely different from that of the corresponding chabazite exchanger indicating that there are different factors affecting the entropy changes in these zeolites. This might be due to the more open structure of the Y zeolite resulting in some of the ions being hydrated to a different extent from those in chabazite.

The only instance where the formation of the mixed exchanger from its components can be regarded as ideal is the Na - Ag exchanger (Fig. 105).

The evaluation of the thermodynamic functions for the formation of a mixed uni-divalent exchanger shows that the factors affecting the formation of the mixed exchanger are different from those when only univalent ions are involved. The function $T\Delta S_x^M - T\Delta S_x^{M(id)}$ is generally negative and can partly be explained by the non-random mixing of the pure components.

From a comparison of the thermodynamic functions for the formation of the mixed exchangers, it appears that the deviations of these functions from ideal behaviour are smaller for the type Y zeolite than for chabazite.

This might be due to the more open structure of the type Y zeolite thus permitting less interaction between the cations in the exchanger.

7.5. Comparison of the ion exchange properties of several zeolites

Considerable data on ion exchange in zeolites have now been obtained and it is of interest to make a comparison of the exchange properties. Although solutions of different concentrations have been used to determine the exchange isotherms, it has been shown (vide section 5.1) that for uni-univalent exchanges the isotherm is almost independent of solution strength. The exchange isotherms for the Na - Li and Na - K exchanges are shown in Figs. 107 and 108 respectively. Complete exchange is possible in all the exchangers, and reversibility has been shown in several cases. Also no evidence of limited mutual solubility of the end members was obtained. For the Na - Li exchange the preferred ion is generally Na^+ , while in the Na - K exchange the preferred ion is generally K^+ although the exchangers in basic cancrinite and basic sodalite are exceptions. A qualitative estimate of the relative powers of the exchangers for the ion of larger crystallographic radius can be made. Thus for the Na - Li exchange

Chabazite > NaY > NaX(15) $\approx$ NaA(51) > Basic Sodalite (9)
> Basic cancrinite

and for the Na - K exchange

Chabazite > Mordenite (109) $\approx$ Phillipsite (69) > NaY > NaX (15) > NaA (51) > Basic Sodalite (9).

Although several of the isotherms have been determined at different temperatures, it seems reasonable to compare the results obtained since the temperature dependence of ion exchange equilibria is small.

The Na - Rb and Na - Cs exchanges are complicated by the limited exchanges that are present when these larger monovalent ions are involved (Figs. 109, 110). It might be expected that the more open zeolites i.e. NaX and NaY would be able to exchange freely with these ions since the channel dimensions are greater than the diameters of these ions. The behaviour of the large cations in these faujasite-type exchangers can be explained in terms of the heterogeneity of the cation sites in these zeolite (vide section 7.2). However, it is possible to compare qualitatively the 'gettering powers' of the zeolites by comparing the values of Rb_s (or Cs_s) at some arbitrary value of Rb_z (or Cs_z). Thus at $Rb_z = 0.3$ the order is Chabazite > Mordenite (109) > NaY $\approx$ NaX (15) > NaA (51) and at $Cs_z = 0.3$ Chabazite $\approx$ Clinoptilolite (63) $\approx$ Mordenite (109) > NaY > NaX (15) > NaA (51).

The isotherm for the Na - Cs exchange on clinoptilolite has been determined at two temperatures and exhibits an appreciable difference over the latter part of the exchange. Consequently the heat of ion exchange evaluated from the temperature dependence of the thermodynamic equilibrium constant is large (-4.92 kcal/gm.eq.).

To generalize the results of ion exchange equilibria involving alkali metal ions it appears that the zeolites with the higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios have the greater preference for the ion of larger crystallographic radius, although the position of chabazite for the Na - Cs and Na - Rb exchanges is anomalous. It might be expected that the reverse would occur. Zeolites of lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio have the higher framework charge, so that changes in the interaction of the ions with the frameworks would be greater. However, no consideration is taken of the different framework structures and different cation sites in the exchangers, and therefore this argument cannot be extended further.

High selectivity for the cation of larger crystallographic radius is also shown for the Na - Ag and Na - Tl exchanges on several zeolites eg. NaA (50) (107), NaX (59) chabazite and NaY (this work); and also on the organic exchange resin Dowex-50 (71). Among the inorganic ion exchangers the greatest overall affinity for the Ag^+

ion is shown by the exchangers of the lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. This is opposite to the generalization made for the alkali metal ion exchanges. The relative order of 'gettering' of silver from solution is therefore
Basic Sodalite $\approx$ NaA $\approx$ NaX $>$ Chabazite $>$ NaY.

The Na - Tl exchange isotherms in NaA and NaY exhibit limited exchange which can be interpreted by the distribution of the cations in various sites in these zeolites. The relative 'gettering' powers of the exchangers for the Tl^+ ion is

Chabazite $>$ NaA $\approx$ NaX $>$ NaY.

The overall high affinities of the Ag^+ and Tl^+ ions for the exchangers might be due in part to their high polarizabilities.

It is difficult to make an overall comparison of the affinity of divalent ions owing to the differing upper limits to the extent of exchange. Values of K_a can be calculated on the exchange capacities corresponding to these limits, and on this basis some comparison can be made. Thus for the Na - Ca exchange

NaX (15) $>$ NaA (51) $>$ chabazite $>$ NaY,

for the Na - Sr exchange

NaX (15) $>$ NaY $>$ chabazite

and for the Na - Ba exchange

NaX (15) $>$ NaY $>$ chabazite.

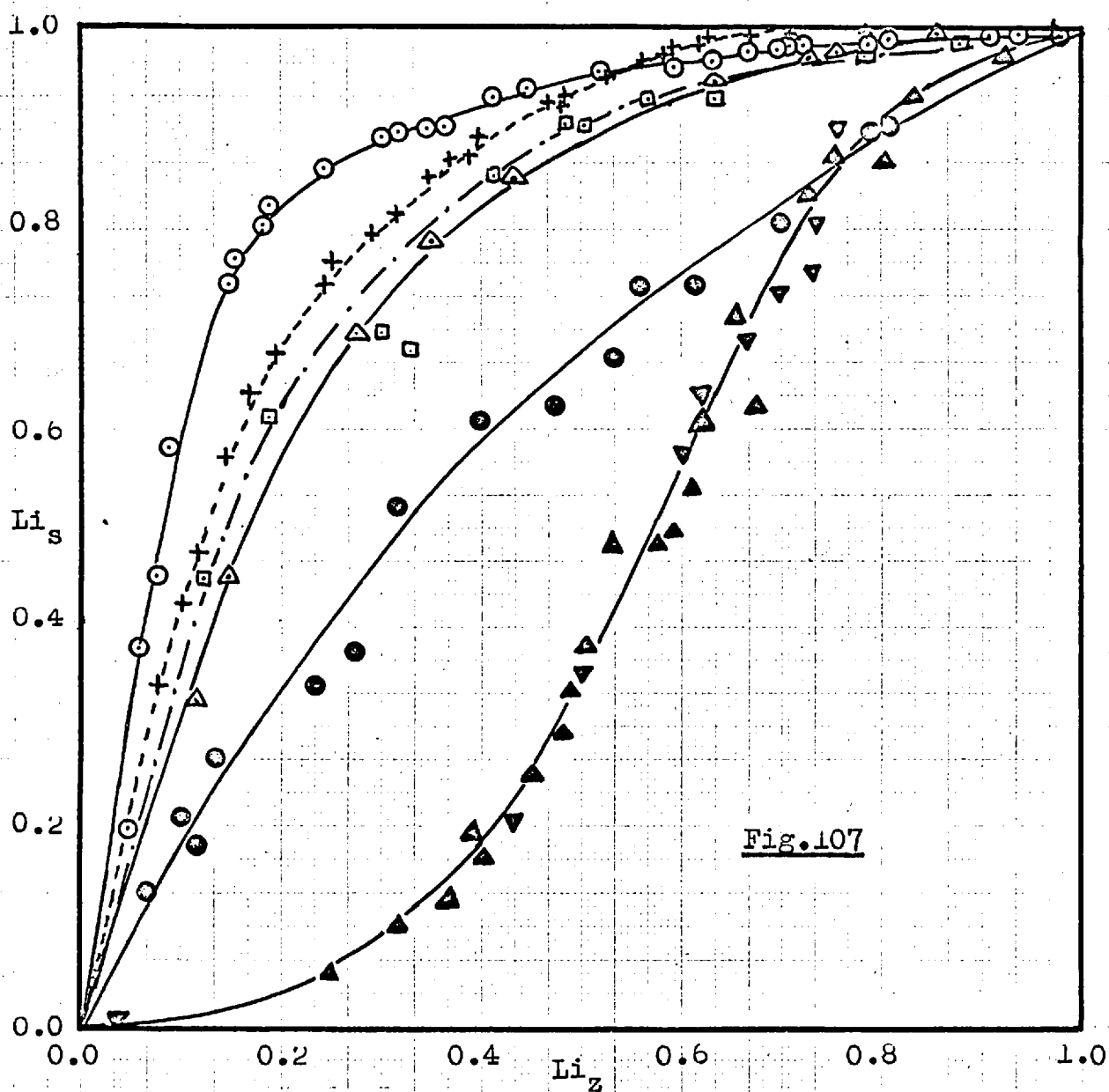
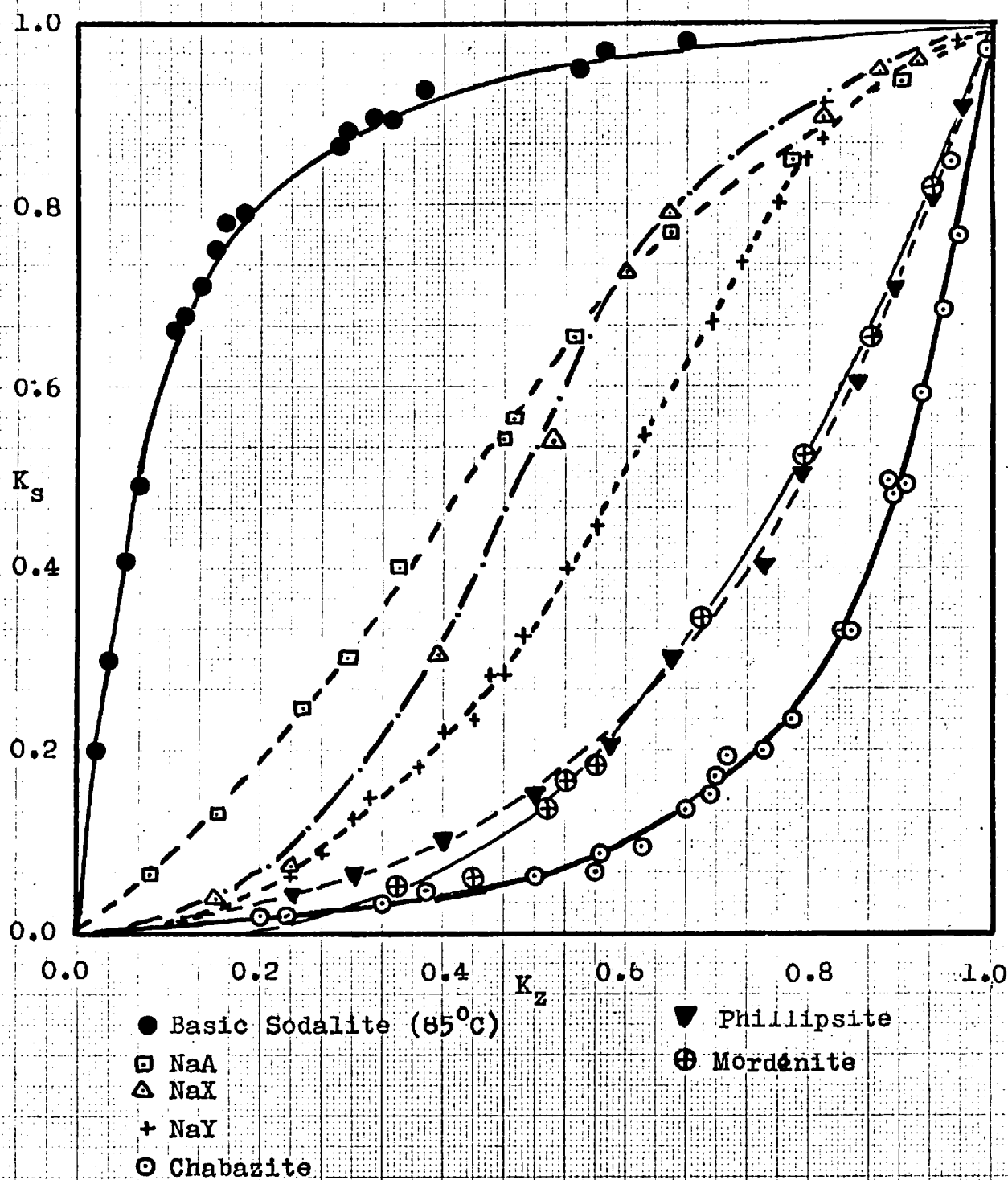


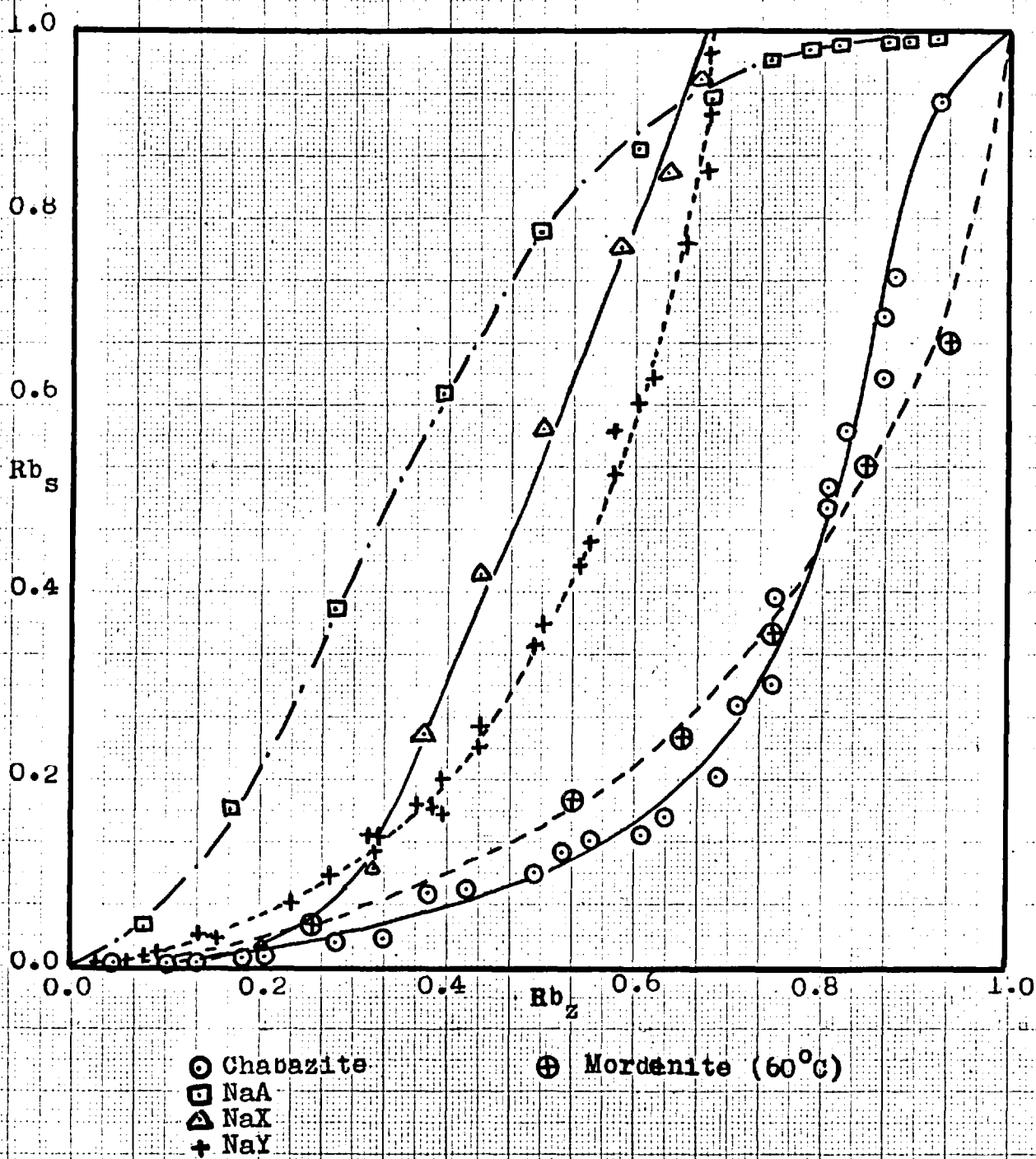
Fig. 107

- | | |
|---------------------------|-------|
| ● Basic Sodalite (85°C) | □ NaA |
| ▲ Basic Cancrinite (85°C) | △ NaX |
| ▼ Basic Cancrinite (25°C) | + NaY |
| ○ Chabazite | |

Na-K exchange isotherms on several zeolites at 25°C



Na-Rb exchange isotherms on several zeolites at 25°C



Na-Cs exchange isotherms on several zeolites at 25°C

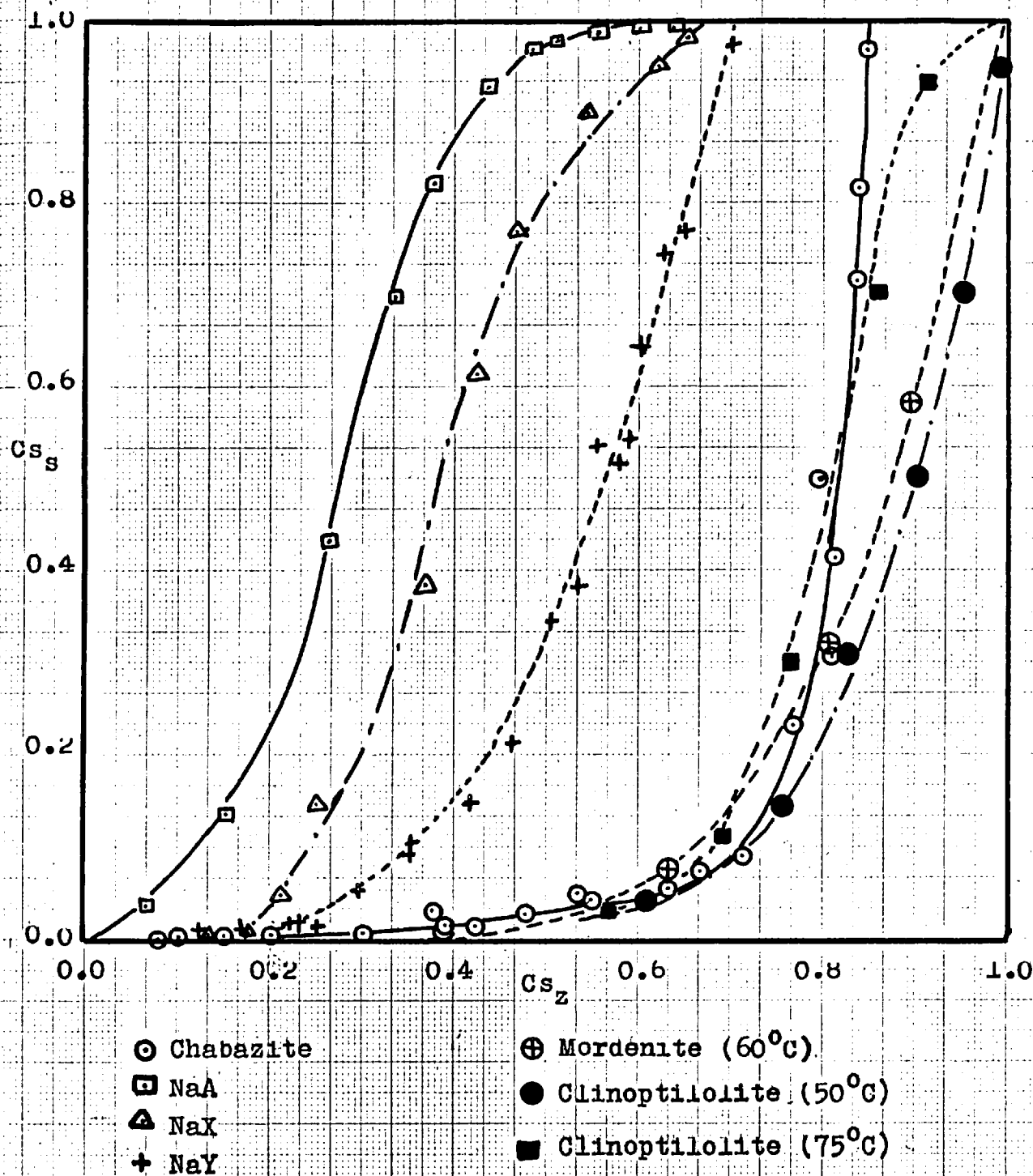


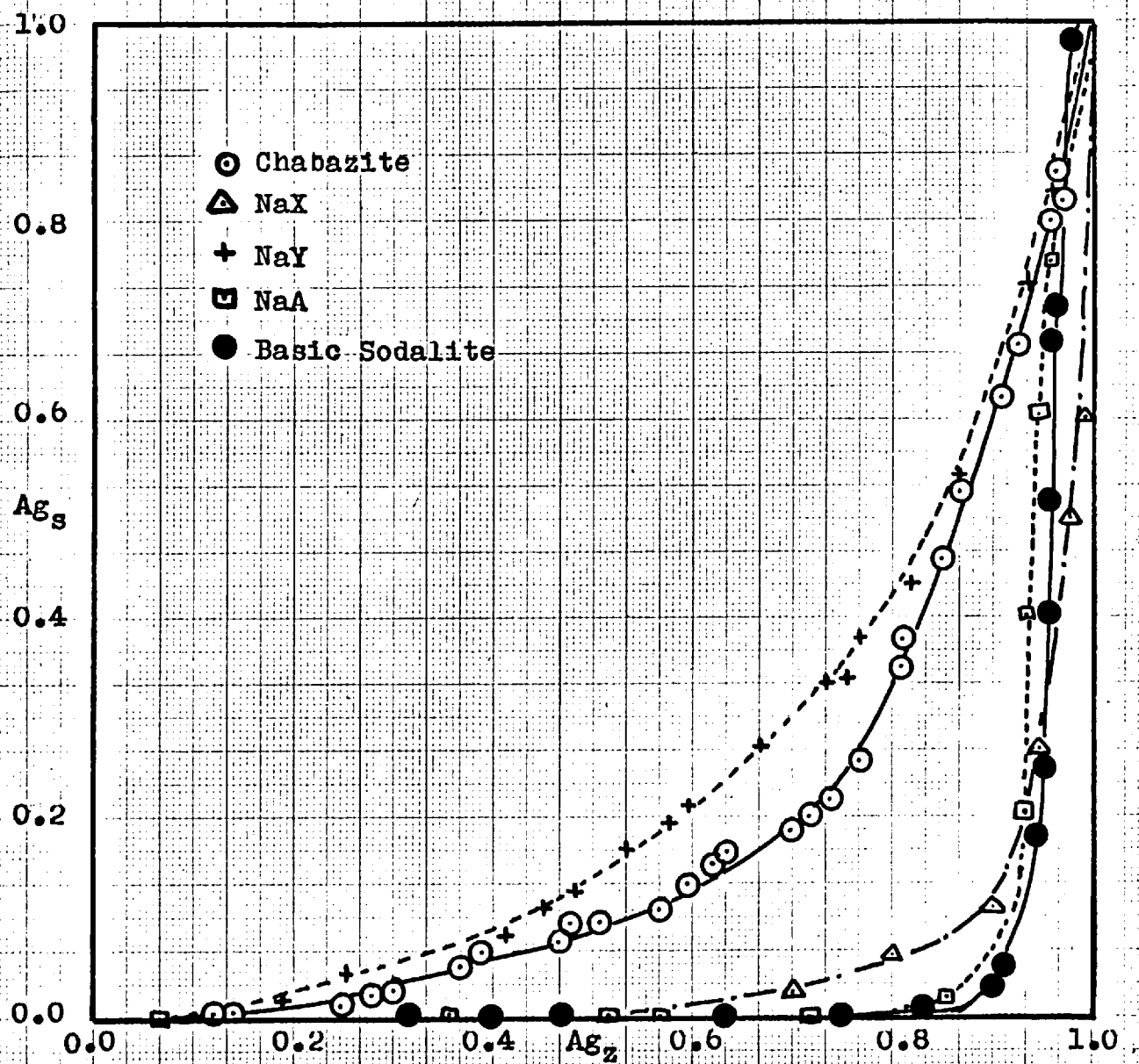
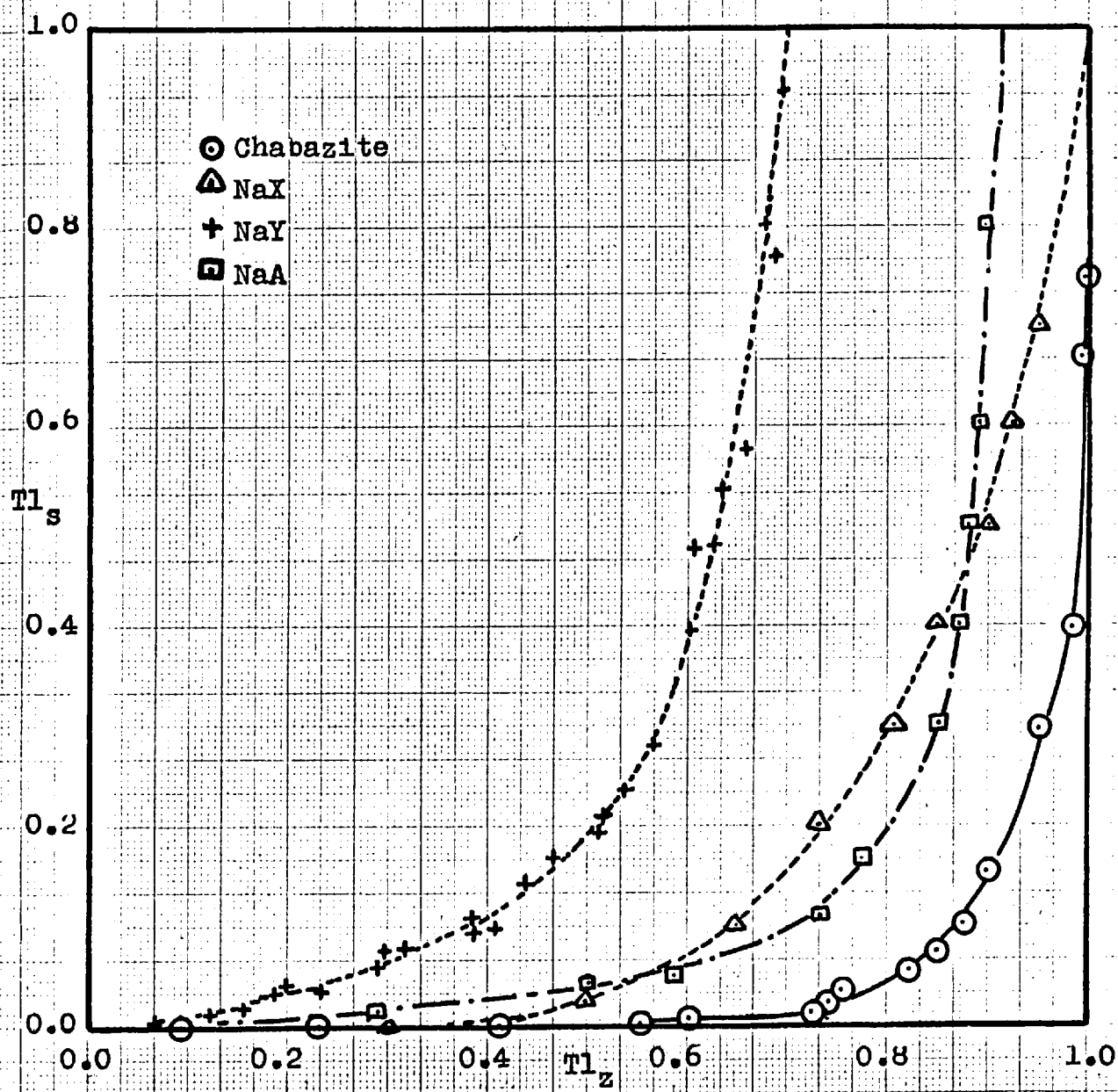
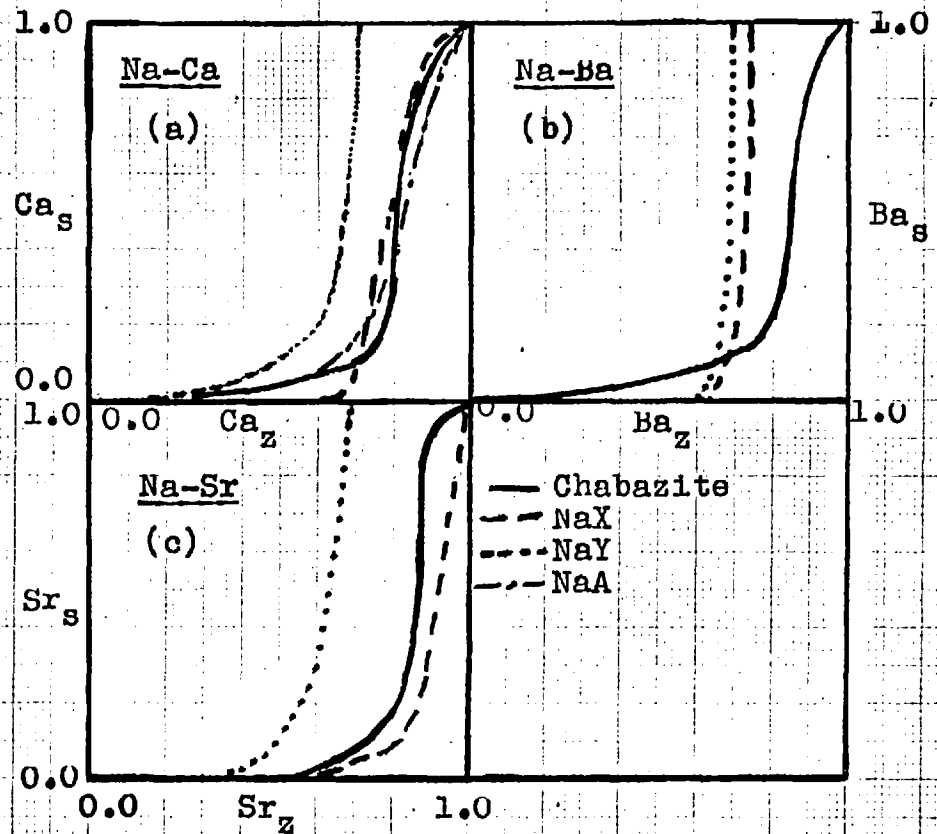
Fig.111Na-Ag exchange isotherms on several zeolites at 25°C

Fig. 112

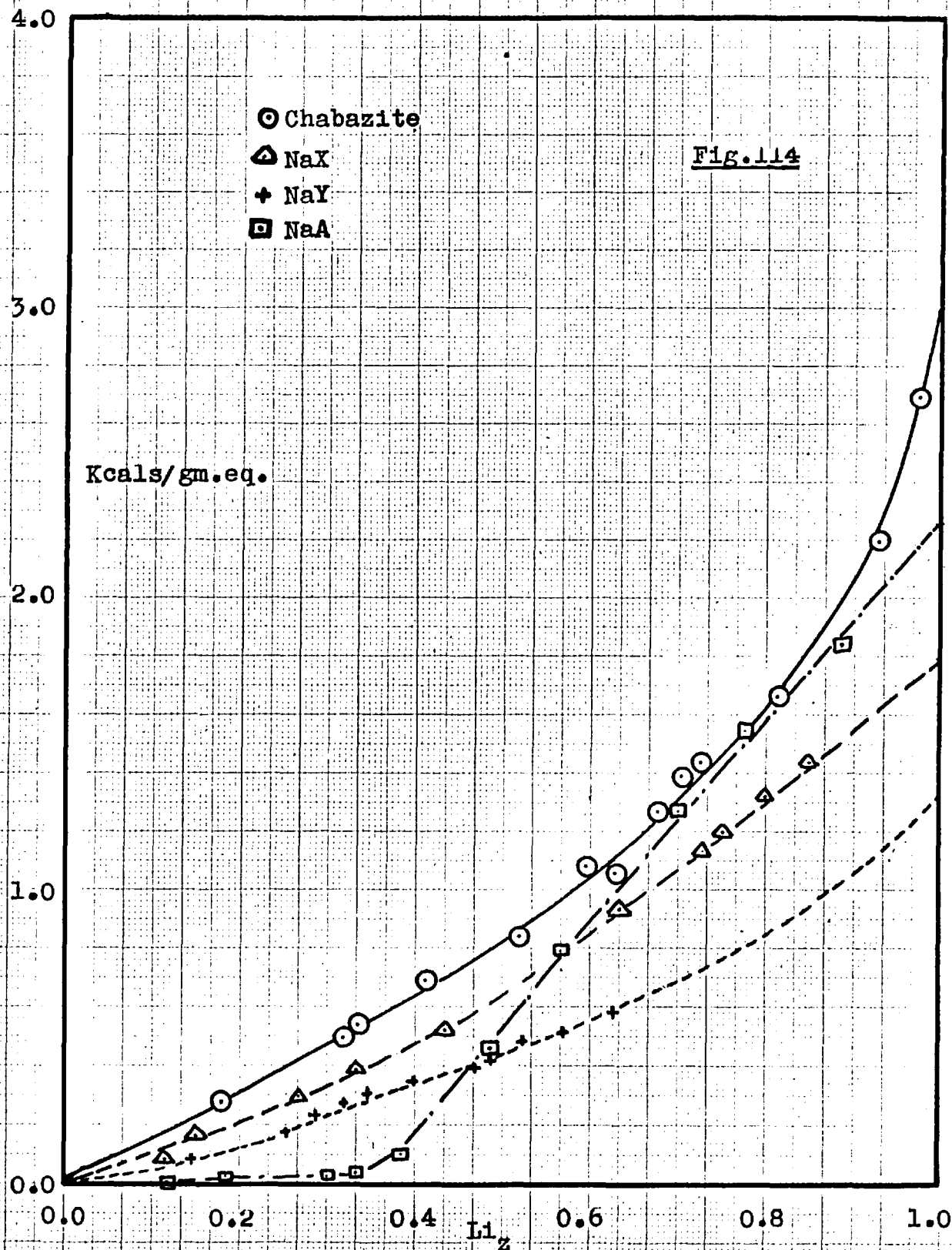
Na-Tl exchange isotherms on several zeolites at 25°C

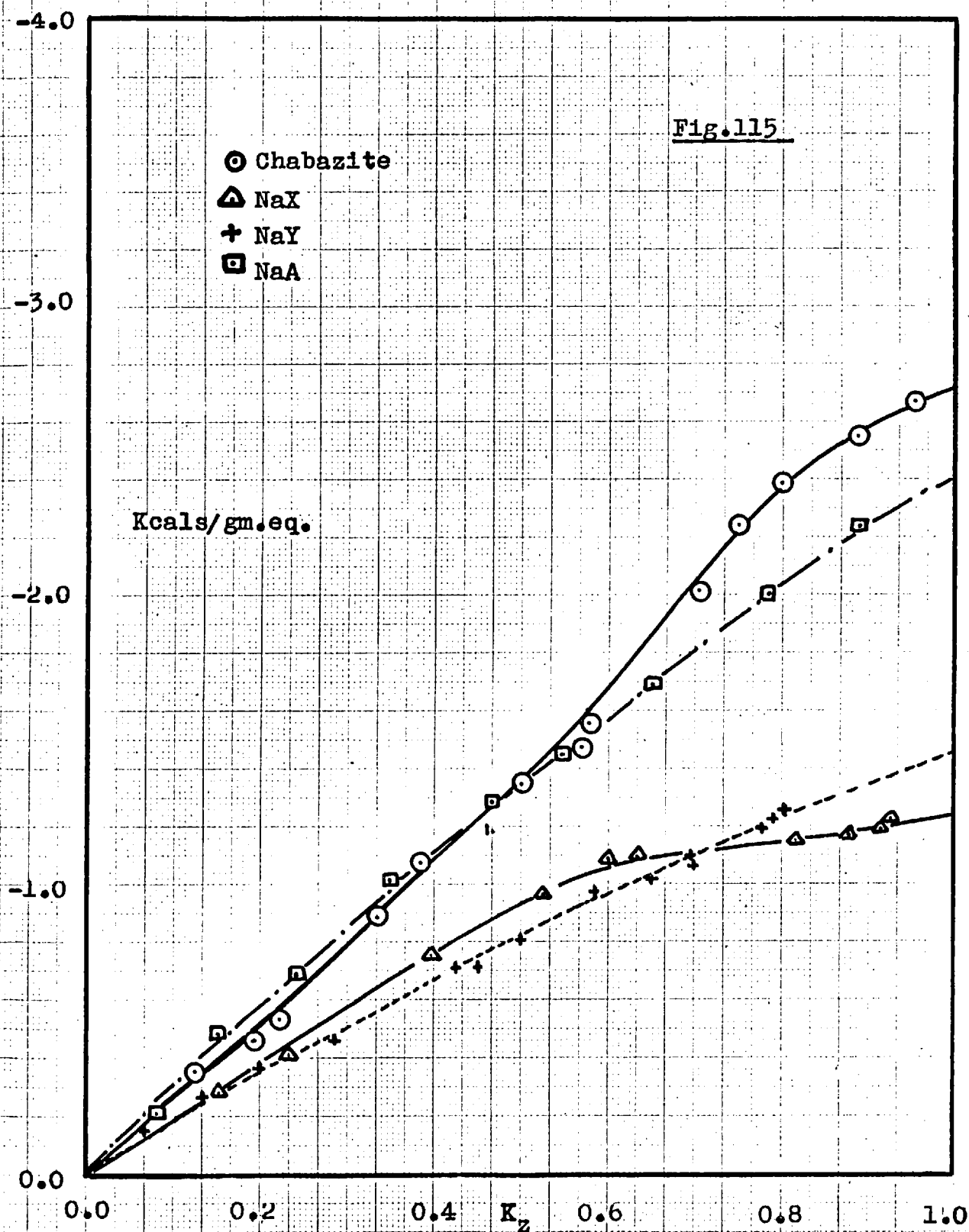


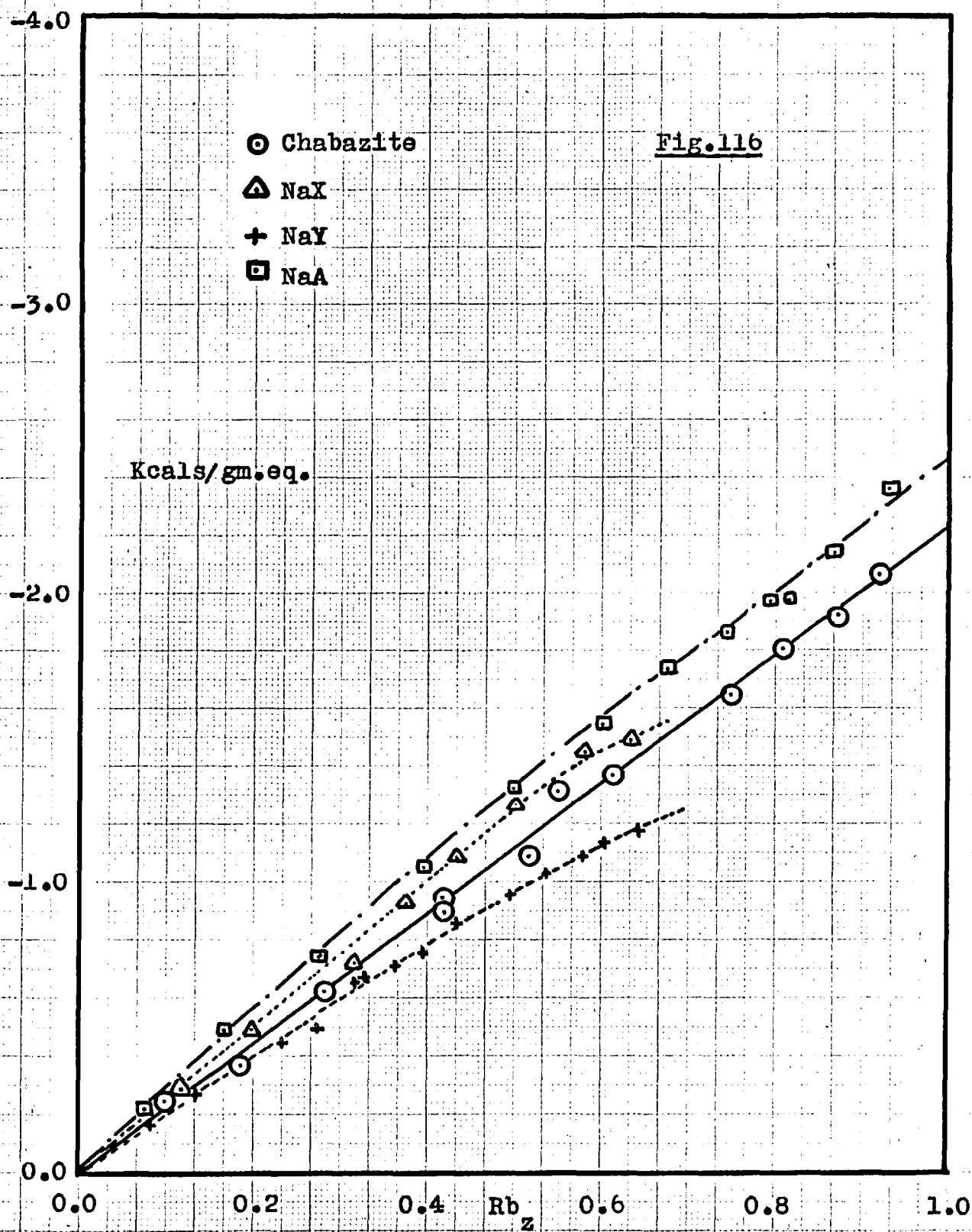
Comparison of uni-divalent exchange isotherms
on several zeolites at 25°C

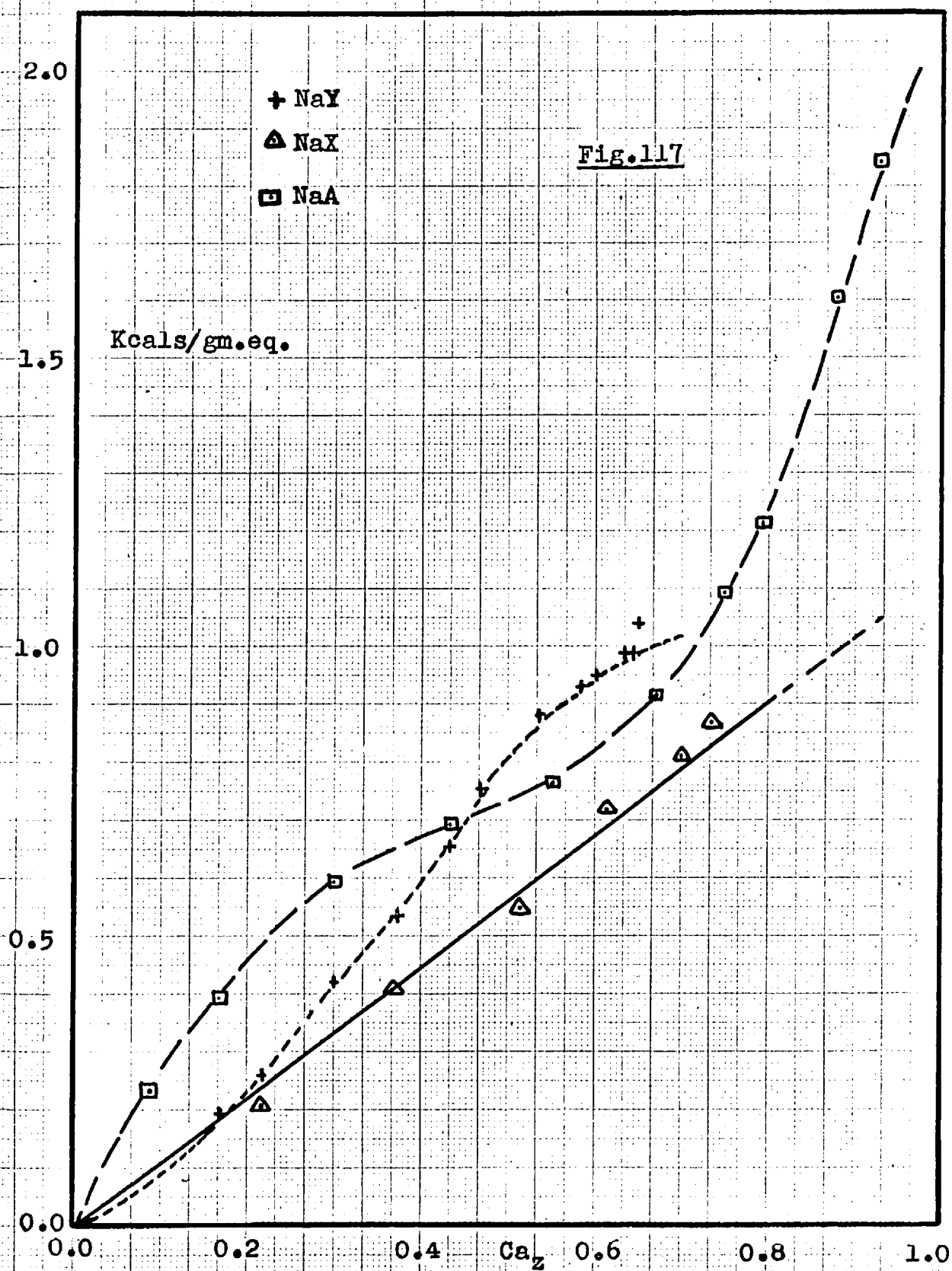


Na-Ca and Na-Sr exchange isotherms on
Chabazite determined at 50°C



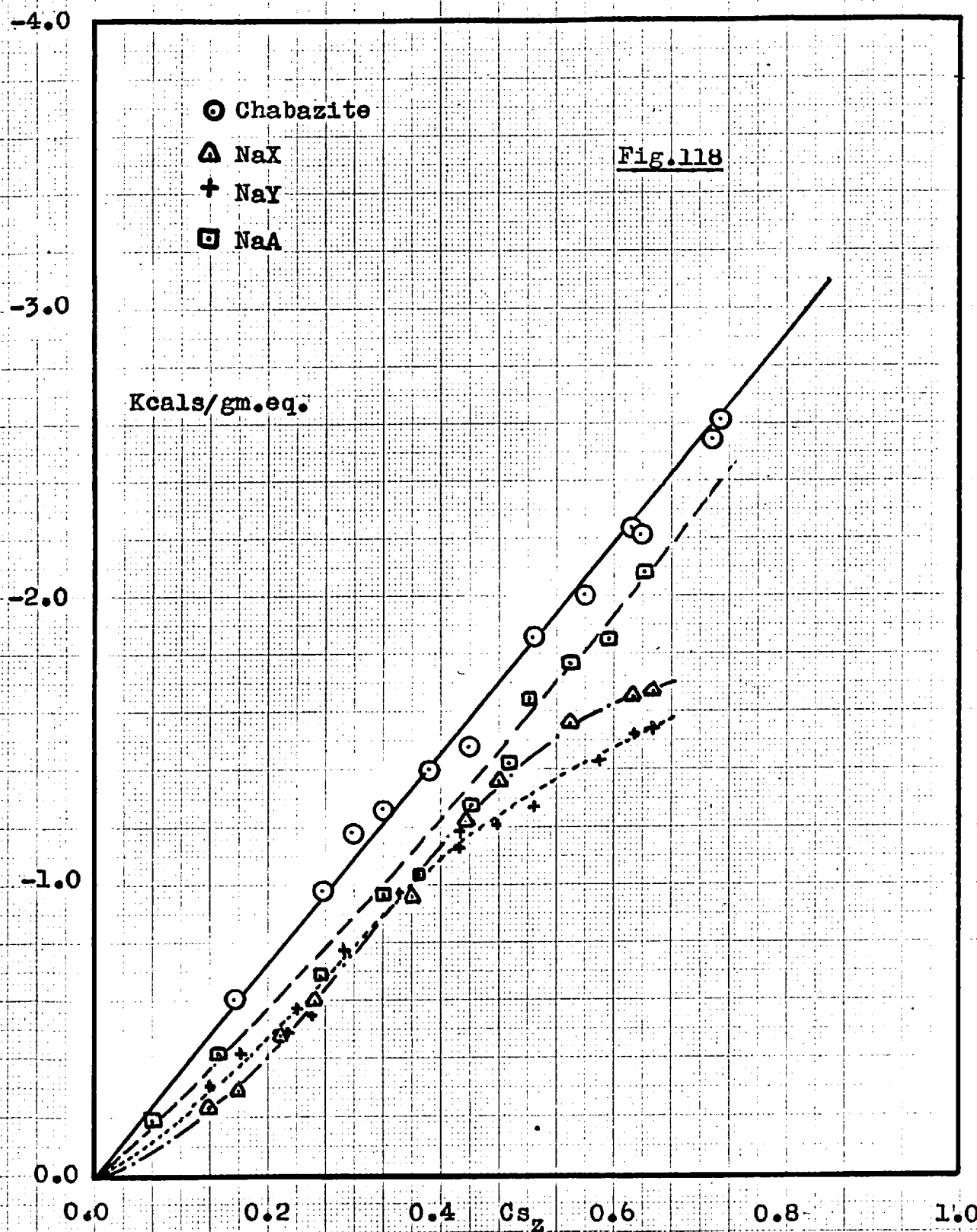






Standard Heats of partial ion exchange for the
Na-Cs exchange on several zeolites.

318



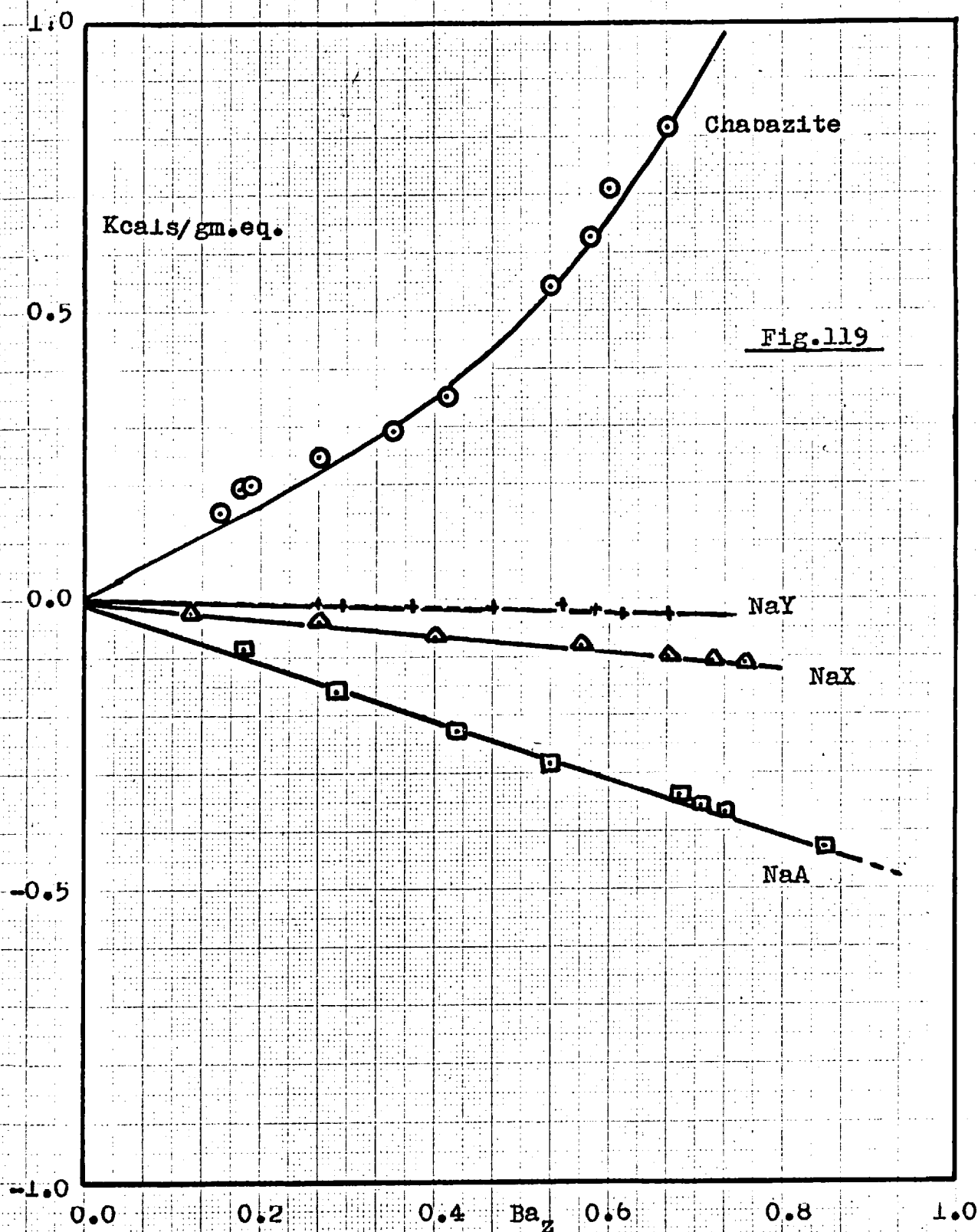
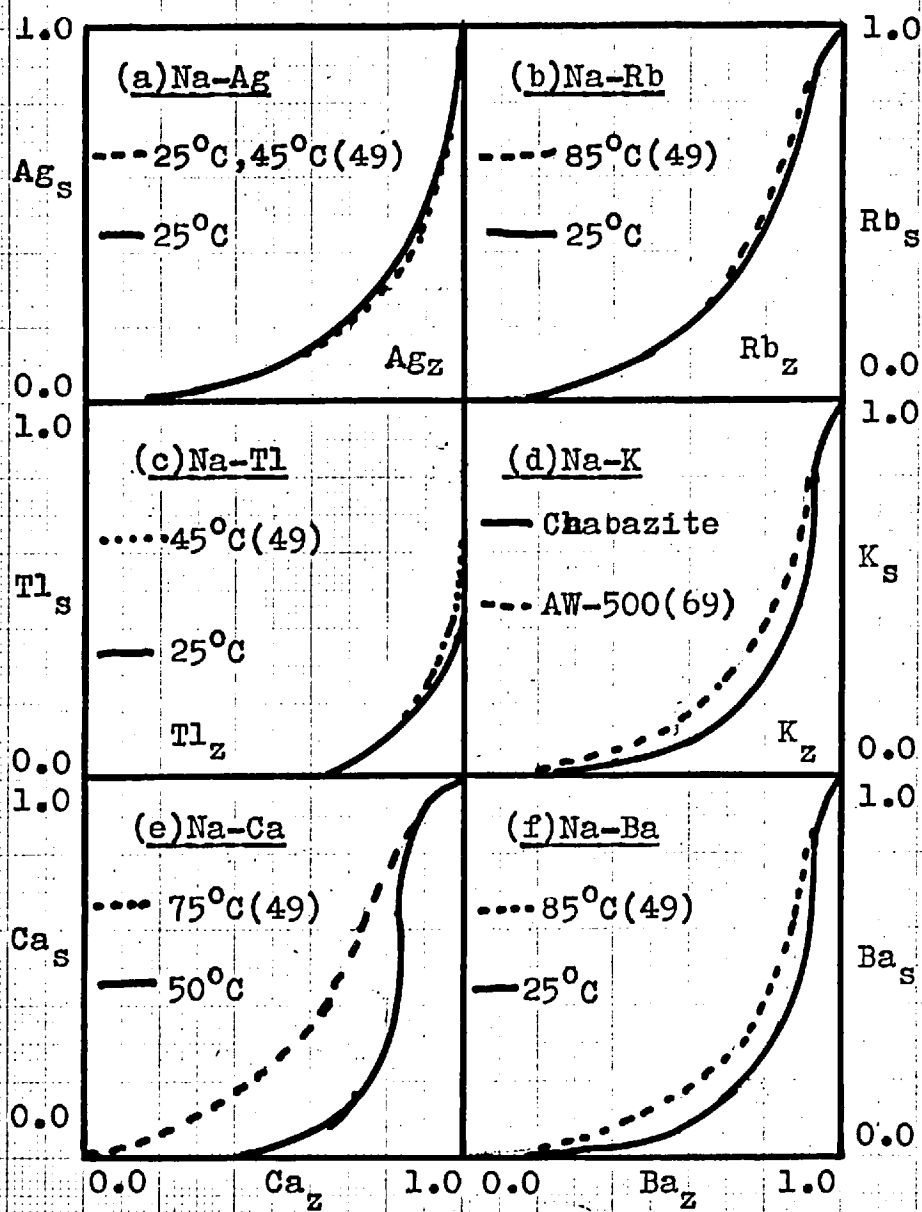
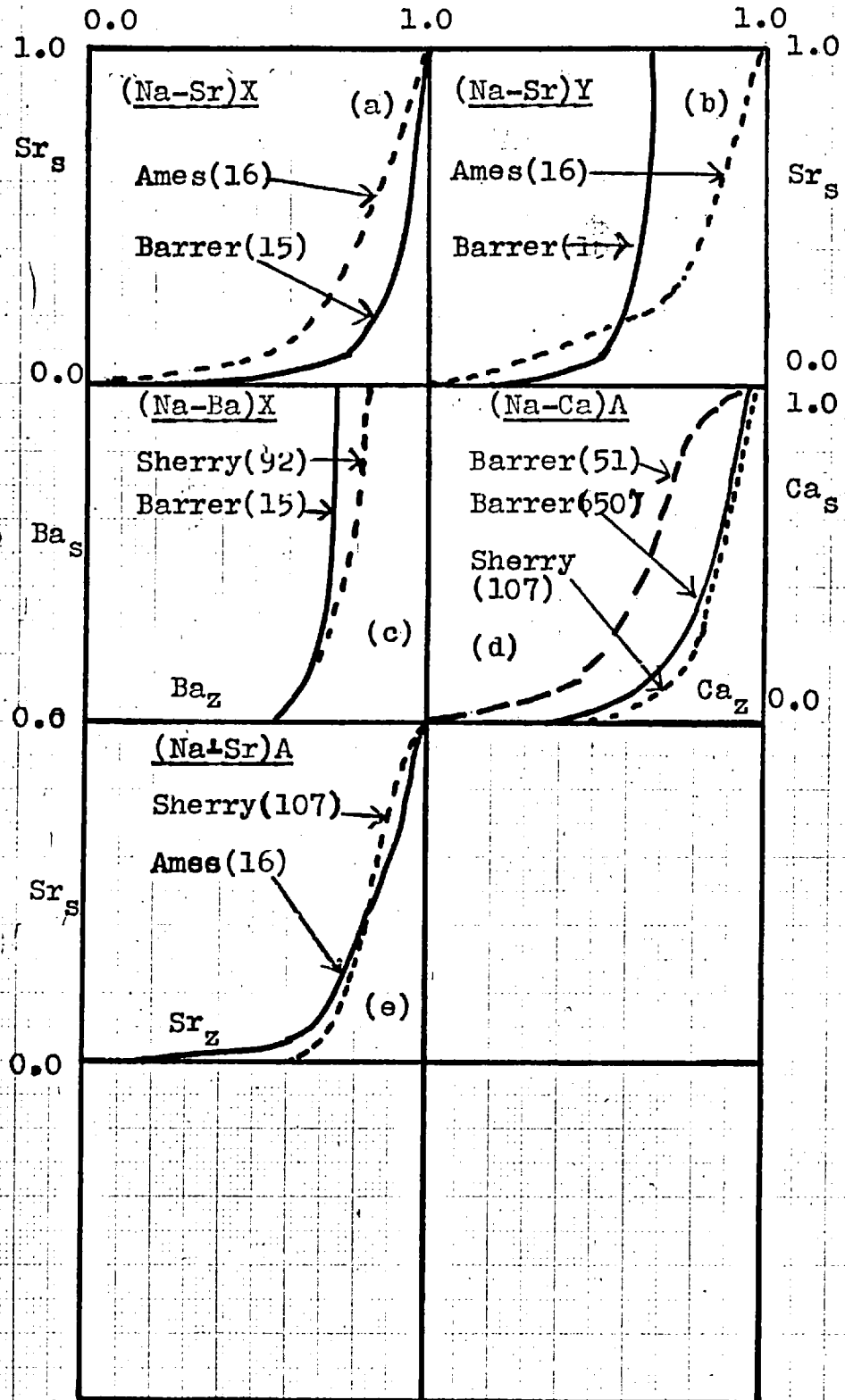


Fig.120 Exchanges in Chabazite

Exchanges in NaX, NaY and NaA



Among these exchangers it appears that the affinity of the divalent ions for the exchanger is greatest for those exchangers that have low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, i.e. high framework charges.

Determination of the heats of ion exchange by a calorimetric method has been restricted to the work of Barrer et al. (15) (51). Several experimenters (63), (69), (70), (107), have attempted to measure heats of ion exchange in zeolites by observing the temperature dependence of ion exchange equilibrium, although this method cannot be considered as reliable.

The variation of the standard heats of partial ion exchange with cationic composition of the exchanger for several Na - alkali metal ion and the Na - Ca exchanges in the zeolites NaA, NaX, NaY and chabazite are shown in Figs. 114 - 118. For a given ion pair the heats have the same signs and are of similar magnitudes i.e. 1 - 3 kcals/gm. eq. of exchanger. Generally, the standard heats are smaller for the exchanges in the faujasite type zeolites i.e. NaX and NaY, than for the corresponding exchanges in NaA and chabazite. Factors that must be taken into consideration when comparing these values are the average framework charges, and the degree of openness of the frameworks. It might be expected that the heats of ion exchange would be greater for the zeolites

of lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, i.e. NaX and NaA, since these zeolites have greater framework charges and would produce greater binding of the cations to the centres of negative charge. If the degree of openness of the zeolite structures is considered, then in the more open zeolites i.e. NaX and NaY, some of the cations would be hydrated more than in NaA and chabazite, and therefore less able to approach the centres of negative charges closely. A balance must be found between these two contributions. Since the heats of ion exchange in the faujasite zeolites are generally smaller than those in NaA and chabazite, it appears that the openness of the structure is the more important for the exchanges involving the alkali metal ions.

For exchanges involving the Na^+ and Ag^+ ions it appears that the energy of binding of the cations to the framework is the more important. The calorimetric heat of ion exchange for the zeolites NaY and chabazite was found to be small in both cases, approximately -0.5 kcal/gm. eq. The heat of exchange involving these ions has not been measured calorimetrically for a zeolite of lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, although Sherry and Walton (107) have reported a value of -2.78 ± 0.45 kcal/gm. eq. for this exchange in NaA, from observations of the temperature dependence of the thermodynamic equilibrium constant.

Thus in a zeolite of higher framework charge density, considerable binding of the Ag^+ ions with the anionic framework occurs.

The Na - Ca exchange isotherm is endothermic for NaA (51), NaX (15) and NaY. The more open zeolites i.e. NaX and NaY have the smaller heats of exchange. From a consideration of the framework charge both NaX and NaA would be expected to have the larger heats of exchange. As before, the degree of openness of the faujasite zeolites permits some of the ions to be hydrated inside the exchanger and unable to approach closely to the centres of negative charge.

The Na -Ba exchange is unusual in that the signs of the heat of exchange are different in the different zeolites (Fig. 119). No explanation of this behaviour can be given.

As well as comparing the exchange isotherms for a given ion pair in the different zeolites, it is of interest to compare exchange isotherms for a given ion pair on the same zeolite as determined by different experimenters. Uni-univalent exchange equilibria in chabazite have been studied by Barrer and Sammon (49). Excellent agreement has been found between their results and those of this work, Fig. 120 (a) (b) (c). Although they have used solutions of fixed normality in their determinations

whereas those in this thesis have been obtained with solutions of varying molalities this agreement is expected (vide section 5.1). The Na - K exchange isotherm has been determined by Ames (69) in a synthetic zeolite AW - 500, which is of the chabazite structural type and of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio 4 - 5. Slight differences occur between this isotherm and the corresponding isotherm in natural chabazite, Fig. 120 (d). This might partly be due to the fact that Ames has used bonded pellets whereas a finely divided powder has been employed in this work. Possibly the binder in these pellets hinders the free migration of the ions in the crystal. Uni-univalent exchanges in Linde Sieves X and Y have been studied by Barrer et al. (15) (this work) and Sherry (59). Excellent agreement has been found between the results of these experimenters.

The greatest deviations from reproducibility of the exchange isotherms has been found in the uni-divalent exchanges. The Na - Ca and Na - Ba exchange isotherms in chabazite are shown in Figs. 120 (e) (f) respectively and are compared with those obtained by Barrer and Sammon (49). The agreement between the isotherms is not good. This is due, at least in part, to the fact that Barrer and Sammon have used electrolyte solutions of 0.5 total normality in their determinations, whereas in this work

solutions of varying molalities have been used. As shown in section 5.1, uni-divalent exchange isotherms are dependent on solution strength. A similar behaviour has been observed in the Na - Ca exchange in NaA. This exchange system has been investigated by three sets of experimenters (50) (51) (107), and three different exchange isotherms have been reported. The samples used by all three experimenters had similar $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios and similar unit cell compositions, so it would be expected that the exchange isotherms would be identical. Again, however, the discrepancy is due at least in part to the fact that solutions of different molalities have been used in their determinations.

A second point of controversy that has arisen in exchange isotherms is the limit to exchange when incomplete exchange has been observed. The Na - Ba exchange in NaX is a prime example of this effect. Barrer, Buser and Grutter (14) have found that the maximum amount of exchange was 85%; Barrer, Rees and Shamsuzzoha (15) and Rees and Williams (114) have found the limit to be 74%; whereas Sherry (92) considered 82% to be the maximum amount of exchange. These variable limits to exchange cannot be readily explained, unless it is considered that other processes besides the Na - Ba exchange are occurring eg. salt occlusion, and exchange involving

hydrogen ions. The limit to exchange is an important quantity that must be obtained as accurately as possible, since interpretation of the exchange process in terms of the heterogeneity of sites in the exchanger depends on this quantity.

7.6

SUMMARY

A calorimeter, based on the D.T.A. apparatus of Borchardt and Daniels (91) has been used to measure the heats of reaction in the range 0 to 4 cal. with an accuracy of ± 0.05 cal. A calorimeter has also been designed which utilizes the resistance change of a small thermistor during the course of an ion exchange reaction. Heats of reaction in the range 0 - 4 cal have been measured to an accuracy of ± 0.04 cal.

The variation of the standard heat of ion exchange with cationic composition of the exchanger has been measured for the exchanges Na - Li, Na - K, Na - Rb, Na - Cs, Na - Ag, Na - Ca, Na - Sr and Na - Ba on both chabazite and NaY; and Na - NH_4 on chabazite. Also heats have been measured for the Na - Tl exchange on both chabazite and NaY, and the Na - Pb exchange on chabazite. The standard heats of ion exchange were in the range 0 to 3 kcals/gm. eq. of exchanger, the sign depending on the ions involved in the exchange. Among the uni-univalent exchanges, the reactions were exothermic in all cases when the ion of larger crystallographic radius replaced a smaller one in the zeolite. The uni-divalent exchanges were all endothermic when the divalent ion entered the crystal, except the Na - Ba exchange in NaY which was virtually athermal.

Activity coefficients of the components forming the mixed exchanger have been determined. In most of the exchanges studied the activity coefficients differ from unity thereby indicating non-ideality of behaviour in the mixed exchanger. For several of the uni-univalent exchanges the activity coefficients of the components in the mixed exchangers were represented by Kielland's relation.

The thermodynamic functions for the formation of the mixed exchanger from the pure components have also shown that the mixed exchanger cannot be regarded as an ideal solution of its components.

The thermodynamic data presented in this thesis for ion exchanges in chabazite and NaY indicate the complex nature of the ion exchange process. Comparison of the thermodynamic data with those obtained for ion exchanges in other zeolites, mainly (15) and (51) indicate that the causes of non-ideal behaviour are not always comparable. Not only do the framework structures of the zeolites differ, but so also do the numbers and positioning of the cations in the exchangers. Thus the derivation of a generalized picture of the ion exchange process does not seem likely without a better understanding of the individual processes that contribute to the overall process.

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APPENDIX

RESULTS

CALIBRATION DATA

Thermistor

Heat of Solution of KCl at 25°C

Molality of solution	Heat of solution cal/mole	ΔH cal	A sq. cm.	Calibration constant k_r cal/cm ²
0.00139	4120	0.1413	-9.005	-0.01902
0.00291	4130	0.3610	-20.78	-0.01732
0.00344	4136	0.4270	-23.67	-0.01804
0.00501	4140	0.6219	-35.05	-0.01774
0.00613	4144	0.7607	-45.63	-0.01667
0.00711	4146	0.8837	-47.55	-0.01858
0.00653	4144	0.8111	-47.89	-0.01694
0.00814	4148	1.0113	-59.68	-0.01697
0.00894	4150	1.113	-63.41	-0.01755
0.01019	4153	1.270	-70.18	-0.01810
0.01046	4154	1.304	-75.05	-0.01738
0.01100	4155	1.371	-79.46	-0.01725
0.01390	4162	1.732	-97.65	-0.01778
0.01569	4165	1.960	-111.76	-0.01754
0.01015	4152	1.254	-74.32	-0.01701

Mean Value $k_r = -0.01759$ cal/cm²

Thermocouple 1

Heat of Solution of KCl at 25°C

Molality of solution	Heat of solution cal/mole	ΔH cal	A cm ²	Calibration constant kr cal/cm ²
0.00456	4138	0.566	-10.91	-0.05188
0.00483	4138	0.599	-11.68	-0.05132
0.00778	4147	0.9678	-18.29	-0.05292
0.00851	4153	1.097	-20.48	-0.05356
0.00984	4154	1.225	-23.76	-0.05156
0.01164	4157	1.450	-28.65	-0.05061
0.01422	4162	1.775	-35.03	-0.05067
0.01622	4165	2.028	-37.67	-0.05384
0.01592	4165	1.989	-38.64	-0.05147
0.01730	4167	2.163	-41.38	-0.05227
0.01779	4168	2.225	-43.23	-0.05147
0.01967	4170	2.461	-47.03	-0.05233
0.01953	4169	2.444	-48.78	-0.05010
0.02244	4172	2.809	-55.32	-0.05078
0.02302	4173	2.882	-55.03	-0.05237
0.02548	4175	3.192	-63.76	-0.05006

Heat of Solution of NaCl at 25°C

0.03375	994	1.007	-19.00	-0.05300
0.1035	1017	3.159	-59.53	-0.05306

Mean Value $k_r = -0.05180 \text{ cal/cm}^2$

Thermocouple 2

Heat of Solution of KCl at 25°C

Molality of Solution	Heat of Solution cal/mole	ΔH cal	A cm ²	Calibration constant kr cal/cm ²
0.00536	4140	0.6109	-9.41	-0.06492
0.006393	4142	0.7944	-11.86	-0.06598
0.007868	4146	0.9787	-15.98	-0.06125
0.01225	4159	1.528	-24.85	-0.06149
0.01265	4159	1.579	-25.50	-0.06192
0.01355	4160	1.691	-25.72	-0.06575
0.01605	4165	2.005	-32.84	-0.06106
0.01739	4167	2.174	-32.92	-0.06604
0.01806	4168	2.258	-35.94	-0.06287
0.02052	4170	2.567	-40.97	-0.06266
0.02159	4172	2.703	-41.26	-0.06551
0.02271	4173	2.843	-44.71	-0.06359
0.02499	4175	3.130	-48.72	-0.06425
0.02580	4176	3.230	-50.09	-0.06448
0.02459	4174	3.079	-50.47	-0.06101
0.02839	4178	3.557	-53.99	-0.06588
0.02934	4179	3.665	-57.73	-0.06349
0.03076	4180	3.856	-61.61	-0.06259

Heat Solution of NaCl at 25°C

0.09956	1016	2.991	-46.85	-0.06384
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Mean Value kr = -0.06358 cal/cm²

Na-Li Exchange on Chabazite at 25°C

(particle size 150 - 200 mesh)

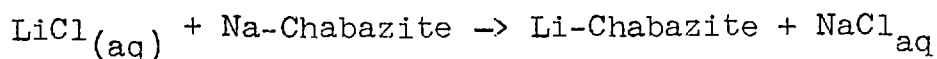
Calorimeter Data

Initial molality m_A^o	$Li_x = Li_z$	Li_s	ΔH_x k cal/gm.eq.of exchanger	ΔH_x^o
<u>Na → Li Exchange</u>				
0.0501	0.1800	0.4016	0.249	0.280
0.1016	0.3178	0.8937	0.445	0.498
0.0820	0.3447	0.9127	0.473	0.524
0.1016	0.3327	0.9085	0.492	0.546
0.1640	0.4123	0.9388	0.614	0.686
0.1640	0.4504	0.9421	0.582	0.654
0.4885	0.5207	0.9600	0.731	0.840
0.410	0.5956	0.9681	0.976	1.095
0.4885	0.6365	0.9725	0.922	1.056
0.4885	0.6701	0.9776	1.152	1.291
0.7327	0.7068	0.9775	1.226	1.397
0.820	0.7242	0.9768	1.266	1.446
1.646	0.7818	0.9878	1.277	1.541
1.646	0.8115	0.9907	1.394	1.667
2.716	0.7887	0.9960	1.388	1.670
2.716	0.9210	0.9937	1.801	2.198
4.195	0.9735	0.9975	2.124	2.694
<u>Li → Na exchange</u>				
0.1005	0.0789	0.4016	-2.962	-2.910

Ion Exchange Equilibria Data (4 days)

Initial molality m_A^o	Li_z	Li_s	Initial molality	Li_z	Li_s
<u>Na $\rightarrow$ Li exchange</u>					
0.00217	0.0499	0.1978	0.06773	0.2485	0.8585
0.00677	0.0592	0.3725	0.06773	0.3639	0.9030
0.00677	0.0724	0.4455	0.1016	0.3518	0.9085
0.01016	0.0810	0.5850	0.2443	0.4109	0.9427
0.03386	0.1435	0.7569	0.4885	0.5180	0.9605
0.03386	0.1525	0.7771	0.7327	0.6939	0.9780
0.05008	0.1726	0.8076	1.646	0.9117	0.9921
0.06773	0.1877	0.8240	2.716	0.9339	0.9937
0.06673	0.3024	0.8934			
<u>Li $\rightarrow$ Na exchange</u>					
0.01217	0.5590	0.9454	0.0335	0.6250	0.9747
0.0335	0.3063	0.8677			

For the reaction at 25°C



$$\Delta H^\circ = 3.05 \text{ kcal/gm.eq.}$$

$$\Delta G^\circ = 1.72 \text{ kcal/gm.eq.}$$

$$T \Delta S^\circ = 1.32 \text{ kcal/gm.eq.}$$

Thermodynamic Functions for the reaction

x Li-Chabazite + $(1-x)$ Na-chabazite

$\rightarrow \text{Li}_x \text{Na}_{1-x} \text{Chabazite}$

and the differential heat of exchange $\frac{\partial \Delta H_x^0}{\partial x}$

$\text{Li}_x = \text{Li}_z$	ΔG_x^M	ΔH_x^M	$T\Delta S_x^M$	$\frac{\partial \Delta H_x^0}{\partial x}$
	k cal/gm.eq. of exchanger			
0.1	-0.193	-0.150	0.043	1.40
0.2	-0.296	-0.299	0.003	1.42
0.3	-0.362	-0.444	-0.082	1.54
0.4	-0.398	-0.563	-0.165	1.68
0.5	-0.410	-0.653	-0.243	1.77
0.6	-0.398	-0.748	-0.350	2.26
0.7	-0.362	-0.782	-0.420	2.69
0.8	-0.296	-0.787	-0.491	3.58
0.9	-0.193	-0.661	-0.468	5.32
0.95	-0.117	-0.484	-0.367	6.78

Na-K Exchange on Chabazite at 25°c

(Particle size 150-200 mesh)

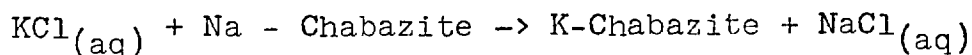
Calorimeter Data

Initial molality	K _Z	K _S	ΔH_x kcal/gm-eq.	ΔH_x°
<u>Na → K Exchange</u>				
0.0052	0.1211	0.008	-0.452	-0.366
0.0052	0.1917	0.0152	-0.540	-0.454
0.00725	0.2226	0.0143	-0.625	-0.539
0.0100	0.336	0.031	-0.970	-0.887
0.0140	0.3833	0.0495	-1.160	-1.077
0.0200	0.5001	0.0601	-1.435	-1.351
0.0333	0.5715	0.0629	-1.545	-1.472
0.0333	0.5754	0.0887	-1.645	-1.565
0.0333	0.7047	0.1706	-2.110	-2.030
0.0333	0.7543	0.1958	-2.305	-2.237
0.0500	0.8023	0.3309	-2.468	-2.391
0.0500	0.8859	0.4989	-2.629	-2.549
0.336	0.9568	0.9097	-2.690	-2.654
<u>K → Na Exchange</u>				
0.1000	0.6838	0.1205	0.493	0.625
0.0333	0.7955	0.2465	1.09	0.225

Ion Exchange Equilibrium Data (4 days)

Initial molality	K_z	K_s	Initial molality	K_z	K_s
<u>Na $\rightarrow$ K exchange</u>					
0.0334	0.6665	0.1330	0.0668	0.9285	0.5888
0.0334	0.5572	0.1850	0.1002	0.9507	0.6864
0.0400	0.9087	0.5150	0.1002	0.9651	0.7631
0.0500	0.8502	0.3383	0.3357	0.9582	0.8501
0.0500	0.8909	0.4850	0.6713	0.9716	0.9600
0.0500	0.9101	0.4943	1.007	0.9974	0.9719
<u>K $\rightarrow$ Na exchange</u>					
0.0927	0.7102	0.1921	0.03091	0.8366	0.3305
0.0993	0.6972	0.1489	0.01217	0.8977	0.4580
0.0618	0.7873	0.2365	0.3053	0.6286	0.0880

For the reaction at 25°C



$$\Delta H^\circ = - 2.61 \text{ kcals/gm.eq.}$$

$$\Delta G^\circ = - 1.60 \text{ kcals/gm.eq.}$$

$$T \Delta S^\circ = - 1.01 \text{ kcals/gm.eq.}$$

Thermodynamic Functions for the reaction

x K-Chabazite + $(1-x)$ Na - Chabazite

$\rightarrow K_x \cdot Na_{1-x}$ - Chabazite

and the differential heat of exchange

K_x	ΔG_x^M	ΔH_x^M	$T\Delta S_x^M$	$\frac{\partial \Delta H_x^0}{\partial x}$
	kcal/gm.eq. of exchanger			
0.1	-0.220	0.002	0.222	-2.50
0.2	-0.347	0.003	0.350	-2.62
0.3	-0.425	-0.005	0.420	-2.70
0.4	-0.472	-0.008	0.464	-2.73
0.5	-0.487	-0.011	0.476	-2.80
0.6	-0.472	-0.030	0.442	-2.90
0.7	-0.425	-0.178	0.247	-3.02
0.8	-0.347	-0.286	0.061	-2.40
0.9	-0.220	-0.215	0.005	-1.56

Na - Rb exchange on Chabazite at 25°c

(Particle Size 150 - 200 mesh)

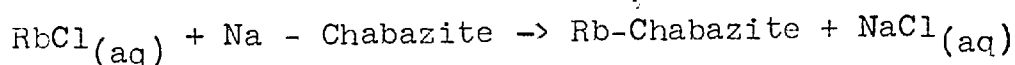
Calorimeter Data

Initial molality	Rb _z	Rb _s	ΔH_x kcal/gm.eq.	ΔH_x°
<u>Na → Rb exchange</u>				
0.005	0.1043	0.0051	-0.335	-0.249
0.0071	0.1834	0.0080	-0.443	-0.358
0.00944	0.2839	0.0233	-0.725	-0.638
0.01416	0.4208	0.0705	-1.018	-0.937
0.01888	0.4202	0.0789	-0.967	-0.881
0.02832	0.525	0.1270	-1.153	-1.070
0.02832	0.5457	0.1407	-1.401	-1.315
0.02832	0.6107	0.1454	-1.449	-1.362
0.0337	0.7453	0.3917	-1.738	-1.653
0.1011	0.8717	0.7359	-1.998	-1.916
0.3827	0.9202	0.9208	-2.145	-2.069

Ion Exchange Equilibrium Data (4 days)

Initial Molality	Rb _z	Rb _s	Initial Molality	Rb _z	Rb _s
<u>Na → Rb exchange</u>					
0.00156	0.0418	0.00165	0.02832	0.6990	0.2091
0.00333	0.0765	0.0030	0.02832	0.7035	0.2833
0.00333	0.1340	0.0060	0.0337	0.7481	0.3085
0.00708	0.1875	0.0089	0.0505	0.8085	0.5152
0.0050	0.2141	0.0176	0.0505	0.8269	0.5719
0.00994	0.3304	0.0279	0.1011	0.8609	0.6944
0.01888	0.3757	0.0704	0.0674	0.8635	0.6273
0.01888	0.4904	0.0971	0.5741	0.9405	0.9550
0.02832	0.6344	0.1580			
<u>Rb → Na exchange</u>					
0.1017	0.6244	0.1038	0.1017	0.5505	0.1030
0.1017	0.6661	0.1289	0.0678	0.6374	0.1370

For the reaction at 25°C

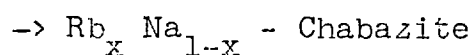
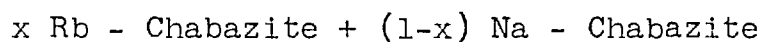


$$\Delta H^{\circ} = -2.24 \text{ kcal/gm.eq.}$$

$$\Delta G^{\circ} = -1.34 \text{ kcal/gm.eq.}$$

$$T \Delta S^{\circ} = -0.90 \text{ kcal/gm.eq.}$$

Thermodynamic Functions for the reaction



and the differential heat of exchange

Rb_x	ΔG_x^M	ΔH_x^M	$T\Delta S_x^M$	$\frac{\delta \Delta H_x^0}{\delta x}$
0.1	-0.270	0.064	0.334	-2.24
0.2	-0.435	0.058	0.493	-2.24
0.3	-0.543	0.052	0.595	-2.24
0.4	-0.606	0.041	0.647	-2.24
0.5	-0.626	0.040	0.666	-2.24
0.6	-0.606	0.029	0.635	-2.24
0.7	-0.543	0.013	0.556	-2.24
0.8	-0.435	0.017	0.452	-2.24
0.9	-0.270	0.006	0.276	-2.24

Na - NH₄ exchange on Chabazite at 25°C

(Particle size 150 - 200 mesh)

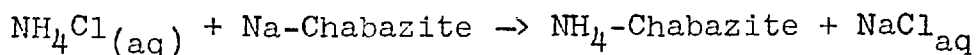
Calorimeter Data

Initial Molality	(NH ₄) _z	(NH ₄) _s	ΔH_x kcal/gm.eq.	ΔH_x^0
<u>Na → NH₄ exchange</u>				
0.0070	0.2057	0.0350	-0.160	-0.074
0.0105	0.2813	0.0611	-0.229	-0.143
0.0105	0.3953	0.0869	-0.381	-0.295
0.0210	0.4295	0.1180	-0.418	-0.332
0.0210	0.4660	0.1184	-0.427	-0.342
0.0210	0.5078	0.1825	-0.486	-0.401
0.0210	0.5824	0.2113	-0.641	-0.556
0.0254	0.5853	0.2502	-0.600	-0.511
0.05075	0.6030	0.2305	-0.646	-0.560
0.03383	0.7028	0.3379	-0.862	-0.777
0.05075	0.7343	0.4587	-0.907	-0.821
0.03383	0.6952	0.3320	-0.816	-0.730
0.0676	0.8334	0.6319	-1.063	-0.976
0.1015	0.8897	0.7550	-1.150	-1.060
0.1818	0.9110	0.8201	-1.146	-1.064
0.3636	0.9692	0.934	-1.274	-1.193
<u>NH₄ → Na exchange</u>				
0.0991	0.5508	0.1737	0.730	0.789

Ion Exchange Equilibrium Data (4 days)

Initial Molality	(NH ₄) _z	(NH ₄) _s	Initial Molality	(NH ₄) _z	(NH ₄) _s
<u>Na → NH₄ exchange</u>					
0.0070	0.1819	0.0257	0.03383	0.6932	0.3320
0.0140	0.2816	0.0562	0.06786	0.8363	0.5881
0.05075	0.6717	0.2851	0.05075	0.7924	0.4992
0.03383	0.6818	0.3858	0.05075	0.7261	0.3818
0.03383	0.6175	0.2374	1.0907	0.9841	0.9751
<u>NH₄ → Na exchange</u>					
0.3053	0.3683	0.0753	0.09906	0.6268	0.2453
0.3053	0.3805	0.0868	0.09906	0.6679	0.3052
0.2036	0.4933	0.1477	0.06604	0.6080	0.2740
0.09906	0.5082	0.1468	0.06604	0.7056	0.3748
0.09906	0.5508	0.1737	0.03302	0.7718	0.4535
0.09906	0.5702	0.2391	0.03302	0.8116	0.5238
0.09906	0.5709	0.2545			

For the reaction at 25°C



$$\Delta H^\circ = -1.24 \text{ kcal/gm.eq.}$$

$$\Delta G^\circ = -0.99 \text{ kcal/gm.eq.}$$

$$T\Delta S^\circ = -0.25 \text{ kcal/gm.eq.}$$

Thermodynamic Functions for the reaction
 $x \text{ NH}_4 - \text{Chabazite} + (1-x) \text{ Na} - \text{Chabazite}$
 $\rightarrow (\text{NH}_4)_x \text{ Na}_{1-x} - \text{Chabazite}$
 and the differential heat of exchange

$(\text{NH}_4)_x$	ΔG_x^M	ΔH_x^M	$T\Delta S_x^M$	$\frac{\partial \Delta H_x^O}{\partial x}$
	kcal/gm.eq. of exchanger			
0.1	-0.239	0.100	0.339	-0.400
0.2	-0.378	0.180	0.558	-0.640
0.3	-0.470	0.215	0.683	-0.950
0.4	-0.524	0.215	0.739	-1.186
0.5	-0.539	0.215	0.754	-1.370
0.6	-0.524	0.175	0.699	-1.620
0.7	-0.470	0.125	0.595	-1.750
0.8	-0.378	0.085	0.463	-1.760
0.9	-0.239	0.050	0.289	-1.760

Na - Cs exchange on Chabazite at 25°c

(Particle Size 150 - 200 mesh)

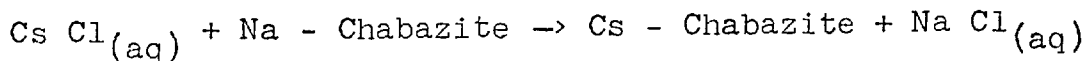
Calorimeter Data

Initial Molality	Cs _z	Cs _s	ΔH_x kcal/gm.eq. of exchange	ΔH°_x
<u>Na - Cs exchange</u>				
0.00508	0.1540	0.0006	-0.609	-0.523
0.00678	0.2500	0.0125	-0.964	-0.878
0.00846	0.3037	0.0155	-1.198	-1.112
0.01269	0.3319	0.0244	-1.267	-1.183
0.01269	0.3875	0.0517	-1.397	-1.314
0.01535	0.4334	0.0519	-1.472	-1.389
0.01692	0.5096	0.1237	-1.862	-1.779
0.01692	0.5671	0.0995	-1.998	-1.916
0.03383	0.6221	0.4114	-2.238	-2.162
0.03383	0.6344	0.5520	-2.206	-2.130
0.07977	0.7119	0.7328	-2.559	-2.494
0.2393	0.7278	0.9088	-2.611	-2.554

Ion exchange equilibria data (4 days)

Initial Molality	Cs _z	Cs _s	Initial Molality	Cs _z	Cs _s
<u>Na → Cs exchange</u>					
0.00508	0.0881	0.0010	0.02538	0.6376	0.0592
0.00508	0.1007	0.0014	0.02538	0.6773	0.0780
0.00508	0.1561	0.0028	0.02538	0.7649	0.2335
0.00508	0.2067	0.0015	0.01692	0.7102	0.0897
0.01269	0.3020	0.0068	0.05075	0.7978	0.4979
0.01269	0.3770	0.0333	0.05075	0.8117	0.4190
0.01269	0.3970	0.0165	0.07977	0.8329	0.7246
0.01269	0.4250	0.0200	0.0338	0.8136	0.3184
0.01692	0.4744	0.0296	0.1197	0.8379	0.8179
0.01692	0.5332	0.0478	0.2393	0.8358	0.9261
0.01269	0.5001	0.0300	0.5863	0.8320	0.9674
0.01692	0.5453	0.0465			

For the reaction at 25°C



$$\Delta G^{\circ} = -2.50 \text{ kcal/gm. eq.}$$

$$\Delta H^{\circ} = -2.89 \text{ kcal/gm. eq.}$$

Na - Ag exchange on Chabazite at 25°c

(Particle size 150 - 200 mesh)

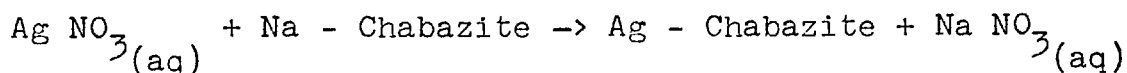
Calorimeter Data

Initial Molality	Ag _z	Ag _s	ΔH_x kcal/gm.eq. of exchanger	ΔH_x°
<u>Na → Ag exchange</u>				
0.00667	0.1319	0.0095	-0.208	-0.121
0.01001	0.2084	0.0100	-0.236	-0.150
0.01335	0.2980	0.0267	-0.262	-0.177
0.02003	0.3733	0.0690	-0.284	-0.198
0.02003	0.4750	0.0675	-0.275	-0.190
0.02003	0.5076	0.0907	-0.274	-0.188
0.02003	0.5296	0.1028	-0.318	-0.233
0.03335	0.6223	0.1493	-0.311	-0.229
0.03335	0.8103	0.3710	-0.427	-0.344
0.10015	0.9709	0.8283	-0.491	-0.414

Ion Exchange Equilibria Data (4 days)

Initial Molality	Ag _Z	Ag _S	Initial Molality	Ag _Z	Ag _S
<u>Na → Ag exchange</u>					
0.00667	0.1268	0.0075	0.03338	0.7379	0.2160
0.01001	0.2785	0.0200	0.03338	0.8045	0.3446
0.01335	0.3661	0.0425	0.05008	0.8481	0.4577
0.02003	0.4630	0.0739	0.03338	0.7681	0.2576
0.01669	0.4798	0.0978	0.06677	0.8676	0.5224
0.02003	0.5602	0.1032	0.06677	0.9073	0.6201
0.03338	0.5957	0.1268	0.10016	0.9228	0.6770
0.02003	0.6302	0.1653	0.10016	0.9594	0.7989
0.03338	0.7188	0.2013	0.10016	0.9589	0.3446
<u>Ag → Na exchange</u>					
0.0999	0.5572	0.1081	0.0333	0.7512	0.2022
0.0999	0.5704	0.1249	0.0999	0.4350	0.0677

For the reaction at 25°C



$$\Delta H^\circ = -0.44 \text{ kcals/gm. eq.}$$

$$\Delta G^\circ = -1.44 \text{ kcals/gm. eq.}$$

$$T\Delta S^\circ = 1.00 \text{ kcals/gm. eq.}$$

Thermodynamic Functions for the reaction

x Ag - Chabazite + $(1-x)$ Na - Chabazite

$\rightarrow$ $\text{Ag}_x \text{Na}_{1-x}$ - Chabazite

and the differential heat of exchange

Ag_x	ΔG_x^M k cals/gm. eq.	ΔH_x^M	$T\Delta S_x^M$	$\frac{\partial \Delta H_x^0}{\partial x}$
0.1	-0.230	-0.046	0.184	-0.650
0.2	-0.364	-0.062	0.302	-0.360
0.3	-0.449	-0.038	0.411	-0.250
0.4	-0.499	-0.004	0.495	-0.200
0.5	-0.515	+0.020	0.535	-0.200
0.6	-0.499	+0.044	0.543	-0.260
0.7	-0.449	+0.048	0.497	-0.390
0.8	-0.364	+0.022	0.386	-0.450
0.9	-0.230	+0.006	0.236	-0.480

Na - Tl exchange on Chabazite at 25°c

(Particle size 150 - 200 mesh)

Calorimeter Data

Initial Molality	Tl _z	Tl _s	ΔH_x kcal/gm.eq. of exchanger	$\Delta H'_x$
<u>Na → Tl exchange</u>				
0.0067	0.1137	0.0027	-0.330	-0.244
0.01007	0.1965	0.0032	-0.502	-0.416
0.01007	0.2945	-	-0.645	-0.565
0.01007	0.3462	0.0056	-0.798	-0.712
0.01007	0.4811	0.0101	-1.053	-0.966
0.0204	0.5493	-	-1.165	-1.079
0.0252	0.6528	0.0130	-1.362	-1.276
0.0336	0.7236	0.0150	-1.485	-1.399
0.0336	0.7697	0.0299	-1.563	-1.477
0.0336	0.8435	0.0687	-1.719	-1.633
0.0503	0.9555	0.3032	-1.916	-1.830

Ion exchange equilibria data (4 days)

Initial Molality	Tl _z	Tl _s	Initial Molality	Tl _z	Tl _s
<u>Na → Tl exchange</u>					
0.0067	0.0977	0.0026	0.0336	0.7594	0.0314
0.0033	0.0833	0.0012	0.0336	0.8709	0.0918
0.0100	0.2284	0.0030	0.0336	0.9001	0.1551
0.0100	0.4149	0.0059	0.0503	0.9432	0.2922
0.0100	0.5488	0.0088	0.0503	0.9811	0.3915
0.0100	0.6003	0.0150	0.1007	0.9978	0.6696
0.0100	0.7413	0.0251	0.1007	0.9989	0.7474
0.0336	0.7263	0.0144			
<u>Tl → Na exchange</u>					
0.0666	0.8250	0.0509			

For the reaction at 25°C

$$\Delta G^\circ = -2.62 \text{ kcals/gm. eq. of exchanger}$$

$$\Delta H' = -1.90 \text{ kcals/gm. eq. of exchanger}$$

$$T\Delta S' = 0.72 \text{ kcals/gm. eq. of exchanger}$$

Na - Li Exchange on NaY at 25°C

(particle size 150-200 mesh)

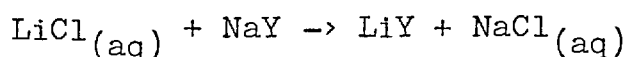
Calorimeter Data

Initial molality	Li _z	Li _s	ΔH_x kcal/gm.eq. of exchanger	ΔH_x°
<u>Na → Li exchange</u>				
0.01006	0.1426	0.5620	-	0.099
0.03354	0.2443	0.7489	0.064	0.166
0.06707	0.3178	0.8322	0.158	0.269
0.0805	0.3425	0.8567	0.194	0.310
0.0503	0.2850	0.7951	0.125	0.231
0.1006	0.3940	0.8861	0.239	0.346
0.1006	0.3640	0.8643	0.207	0.313
0.2041	0.4750	0.9250	0.281	0.430
0.2551	0.4654	0.9356	0.236	0.391
0.3402	0.5246	0.9504	0.314	0.489
0.5102	0.5601	0.9677	0.315	0.510
1.0205	0.6276	0.9837	0.310	0.576
1.0205	0.5849	0.9822	0.341	0.600
<u>Li → Na exchange</u>				
0.03334	0.2583	0.7292	-1.240	-1.149
0.03334	0.2575	0.7266	-1.233	-1.141
0.01666	0.5864	0.9671	-0.935	-0.843

Ion Exchange Equilibria Data (4 days)

Initial molality	Li _z	Li _s	Initial molality	Li _z	Li _s
<u>Na → Li Exchange</u>					
0.005	0.0778	0.3426	0.2041	0.4696	0.9240
0.01006	0.1020	0.4284	0.3803	0.5834	0.9734
0.01006	0.1198	0.4682	1.0205	0.6230	0.9842
0.02012	0.1692	0.6302	1.0205	0.6111	0.9812
0.03354	0.1971	0.6713	3.344	0.6628	0.9943
0.03354	0.2482	0.7654	3.344	0.6893	0.9968
0.06707	0.3167	0.8137	6.259	0.7183	0.9980
0.1006	0.3834	0.8703	6.259	0.7750	0.9972
0.1006	0.3952	0.8861			
<u>Li → Na Exchange</u>					
0.0200	0.3717	0.8594			

For the reaction at 25°c

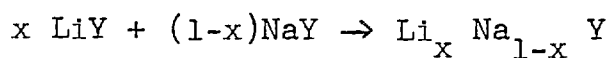


$$\Delta H^{\circ} = + 1.35 \text{ kcals/gm.eq.}$$

$$\Delta G^{\circ} = + 2.86 \text{ kcals/gm.eq.}$$

$$T \Delta S^{\circ} = - 1.51 \text{ kcals/gm.eq.}$$

Thermodynamic Functions for the reaction



and the differential heat of ion exchange

Li_z	ΔG_x^M	ΔH_x^M	$T\Delta S_x^M$	$\frac{\partial \Delta H_x^0}{\partial x}$
	kcal/gm.eq. of exchanger			
0.1	-0.305	-0.075	0.230	0.760
0.2	-0.527	-0.136	0.391	0.820
0.3	-0.662	-0.156	0.506	0.960
0.4	-0.781	-0.192	0.589	1.100
0.5	-0.850	-0.227	0.623	1.140
0.6	-0.868	-0.242	0.626	1.280
0.7	-0.800	-0.248	0.552	1.480
0.8	-0.645	-0.233	0.412	1.680
0.9	-0.389	-0.179	0.210	1.840

Na - K exchange on NaY at 25°c

(Particle size 150-200 mesh)

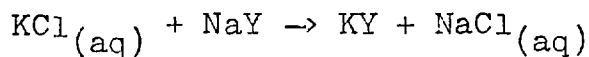
Calorimeter Data

Initial Molality	K _Z	K _S	ΔH_x kcal/gm.eq. of exchanger	ΔH_x^0
<u>Na → K exchange</u>				
0.0025	0.064	-	-0.245	-0.153
0.0050	0.1349	0.0140	-0.362	-0.269
0.0083	0.1981	0.0416	-0.463	-0.371
0.0100	0.2828	0.1070	-0.560	-0.467
0.0208	0.4282	0.2556	-0.808	-0.714
0.0200	0.4406	0.2728	-0.803	-0.709
0.0200	0.4990	0.3678	-0.902	-0.808
0.0500	0.5856	0.5105	-1.074	-0.972
0.0500	0.6501	0.6181	-1.124	-1.019
0.08333	0.6960	0.7167	-1.176	-1.094
0.1000	0.6969	0.7549	-1.154	-1.069
0.2500	0.7715	0.9238	-1.257	-1.186
0.2500	0.8036	0.9091	-1.326	-1.256
0.5000	0.7869	0.9579	-1.272	-1.227
0.5026	0.7822	0.9570	-1.273	-1.228
<u>K → Na exchange</u>				
0.03334	0.6752	0.3428	0.425	0.405

Ion Exchange Equilibria Data (4 days)

Initial Molality	K _Z	K _S	Initial Molality	K _Z	K _S
<u>Na → K Exchange</u>					
0.0050	0.1167	0.0173	0.0250	0.5386	0.4044
0.0100	0.2306	0.0600	0.0838	0.6868	0.6654
0.0100	0.2380	0.0613	0.1000	0.7248	0.7294
0.0100	0.2642	0.0830	0.1000	0.7602	0.8003
0.0100	0.3009	0.1210	0.1675	0.7967	0.8488
0.0100	0.3215	0.1553	0.1675	0.8190	0.8607
0.0250	0.4376	0.2387	0.2500	0.8951	0.9236
0.0250	0.4885	0.3228	1.0034	0.9600	0.9804
0.0250	0.4704	0.2871			
<u>K → Na Exchange</u>					
0.0033	0.8623	0.9154	0.03334	0.5636	0.4410
0.0033	0.7963	0.8630	0.06667	0.4495	0.2830
0.0067	0.7832	0.8053	0.1001	0.4066	0.2247
0.0200	0.6284	0.5459	0.1001	0.3712	0.1762

For the reaction at 25°C

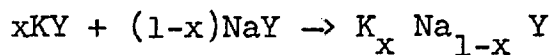


$$\Delta H^{\circ} = -1.45 \text{ kcal/gm.eq.}$$

$$\Delta G^{\circ} = -0.37 \text{ kcal/gm.eq.}$$

$$T\Delta S^{\circ} = -1.08 \text{ kcal/gm.eq.}$$

Thermodynamic Functions for the reaction



and the differential heat of exchange

K_z	ΔG_x^M	ΔH_x^M	$T\Delta S_x^M$	$\frac{\partial \Delta H_x^O}{\partial x}$
	kcal/gm.eq. of exchanger			
0.1	-0.272	-0.072	0.200	-1.716
0.2	-0.438	-0.094	0.354	-1.590
0.3	-0.547	-0.106	0.441	-1.550
0.4	-0.610	-0.108	0.502	-1.433
0.5	-0.631	-0.120	0.511	-1.400
0.6	-0.610	-0.142	0.468	-1.320
0.7	-0.547	-0.114	0.433	-1.280
0.8	-0.438	-0.076	0.362	-1.240
0.9	-0.272	-0.036	0.236	-1.205

Na - Rb Exchange on NaY at 25°c

(Particle size 150-200 mesh)

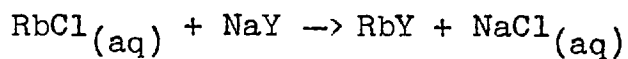
Calorimeter Data

Initial Molality	Rb _z	Rb _s	ΔH_x kcal/gm. eq.	ΔH_x^o
<u>Na → Rb exchange</u>				
0.00333	0.0819	0.0110	-0.255	-0.163
0.00667	0.1375	0.0349	-0.365	-0.274
0.0100	0.2305	0.0656	-0.549	-0.457
0.0100	0.2708	0.0932	-0.587	-0.495
0.01335	0.3192	0.1400	-0.737	-0.652
0.01668	0.3269	0.1434	-0.759	-0.677
0.01668	0.3625	0.1687	-0.789	-0.706
0.01668	0.3924	0.1535	-0.835	-0.752
0.0200	0.4348	0.2567	-0.936	-0.851
0.03337	0.4971	0.3419	-1.040	-0.960
0.03337	0.5365	0.4290	-1.111	-1.024
0.0500	0.5766	0.5785	-1.180	-1.098
0.0500	0.6037	0.6051	-1.233	-1.159
0.1001	0.6400	0.7773	-1.267	-1.198

Ion Exchange Equilibria Data (4 days)

Initial Molality	Rb _z	Rb _s	Initial Molality	Rb _z	Rb _s
<u>Na → Rb exchange</u>					
0.0010	0.0253	0.0044	0.01668	0.4343	0.2264
0.00166	0.0539	0.0096	0.03337	0.5067	0.3623
0.0033	0.0789	0.0160	0.03337	0.5478	0.4435
0.005	0.1420	0.0266	0.03337	0.5747	0.5241
0.01001	0.3279	0.1179	0.0500	0.6104	0.6244
0.01668	0.3853	0.1672	0.1001	0.6770	0.8505
0.01668	0.3948	0.1942	0.3333	0.6832	0.9136
0.01668	0.3643	0.1707	1.0001	0.6784	0.9797

For the reaction at 25^oc

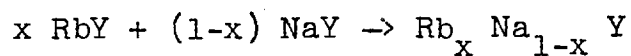


$$\Delta G^{\circ} = -1.06 \text{ kcals/gm.eq.}$$

$$\Delta H^{\circ} = -1.22 \text{ kcals/gm.eq.}$$

$$T\Delta S^{\circ} = -0.16 \text{ kcals/gm.eq.}$$

Thermodynamic Functions for the reaction



and the differential heat of exchange

(Based on 69°/o Na exchangeable)

Rb_z	ΔG_x^M	ΔH_x^M	$T \Delta S_x^M$	$\frac{\partial \Delta H_x^0}{\partial x}$
	k cals/gm.eq. of exchanger			
0.1	-0.220	-0.018	0.202	-1.37
0.2	-0.325	-0.031	0.294	-1.37
0.3	-0.401	-0.044	0.357	-1.37
0.4	-0.434	-0.052	0.382	-1.37
0.5	-0.454	-0.070	0.384	-1.35
0.6	-0.434	-0.078	0.356	-1.27
0.7	-0.401	-0.086	0.315	-1.19
0.8	-0.325	-0.084	0.241	-1.10
0.9	-0.220	-0.052	0.168	-0.88

Na - Cs exchange on NaY at 25°C

(particle size 150-200 mesh)

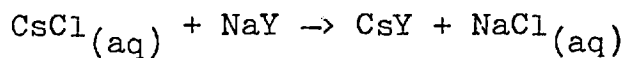
Calorimeter Data

Initial Molality	Cs _z	Cs _s	ΔH_x kcal/gm.eq.	ΔH_x° of exchange
<u>Na → Cs exchange</u>				
0.00338	0.1259	0.0154	-0.393	-0.300
0.00338	0.1674	0.0101	-0.513	-0.420
0.00508	0.2251	0.0150	-0.574	-0.482
0.00833	0.2329	0.0150	-0.666	-0.575
0.00508	0.2465	0.0154	-0.640	-0.548
0.00677	0.2878	0.0522	-0.871	-0.778
0.00846	0.3512	0.0855	-1.063	-0.971
0.01015	0.4175	0.1557	-1.264	-1.180
0.01667	0.4150	0.1460	-1.269	-1.177
0.01667	0.4600	0.2182	-1.298	-1.204
0.01692	0.5075	0.3495	-1.360	-1.272
0.02538	0.5892	0.5491	-1.511	-1.426
0.05075	0.6279	0.7431	-1.594	-1.523
0.05075	0.6422	0.7635	-1.607	-1.539

Ion Exchange Equilibria Data (4 days)

Initial Molality	Cs _z	Cs _s	Initial Molality	Cs _z	Cs _s
<u>Na → Cs exchange</u>					
0.00503	0.2500	0.0250	0.03383	0.5552	0.5328
0.01667	0.3550	0.0996	0.02538	0.5748	0.5274
0.01692	0.5066	0.3529	0.03383	0.6076	0.6461
0.01015	0.4652	0.2167			

For the reaction at 25°c

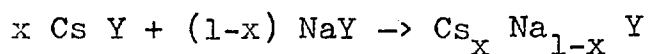


$$\Delta H^{\circ} = -1.61 \text{ kcal/gm. eq.}$$

$$\Delta G^{\circ} = -1.42 \text{ kcal/gm.eq.}$$

$$T\Delta S^{\circ} = -0.19 \text{ kcal/gm. eq.}$$

Thermodynamic Functions for the reaction



and the differential heat of exchange

(Based on 71% Na exchangeable)

Cs_z	ΔG_x^M	ΔH_x^M	$T \Delta S_x^M$	$\frac{\partial \Delta H_x^0}{\partial x}$
	kcal/gm. eq. of exchanger			
0.1	-0.289	0.003	0.292	-1.70
0.2	-0.468	0	0.468	-1.82
0.3	-0.587	-0.013	0.574	-1.88
0.4	-0.656	-0.120	0.536	-2.34
0.5	-0.679	-0.158	0.521	-1.94
0.6	-0.656	-0.139	0.517	-1.56
0.7	-0.587	-0.143	0.444	-1.39
0.8	-0.468	-0.105	0.363	-1.21
0.9	-0.289	-0.068	0.221	-1.04

Na - Ag exchange on NaY at 25°c

(Particle size 150-200 mesh)

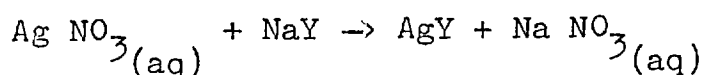
Calorimeter Data

Initial Molality	Ag _z	Ag _s	ΔH_x kcal/gm.eq. of exchanger	ΔH_x°
<u>Na → Ag exchange</u>				
0.0050	0.1388	-	-0.180	-0.088
0.0067	0.2226	0.0265	-0.238	-0.145
0.0100	0.2921	0.0540	-0.270	-0.178
0.0100	0.3708	0.0880	-0.312	-0.220
0.0100	0.3875	0.1063	-0.330	-0.239
0.0150	0.4203	0.1140	-0.315	-0.225
0.0250	0.5822	0.2360	-0.376	-0.286
0.0250	0.6079	0.2183	-0.411	-0.320
0.0500	0.7898	0.4248	-0.476	-0.387
0.0667	0.8575	0.5846	-0.547	-0.457
0.1000	0.8811	0.7387	-0.533	-0.450
0.1000	0.9024	0.7583	-0.551	-0.468

Ion Exchange equilibria data (4 days)

Initial Molality	Ag _Z	Ag _S	Initial Molality	Ag _Z	Ag _S
<u>Na → Ag exchange</u>					
0.0067	0.1372	0.0078	0.0200	0.5910	0.2122
0.0067	0.1792	0.0199	0.0333	0.5750	0.1940
0.0100	0.2107	0.0254	0.0333	0.6699	0.2720
0.0100	0.2530	0.0487	0.0333	0.7472	0.3354
0.0100	0.3005	0.0576	0.0500	0.7691	0.3845
0.0133	0.3590	0.0750	0.0333	0.7347	0.3346
0.0133	0.4145	0.1231	0.0500	0.8188	0.4302
0.0200	0.4504	0.1148	0.0666	0.8641	0.5392
0.0200	0.4863	0.1252	0.1004	0.9392	0.7316
0.0200	0.5353	0.1666	0.1004	0.9599	0.8224
<u>Ag → Na exchange</u>					
0.1000	0.3903	0.1080	0.0333	0.6818	0.2550
0.0666	0.5616	0.1681	0.0333	0.7169	0.2907

For the reaction at 25°C

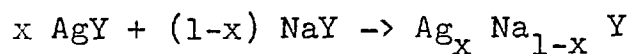


$$\Delta G^\circ = -1.08 \text{ kcal/gm.eq. of exchanger}$$

$$\Delta H^\circ = -0.50 \text{ kcal/gm.eq. of exchanger}$$

$$T\Delta S^\circ = 0.58 \text{ kcal/gm.eq. of exchanger}$$

Thermodynamic Functions for the reaction



and the differential heat of exchange

Ag_z	ΔG_x^M	ΔH_x^M	$T \Delta S_x^M$	$\frac{\partial \Delta H_x^0}{\partial x}$
	kcal/gm. eq. of exchanger			
0.1	-0.202	-0.020	0.182	-0.640
0.2	-0.314	-0.020	0.294	-0.590
0.3	-0.384	-0.030	0.354	-0.520
0.4	-0.423	-0.030	0.393	-0.460
0.5	-0.437	-0.030	0.407	-0.435
0.6	-0.423	-0.020	0.403	-0.435
0.7	-0.384	-0.020	0.364	-0.435
0.8	-0.314	-0.020	0.294	-0.425
0.9	-0.202	-0.015	0.187	-0.390

Na - Tl exchange on NaY at 25°C

(Particle size 150-200 mesh)

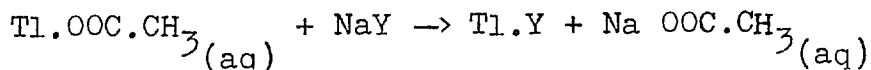
Calorimeter Data

Initial Molality	Tl _z	Tl _s	$\Delta \bar{H}_x$ kcal/gm. eq. of exchanger	$\Delta H'_x$
<u>Na → Tl exchange</u>				
0.0050	0.1043	-	-0.348	-0.255
0.0050	0.1122	-	-0.351	-0.259
0.0050	0.1310	-	-0.405	-0.312
0.0075	0.2331	0.0338	-0.600	-0.507
0.0100	0.2903	0.0743	-0.734	-0.642
0.0100	0.3114	0.0793	-0.772	-0.679
0.0150	0.3886	0.1134	-0.953	-0.860
0.0133	0.4006	0.0963	-0.966	-0.874
0.0150	0.4376	0.1422	-0.981	-0.888
0.0200	0.5170	0.2132	-1.122	-1.030
0.0200	0.5300	0.2366	-1.208	-1.116
0.0334	0.6061	0.4801	-1.307	-1.215
0.1003	0.6861	0.8003	-1.468	-1.376

Ion Exchange Equilibria Data (4 days)

Initial Molality	Tl _z	Tl _s	Initial Molality	Tl _z	Tl _s
<u>Na → Tl exchange</u>					
0.0040	0.0636	0.0060	0.0167	0.5189	0.1923
0.0080	0.1155	0.0120	0.0200	0.5643	0.2860
0.0080	0.1526	0.0173	0.0334	0.6017	0.3959
0.0080	0.1894	0.0306	0.0334	0.6247	0.4809
0.0100	0.1972	0.0424	0.0502	0.6354	0.5248
0.0100	0.2863	0.0532	0.0502	0.6597	0.5737
0.0151	0.3883	0.1037	0.1003	0.6866	0.7630
0.0167	0.4661	0.1726	0.2501	0.6854	0.9361

For the reaction at 25°C



$$\Delta G^\circ = -1.49 \text{ kcals/gm. eq. of exchanger}$$

$$\Delta H^\circ = -1.38 \text{ kcals/gm. eq. of exchanger}$$

$$T\Delta S^\circ = 0.11 \text{ kcals/gm. eq. of exchanger}$$

Na - K exchange on NaY at 25°C

(Methanol as solvent)

Calorimeter Data

Initial Molality	K_z	K_s	ΔH_x kcal/gm.eq. of exchanger	$\Delta H_x - \Delta H_{NaY}^W$
0.0067	0.1426	0.1185	-0.473	-0.393
0.0100	0.2149	0.1957	-0.558	-0.478
0.0167	0.2649	0.3210	-0.724	-0.644
0.0167	0.2747	0.4434	-0.719	-0.639
0.0333	0.3423	0.5771	-0.845	-0.765
0.0500	0.4514	0.6880	-1.100	-1.020
0.06675	0.5211	0.7297	-1.234	-1.154
0.1001	0.6343	0.7939	-1.411	-1.331
0.2500	0.6966	0.9219	-1.596	-1.516
0.2500	0.7523	0.9236	-1.735	-1.655

$$\Delta H_{NaY}^W = -0.08 \text{ kcal/gm. eq.}$$

$$\Delta H'_x = -2.05 \text{ kcal/gm. eq.}$$

$$\Delta G^{\ddagger} = -0.25 \text{ kcal/gm. eq.}$$

Na - K exchange on NaY at 25^oc

(Methanol as solvent)

Ion exchange equilibria data

Initial Molality	K _Z	K _S	Initial Molality	K _Z	K _S
0.00333	0.1006	0.0647	0.03334	0.5623	0.4235
0.00333	0.1117	0.0401	0.03334	0.5720	0.4394
0.00667	0.1456	0.0684	0.03337	0.5874	0.4274
0.01001	0.2336	0.1155	0.06675	0.6588	0.5813
0.01001	0.3146	0.1490	0.06637	0.7195	0.7115
0.01669	0.3250	0.1696	0.06675	0.7092	0.6958
0.01669	0.3538	0.1805	0.1000	0.7427	0.7816
0.01669	0.4013	0.2125	0.1001	0.7728	0.8085
0.01669	0.4457	0.2591	0.2500	0.8651	0.9189
0.03337	0.5034	0.3117			

Na - Ca exchange on Chabazite

(Particle size 350-400 mesh)

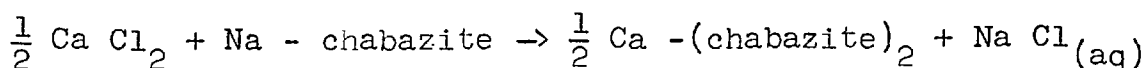
Calorimeter Data (25°C)

Initial Molality	Ca _z	Ca _s	ΔH_x kcal/gm.eq. of exchanger	ΔH_x°
0.1246	0.233	-	-0.041	0.091

Ion exchange equilibria data at 50°C (2 weeks)

Initial Molality	Ca _z	Ca _s	Initial Molality	Ca _z	Ca _s
<u>Na → Ca exchange</u>					
0.00416	0.1371	0.0026	0.01246	0.7093	0.1012
0.00623	0.2579	0.0072	0.02078	0.7898	0.4809
0.00623	0.3115	0.0075	0.06232	0.8250	0.8457
0.00623	0.3528	0.0082	0.1246	0.8653	0.8984
0.00623	0.4606	0.0131	0.1246	0.8800	0.9264
0.01246	0.6346	0.0400	0.5740	0.8860	0.9750
0.01246	0.7035	0.0824			
<u>Ca → Na exchange</u>					
0.01668	0.8218	0.3943	0.06674	0.7106	0.1348
0.03337	0.7937	0.2435			

For the reaction



$$\Delta G^\circ = 0.09 \text{ kcal/gm. eq. of exchanger}$$

Na - Sr exchange on Chabazite

(Particle size 350-400 mesh)

Calorimeter Data (25°C)

Initial Molality	Sr _z	Sr _s	ΔH_x kcal/gm.eq. of exchanger	ΔH_x°
0.00667	0.1526	0.4835	-0.027	0.067
0.1001	0.1568	0.9671	-0.041	0.077

Ion exchange equilibria data at 50°C (2 weeks)

Initial Molality	Sr _z	Sr _s	Initial Molality	Sr _z	Sr _s
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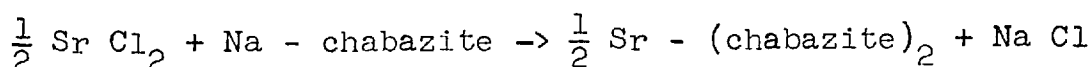
Na → Sr exchange

0.00373	0.1078	0.0061	0.0200	0.7930	0.2689
0.00560	0.1836	0.0060	0.0200	0.8252	0.2113
0.00560	0.1917	0.0080	0.0200	0.8079	0.3392
0.00914	0.3858	0.0098	0.01848	0.8428	0.2724
0.01097	0.5264	0.0190	0.02743	0.8414	0.4428
0.00914	0.5834	0.0166	0.0400	0.8482	0.4534
0.01334	0.5336	0.0170	0.03656	0.8549	0.5505
0.01097	0.6316	0.0383	0.0200	0.8320	0.3173
0.01371	0.6536	0.0345	0.06676	0.8618	0.7887
0.01334	0.7274	0.0397	0.1001	0.8770	0.8291
0.01334	0.7878	0.1271	0.2002	0.8899	0.9152
0.01828	0.7780	0.1217	0.2002	0.9134	0.9613

Sr → Na

0.0333	0.8145	0.2037	0.0333	0.8326	0.1645
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For the reaction



$$\Delta G^\circ = 0.043 \text{ kcal/gm. eq. of exchanger}$$

Na - Ba exchange on Chabazite at 25°c

(Particle size 150 - 200 mesh)

Calorimeter Data

Initial Molality	Ba _z	Ba _s	ΔH_x kcal/gm.eq. of exchanger	ΔH_x°
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Na → Ba exchange

0.00334	0.1834	0.002	0.116	0.200
0.00334	0.1661	0.002	0.055	0.150
0.00334	0.1967	0.002	0.108	0.202
0.0050	0.2708	0.004	0.157	0.256
0.0050	0.3538	0.0398	0.179	0.281
0.00668	0.4096	0.0384	0.247	0.355
0.01003	0.5361	0.2881	0.422	0.541
0.03343	0.5787	0.6793	0.495	0.633
0.0500	0.6000	0.8363	0.568	0.714
0.1003	0.6599	0.9083	0.651	0.822

Ion Exchange equilibria data (7 days)

Initial Molality	Ba _z	Ba _s	Initial Molality	Ba _z	Ba _s
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Na - Ba exchange

0.00334	0.1500	0.0025	0.01666	0.7573	0.1325
0.00500	0.2603	0.0074	0.01188	0.7921	0.1897
0.00668	0.3348	0.0217	0.02501	0.8684	0.4692
0.01003	0.3727	0.0255	0.0500	0.8758	0.5714
0.00668	0.3077	0.0150	0.0396	0.8988	0.7036
0.01003	0.4748	0.0408	0.0594	0.8997	0.7650
0.01003	0.6167	0.0526	0.1003	0.8922	0.8573
0.01003	0.6782	0.0545	0.1003	0.9124	0.8669
0.01666	0.7257	0.1229	0.5189	0.9407	0.9788

Na - Pb exchange on Chabazite at 25°C

(Particle size 150 - 200 mesh)

Calorimeter data

Initial Molality	Pb _z	Pb _s	ΔH_x kcal/gm.eq.	ΔH_x^i of exchanger
0.00333	0.1713	-	0.102	0.188
0.0050	0.2610	-	0.183	0.269
0.00666	0.3755	-	0.332	0.418
0.00666	0.4110	-	0.360	0.446
0.0100	0.5386	-	0.559	0.645
0.0100	0.5500	-	0.553	0.639
0.0100	0.5589	-	0.611	0.698
0.0100	0.4669	0.0213	0.429	0.515
0.0150	0.7402	0.0820	0.779	0.865
0.0250	0.7016	0.4461	0.753	0.839
0.0333	0.7019	0.5940	0.757	0.843
0.0666	0.7107	0.8101	0.767	0.857
0.1000	0.7975	0.8547	0.832	0.918

Ion exchange equilibria data (7 days)

Initial Molality	Pb _z	Pb _s	Initial Molality	Pb _z	Pb _s
0.00214	0.0987	0.0057	0.0200	0.8865	0.0839
0.00429	0.2036	0.0077	0.0200	0.8889	0.2603
0.00429	0.2370	0.0078	0.0250	0.8805	0.2861
0.00643	0.3042	0.0080	0.0250	0.8974	0.3378
0.00643	0.3537	0.0084	0.0333	0.9210	0.4731
0.00857	0.4383	0.0090	0.0333	0.9276	0.4398
0.00857	0.5218	0.0173	0.0666	0.9365	0.7506
0.01286	0.6453	0.0181	0.1000	0.9327	0.8295
0.01286	0.7461	0.0283	0.1000	0.9299	0.8309
0.0200	0.7557	0.0286	0.2500	0.9375	0.9314

Na - Ca exchange in NaY at 25°c

(Particle size 150-200 mesh)

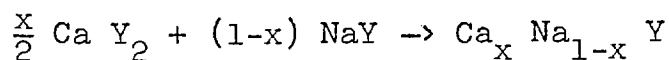
Calorimeter Data

Initial Molality	Ca _z	Ca _s	ΔH_x kcal/gm. eq.	ΔH_x°
0.00249	0.2161	0.005	0.162	0.262
0.00208	0.1726	0.0069	0.100	0.193
0.00332	0.3057	0.0133	0.324	0.426
0.00416	0.3740	0.0233	0.421	0.531
0.00623	0.4305	0.0508	0.533	0.646
0.00623	0.4622	0.0712	0.641	0.755
0.00623	0.5365	0.0930	0.767	0.886
0.00831	0.5878	0.2310	0.808	0.933
0.01039	0.6077	0.3697	0.818	0.946
0.02078	0.6415	0.6821	0.836	0.980
0.04155	0.6501	0.8333	0.819	0.981
0.06232	0.6532	0.9014	0.870	1.041

Ion exchange equilibria data (4 days)

Initial Molality	Ca _z	Ca _s	Initial Molality	Ca _z	Ca _s
0.00208	0.1210	0.0040	0.02078	0.6718	0.7895
0.00249	0.2217	0.0081	0.06232	0.6754	0.8850
0.00416	0.3315	0.0235	0.06232	0.6755	0.8829
0.00623	0.4777	0.0677	0.1246	0.6789	0.9354
0.01039	0.5798	0.2209	0.1246	0.7100	0.9367
0.01039	0.6533	0.5090	0.5740	0.7127	0.9854

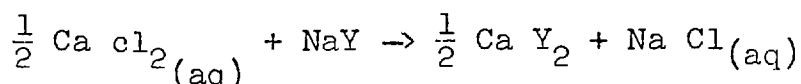
Thermodynamic Functions for the reaction



and the differential heat of exchange

Ca_x	ΔG_x^M kcal/gm. eq. of exchanger	ΔH_x^M	$T\Delta S_x^M$	$\frac{\partial \Delta H_x^0}{\partial x}$
0.1	-0.084	-0.047	0.037	0.730
0.2	-0.136	-0.074	0.062	0.860
0.3	-0.179	-0.061	0.118	1.086
0.4	-0.211	-0.043	0.168	1.250
0.5	-0.234	-0.025	0.209	1.375
0.6	-0.259	0.018	0.277	1.1617
0.7	-0.250	0.076	0.326	1.480
0.8	-0.246	0.064	0.310	0.910
0.9	-0.159	0.027	0.186	0.475

For the reaction at 25°C



$$\Delta G^0 = 0.17 \text{ kcal/gm. eq.}$$

$$\Delta H^0 = 1.09 \text{ kcal/gm. eq.}$$

$$T\Delta S^0 = 0.92 \text{ kcal/gm. eq.}$$

Na - Sr exchange in NaY at 25°C

(Particle size 150-200 mesh)

Calorimeter Data

Initial Molality	Sr_z	Sr_s	ΔH_x kcal/gm. eq.	ΔH_x°
0.00267	0.1774	0.0100	0.117	0.215
0.00335	0.1823	0.0125	0.131	0.231
0.00667	0.3188	0.0245	0.260	0.369
0.01000	0.4691	0.2247	0.381	0.500
0.01000	0.5317	0.2492	0.492	0.616
0.02001	0.5669	0.5347	0.499	0.636
0.04002	0.6349	0.7722	0.696	0.850
0.1001	0.6763	0.8911	0.778	0.959

Ion exchange equilibria data (7 days)

Initial Molality	Sr_z	Sr_s	Initial Molality	Sr_z	Sr_s
0.00267	0.1386	0.0020	0.01005	0.4751	0.0498
0.00400	0.2086	0.0055	0.01005	0.5840	0.1724
0.00400	0.2274	0.0060	0.01334	0.6218	0.4599
0.00400	0.3564	0.0103	0.00800	0.5707	0.2028
0.00400	0.3906	0.0205	0.02001	0.6286	0.3982
0.00400	0.2667	0.0103	0.04002	0.6456	0.6992
0.00400	0.4690	0.0530	0.04002	0.6666	0.7736
0.00800	0.4176	0.0310	0.1001	0.6722	0.9068
0.00667	0.4526	0.0350	0.2003	0.6766	0.9376

Na-Ba exchange in NaY at 25°C

(Particle size 150-200 mesh)

Calorimeter Data

Initial Molality	Ba _z	Ba _s	ΔH_x kcal/gm. eq.	ΔH_x°
0.00396	0.2654	0.0051	-0.015	-0.005
0.00396	0.2909	0.0256	-0.024	-0.012
0.00594	0.3738	0.0441	-0.032	-0.014
0.00792	0.4670	0.1132	-0.036	-0.017
0.00792	0.5459	0.1620	-0.032	-0.010
0.00792	0.5806	0.1570	-0.040	-0.021
0.01188	0.6192	0.3627	-0.065	-0.029
0.03960	0.6782	0.8022	-0.094	-0.030

Ion Exchange Equilibria data (7 days)

Initial Molality	Ba _z	Ba _s	Initial Molality	Ba _z	Ba _s
0.00396	0.0869	0.0009	0.00594	0.6094	0.0301
0.00396	0.1804	0.0031	0.01188	0.6267	0.1127
0.00594	0.1519	0.0025	0.00792	0.6485	0.2376
0.00396	0.2431	0.0046	0.01188	0.6540	0.1560
0.00396	0.3134	0.0051	0.02970	0.6648	0.6772
0.00594	0.4192	0.0073	0.01188	0.6746	0.4457
0.00594	0.4886	0.0079	0.0594	0.7106	0.8828
0.00792	0.6065	0.0080	0.1188	0.6980	0.9371