

NEUTRON IRRADIATION
OF
LINDE ~~MOLECULAR~~ SIEVE 13-X

by

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ABSTRACT

Linde Molecular Sieve 13-X is a synthetic zeolite commonly known as NaX. It possesses a very open, stable, crystalline lattice which allows it to function as an excellent, specific cation exchanger, and as a gas adsorbent.

The purpose of examining the effects of neutron irradiation to this material, was chiefly to ascertain whether an inorganic exchanger such as a zeolite, is more capable of withstanding the damaging effects of radiation, than its organic counterparts. Organic resin exchangers employed for the separation of highly radioactive material, are rendered useless quite rapidly by the various radiations to which they are subjected. Little work on the effects of particle bombardment on the more stable inorganic ion exchangers has previously been carried out.

NaX was examined with respect to its cation exchange properties by briefly studying the exchange equilibria with the ions Cs^+ , Ba^{++} and UO_2^{++} . It was found to possess certain excellent, high specific exchange properties, but was unstable in solutions of pH lower than 5.

A Volumetric apparatus was constructed to study the sorption of an inert gas by NaX, over a wide range of temperature. From the isotherms, isosteric heats of sorption were calculated. The isotherms measured at low temperatures were

analyzed by applying them to various limiting isotherm models from which the corresponding entropy functions were obtained. The model based on localized sorption, with molecule - molecule interactions, and including a configurational entropy term was found to provide the best fit to the experimental data.

The neutron irradiation resulted in no observable change in the sorbent properties of NaX, provided the dose was less than 5×10^{17} neutrons/cm². Beyond this dose, a progressive loss in sorption capacity was observed. However the zeolite still retained excellent sorbent properties even after a dose of 2×10^{19} n/cm². No conclusive changes in the cation exchange properties were observed below a dose of 1.9×10^{19} n/cm²; however, even at this dosage, it still functioned as a cationic exchanger, with slightly reduced capacity. The highest dose received by any sample, 7×10^{19} n/cm², was found by X-rays, to have rendered it completely amorphous; it was then found to sorb very little argon at 90°K, and have little ion exchange capacity.

The cation exchange and gas adsorption results thus indicate that NaX can withstand very high neutron doses, before these properties are appreciably affected. A critical point is reached around 5×10^{19} n/cm², after which the zeolite suffers major structural damage resulting in large decreases in sorption and cation exchange capacities.

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PART 1INTRODUCTION AND LITERATURE SURVEY.

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1.0GENERAL INTRODUCTION.

It may fairly safely be assumed that prolonged irradiation with energetic radiation (particles or photons) of any material, will eventually bring about some changes in the physical and chemical properties of that substance. The susceptibility to radiation effects is a function of the particular material. In solids, one would expect lattice imperfections to arise, e.g. vacant lattice sites and the formation of impurity atoms. These phenomena may be included under the general heading of "radiation damage".

It is appropriate at this point, to define radiation damage, to mean any physical, chemical or biological change of more than a mere transitory nature, brought about by the bombardment of the material, with particles such as neutrons or protons, or electromagnetic radiation such as gamma-rays. The term 'damage' usually infers injury or destruction impairing the value or usefulness of a material. Although this is not necessarily true, e.g. the increased hardness and improved electrical properties of many metals upon irradiation, the study of damage as a result of irradiation may still enable the physical chemist to glean further information on the

fundamentals of the solid state, and on the properties of imperfections in solids.

Damage to solids may be studied in various ways depending on the type of solid under study. In this work, we are concerned with the effects of neutron irradiation of an aluminosilicate material, and have measured the degree of radiation damage from the change in its capacity as an inorganic exchanger, but more important, from the change in its gas adsorbent properties. Several cation exchange systems, and the sorption of argon and krypton over a wide range of temperature and degree of saturation, have been studied.

It is a well established fact that both organic materials such as sulphonated polystyrenes and phenolic resins, and inorganic materials such as aluminosilicates and zeolites, are extremely efficient as ion exchange media. However, the crystal frameworks of the latter result in far more rigid, stable and well defined structures than the polymeric structures of the organic resins. It thus appears strange that comparatively little work has been done with inorganic exchange materials and their applications towards the separation and purification of radioactive substances, especially when considering the amount of literature available on similar work with organic exchangers.

The purpose of this research work was therefore to determine whether the stability of zeolites towards irradiation, was far in excess of the stability of corresponding organic exchangers, and hence to indicate the latent importance of these aluminosilicates in the separation and purification of highly radioactive materials.

However the purpose was not merely to make a comparison between the two types of exchangers, but also to consider some more fundamental aspects. Interest was directed towards the energetics of sorption of inert gases in order to determine which, if any, of the sorption sites were most affected by irradiation. For this purpose a volumetric gas sorption system was employed to study the physical adsorption of gases from zero coverage up to saturation.

Interest has been shown recently in the use of ion exchangers to decontaminate the water coolant systems in the reactors of nuclear submarines. Much work has already been conducted on the separation of fissile material, the purification of fuel elements, and the decontamination of effluent streams. However, in all of these modern radiochemical procedures, little attention has been paid to the inherent importance of inorganic exchange materials such as zeolites. The work presented here is a step in this direction.

ZEOLITES.

Introduction. Silica is constructed of a regular arrangement of the tetrahedral building unit SiO_4^{4-} , each tetrahedron being linked to four others. Isomorphous replacement of silicon by aluminium results in the group of minerals known as aluminosilicates. The AlO_4^{5-} and SiO_4^{4-} tetrahedra have almost identical dimensions and thus replacement of the silicon is possible with very little lattice distortion. Loewenstein (ref.1.) has shown that two aluminium atoms cannot share the same oxygen atom, whilst retaining a co-ordination of 4, hence Al-O-Al bridges are impossible. The net unit negative charge on each AlO_4^- tetrahedron is balanced by a cation located in the lattice framework, thus ensuring electrical neutrality.

Depending on the manner in which the AlO_4^{5-} and SiO_4^{4-} tetrahedra are linked, the zeolites may be divided into three classes :-

- (a) fibrous zeolites, e.g. natrolite.
- (b) lamellar zeolites, e.g. heulandite.
- (c) three dimensional zeolites, e.g. faujasite and mordenite.

In this work, we are only concerned with type (c), and these may be described by the general formula:- $\text{M}_{x/n} (x.\text{AlO}_2.y.\text{SiO}_2) z \text{H}_2\text{O}$. where x/n = no. of exchangeable cations M, of valency n.

This type of zeolite possesses several

important properties including :-

(a) the ability to undergo dehydration with little or no change in lattice dimensions.

(b) ion exchange properties, zeolites such as faujasite being capable of separating relatively large ions due to its very open lattice.

(c) physical adsorption of gases and vapours after dehydration, with molecular sieve action towards molecules of different sizes.

These three properties will now be discussed in more detail :-

(a) all zeolites are hydrated; the water present in the interstices of the crystal, may be removed by heating and evacuation. Zeolites of types (a) and (b) tend to shrink and collapse upon dehydration because they are only rigid in one and two directions in space respectively, but the robust three dimensional zeolites are generally stable up to temperatures as high as 700°C . Details of the dehydration process employed for these zeolites will be given in the experimental section. The zeolitic water may occupy definite sites in the lattice as with hydrates, forming a series of solid solutions during dehydration; alternatively, it may be completely mobile occupying no definite positions, and thirdly it may be held interstitially by physical adsorption. It differs from water of crystallization and chemisorbed water.

Electrical conductivity is occasionally attributed to zeolitic water which infers that it is mobile. Clusters of up to 32 molecules of water exist in faujasite, and due to the interconnecting channels it forms an intracrystalline fluid.

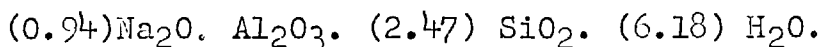
(b) Electrical conductivity measurements (ref.2) have also attributed the conductivity in some zeolites, to the mobile cations. The open lattice of zeolites facilitates ease of movement of ions and also therefore, cation exchange. Faujasite, with its particularly spacious intracrystalline channels and cavities, should thus be expected to possess particularly useful properties as a cation exchange medium.

(c) The fact that the "supercages" of synthetic faujasite can accommodate 32 molecules of water, and molecules as large as iso-octane, illustrates the enormous capacity for the sorption of gases and vapours. (For further details on sorptive properties of zeolites, see section 1.2.)

LINDE MOLECULAR SIEVE 13-X. or NaX

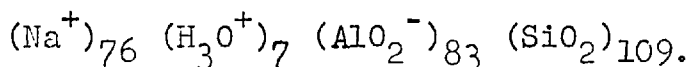
Faujasite contains both sodium and calcium ions in the approximate ratio of 2:1, but the synthetic form only contains Na^+ ions. NaX is manufactured by the Linde Air Products Company of America, and is known commercially as "Linde Molecular sieve 13X" - or sometimes as "NaX". It was supplied in the form of a fine

white powder. It has a silica to alumina ratio of between 2.1 and 3.0; analysis of the sample used in this work gave the formula :

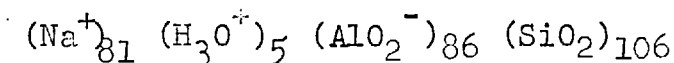


The percentage of sodium was determined radio-chemically (vide section 3.1.4), the alumina and silica by chemical analysis (vide section 3.1.1.), and the water by ignition of a sample in a platinum crucible to constant weight.

Cation Deficiency. NaX is synthesised from sodium hydroxide, silica and alumina in aqueous solution, and it is possible for the final product to possess a deficiency of Na^+ ions, the balance being made up by hydronium ions (H_3O^+). In some cases, cation deficiency (refs.3-8) may be as much as 15%. The sample of NaX used by Szymanski et al. (5) had the following unit cell composition:



The sample used in this work corresponds to :



Frohnsdorff & Kington (9) suggested that this water may be strongly hydrogen bonded to the oxygen atoms of the aluminosilicate structure.

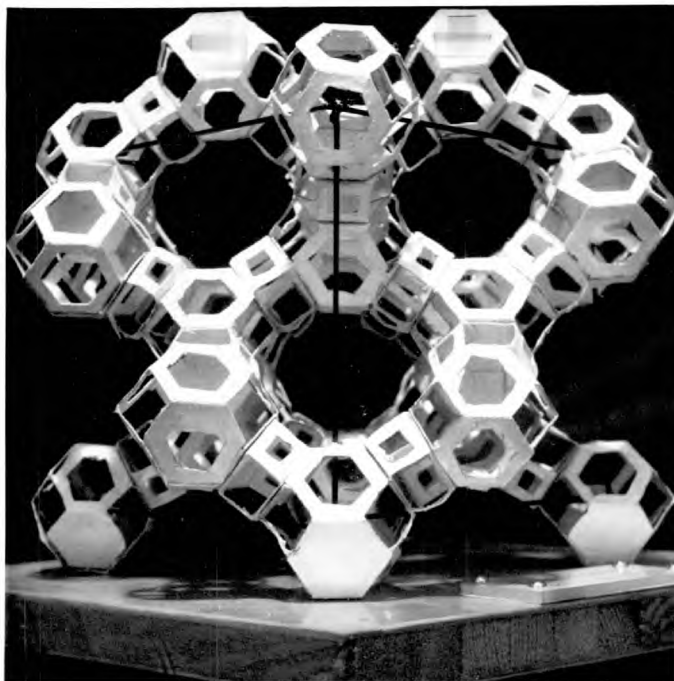
The structure of NaX is cubic ($a = 25 \text{ \AA}$). It consists of very large cubo-octahedral cavities, see fig.1, which are linked in tetrahedral co-ordination similar to the carbon atoms of the diamond lattice.

These cavities have "free diameters" of between 12-13 Å and are connected tetrahedrally to each other via wide windows consisting of 12 silica and alumina tetrahedra; the "free diameter" of these windows, which is the smallest diameter in the actual interconnecting system of "super" cavities and channels, is 7.5 Å. By "free diameter", we mean 'unoccupied', even by the peripheries of framework oxygen atoms,

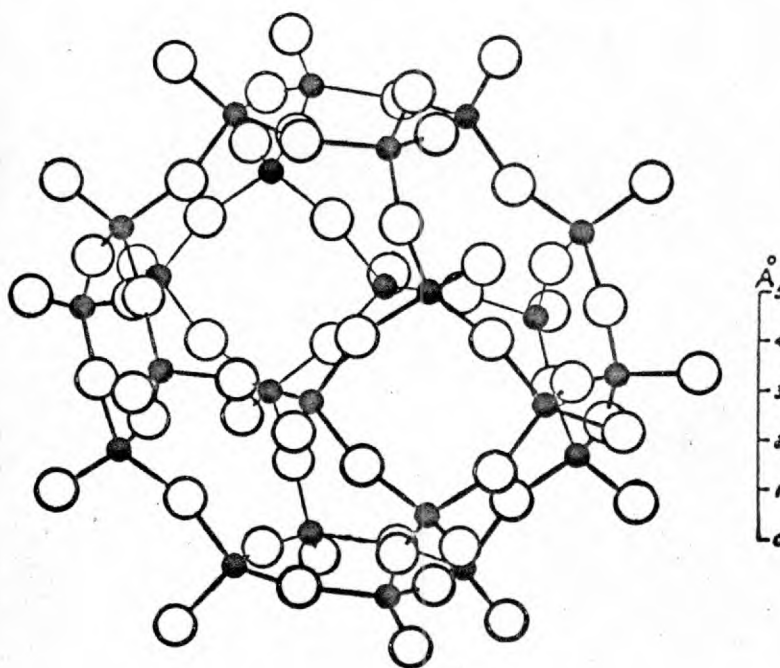
The lattice also consists of smaller cubo-octahedral cavities of free diameter 6.6 Å, called sodalite cages, see figure 2, linked tetrahedrally with each other through hexagonal prisms. These prisms are bounded by two 6-membered rings of free diameter 2.2 Å, and six 4-membered oxygen rings. Thus three types of cages exist in the NaX lattice:-

- (a) "super cages" : cubo-octahedra of free diameter 12-13 Å, joined tetrahedrally through windows of free diameter 7.5 Å.
(see figure 1.)
- (b) sodalite cages : cubo-octahedra of free diameter 6.6 Å. (see figure 2.)
- (c) hexagonal prisms : interconnecting cavities between the sodalite cages, (see figure 1).

Unit cell. The unit cell of NaX comprises 8 super cages, 8 sodalite cages, and 16 hexagonal prisms, and has the composition :

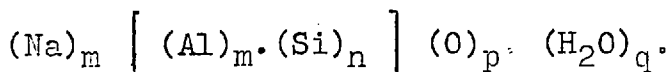
FIGUREI

MODEL OF SYNTHETIC FAUJASITE = NaX
 (wire framework shows cubic unit cell)

FIGURE2

Cubo-octahedral SODALITE CAGE

(open circles = Oxygen,
 full circles = Aluminium, Silicon)



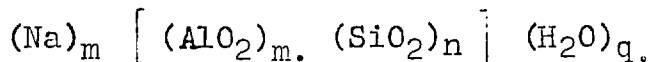
where m. n. p. q have the variable values shown below.

Variable Composition of NaX.

<u>Symbol.</u>	<u>Range of values.</u>	<u>Sample used in this work.</u>
m	80 - 88	86
n	104 - 110	106
p	384 (constant)	384
q	240 - 260	250 - 260

As mentioned earlier, electrical neutrality is achieved by an equal number of cationic charges as aluminium atoms present in the lattice; if there is a deficiency of metal cations, H_3O^+ ions make up the balance.

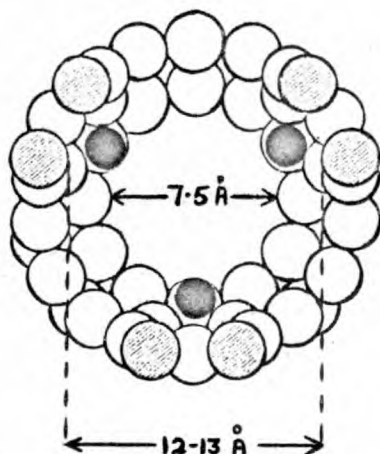
The general formula may also be written:-



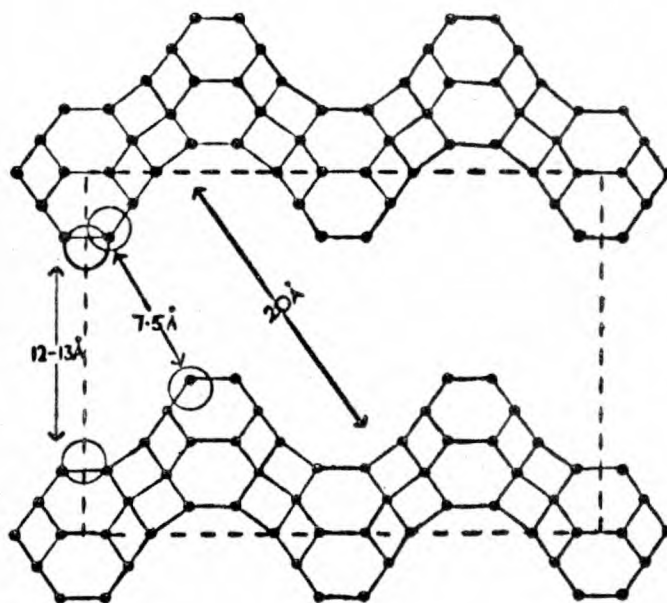
Substitution of $(\text{M})_{m/x}$ for $(\text{Na})_m$ gives the generalised formula for all zeolites, x being the valency of metal M.

Cation positions in NaX.

Broussard & Shoemaker (10) have analysed the NaX lattice by X-ray diffraction and 3-dimensional Fourier analysis. They found that one Na^+ ion occupies each of the 16 hexagonal prisms. Of the 86 Na^+ ions per unit cell, this leaves 70 Na^+ ions occupying the larger cavities. Each of the sodalite cages possesses 8 hexagonal windows; 4 of these form the sides of the hexagonal prisms and the other 4 face out into the supercages. Broussard &

FIGURE3

CROSS SECTION OF "SUPERCAGE" IN NaX
 (from ref.10. Full circles = Na⁺ ions)

FIGURE4

Projection on the (011) plane of Al and Si atoms of NaX, showing some important free distances, and the exceptional open-ness of NaX (ref.27)

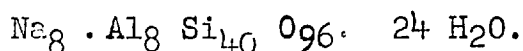
Shoemaker (10) actually found these windows to consist of distorted hexagons (rather like cyclohexane in the "chair" form), formed by two parallel planes of 3 oxygen atoms per plane, and considered the Na^+ ions to be situated in the centre of this structure, in the dehydrated zeolite. In the hydrated form, due to the water of hydration surrounding the Na^+ ions, and its polarizability, it is found that the Na^+ ion is actually displaced a little towards the supercage. The remaining 38 Na^+ ions are considered to be randomly distributed throughout the open lattice. It was originally postulated by Breck et al. (4) in 1958, that NaX contained more than just one type of cation site; Freeman and Stamires (11) in measuring the activation energy for conduction of the cations in the zeolite lattices, showed that at least two different sites existed in NaX, but could not definitely prove the existence of three. Cation exchange studies employing uni- & divalent ions of varying radii are helping to throw some light on this matter (12).

Zeolon (Na^+ form).

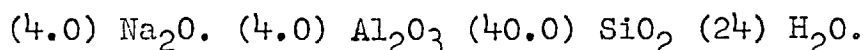
This zeolite is the synthetic form of the mineral mordenite. Although the latter contains Na^+ , K^+ , and Ca^{++} ions, zeolon contains only Na^+ ions. It is synthesized by the Norton Co. Ltd. of America, and known commercially as Zeolon (Na^+ form). However, throughout this thesis, it will be referred to as 'mordenite'.

Detailed X-ray analysis has been carried out by Meier (13) on the natural zeolite, and it was found that the synthetic variety had an almost identical X-ray diffraction pattern. The natural mordenite was a calcium-rich specimen which he percolated with concentrated sodium nitrate solutions to exchange it to the pure Na^+ form.

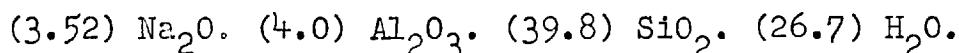
Analysis: Mordenite has a silica to alumina ratio of 10:1 and Meiers' analysis agreed well with the formula:



This may be written as :-



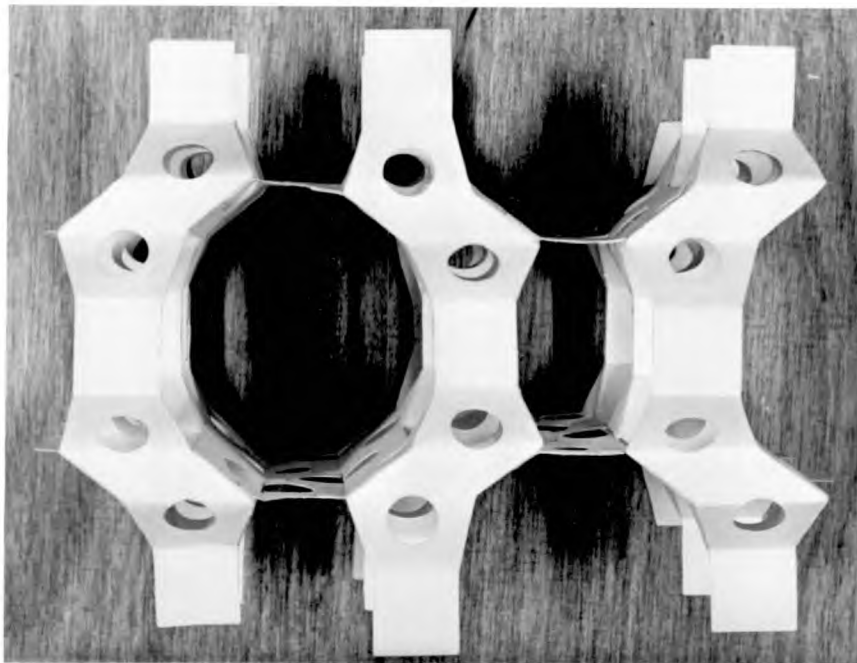
Analysis of the synthetic sample used in this work gave the following composition :



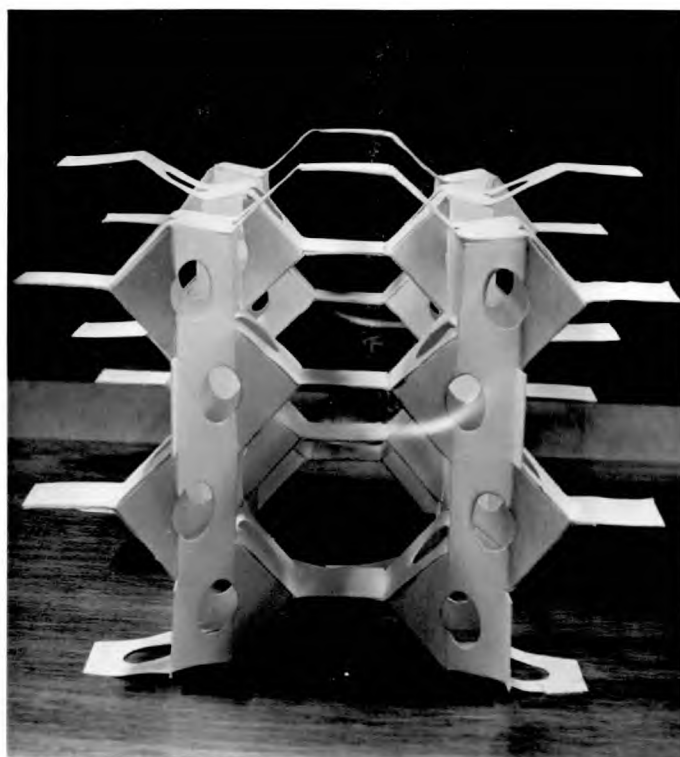
The Na was determined radiochemically and SiO_2 , Al_2O_3 and H_2O by conventional chemical methods of analysis. (vide section 3.1.1.)

Cation Deficiency:

The sample of synthetic mordenite used in this work is deficient in Na^+ , and since it was not percolated with NaCl , this may be explained as a cation deficiency frequently found in synthetic zeolites (see previous section in NaX, and refs. 3-8). The missing Na^+ ion per unit cell is assumed to be replaced by H^+ or H_3O^+ , since the synthesis is performed in aqueous solution. The aluminosilicate network consists of characteristic chains

FIG.5

MODEL OF SYNTHETIC MORDENITE = ZEOLON (Na⁺ FORM)
(showing large channels, diameter 6.6 Å).

FIGURE6

Same model, viewed through channels of
diameter 4.0 Å.

enclosing channels of free diameter $6.6 \text{ \AA}$, which give mordenite its molecular sieve properties. These channels are formed by a ring of twelve tetrahedra comparable to those existing in faujasite; however, the latter has cavities, whereas mordenite is characterized by channels of uniform diameter parallel to the (001) direction. These channels are interconnected by smaller channels of free diameter $2.8 \text{ \AA}$ parallel to the (010) direction. Actually, these interconnecting channels have free diameters of approx: $4 \text{ \AA}$, with periodic windows of $2.8 \text{ \AA}$ diameter. Each $(\text{Al}, \text{Si})\text{O}_4$ tetrahedron is part of one or more five membered rings in the frame-work, and the numbers of 4-, 5-, 6- and 8-membered loops of tetrahedra per unit cell are 4, 48, 16 and 16 respectively. The prevailing number of 5-membered rings is an outstanding feature of the mordenite framework. It has been shown (14) that the most stable loops in silicates (i.e. lowest energy) are of 5 or 6 tetrahedra. This predominance of 5-loops and the high silica to alumina ratio account for the extraordinary stability of mordenite compared with other zeolites.

Stacking faults: Although the free diameter of the main channels is $6.6 \text{ \AA}$, mordenite does not sorb molecules whose critical diameters exceed $4.4 \text{ \AA}$. This suggests that crystal imperfections exist, e.g. stacking faults, of which only comparatively few would be necessary to

inhibit diffusion. These stacking faults reduce the effective diameter of the main channels to 4.4 Å.

Positions of Cations : Of the 8 Na^+ ions per unit cell, only four have been definitely located; they lie in the windows (2.8 Å diameter) of the interconnecting channels.

The remaining four Na^+ ions have not been assigned definite positions and are therefore assumed to be randomly distributed within the large channels, (c.f. the 38 Na^+ ions per unit cell of NaX).

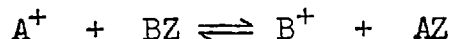
1.1.CATION EXCHANGE.1.1.1. Ion Exchange in Zeolites.

The first systematic studies of the exchange of one metal for another, were made by Way (15) in the 1850's, by passing a salt solution through a column of soil. He observed that some metals were exchanged more readily than others; that chemically equivalent amounts of the exchanging metals were involved, and that the process must therefore be a chemical one, with the aluminosilicates in the soil being responsible for these phenomena. Synthetic aluminosilicates which he prepared possessed similar properties.

Gans (16) employed natural and synthetic aluminosilicates for industrial water softening as early as 1905. Adams & Holmes (17) in 1934, showed that organic ion exchange resins could be synthesized, and, from this time on, rapid improvements have been made in their stabilities and exchange capacities. The exchange capacity of a cation exchanger is usually expressed as the number of milligram equivalents of Na^+ ion which are absorbed per gm. of dry resin in the H^+ form; or in the case of the Na^+ form of the exchanger, as the number of milligram equivalents of Na^+ ion which may be eluted by hydrochloric acid per gm. of dry resin (Na^+ form). In general terms, it is the number of ionogenic groups per

specified amount of exchanger.

The ion exchange process itself involves the replacement of the exchangeable ions in the zeolite, by ions (counter-ions) of like charge in the solution. It may be represented by :



where Z refers to the anionic framework of the zeolite or resin, and A^{+} and B^{+} are the exchanging ions.

The extent to which one ion is absorbed in preference to another, i.e. the selectivity, is of fundamental importance, e.g. it determines the efficiency of recovery of ions from solution for the purpose of concentration of liquors; the ease with which very similar ions may be separated by ion exchange chromatography; and the ease with which ions are eluted from the exchanger after absorption.

Some of the more important factors which often determine the distribution of ions between the exchange medium and a solution, are summarized below :-

(1) Nature of exchanging ion.

- (a) charge: in dilute solutions, the affinity of a cation for the exchanger increases with increasing valency, i.e. $Ba^{++} > Cs^{+}$.
- (b) size: the larger the ion, the less chance of penetrating the exchange lattice, therefore since Cs^{+} is larger than Ba^{++} , the latter should exchange more easily.
- (c) polarizability: the higher the polarizability the more strongly will the ion be absorbed. e.g. $Cs^{+} > Na^{+}$.

- (d) hydration: the lower the degree of hydration the more strongly will be ion be absorbed, e.g.
 $\text{Cs}^+ > \text{Na}^+$.

(2) Concentration of solution: it has been observed that a cation exchange resin may preferentially absorb a divalent ion from a dilute solution also containing a monovalent cation, whereas the latter is preferentially absorbed at high concentrations.

(3) Nature of the cation exchanger:

- (a) number of exchangeable ions: in aluminosilicates the number of cations is equal to the number of AlO_4^{3-} tetrahedral units present, hence the greater the ratio of Al to Si, the larger the number of exchangeable cations.

- (b) availability of cations: if small cations are trapped inside small cavities within the lattice, large ions will not be able to replace them.

Various cation exchange studies have previously been made with synthetic faujasite, notably those of Barrer, Buser & Grutter (18). The following ions were found to be readily exchanged; univalent metal ions: K, Tl, Ag; divalent metal ions: Mg, Ca, Sr, Ba, Co, Ni, Cu; also $\text{Cu}(\text{NH}_3)_4^{++}$ and the alkyl ammonium ions: NH_4^+ , NH_3Me^+ , NH_3Et^+ , NH_2Me_2^+ , NHMe_3^+ and NMe_4^+ . The extent of exchange for the latter series, decreases with increasing alkyl content, i.e. in the order given. The ion NEt_4^+ is too large to be exchanged by NaX. The relative affinities of metal ions in NaX can be expressed according to their selectivity coefficients at 50% exchange; for the univalent ions we have: $\text{Ag} > \text{Tl} > \text{K} > \text{Na}$. and for the

divalent ions: $Ba > Sr > Ca > Mg$ (18); however, these cation exchange studies were largely qualitative, i.e. no attempt was made by these workers to construct exchange isotherms. The exchange studies carried out with NaX and mordenite in this work were quantitative, and isotherms were constructed for each system.

1.1.2. Inorganic Exchange Materials other than Zeolites.

Kraus et al. (19,20) in 1956, conducted some anion exchange studies on hydrous zirconium oxide. It was found to be particularly suitable as it is extremely insoluble and almost insensitive to attack by acids, bases, oxidizing and reducing agents. In basic solution, it acts as a cation exchanger; it is therefore an amphoteric exchanger. Zirconium phosphate was also found to show excellent exchange properties for alkali and alkaline earth metals, and it possesses quite an appreciable exchange capacity.

Amphlett et al. (21) first suggested the use of natural soils for the treatment of radioactive materials; exchange studies were carried out with various inactive ions, such as caesium, strontium and sodium. Radioactivity may enter the soil in various ways, e.g. by leakage of radioactive solutions, from a reactor accident, by fall-out from a nuclear explosion and so on, and it was reasoned (22) that ion exchange within the soil could play

an important role in delaying the spread of contamination. On the other hand, this might be a disadvantage as relatively high concentrations of activity would be localized, and hence become available to plants and livestock, and thence to man.

The question of disposal of radioactive material by absorption on various materials such as clays and zeolites, followed by fixing them against leaching by firing at high temperature, has also been considered (22,23). Pilot plants for this process are already in operation.

Amphlett et al. (24) in 1957, turned their attention towards the use of zirconium phosphate and hydrous zirconium oxide for cation exchange separations. The resins and zeolites then available had limitations, such as radiation instability in the former instance and instability in mildly acid solutions in the latter. Zirconium phosphate was found to be extremely stable over a wide range of temperature and pH. Other exchange media studied include the phosphates, molybdates, arsenates, and tungstates of zirconium, titanium, and thorium, i.e. acid salts formed by polybasic acids and certain hydrolyzable polyvalent cations. All were found to exhibit cation exchange properties, and are extremely insoluble in most reagents.

Ahrland et al. (25) investigated the selective sorption by silica gel, for the separation of uranium, plutonium and fission products from acid solutions of neutron irradiated uranium. After a cooling period of 100 days, the only appreciable activities other than from uranium and plutonium, are caesium - 137 (gamma-active) and strontium - 90 (beta-active). By a suitable choice of pH and flow rate, quantitative separations of uranium and plutonium were made. However, no mention was made of any damage sustained by the silica gel due to these radioactive materials in contact with it. Obviously, the more stable the ion exchange medium employed, the shorter the cooling period.

Separation of Radioactive Materials: For this purpose, there are several methods at present in large scale use, e.g. ion exchange, solvent extraction and precipitation. The advantages of ion exchange techniques include their simplicity and rapidity for decontamination, separation of trace elements and volume reduction (i.e. concentration of liquors). Organic exchangers in bead form allow rapid flow rates, and mixed bed resins can separate cations as well as anions. However, they suffer damage as a result of the radiation (vide section 1.3.1.) often releasing impurities into the effluent stream. Gas evolution produces "channelling" in the resin bed with consequent losses in efficiency. Inorganic exchangers in pellet or

granule form allow rapid flow rates, are able to withstand high temperatures (up to 300°C), and sustain far less damage as a result of the irradiation. Some zeolites are unstable in mildly acid solutions, but zirconium phosphate or oxide as already mentioned, would be quite stable under these conditions.

One of the most important uses of ion exchange procedures nowadays in the field of radiochemistry, is undoubtedly the decontamination of the vast volumes of solution resulting from the various processes involved in radiation chemistry. Most of the active materials are removed from solution by precipitation, the smaller proportions of other contaminants being separated by solvent extraction or ion exchange procedures. In the main, the United Kingdom Atomic Energy Authority decontaminate effluent streams, i.e. any active solutions from which it would be uneconomical to extract individual constituents, by passing the solutions through mixed bed exchange columns. These invariably consist of a mixture of the cation exchanger Zeo-Karb 225 and the anion exchanger De-Acidite FF 530 (ref.26). When these exchangers are almost completely spent i.e. , all the exchangeable ions have been replaced by the radioactive ions in the solution, they are radioactively speaking quite "hot". However, all the activity has thus been concentrated into a comparatively small volume, and disposal of this material offers no

difficulties at all compared with the disposal of large volumes of liquid. In fact, the spent resins are sealed into steel drums lined with concrete, and simply deposited in the Irish Sea.

1.2.GAS ADSORPTION.

We have already seen from the discussion of zeolite structures (vide section 1.0), that dehydration results in a lattice framework interlaced with regularly spaced cavities and channels of molecular dimensions. Zeolites are known as "molecular sieves" because they have the property of adsorbing some molecules but not others; this was first recognised by McBain in 1920. As to whether or not a specific molecule may enter the pores of a zeolite, is decided by its size and shape in relation to the pore size of the zeolite. It should be remembered that many molecules possess two 'sizes', i.e. the diameter of the nitrogen molecule measured normal to its longitudinal axis is $3.0\text{\AA}$, whereas the longitudinal is $4.1\text{\AA}$. Consequently, the rate of sorption might be low, allowing time for the gas molecules to orientate themselves in a suitable manner for diffusion throughout the lattice. The molecular sieve action is also decided upon by the cations of the zeolite (27), e.g. the sodium aluminosilicate known as "4A" is capable of adsorbing molecules of diameters up to $4\text{\AA}$. Exchanging approx. one third of the Na^+ ions with Ca^{++} ions, and we have the zeolite "5A", which can sorb molecules up to $5\text{\AA}$ in diameter. This behaviour does not depend on cation size, since Na^+ and Ca^{++} have very nearly the same radii, but results from the fact that one Ca^{++} replaces two Na^+ ions.

It is considered (10,28,29,) to be due to some Na^+ ions blocking channels and cavities, so hindering the passage of adsorbate molecules above a certain size, whereas the calcium ions are so positioned as to permit free passage of the gas or vapour.

Resulting from the large number of studies of occlusion by zeolites made by Barrer et al., the zeolites have been classified into five groups (28), depending upon the size of the molecules which they are able to sorb. NaX alone falls into class one, and is capable of sorbing in larger amounts, all those gases and vapours which are sorbed by other zeolites, e.g. aromatic hydrocarbons, naphthenes, isoparaffins etc., the largest molecule so far studied being iso-octane (2.8 molecules per supercage of NaX). The exceptional porosity of NaX arises from the presence of the supercages, of free diameter 12-13Å, and interconnecting windows 7.5Å in diameter. The total intracrystalline pore space amounts to about 0.53cc./cc. NaX.

The pores of NaA are too small to admit Xenon or krypton, but it is possible to sorb argon. However, it is found (30) that at -100°C , the sorption of argon is a function of time, because the adsorption process is one of activated diffusion.

The question thus arises as to how to decide which type of sorption process is occurring, i.e.

absorption or adsorption and physical or chemical.

Adsorption is taken to mean the gas is sorbed only on the outer surfaces of the sorbent, whereas absorption infers that the gas actually enters the electrical field between constituent atoms of the sorbent structure, so forming a solid solution or possibly a chemical compound. Molecules sorbed on the outside of the sorbent only, may experience a weak Van de Waal's attraction, or a much stronger activated or chemical adsorption (chemisorption). A number of differences between physical adsorption and chemisorption will now be outlined:

- (a) The fundamental difference arises in the nature of the forces involved between sorbent and sorbate; in physical adsorption, they are the same as those for condensation and liquefaction, i.e. Van de Waal's forces. In chemisorption, they are the same as valency forces etc.
- (b) The heat of adsorption for physical adsorption is of the same order as the heat of condensation; for chemisorption, it is of the same order of magnitude as for the heat of chemical reaction, (this may exceed the heat of condensation by a factor of 10).
- (c) The rate of physical adsorption is rapid, especially at low temperatures, equilibrium may be achieved in seconds or minutes. In chemisorption, the rate of adsorption is controlled by the resistance to surface reaction, and is therefore slow; a high activation

energy must be applied before chemisorption occurs, i.e. the higher the temperature, the faster the rate.

Since for the majority of sorbent/sorbate systems involving zeolites, the heats of sorption may be explained in terms of Van de Waal's forces, and are of the same order of magnitude as heats of liquefaction, and the rate of adsorption is invariably quite rapid, the sorption of gases and vapours by zeolites, is therefore considered to be physical adsorption.

Since the cavities and channels in a zeolite are interconnecting, the sorbed gas or vapour may be likened to a sorbed fluid (27), i.e. it may exhibit properties characteristic of the bulk liquid. (vide section 4.2.3.)

At a given temperature and pressure, the amount of gas or vapour adsorbed, is a function of the adsorbent and adsorbate, or conversely, for a given adsorbent/adsorbate system, the amount sorbed is a function of temperature and pressure, i.e.

$$V = f(p, T)$$

The usual method of expressing adsorption equilibria is in the form of adsorption isotherms, i.e. a plot of amount sorbed at constant temperature vs. the equilibrium pressure, i.e.

$$V = f(p) \quad (T = \text{constant})$$

At small adsorptions, Henry's law is valid: $V = kp$.

i.e. the isotherms are straight lines. In general, adsorption isotherms may be classified according to the Brunauer (31) classification; the distinction arises mainly from differences in the structure of the sorbent and sorbate - sorbate interaction. Type I represents unimolecular sorption of the Langmuir type, and type II is sigmoid in shape, being attributed to multilayer formation. All isotherms in this work were either straight lines or of type I. The various theoretical limiting isotherm models are discussed in section 2.2.4.

Interest has been centred recently (32-35) on the use of thermodynamical methods of investigating the physical state of molecules, occluded within the intracrystalline channels of robust zeolites such as faujasite. This approach is particularly favourable for such systems, as the heterogeneities which might complicate the energetics of sorption in analogous systems, are absent. Such heterogeneities include surface irregularities and multilayer formation. However, an adequate analysis may only be made if data is available over a wide, if not complete, range of θ (where θ is the degree of saturation of the intracrystalline pore space). This study describes the occlusion of the rare gas krypton, on the synthetic form of faujasite known as NaX. The isotherm data is analysed in terms of the various ideal isotherm models, in an attempt to decide whether the sorption is localized

or mobile, and whether or not, the interactions between adsorbate molecules are significant. The isosteric heat data provides interesting results, and an attempt has been made to explain these in terms of the potential energies of occluded molecules, i.e. the potential energies of interaction both with the framework atoms of the zeolite, and with the mutually sorbed gas molecules.

1.3.NEUTRON IRRADIATION.

Present day interest in the effects of neutron irradiation of materials, stems from an observation by Wigner during wartime research on nuclear reactor development. He realised that the energetic neutrons born in the fission process, would have the ability to displace atoms from equilibrium positions in the crystal lattices of solids, and hence result in deleterious effects in their properties. Technologically, these effects could be very serious.

Early experimental studies confirmed these observations and it soon became obvious that radiation damage was to be expected in all solid materials, to an extent depending on parameters such as type of radiation, flux, temperature and characteristics of the particular solid. The Atomic Energy Commission of America therefore established research programmes to study the effects of radiation (a) on reactor materials, such as metals, graphite, concrete and other constructional materials;

(b) on reactor fuel elements, to determine whether damage resulted in loss in efficiency of power production; and more relevant to this work,

(c) on processing materials, required to separate, decontaminate and purify still-fertile material, and particular fission products. Consequently,

most of the literature published in this field is to be found since about 1955.

When a substance is irradiated in a nuclear reactor, it can be subjected to bombardment by heavy particles, both charged and uncharged, by β - and γ -rays and also by fission fragments. The quantity of any one type of radiation depends upon factors such as position in relation to the core of the reactor, amount of moderator between source and sample, radiation flux etc. Linear accelerators and cyclotrons may also be employed for irradiation purposes.

Radiation damage may arise in two ways (36) :-

- a) through the elastic collisions between lattice atoms and bombarding particles, and
- b) ionization effects, brought about by the coulombic interactions between lattice nuclei and bombarding charged particles; by the displacement of electrons from their normal orbital positions; by the movement of displaced atoms and ions throughout the lattice, and so on. Gamma rays are predominantly responsible for ionization by the displacement of orbital electrons. Neutrons, being uncharged, can however only cause ionization indirectly.

The physical consequences of these interactions upon irradiation of a solid, are that several types of defects are introduced which affect the

properties of the solid to a large or small extent, depending upon the material, type of radiation etc.

Examples of these defects will now be briefly discussed:-

Vacant lattice Sites: these may be created by collisions of fast neutrons with the atoms in the solid lattice.

The recoiling atom will usually possess sufficient energy to cause further vacant sites in the lattice by subsequent collisions. Thus each 'primary collision' may result in a series of collisions known as 'cascades', creating many vacancies. The passage of these atoms and ions throughout a lattice will also cause extensive ionization and electronic excitation, which in turn will lead to bond rupture and free radical formation. Such effects are most important in various materials such as insulators, ionic crystals and organic high polymers.

Interstitial Atoms: these may arise from displaced atoms coming to rest in non equilibrium positions in the lattice. Frequently however, they immediately recombine with a nearby vacancy. If the replacing atom is not the same as the displaced atom, it will still constitute a defect, and even if the two atoms concerned are identical, there may be insufficient energy for it to recombine or reform all the broken bonds. The name Frenkel-defect is given to an interstitial-vacancy pair.

Impurity Atoms: these arise from neutron capture by an atomic nucleus, i.e. nuclear transmutations, or by the

introduction of fission fragments from the fission process. However, these two mechanisms are considered to be of little significance compared with other effects. The explanation of various terms will now be given;

Cross Sections: when a material is bombarded with neutrons, there is a finite probability of either scattering, absorption or nuclear reaction. This probability is expressed as a cross section σ , measured in barns (where 1 barn = 10^{-24} cm²). The cross section of an atomic nucleus may be thought of as a circular disc, centred on the nucleus, on a plane normal to the incident beam. If the neutron passes through this 'area', then interaction or absorption occurs, otherwise scattering occurs. The scattering cross sections of most nuclei, for high energy neutrons, is about 3 barns, i.e. 3×10^{-24} cm².

Neutron Flux: the term 'neutron flux' or 'neutron flux density', also known as 'instantaneous flux', is abbreviated as (nv) or ϕ , where n = the number of neutrons per unit volume in the sample being irradiated (n/cm^3) and v = the mean velocity of the bombarding neutrons; therefore the units of flux density are $n/\text{cm}^3 \cdot \text{cm}/\text{sec} = n/\text{cm}^2/\text{sec}$. However, this refers to a time interval of only one second (hence the name 'instantaneous flux').

The so-called "dose of bombardment" or "neutron irradiation exposure", best known as "integrated neutron flux density", refers to a time interval of more than one second, and is expressed by the symbols (nvt). The units are therefore $\text{n/cm}^3 \cdot \text{cm/sec} \cdot \text{sec} = \text{n/cm}^2$. For reactor irradiations, we may express the neutron flux in the following ways depending on which is appropriate, e.g. 10^{18} nvt (total) or 10^{18} nvt (fast) or 10^{18} nvt (thermal).

The integrated flux density may be defined as the number of neutrons that traverse an imaginary sphere of cross sectional area, 1 cm^2 , within the sample; it is not the number of neutrons crossing a flat surface of the same area.

Fast Neutrons.

The reason for the widespread interest into the effects of neutron bombardment stems from reactor technology, and the need to know the effects upon all types of reactor materials. The neutrons that are of primary interest are those originating from nuclear fission; they possess an average energy of approximately 1 MeV, though the actual energies vary through a wide spectrum. Slow or thermal neutrons are the result of the fission (fast) neutrons, being slowed down ("thermalized") by the moderator, and they cause radiation damage by the formation of impurity atoms resulting from neutron absorption, i.e. nuclear

transmutations. Fast neutrons, however, cause extensive damage throughout the lattice by suffering elastic collisions with lattice atoms, resulting in displacements, interstitials etc. Such radiation-induced defects are much more numerous than impurity atoms produced by thermal n-capture, because the neutron scattering sections are larger than the absorption cross sections. Also, there are several hundreds of dislocations for every bombarding neutron (37,38,). In most reactor irradiations there are several times more thermal neutrons than fast neutrons. The immediate vicinity of the fuel element in a reactor is obviously the most suitable to obtain high fast neutron fluxes.

Due to the lack of charge, a high energy neutron has a longer mean free path (of the order of 1 cm.) than that possessed by heavy charged particles or electrons. This is a great advantage, as massive samples may be irradiated instead of the very thin sections usually required for proton bombardment. The damage then sustained by the sample is free from spurious effects due to surface damage only; fast neutron irradiation can therefore be thought of as producing homogeneous damage effects. Actually, on a microscopic scale, the damage will tend to be highly concentrated, due to thermal spikes for example (see later).

During the fission process, γ -photons will accompany the emission of fast neutrons, and they are generally assumed to be about 3 times as numerous as the latter. Gammas cannot be filtered out of this mixture without seriously decreasing the neutron flux and, consequently, the radiation damage resulting from γ -irradiation must always accompany the effects due to neutrons. The problem of "gamma heating" may also arise, due to decaying radionuclides, and may require adequate cooling of the sample to prevent fusion or melting.

Displacement Spikes: On average, a displaced lattice atom will possess an energy of the order of several hundreds of eV, and will suffer approximately 10 - 100 collisions before becoming a trapped interstitial atom. It is therefore only a few interatomic distances away from the vacancy which was its original position. Consequently, the path of a projectile atom is an area of a comparatively high degree of damage comprising many interstitials and vacancies. This is the type of damage to be expected from fast neutron bombardment. Most of the energy transferred to a displaced atom reappears as lattice vibration, confined to an area close to the paths of the projectiles. Brinkman (39) proposed the name "displacement spike" for the volume of the lattice, disordered and heated in the above manner. He suggested that this volume may be actually

raised in temperature to the melting point, for the order of 10^{-11} secs. and then rapidly recrystallize to the original form, involving in all about 10^3 - 10^4 atoms per spike.

Thermal Spikes: this term, proposed by Seitz (40), refers to the situation where the lattice atoms only vibrate about their mean positions, and do not actually move about producing vacancies and interstitials. The temperature may attain the melting point of the solid for the order of 10^{-12} second, but only involves about 10^2 - 10^3 atoms per spike. There is just a rapid local heating and quenching within a very small volume, with no atomic rearrangements as found in displacement spikes.

Thermal Neutrons:

Irradiation of a material in a nuclear reactor necessarily incurs the bombardment by slow, thermal neutrons, as well as fast neutrons. In most reactor irradiations, there will be several times as many slow as fast neutrons. Thermal neutrons possess energies of the order of .05 eV and are produced by the thermalizing effect of the moderator. They are usually absorbed by the lattice atoms resulting in nuclear transmutations, i.e. the formation of stable and unstable isotopes of higher mass. γ -radiation is frequently emitted in this process, a typical reaction being expressed as follows: $A_Z^w(n, \gamma)B_Z^{w+1}$, where the atom A of atomic number z and atomic weight w, has absorbed a single neutron to form

a higher isotope B, (same atomic number as A) of atomic weight $w + 1$. Examples of nuclear transmutations that may occur upon thermal neutron irradiation of an aluminosilicate structure such as NaX, will be discussed in section 2.3.3.

1.3.1. Radiation Effects in Exchange Materials.

Cathers (41) published the first paper on the effects of radiation of organic ion exchange materials, at the United Nations Conference on the Peaceful Uses of Atomic Energy in Geneva (1955). The purpose of his work was to study :-

- (a) the effects of radiation damage on the materials used for the recovery of fissile and fertile material, and the decontamination of this material from fission products.
- (b) the process cost, of obvious importance for radio-chemical processing at high activity levels. The high radiation stability of some processing materials is, unfortunately, counterbalanced by their relatively poor chemical stability, and vice versa.

Preliminary work by Cathers showed the initial effect on the exchange resins was a loss in exchange capacity. Other properties which must however be considered are swelling behaviour, selectivity for various ions, physical damage to the resins such as cracking of the globules, chemical rearrangements due to chain scission or cross linking, and contamination of the effluent stream. Examples of the latter include the release of ammonia and primary amines from the quaternary ammonium polystyrene resins due to chemical breakdown, and the exchange of hydrogen in the resin for

deuterium of the heavy water moderating solutions which are usually decontaminated by ion exchange.

In order to compare the sensitivities of various materials towards irradiation, we require a convenient unit of dosage. For high intensity work, Bruce & Cathers proposed the "watt hour of radiation energy absorbed per gram of dry resin". This unit is related to others as follows:-

1 watt hour of energy absorbed / gm.

$$= 3.60 \times 10^8 \text{ rads. / gm.}$$

$$= 3.60 \times 10^{10} \text{ ergs. / gm.}$$

$$= 8.60 \times 10^2 \text{ calories / gm.}$$

$$= 2.25 \times 10^{22} \text{ eV / gm.}$$

The following table of results (reproduced in part from ref.42), and due partly to Cathers, (41), compares the loss in exchange capacities of various resins due to the absorption of 1 watt hour of radiation energy.

Type of Resin.	Commercial Name.	% Capacity Loss.
strong acid	Dowex-30	1
	Amberlite 1R-120	10
weak base	Dowex-3	20
strong base	Permutit S2	40
	Dowex-1	40
weak acid	Amberlite 1RC-50	100
	Permutit H 70	100

Unfortunately, the relatively high radiation stability

of Dowex - 30 is counterbalanced by poor chemical stability. The radiation in these cases was obtained from a cobalt-60 γ -source, or β -emission resulting from Ce^{144} and Pr^{144} sorbed on the resin (43).

Kiselev et al. (44) bombarded an organic cation exchange resin (KU-2) with accelerated electrons, up to doses of 50 watt hours of energy absorbed per gm., both in the dry state and in aqueous acid solution. Decomposition of the material was observed in the form of free sulphur and sulphuric acid, and partial solubility of the resin. The exchange capacity was considerably diminished. Organic resins have also been subjected to X- irradiation and nuclear reactor irradiation, the damage resulting from each type being approximately equivalent in terms of capacity loss.

Ferguson (45) has studied the problems of a cyclic processing plant for the experimental homogeneous reactor at the Oak Ridge National Laboratory. This reactor employs uranyl sulphate in heavy water as fuel solution, i.e. ($\text{U}^{233} \text{O}_2 \cdot \text{SO}_4 / \text{D}_2\text{O}$). To maintain the level of neutron absorbing fission products at an acceptable level, and thus maintain the power production of the order of 100,000 kw. of useful electricity, it is necessary to process the fuel solution frequently. These neutron absorbers include caesium and the rare earth elements created in the fission process. The

chemical process employed consisted of removing a large volume of fuel solution from the reactor each day, storing for 5 days to allow decay of the short lived fission products, and then passing through an organic cation exchange resin of the sulphonated phenol type. This resin sorbed the neutron poisons so efficiently that the treated solution could be returned directly to the reactor. The principal advantages of this process are its efficiency and simplicity, but the chief disadvantages result from the radiation damage to the resin, and the appreciable inventories of D_2O and U^{233} necessitated by the 5 day decay period before processing.

The phenolic resins such as Dowex-30 and Amberlite IR - 105, are the most stable of the organic exchange resins, losing approximately 1% of their capacity when exposed to 1 watt hr. of ionising radiation / gm. dry resin. The process outlined above results in the resin being exposed to approximately 10 watt hrs/gm., corresponding to ca.10% loss in capacity. Hence it would be discarded after only one operation. Less stable resins would necessitate a longer cooling period before processing, thus further increasing storage costs. Since suitable radiation resistant ion exchangers were not known of, other more costly techniques were employed for the cyclic processing of this fuel solution. Another problem which arose through the use of organic resins to

process this reactor fuel solution, was that hydrogen from the resin contaminated the deuterium of the heavy water. Ferguson realised that use of an inorganic exchanger, of high relative radiation stability, would eliminate these problems.

Ferguson (45) also observed that uranium, protoactinium and thorium, can be effectively separated by anion exchange on a quaternary amine polystyrene. Again the chief limitation arises from radiation damage; a decay period of 100 days is required to limit the resin capacity loss to 10%, and even then it has to be replaced.

For the second International Conference on the Peaceful Uses of Atomic Energy (Geneva 1958), Nater (46) published a paper containing a table of comparative results for the irradiation of both organic and inorganic exchangers. The most stable organic resin studied, Dowex-50, sustained a 30% loss in capacity from a dose of 19.5×10^8 rads; Stamex-S, a strong anion exchanger suffered a 100% capacity loss from only 5.7×10^8 rads. Nater realised that the exchange properties of stable inorganic exchangers will deteriorate only after much larger radiation doses.

Actual physical damage sustained by resins has also been observed by several workers. Utley (47) observed that the rate of diffusion of lithium ions into resin particles (20-50 mesh), showed an initial

increase to precede the subsequent decrease. This initial increase was due to an increase in surface area of the particles arising from radiation induced cracking and shattering of the resin spheres.

Other materials possessing ion exchange properties include the insoluble acid salts of polybasic acids with certain hydrolysable polyvalent cations, e.g. the phosphates, arsenates, tungstates and molybdates of zirconium, thorium and titanium (24). The exchange characteristics for ions ranging in size from Na^+ to UO_2^{++} have been determined, and in view of the extreme insolubility of these exchangers and their resistance towards irradiation damage, they are considered of increasing importance for the separation, concentration, purification etc. of radioactive effluents, wastes and fuel solutions (49).

Summarizing : (a) the order of stability of organic exchange media towards radiation is :-

weak acid < strong base < weak base < strong acid, the latter suffering approximately one fifth of the capacity loss of the former for the same dosage.

(b) the greater the degree of cross-linking, the greater the stability towards irradiation.

(c) The most radiation resistant organic exchangers unfortunately suffer from relatively poor chemical stability, and in general they are less radiation resistant than their inorganic counterparts.

1.3.2. Radiation Effects in Silica, Quartz etc.

This section of the literature survey briefly describes the work carried out on the effects of radiation upon materials similar in structure to zeolites, e.g. quartz, vitreous silica, diamond and alumina.

Quartz changes from its crystalline form (α -quartz) to an amorphous structure similar to silica glass; this occurs with a dose of approximately 2×10^{20} fast neutrons/cm² and is accompanied by a large decrease in density of ca. 15%(50). It is interesting to note that no macroscopic defects were observed; however, Crawford & Wittels (51) observed the formation of macroscopic holes in quartz, after irradiation to a dose of only 8×10^{19} n/cm², with subsequent annealing at 950° C. The quartz lattice is disordered in a manner known to mineralogists as "metamict". The lattice expansion may be due to atoms lodging in parts of the structure not large enough to accommodate them (52). The damage is known to arise in two stages (53); up to 3×10^{19} n./cm², the lattice damage is predominantly point defects and small disordered regions. The lattice vacancies and interstitial atoms are assumed to be almost entirely due to oxygen atoms, since more energy would be required to displace Si atoms. At higher exposures, the shear strains set up by the

disordered regions spread throughout the crystal, rendering it completely amorphous.

Vitreous Silica, in contrast to quartz, shows an increase in density upon neutron irradiation, resulting in the same final product in the amorphous state (54). The complete change, either from quartz or silica to the amorphous state requires a dose of ca. 2×10^{20} fast neutrons/cm². These changes are attributed to ionization and to atomic displacements. Primak et al. (52), suggest that in vitreous silica, displaced atoms of O and Si lodge in the cavities within the structure, and permit the SiO₄ tetrahedra to relax into a more compact arrangement, thus increasing the density. These atoms, however, seem to be loosely held or even uncombined, since on annealing by heating, the original density is restored (55).

Simon (56) studied the Debye-Scherrer X-ray diffraction patterns of silica, before and after neutron irradiation, and suggested that the decreased Si-Si bond distance in the irradiated material was due to a smaller Si-O-Si bond angle (138° as opposed to 142°). The Si-O bond length appears to be unaffected by the irradiation. Coesite; Wittels & Sherrill (50) first observed that prolonged neutron bombardment of crystalline solids containing the SiO₄ tetrahedral group such as quartz and silica, reduced them to a common amorphous substance.

Since these two materials consist of 50% or more of void space, it was considered of interest to determine whether radiation damage is related to the openness of structure. For this purpose, polycrystalline specimens of coesite, a high density synthetic silica ($d = 3.01$ g./cc.) were exposed to 2×10^{20} n/cm²., the dosage which is sufficient to vitrify silica and quartz (57). Before and after irradiation, Debye-Scherrer X-ray diffraction patterns were taken to ascertain whether any structural changes had occurred in the material as a result of the neutron bombardment; no damage was observed. Wittels therefore suggested that the radiation stability of coesite offered evidence supporting the belief that both the rate of damage, and the location of lattice defects have a structure dependence in neutron irradiated solids. Several naturally occurring silicate and aluminosilicate materials have been investigated, and it is found that the greater the degree of covalent bonding the greater the response to irradiation.

Diamond, has been observed (58) firstly to suffer from the formation of vacancies and interstitials, and then to lose its crystallinity after prolonged fast neutron bombardment (ca. 10^{21} n/cm².) Since this has important implications in the use of covalent refractory materials further studies were carried out, notably those of Crawford & Wittels (51) and the etching studies of Chang (59).

Effects of Neutron Irradiation upon the Catalytic Activity of Silica and Alumina.

Pure Silica is known to be catalytically inert; however, it can acquire considerable catalytic activity in the presence of such elements as aluminium, magnesium, zirconium etc.; these elements are therefore called "promoters". Taylor & Wethington (60) suggested that catalytic properties might even be induced by bombardment of a solid with energetic particles, so producing lattice defects and/or impurity atoms. Weisz & Swegler (61) irradiated a pure sample of porous silica gel, and showed that the catalytic activity towards the double bond isomerization of n-hexene-1, was very slightly increased, as a result of a dose of about 7.5×10^{18} fast neutrons/cm². Conditions were such that this induced activity could be explained in terms of lattice defects and not by the impurity atoms which are produced by nuclear transmutations, i.e. the proportion of slow to fast neutrons was very small. Silica and oxygen atoms possess such small neutron-absorption cross sections, that nuclear transmutations are unlikely to result in significant amounts of chemical impurities, (i.e. Al, P, F). If the neutron-absorption cross sections for Si and O are taken as 10^{-27} cm² and the total neutron dose equals 7.5×10^{18} n/cm², the fraction of neutron induced impurity atoms equals the product of these two

figures, i.e. 7×10^{-9} . However, the fraction of dislocated atoms, approaches one per cent of the normal lattice sites; this was calculated (61) using the observation that in germanium crystals, several hundreds of dislocations result from one scattered neutron (38); therefore the fraction of dislocations equals the neutron dose ($7.5 \times 10^{18} \text{ n/cm}^2$) multiplied by the scattering cross section ($1.7 \times 10^{-24} \text{ cm}^2$) and the factor of $10^2 - 10^3$; i.e. 1.0 to 0.1 % of the normal lattice atoms are dislocated. Hence the above assumption that neutron-induced dislocations are the cause of the enhanced catalytic properties of silica gel towards the isomerization of hexene-1. However, Lucchesi et al. (62,63,) used a silica-alumina (13 wt.% Al_2O_3) catalyst for the isomerization of butene-1 to butene-2, and found that neutron irradiation of the catalyst with a dose of ca. $7 \times 10^{18} \text{ n/cm}^2$ decreased the catalytic activity. It is interesting to note that the ratio of cis- and trans-butene-2 so formed, was the same using the non-irradiated and irradiated catalysts; hence only the catalytic activity is affected. The reason for the observed decrease may, as above, also lie in the formation of neutron-induced dislocations. Kohn & Taylor(64) irradiated silica gel with neutrons up to a dose of $2.2 \times 10^{18} \text{ n/cm}^2$, and found a catalytic activity much higher than any obtained by outgassing

procedures alone; this result was confirmed using in all 8 forms of silica. Mikovsky & Weisz (65) increased the neutron dose used by Weisz & Swegler (61) to irradiate a silica-alumina (10%) catalyst, from 7.5×10^{18} n/cm² to ca. 10^{20} n/cm². This tenfold increase in dose resulted in a 1.5 to 3 fold increase in activity towards olefin isomerization, thus confirming the statistically significant (i.e. extremely small) increase previously observed. The same irradiation resulted in an increase in the catalytic activity of pure silica, i.e. by a factor of 10. The surface areas of these catalysts were found to decrease, SiO₂, 395 to 354, and Al₂O₃/SiO₂ 274 to 218 m²/gm, so the increases in catalytic activity are not produced by increases in surface area. Neutron irradiation of silica and silica-alumina catalysts may therefore enhance, decrease or make no difference to their catalytic activities. An attempt was made by Weisz & Mikovsky (65) to explain these observations in terms of atomic displacements; it was suggested that neutron irradiation might well create new active catalytic sites, but also affect existing ones, resulting at lower doses in no net change, and at higher doses in a net activation. Decreases in catalytic activity might be explained by deleterious effects resulting from the neutron bombardment, or the effects of poisons produced during irradiation.

1.3.3. Neutron Irradiation of Alumina :

The first systematic approach to the effects of neutron irradiation on crystalline solids, with subsequent physical gas adsorption studies, is due to Young (66). He analyzed the thermodynamical properties resulting from isotherms of krypton adsorbed on specimens of dehydrated alumina, before and after nuclear reactor irradiation.

Previous work on the etching of solids, showed that particle bombardment caused an increase in the number of surface heterogeneities, at which etch-pits would be formed. Examination of the imperfections produced by radiation was not considered possible by electron microscope or field-ion microscope studies, since the effects are usually too small to be observed by these methods. A more indirect method was thus adopted, that of the physical adsorption of an inert gas at low temperatures, with subsequent analysis in terms of the shape of the adsorption isotherm and the differential molar entropy of the sorbed phase.

A significant increase in isotheric heat was observed resulting from a dose of 2×10^{18} fast neutrons. Young analysed the adsorption results using the isotherm methods of Garden & Kington (67,143), i.e. localized or mobile sorption, with or without adsorbate molecule interactions. The most suitable model appeared to be

one of localized sorption without marked lateral interactions, on surfaces of varying heterogeneity.

1.4. SUMMARY OF PART 1 and
Reasons for Choice of Materials.

The organic ion exchange materials at present employed for the separation and purification of extremely radioactive materials, suffer from the serious disadvantage of being decomposed by the radiation. Since the crystalline zeolites possess very stable lattice frameworks and excellent ion exchange properties, it was considered quite probable that a zeolite such as faujasite should be capable of withstanding the radiation doses which caused serious capacity losses in its organic counterparts.

The exceptional openness of NaX, with its wide interconnecting channels, facilitates the free passage of large ions, such as Cs^+ , Ba^+ and uranyl UO_2^{++} , thus allowing cation exchange of these ions. All three of these cations are readily available and may be considered as fairly representative of the metals constituting a still fertile, fission products mixture from a nuclear reactor. For these reasons, the ion exchange characteristics of the systems NaX/Cs^+ , $\text{NaX}/\text{Ba}^{++}$ and $\text{NaX}/\text{UO}_2^{++}$, were briefly studied. Mordenite, with a higher SiO_2 to Al_2O_3 content than

NaX, possesses greater stability in acid solutions, and was also used for ion exchange studies with these ions. The open lattice structure of NaX also made it possible to study in some detail the thermodynamics of physical adsorption of krypton. Such a study should provide information about any surface heterogeneities in the NaX produced by the radiation. For a complete discussion of the thermodynamics of such a system, we require sorption results over a wide range of θ (= degree of saturation). Constructing isotherms in the region of -150°C , meant that a maximum of $\theta = \text{ca. } 0.5$ could be obtained using argon, whereas with krypton (fr.pt. -158°C), $\theta_{\text{max}} = .95$ was achieved. The advantages of the system NaX/krypton, therefore adopted for the physical adsorption studies are thus apparent.

Regarding the type of radiation employed, i.e. fast neutrons in a nuclear reactor, this choice was largely determined by convenience. Facilities exist whereby Universities and Industry may have samples of various materials irradiated in the reactors at Aldermaston & Harwell. Irradiations to known fluxes are possible and the high pile factors allow high doses to be achieved in relatively short times.

PART 2THEORETICAL.

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2.1.CATION EXCHANGE.2.1.1. Summary of Symbols.

A = exchanging ion (initially in solution)

B = " " (" " zeolite).

Y = anion, common to both cations, A^+ and B^+ .

Z = anionic framework of zeolite; S = solution.

z_A, z_B, z_Y = valencies of ions.

A_Z, B_S etc. = equivalent cation fractions of ions;

e.g.

$$B_S = \left[\frac{z_B \cdot n_B}{z_A \cdot n_A + z_B \cdot n_B} \right]_S$$

n = no. of moles or g.ions.

m = molality of solution. Initial molality of AY is M. At equilibrium, after exchange:

$$m_{AY} = M - m_{BY}$$

$$\text{where } m_{BY} = B_S \times M$$

and B_S is as above.

K = simple law of mass action constant or selectivity coefficient.

K_a = thermodynamic equilibrium constant:

$$K_a = K \cdot \gamma_S / f_Z$$

$$K_C = K \cdot \gamma_S = K_a \cdot f_Z \quad (\text{see text})$$

() = activity of cation enclosed by brackets.

γ = activity coefficient of ion in solution.

f = " " " " " exchanger.

γ_s, f_z = ratio of activity coefficients in solution and exchanger respectively.

$\gamma_{\pm AY}$ = mean molal activity coefficient of AY in solution in the presence of BY.

$\gamma_{\pm AY}$ = activity coefficient of AY in solution of ionic strength I (which is the ionic strength of AY and BY mixed).

$$k_1^0 = z_B (2z_B - z_A + z_Y)$$

$$k_2^0 = z_A (z_B + z_Y)^2 / (z_A + z_Y)$$

$$k_3^0 = z_A z_B z_Y (z_A - z_B)^2 / 2(z_A + z_Y)$$

(the superscript 0 denotes values of k for the forward reaction $(AY + BZ \rightleftharpoons)$. For the reverse reaction $(\leftarrow BY + AZ)$, k_1 k_2 and k_3 are obtained by reversing the letters A and B in the above expressions.

[] = concentrations of ions.

$$I = \text{ionic strength of solution of mixed electrolytes}$$

$$= \frac{1}{2} \sum (z_A^2 m_A + z_{Y_A}^2 m_{Y_A} + z_B^2 m_B + z_{Y_B}^2 m_{Y_B})$$

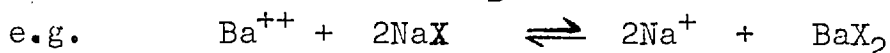
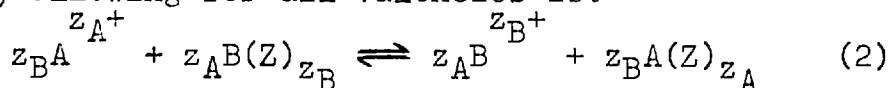
where m_{Y_A} and m_{Y_B} are molalities of anion Y^- in the electrolytes AY and BY respectively.

2.1.2. Introduction to cation exchange theory.

When a cation exchanger is mixed with an electrolyte solution, the equilibrium eventually achieved may be expressed by the equation:



where A^+ and B^+ are univalent cations. The general equation, allowing for all valencies is:-



where $A = Ba^{++}$ and $B = Na^+$

The law of mass action then gives:-

$$K_a = \frac{(A_Z)(B_S)}{(B_Z)(A_S)} \quad \begin{array}{l} \text{- for univalent} \\ \text{cations} \end{array} \quad (3)$$

and
$$K_a = \frac{(A_Z)^{z_B} (B_S)^{z_A}}{(B_Z)^{z_A} (A_S)^{z_B}} \quad \begin{array}{l} \text{- for all} \\ \text{valencies} \end{array} \quad (4)$$

K_a being the thermodynamic equilibrium constant. The bracketted symbols refer to the activities of the respective ions. However the experimentally measurable quantities are not activities, but concentrations, and therefore we must introduce the activity coefficients, both for ions in solution, γ , and in the exchanger, f . For uni- univalent systems:

$$K_a = \frac{A_Z B_S f_{AZ} \gamma_{BS}}{B_Z A_S f_{BZ} \gamma_{AS}} \quad (5)$$

where
$$\frac{A_Z B_S}{B_Z A_S} = K, \text{ the selectivity coefficient.} \quad (6)$$

K is obtained directly from the ion exchange equilibrium data. Thus in order to determine K_a , we require the activity coefficients of A^+ and B^+ in both the solution and exchanger phases.

Single ion activity coefficients such as γ_{B_s} and γ_{A_s} are indeterminate, but the ratio $\gamma_s = \gamma_B / \gamma_A$ is obtainable. If we consider the exchanger at equilibrium to be a non ideal solid solution of the two pure components, i.e. consisting of pure exchangers $A(Z)_{z_A}$ and $B(Z)_{z_B}$, and the solution phase to consist of pure electrolytes $A(Y)_{z_A}$ and $B(Y)_{z_B}$, then the activity of each component can be equated to its mole fraction multiplied by the activity coefficient, i.e. $A_z^{z_B} f_{A(Z)}^{z_B}$ for the ion A^{z_A+} in the exchanger phase, and $m_{AY}^{z_B} \left[\gamma_{\pm AY}^{z_A+1} \right]^{z_B}$ for the ion A^{z_A+} in the solution phase. Therefore the rigorous thermodynamic equilibrium constant K_a , allowing for all valencies, is given by:-

$$K_a = \frac{A_z^{z_B} f_{A(Z)}^{z_B} m_{BY}^{z_A} \left[\gamma_{\pm BY}^{z_B+1} \right]^{z_A}}{B_z^{z_A} f_{B(Z)}^{z_A} m_{AY}^{z_B} \left[\gamma_{\pm AY}^{z_A+1} \right]^{z_B}} \quad (7)$$

For uni- univalent systems:

$$K_a = \frac{A_z f_{A(Z)} m_{BY} \gamma_{\pm BY}^2}{B_z f_{B(Z)} m_{AY} \gamma_{\pm AY}^2} \quad (8)$$

and for uni- bivalent systems: ($z_A = 2, z_B = 1$):

$$K_a = \frac{A_z f_{A(Z)}^2 m_{BY}^2 \gamma_{\pm BY}^4}{B_z^2 f_{B(Z)}^2 m_{AY}^3 \gamma_{\pm AY}^3} \quad (9)$$

If the exchanging solutions are dilute, we can simplify the above expressions for K_a , e.g. for uni- univalent systems, the ratio of activity coefficients in solution,

$$\gamma_s = \frac{\gamma_{\pm BY}^2}{\gamma_{\pm AY}^2}$$

should be almost constant and nearly equal to unity.

Equation 8 then reduces to:

$$K_a = \frac{A_Z f_A(Z) m_{BY} \gamma_s}{B_Z f_B(Z) m_{AY}} \quad (10)$$

$$\therefore K_a \frac{f_Z}{\gamma_s} = \frac{A_Z m_{BY}}{B_Z m_{AY}} = K \quad (11)$$

where K is the law of mass action selectivity coefficient. Thus knowing K , γ_s , $f_A(Z)$, and $f_B(Z)$, we can calculate K_a . The majority of exchange systems previously studied have shown that f_Z cannot like γ_s be assumed to be constant.

2.1.3. Activity Coefficients in Solutions of Two Electrolytes:

The mean molal activity coefficients of the electrolytes employed in the expression for K_a , e.g. $\gamma_{\pm AY_{Z_A}}$, are actually the activity coefficients of the individual electrolytes at the same molality as the molality of the solution of the mixed electrolytes. Strictly speaking they should be the activity coefficient of one electrolyte, e.g. AY_{Z_A} , in the presence of the other, BY_{Z_B} . Numerous activity coefficients of single electrolytes have been tabulated (69), but very few for electrolytes in the presence of another electrolyte.

Glueckauf (70) derived an expression for the activity coefficient of an electrolyte AY, in the presence of a second electrolyte BY, where the anionic group is common:-

$$\log \gamma_{\pm AY} = \log \gamma_{\pm AY}^0 - \frac{[B]}{4I} \left[k_1^0 \log \gamma_{\pm AY}^0 - k_2^0 \log \gamma_{\pm BY}^0 - \frac{k_3^0}{1+I^{-\frac{1}{2}}} \right] \quad (12)$$

- for the forward reaction ($AY + BZ \rightarrow$), and

$$\log \gamma_{\pm BY} = \log \gamma_{\pm BY}^0 - \frac{[A]}{4I} \left[k_1^0 \log \gamma_{\pm BY}^0 - k_2^0 \log \gamma_{\pm AY}^0 - \frac{k_3^0}{1+I^{-\frac{1}{2}}} \right] \quad (13)$$

- for the reverse reaction ($\leftarrow AZ + BY$). (All symbols have already been defined, pages 57-58). If A, B, and Y are all univalent, these expressions reduce to:

$$\log \frac{\gamma_{\pm AY}}{\gamma_{\pm BY}} = \frac{1}{2} \log \frac{\gamma_{\pm AY}^0}{\gamma_{\pm BY}^0} \quad (14)$$

$$\therefore \gamma_s = \frac{\frac{\gamma_{\pm BY}^0}{2}}{\gamma_{\pm AY}} = \frac{\gamma_{\pm BY}^0}{\gamma_{\pm AY}} \quad (15)$$

The ratio γ_s remains constant provided the ionic strength of the solution of the mixed electrolytes remains constant, i.e. γ_s is independent of the relative amounts of the individual electrolytes present. As shown in equation 11 the selectivity coefficient is given by: $K = K_a f_Z / \gamma_s$, therefore since γ_s is constant for uni- univalent systems any variation in K must be explained by a variation in f_Z , the ratio of activity coefficients of A^+ and B^+ in the exchanger. In uni- bivalent systems, the activity coefficients of the electrolytes AY and BY in the presence

of each other, must be calculated directly from the Glueckauf expressions (equations 12 and 13); substitution in equation 7 then yields K_a .

2.1.4. Activity Coefficients in the Exchanger Phase:

The two components of the exchanger phase A(Z) and B(Z) normally form a continuous range of solid solutions, therefore their activities are usually considered to be a function of their concentrations. If a linear relationship exists between these two quantities, i.e. assuming the exchanger is an ideal solid solution of its components, and that γ_s is constant, the simple form of the law of mass action is obtained:

$$K = \frac{A_Z B_S}{B_Z A_S} \quad (z_A = z_B = 1) \quad (6)$$

If the exchanger is not an ideal solution of its components, the activity coefficients of the components in the solid phase are given by Kielland (71) as follows:

$$\log f_A(Z) = C \cdot B_Z^2 \quad \log f_B(Z) = C \cdot A_Z^2 \quad (16)$$

where C is a positive or negative constant depending on the system (see below). Barrer & Sammon (72) substituted these values in the expression for K_a (equ. 7) and obtained the following:

$$\log K_a = \log K_c + C(1 - 2A_Z) \quad (17)$$

where

$$K_c = \frac{A_Z^{z_B} B_Z^{z_A} \left[\gamma_{+BY}^{z_B+1} \right]^{z_A}}{B_Z^{z_A} A_Z^{z_B} \left[\gamma_{+AY}^{z_A+1} \right]^{z_B}} \quad (18)$$

If we then plot $\log K_c$ vs. A_Z , a straight line will be

obtained, of slope $2C$, from which the thermodynamic equilibrium constant may be evaluated, because when $A_Z = \frac{1}{2}$, $\log K_a$ reduces to $\log K_{C\frac{1}{2}}$. This plot is known as the Kielland plot. Also when $C = 0$, $\log K_a = \log K_C$, i.e. $K_a = K_C = K_Y$, which represents the simple form of the law of mass action, and the components of the **ex-**changer phase are then forming ideal solid solutions. Consequently equation 17 is generally applicable to reversible uni- univalent exchanges in crystalline zeolites. It has already been found to represent the ion exchange equilibria in a number of systems, e.g. Na/Rb, Na/Tl and K/Ag in chabazite (73); Na/Li in basic cancrinite (74); Na/K in faujasite (75); and Na/Li, Na/K, Na/Rb, and Na/Cs in NaA (7).

For some systems, the plot of $\log K_C$ vs. A_Z is not a straight line; in these cases, if the exchange is between univalent ions, Kielland's relationships for **the activity** coefficients of the components in the exchanger phase ($\log f_{A(Z)} = C.B_Z^2$) are obviously invalid. These activity coefficients and the value of K_a , are then available using the methods of Ekedahl et al. (76) or Argersinger et al. (77). However since the uni- univalent systems studied in this work did give linear Kielland plots, the above treatments will not be considered further.

The thermodynamic treatment of Gaines & Thomas (79) gives the following expressions for the activity

coefficients of the components in the exchanger phase:

$$\ln f_{A(Z)}^{z_B} = -(z_A - z_B)B_Z - \int_{K_C^0}^{K_C} (1 - A_Z) d.\ln K_C - (a) \quad (19)$$

$$\ln f_{B(Z)}^{z_A} = +(z_A - z_B)A_Z + \int_{K_C^1}^{K_C} (A_Z) d.\ln K_C - (a') \quad (20)$$

For uni- univalent systems, these expressions reduce to those of Ekedahl et al. and Argersinger et al. mentioned above. The terms (a) and (a') involve the activities of water in aqueous solution at infinite dilution, in solutions corresponding to extrapolated values of K_C , at $A_Z = 0$ and 1, and the activity of the water in the mixed exchanger; however these terms are negligible for the zeolitic exchangers, where only small changes in water content occur, and as they are less than the errors involved in the graphical integration (78), they will be neglected; also $K_C = K_C^0$ when $B_Z = 0$, and $K_C = K_C^1$ when $B_Z = 1$. Thus the terms $f_{A(Z)}$ and $f_{B(Z)}$ can be evaluated from the plot of $\log K_C$ vs. A_Z . From the straight line Kielland plots, it can easily be seen that:

$$\log K_C = \log K_C^1 + 2C.A_Z$$

and therefore the expression for $f_{A(Z)}$ reduces to:-

$$\log f_{A(Z)} = C.B_Z^2$$

Likewise for $f_{B(Z)}$, these being the Kielland expressions for the activity coefficients of the components of the exchanger phase (ref. 71; equ.16).

The thermodynamic treatment of Gaines & Thomas (79) also gives the following expression for K_a :-

$$\ln K_a = (z_B - z_A) + \int_0^1 \ln K_c \cdot d.A_z \quad (21)$$

terms involving the activities of the water again being neglected.

A more complete theoretical approach to the thermodynamics of cation exchange has been given by Ward (ref.7). Only the most important results of the theory have been presented here, as the cation exchange studies did not constitute the bulk of this work.

2.2.GAS ADSORPTION.Thermodynamics of Adsorption.2.2.1. Summary of Symbols.

$-\Delta H$ = isosteric heat of adsorption = q_{st}

$$(-\Delta H = \tilde{H}_g - \bar{H}_s)$$

$\tilde{H}_g$ = molar heat content, or enthalpy, of gas molecules in the gas phase, at equilibrium pressure p (cms.Hg) and temperature T ($^{\circ}K$).

$\bar{H}_s$ = differential or partial molar enthalpy of sorbed phase: $\bar{H}_s = \left(\frac{\partial H}{\partial n_s} \right)_{p, T, n_A}$

n_s, n_A = moles sorbent and adsorbate.

R = gas constant.

θ = degree of saturation

= $\frac{\text{volume gas sorbed at equilibrium}}{\text{volume sorbed at saturation (same temp.)}}$

K_1, K_2, K_3, K_4, K_5 = limiting isotherm model constants.

$2w/z$ = interaction energy between two sorbate molecules sorbed on adjacent sites in the crystal lattice.

z = co-ordination number of sorption site, i.e. no. of nearest neighbours occupied by adsorbate molecules.

ΔS = change in entropy of system.

$$(\Delta S = \bar{S}_s - \tilde{S}_g)$$

$\bar{S}_s$ = differential or partial molar entropy of sorbed phase, i.e. gas in host lattice:

$$\bar{S}_s = \left(\frac{\partial S}{\partial n_s} \right)_{p,T,n_A}$$

$\tilde{S}_g$ = molar entropy of gas in gas phase at p,T.

$\tilde{S}_{og}$ = molar entropy of gas at standard pressure (usually one atmosphere) and temp. T.

$\bar{S}_{th}$ = differential thermal entropy.

$\bar{S}_c$ = differential configurational entropy.

$\bar{S}_{th}'$ = residual thermal entropy, related to ${}_1\bar{S}_T$ by: $\bar{S}_s = {}_1\bar{S}_T + \bar{S}_{th}'$

$\bar{S}_{th}''$ = (ditto, where $\bar{S}_s = {}_2\bar{S}_T + \bar{S}_{th}''$)

${}_1\bar{S}_T$ = partial molal entropy resulting from one degree of translational freedom of the guest molecule within the intracrystalline environment.

${}_2\bar{S}_T$ = (ditto, for two degrees of translational freedom).

t = translational degree of freedom.

v = vibrational " " "

k = Boltzmann's constant.

h = Planck's constant.

m = molecular mass of adsorbate, i.e. molecular weight $\times 1.66 \times 10^{-24}$ gm.

V = volume gas adsorbed (cc.S.T.P./g.sorbate)

2.2.2. Adsorption and Solution Thermodynamics:

Two different approaches to the thermodynamics of adsorption may be considered:-

- a). Adsorption Thermodynamics; the sorbed molecules are regarded as a single component phase in the potential field of the solid, which is assumed to be unperturbed by adsorption. This approach leads to the molar thermodynamical quantities, which are usually of more significance than the differential quantities. However the concepts of surface area and surface spreading pressure involved are unrealistic in systems involving zeolites (80,81).
- b). Solution Thermodynamics; the system is regarded as a single condensed phase of two components, sorbate and sorbent, in equilibrium with unadsorbed gas. This approach leads to the partial molar or differential thermodynamical quantities, which Everett (82) and Kington (67,83) have shown to be useful in describing the state of the sorbed phase. In fact, for small differences in the energy of the sorbed molecules, the differential functions are found (83) to be more sensitive than the molar functions.

Recent developments in this field have been adequately reviewed by Hill (80,84), Drain (85), Everett (82,86,87) and Kington (67,88). In this work the solution thermodynamical approach has been adopted.

2.2.3. Isosteric Heat of Adsorption:

By employing standard solution thermodynamics the following expressions may be obtained; the rate of change of pressure with temperature, is given by the Clausius - Clapeyron equation:

$$\left(\frac{\partial \ln p}{\partial T} \right) = \frac{-\Delta H}{RT^2} = \frac{\tilde{H}_g - \bar{H}_s}{RT^2} \quad (22)$$

$$= \frac{-\Delta S}{RT} = \frac{\tilde{S}_g - \bar{S}_s}{RT} \quad (23)$$

where $-\Delta H = q_{st}$ is the isosteric heat of adsorption. This equation assumes that the gas behaves as an ideal gas, and that the volume of the gas in the gas phase greatly exceeds its volume in the sorbed phase, which is usually the case.

The isosteric heat may be determined in the following ways:-

- (a) by direct calorimetry, by measuring the heat evolved for every addition of gas;
- (b) from changes in equilibrium pressure with temp. i.e. by plotting $\log_{10} p$ vs. $1/T$ for a fixed amount sorbed; the slope, or tangent if a curve results, multiplied by $2.303 R$ gives q_{st} , in accordance with the expression:

$$\ln p = \frac{q_{st}}{RT} + c \quad (24)$$

Performing this operation for a series of amounts sorbed leads to a plot of q_{st} vs. V . (volume sorbed at equilibrium).

- (c) plot $\log p$ vs. V for each of a series of isotherms and obtain $\log p_1/p_2$ corresponding to T_1 and T_2 ; then

$$q_{st} = R \left(\frac{T_1 \cdot T_2}{T_1 - T_2} \right) \ln \frac{p_1}{p_2} \quad (25)$$

It is important to obtain an average value of q_{st} for each value of θ , from more than just one pair of isotherms, because q_{st} may vary with temperature, and also, misleading results may easily be obtained in reading the values of $\log p$ from the graphs. In this work, four isotherms (10°C increments) were used to obtain six permutations, i.e. six values of q_{st} .

The nature of the solid does not enter into the derivation of the above expressions, as we have employed the amount of sorbent, not its surface area. It is a perfectly general treatment which applies even if the adsorbent exhibits swelling properties, or if the number of sorption sites varies with temperature or pressure.

2.2.4. Interpretation of the Thermodynamical Properties of sorption in terms of limiting isotherm models:

This is a procedure which has been investigated with considerable success in relation to

sorption by zeolites (27,67,83,89,90). When a gas molecule is adsorbed on the surface of a solid (for zeolites, this includes the interior of the zeolite framework), it is assumed to be subject to the potential field existing on the surface. If the adsorbent is a crystalline zeolite, this field will vary in a regular or periodic manner depending on the crystal structure and nature of the surface. Hence an adsorbate molecule when moving across a surface, will encounter potential energy barriers of varying heights.

Two extreme cases may be described, and the actual state of the adsorbate molecules may exist anywhere between these extremes:

(a) If the thermal energy (kT) of the sorbed molecule is smaller than the height of the potential energy barriers, then it will vibrate about a mean position on the surface. A single molecule may not necessarily be confined to a particular sorption site however; by a process of diffusion or desorption - resorption, it may occupy neighbouring sites, thus although the molecule is mobile over an area consisting of several sites, this will still constitute the state of affairs referred to as localized sorption. The mutual caging effect at large values of θ will also lead to localized sorption systems.

(b) If the thermal energy of the adsorbed molecule is large enough to permit freedom of movement over the potential energy barriers, then such a molecule will be capable of possessing two degrees of translational freedom. Sorbed molecules will not be confined even to a certain number of sites as with localized sorption, but will be completely mobile, giving rise to the state of affairs known as mobile sorption.

Thus the 'surface phase' may be regarded as either localized or mobile, the 'surface phase' here referring to the phase comprising adsorbate molecules within the potential energy field of the surface.

Gas molecules sorbed within the lattice of an aluminosilicate structure cannot possess three degrees of translational freedom, since they are confined within channels and cavities of dimensions similar to their own. (For convenience, t shall now refer to degree of translational freedom, and v , to degree of vibrational freedom; perfectly symmetrical monatomic gas molecules such as krypton do not possess degrees of rotational freedom, r , hence these do not enter into this discussion). It is possible for a gas to possess " $3t$ ", " $2t + 1v$ ", " $1t + 2v$ ", or even " $3v$ ". For the latter system, we may cite the adsorption, hydrogen on metals. The " $2t + 1v$ " system is

frequently found in zeolites, in which the cavities are large compared with the dimensions of the sorbate molecules. If however, these channels and cavities are only slightly larger than the gas molecules, the latter will possess " $1t + 2v$ ". Finally if the cavities are so small as to encage only one gas molecule, then the " $3v$ " system will exist; such a system also exists when localized adsorption occurs.

The most likely systems existing for gas adsorption by zeolites are:-

(i) localized (no translational movement)

(ii) mobile (a) with " $1t$ ",

(b) with " $2t$ ",

and in all three cases, mutual sorbate molecule interactions may or may not be pertinent.

As suggested earlier, the complete sorption process need not be purely localized or mobile; e.g. Kington et al. (67,83) found that at low coverages, argon in chabazite exhibits mobile sorption, whereas at higher values of θ the sorbed gas is localized; this was concluded to be due to the mutual caging of the molecules within the cavities as sorbate concentration increases. Hill (91) has discussed the reverse transition, from a localized to a mobile model, with increase in temperature, e.g. argon sorbed on rutile (92).

It is therefore necessary to consider all possible isotherm models, and so the various models will now be briefly discussed; they describe ideal systems, but a comparison with experimental data provides information concerning the state of the adsorbed phase. Deviations from these ideal models may arise from surface heterogeneities, multilayer formation and the mutual interactions between sorbed molecules. The isotherm and isosteric heat data obtained for the system, krypton sorbed by NaX, showed that effects such as surface heterogeneities and multilayer formation were negligible, thus any deviation from ideality should be explained on the basis of mutual interactions between sorbed molecules.

Perturbation of the solid by physically adsorbed molecules is ignored throughout this discussion, since the rigid lattice frameworks are considered unlikely to be affected by the presence of a potential field due to sorbed gas. This assumption is usually considered an excellent approximation in physical adsorption but it is most unreal for chemisorption (80).

The ideal isotherm equation should satisfy the following criteria:

- (i) it should describe the whole isotherm, not just part of it;

- (ii) it should be applicable over a wide range in temperature, and
- (iii) the corresponding entropy of the system must obey certain criteria (see later).

Localized Sorption Isotherm Models:

The simplest case of physical adsorption of gases arises when the molecules are adsorbed on a surface comprised of energetically homogeneous sites, in the absence of mutual sorbate molecule interactions. Langmuir (93), employing a kinetic approach, in which the adsorbed layer of gas is regarded in dynamic equilibrium with the gas phase, derived the following expression:

$$K_1 = p \frac{(1-\theta)}{\theta} \quad (26)$$

where p = equilibrium pressure (cms.Hg)

and θ = degree of saturation.

A statistical derivation by Fowler (94) related the equilibrium constant K_1 to the partition functions of the sorbed and gaseous molecules. As with any isotherm model, K_1 will be independent of θ over the range in which the model is valid. K_1 may also be expressed:

$$K_1 = \exp. \left(\frac{\Delta H}{RT} - \frac{\Delta S_{th}^0}{R} \right) \quad (27)$$

both ΔH and ΔS_{th}^0 being independent of θ . The assumptions thus made for the Langmuir isotherm model are:-

- (i) sorbate molecules are sorbed on independent sorption sites, all of which are energetically equivalent;
- (ii) these molecules are localized, i.e. each one is confined to a small area of sites within the lattice;
- (iii) no interactions occur between adjacent molecules; this might be expected at low coverage since the sorbed molecules are relatively far apart, but as θ increases, it becomes less likely.
- (iv) the sorption is restricted to a monolayer.

Localized model with mutual sorbate molecule interactions:

Extra energy terms must be considered **if** the sorbate molecules interact with each other. An exponential term involving the interaction energy between 2 molecules adsorbed on adjacent sites $2w/z$ is included in the Langmuir expression, where z = co-ordination number of a sorption site:

$$K_2 = \frac{p(1-\theta)}{\theta} \cdot \exp\left(\frac{-2\theta w}{RT}\right) \quad (28)$$

$$= \exp\left(\frac{\Delta H_0}{RT} - \frac{\Delta S_{th}^0}{R}\right) \quad (\text{see ref.87}) \quad (29)$$

where ΔS_{th}^0 is independent of θ as for K_1 , but

$$\Delta H_0 = \Delta H - 2\theta w \quad (30)$$

When $w = 0$ this expression reduces to the Langmuir model. Molecule - molecule interactions can lead to changes in configurational entropy, hence further modification can be made to the Langmuir model:

$$K_3 = p \frac{(1-\theta)}{\theta} \cdot \left(\frac{\beta+1-2\theta}{2-2\theta} \right)^z \quad (31)$$

$$\text{where } \beta = \left(\frac{1-4\theta(1-\theta) \left(1 - \exp\left(\frac{-2w}{zkT}\right) \right)}{\left(1 - \exp\left(\frac{-2w}{zkT}\right) \right)} \right)^{\frac{1}{2}} \quad (32)$$

which also involves the term $2w/z$; z may be determined from the geometry of the three dimensional lattice. This expression also reduces to the Langmuir model when $w = 0$. Fowler (95,96) derived this expression for K_3 , employing a quasi chemical approach, in which the variation in energy of sites due to mutual interactions is allowed for. The assumptions made in this derivation are as follows:- (a) the interactions between sorbed molecules are constant and additive, and

(b) only nearest neighbour sorbate molecule interactions are allowed for.

Mobile sorption isotherm model:

If the sorbed phase behaves as a perfect two dimensional gas of point particles, the isotherm model derived either from statistical thermodynamics (96) or from an equation of state (87) is:-

$$K'_4 = p\theta \quad (33)$$

This is of course Henry's law (cf. analogous isotherm for solution of gases in liquids), and only applicable to very dilute phases, and at temperatures above the critical temperature of the gas.

If the adsorbed phase is assumed to possess

a finite co-area (= Van de Waal's co-volume^{2/3}), the following expression may be deduced from partition functions (96).

$$K_4 = p \frac{(1-\theta)}{\theta} \cdot \exp\left(\frac{-\theta}{(1-\theta)}\right) \quad (34)$$

This is often referred to as the Volmer equation of sorption since it may also be derived from the Volmer equation of state (87,91,97).

Mobile model with mutual sorbate molecule interactions:

Hill (91) deduced the following expression from the Van de Waal's equation of state, employing a somewhat approximate treatment:

$$K_5 = p \frac{(1-\theta)}{\theta} \cdot \exp\left(\frac{-\theta}{(1-\theta)} + a\theta\right) \quad (35)$$

where $a = 2a/bkT$, a and b being the two-dimensional Van de Waal's constants.

All of these isotherm models are derived assuming that the adsorbent surface is energetically homogeneous. If the heat of adsorption is not independent of the amount sorbed, then these models cannot be rigorously applied. However, useful and interesting information can still be obtained even if the theory can only explain the experimental results over a limited range of θ .

Intracrystalline sorption was originally considered to be localized (Lacher,98); work by Rees

on two component interstitial solid solutions (99) of hydrogen in metals extended this treatment; however the possibility of mobility must not be overlooked, since the free diameters of cavities and channels in several zeolites greatly exceed the size of the adsorbate molecules. It is thus necessary to consider all isotherm models which are physically reasonable.

For any isotherm model to be valid, the isotherm constant K , must be independent of Θ . It should be noted however, that constancy of K , does not necessarily imply that the system conforms to the specified model over the entire range of Θ ; it has frequently been noted that a mere test of the shape of an isotherm is not in itself conclusive. It is also impossible to distinguish between the 1, 2 or 3 translational degrees of freedom implied in the models K_4 and K_5 . It is therefore considered essential to compare thermodynamical quantities such as entropies, configurational and thermal, with the calculated values from the isotherm model under test (82,100).

2.2.5. Entropy of Adsorption.

Earlier the isosteric heat of adsorption was expressed as follows:

$$\left(\frac{\partial \ln p}{\partial T} \right) = \frac{-\Delta H}{RT^2} = \frac{\tilde{H}_g - \bar{H}_s}{RT^2} \quad (22)$$

$$= \frac{-\Delta S}{RT} = \frac{\tilde{S}_g - \bar{S}_s}{RT} \quad (23)$$

$$\therefore \quad \bar{S}_s = \Delta S + \tilde{S}_g \quad (36)$$

$$= \Delta S + \tilde{S}_{og} + R \ln \frac{p^o}{p} \quad (37)$$

where $\tilde{S}_{og}$ = molar entropy of gas molecules at standard pressure p^o (1 atmosphere) and temp. T^oK .

$$\therefore \quad \bar{S}_s = \frac{\Delta H}{T} + \tilde{S}_{og} + R \ln \frac{p^o}{p} + (B) \quad (38)$$

where (B) is an extra term to correct for the non-ideality of the gas (83,101):

$$B = -\frac{27}{32} R \frac{T_c^3}{T^3} \frac{p}{p_c}$$

where subscript "c" denotes critical constant of the sorbed gas. However for the rare gases such as krypton at pressures such as employed in this work, the term B may be ignored (it is less than 0.1 entropy units).

For a monatomic gas, the following expression for $\tilde{S}_g$ may be derived from statistical thermodynamics:

$$\tilde{S}_g = R \ln \frac{kT}{p} + R \ln \left(\frac{2\pi mkT}{h^3} \right)^{3/2} + \frac{5R}{2} \quad (39)$$

(see section 2.2.1. for summary of symbols).

$$\therefore \quad \bar{S}_s = \frac{\Delta H}{T} + R \ln \left(\frac{2\pi mkT}{h^3} \right)^{3/2} \cdot \frac{kT}{p} + \frac{5R}{2} \quad (40)$$

If the sorbed molecules are localized, i.e. do not possess translational motion, then the partial molar entropy may be divided into differential thermal and configurational entropy terms (102):

$$\bar{S}_s = \bar{S}_{th} + \bar{S}_c \quad (41)$$

The thermal entropy for an inert gas sorbed by a zeolite

originates from the electronic states of the molecules and the vibrations about mean positions on a sorption site. The configurational entropy term $\bar{S}_c$, arises when we consider the number of distinguishable arrangements of N molecules sorbed on M sites, in a localized system on a homogeneous surface (87), i.e. $\frac{M!}{N!(M-N)!}$. From

this expression, it may be deduced that:

$$\bar{S}_c = R \ln \frac{(1-\theta)}{\theta} \quad (42)$$

and this configurational entropy term applies to the isotherm models corresponding to K_1 and K_2 (localized without interactions), but K_3 (localized with mutual sorbate interactions) does allow for changes in configurational entropy; these in turn are allowed for in the expression (87,96):

$$\bar{S}_c = R \ln \frac{(1-\theta)}{\theta} \left(\frac{2-2\theta}{\beta+1-2\theta} \right)^2 + \frac{w(\beta-1+2\theta)}{T\beta} \quad (43)$$

The difference between the value of $\bar{S}_c$ obtained using this expression and that obtained from the ideal Langmuir model has been found to be negligible for the system, argon sorbed on chabazite (83). Now that $\bar{S}_s$, $\bar{S}_c$ have been formulated, we can obtain the residual thermal entropy:

$$\bar{S}_{th} = \bar{S}_s - \bar{S}_c \quad (41)$$

$$= \Delta S + \tilde{S}_g - \bar{S}_c \quad (44)$$

$$= \frac{\Delta H}{T} + R \ln \left(\frac{2\pi mkT}{h^3} \right)^{3/2} \cdot \frac{kT}{p} + \frac{5R}{2} - R \ln \frac{(1-\theta)}{\theta}$$

for localized sorption without interactions, and

$$\begin{aligned} \bar{S}_{th} = \frac{\Delta H}{T} + R \ln \left(\frac{2\pi mkT}{h^3} \right)^{3/2} \cdot \frac{kT}{p} + \frac{5R}{2} - \\ R \ln \frac{(1-\theta)(2-2\theta)^2}{\theta(\beta+1-2\theta)} - \frac{w(\beta-1+2\theta)}{T\beta} \end{aligned} \quad (45)$$

for localized sorption with interactions.

The thermal entropy must satisfy certain criteria (67):

- (a) it must be positive, having reasonable physical magnitudes;
- (b) it must be independent of θ (over the range in which the sorption model is valid).

As shown earlier, $K_1 = p \frac{(1-\theta)}{\theta}$, may be expressed alternatively as:-

$$K_1 = \exp \left\{ \frac{\Delta H}{RT} - \frac{\Delta S_{th}^0}{R} \right\} \quad (27)$$

$$\begin{aligned} \text{where } \Delta H = \bar{H}_s - \tilde{H}_g, \text{ and } \Delta S_{th}^0 = \bar{S}_{th} - \tilde{S}_g^0 \\ = \bar{S}_s - \bar{S}_c - \tilde{S}_g^0 \\ = \Delta S^0 - \bar{S}_c \end{aligned}$$

in this case, $\bar{S}_c$ being equal to $R \ln \frac{(1-\theta)}{\theta}$. If ΔH and ΔS_{th}^0 are independent of θ , then K_1 is constant; however if only ΔS_{th}^0 is independent of θ , and $\Delta H = \Delta H^0 + 2\theta w$, then we have:

$$K_2 = \exp \left\{ \frac{\Delta H^0}{RT} - \frac{\Delta S_{th}^0}{R} \right\} \quad (46)$$

corresponding to the isotherm model K_2 . The assumption made above for ΔH ($\Delta H = \Delta H^0 + 2\theta w$) means that a change

in ΔH is a result only of sorbate molecule interactions. For non-polar molecules, this is a valid assumption since there is no observable decrease in ΔH initially, an effect usually indicative of surface homogeneity.

For non-localized systems, i.e. mobile sorption we have two expressions:

$$\bar{S}_s = {}_1\bar{S}_T + \bar{S}_{th}' \quad (47)$$

$$\bar{S}_s = {}_2\bar{S}_T + \bar{S}_{th}'' \quad (48)$$

where ${}_1\bar{S}_T$ and ${}_2\bar{S}_T$ are the partial molal translational entropies resulting from one and two degrees of translational freedom of the guest molecules within their intracrystalline environment respectively. For the isotherm models K_4 and K_5 (mobile sorption without, and with, sorbate molecule interactions), ${}_1\bar{S}_T$ and ${}_2\bar{S}_T$ may be formulated:-

$${}_1\bar{S}_T = R \ln \left(\frac{2\pi mkT}{h} \right)^{\frac{1}{2}} \cdot L \frac{(1-\theta)}{\theta} + R \left(\frac{1}{2} - \frac{\theta}{1-\theta} \right) \quad (49)$$

$${}_2\bar{S}_T = R \ln \left(\frac{2\pi mkT}{h^2} \right) \cdot a \frac{(1-\theta)}{\theta} + R \left(1 - \frac{\theta}{1-\theta} \right) \quad (50)$$

where L = co-length of a sorbed molecule (= co-volume $b^{1/3}$), and a = co-area (= $b^2/3$). Thus knowing $\bar{S}_s$ and ${}_1\bar{S}_T$ (or ${}_2\bar{S}_T$), the residual differential thermal entropy $\bar{S}_{th}'$ (or $\bar{S}_{th}''$) is obtainable.

It is thus apparent from the above discussion that calculation of the thermal entropies depends upon the model of the sorption isotherm chosen. However calculation of $\bar{S}_s$ involves a quite general argument only.

2.2.6. Interpretation of Heats of Adsorption in terms of Intermolecular Forces.

The heat of sorption is the difference between the sum of the heat contents of the completely separated adsorbate and adsorbent, and the heat content of the two component phase resulting from adsorption. During the adsorption process, energy is released as heat, and is consequently known as the heat of sorption or occlusion. At low coverage, the mutual interactions between adsorbed molecules will be small, hence the initial heat of occlusion results chiefly from the interactions between occluded molecules and the atoms of the lattice framework. A consideration of the attractive and repulsive forces between the gas and solid, should therefore provide information on the sorption process (103). Recent developments in this field have been extensively reviewed by Hirschfelder, Curtiss and Bird (104).

Numerous attempts have been made to relate the experimental heat of adsorption to the calculated intermolecular forces. Progressive refinements have been developed as the importance of more significant terms has been realized. London (105,106) first introduced the effects of dispersion forces. Kiselev et al. (107) made detailed calculations of the heats of sorption for the systems of inert gases sorbed on

graphitized carbon blacks. The theoretical calculation of heats of sorption involves certain problems which may or may not be resolvable, e.g.

- (i) charge distribution of sorbate and sorbent,
- (ii) equilibrium distance between " " " ,
- (iii) perturbing effects of sorbate on sorbent.

Kington (108) studied the systems, argon sorbed on natural and calcium chabazites. He showed that clusters of argon molecules in the chabazite cavities are associated with an increasing isosteric heat, due to mutual interactions, whereas at higher sorbate concentrations, the 'squeezing' of the gas molecules into cages, was associated with a decreasing isosteric heat. The agreement between experimental and calculated values was not exact; however a comparison does lead to some interesting and useful information. The magnitudes of the theoretical and observed maxima (108) were in qualitative agreement, but the experimental maximum occurred at higher concentrations than the theoretically calculated maximum. However the card-index system employed by Kington to determine the random distribution of the sorbate molecules produced an artificially high number of molecules which are squeezed into the smaller chabazite cavities. Less of this effect improves the position of the theoretical maximum, i.e. it moves towards higher θ values, (for further discussion on Kington's work with chabazite, see section 4.2.4.).

The isosteric heat q_{st} , at temperature T , has been defined by Hill (109) as follows:-

$$q_{st} = \tilde{E}_g - \bar{E}_s + RT \quad (51)$$

$$= \tilde{E}_g - \tilde{E}_s + n_s \left(\frac{\partial E_s}{\partial n_s} \right)_{p.T.n_A} + RT \quad (52)$$

where $\tilde{E}_g$ = molar energy content of gas in gas phase;

$\tilde{E}_s$ = " " " " " " sorbed " ;

$\bar{E}_s$ = partial molar energy " " " " " ;

n_s, n_A = number of moles of sorbed gas and sorbate.

When $\tilde{E}_s$ is independent of n_s :

$$q_{st} = \tilde{E}_g - \tilde{E}_s + RT \quad (53)$$

This is also valid at $n_s = 0$, i.e. zero coverage.

At $0^\circ K$, only potential energy $\emptyset$ need be considered,

when, neglecting zero point energy (which usually

amounts to about 0.1 Kcals/mole), the isosteric heat

$$\text{is given by: } q_{st}^0 = -\tilde{E}_s = -\emptyset \quad (54)$$

$$\therefore q_{st} - q_{st}^0 = \tilde{E}_g + RT \quad (55)$$

$$= -\Delta H$$

$$= -\int_0^T \Delta C_p \cdot dT$$

$$\therefore q_{st} = q_{st}^0 - \int_0^T \Delta C_p \cdot dT \quad (56)$$

where $-\Delta C_p = \tilde{C}_g - \bar{C}_s$

$\tilde{C}_g$ = molar heat capacity of gas in gas phase,

$\bar{C}_s$ = partial molar heat " " " " sorbed ".

Thus in order to relate q_{st} to $\emptyset$, we require to know

$\tilde{C}_g$ and $\bar{C}_s$. However Orr (110), using an empirical

formula to represent the heat capacity of the sorbate, showed that at low temperature, there is a negligible variation of heat of sorption. Thus within experimental error, the isosteric heat may be directly related to the potential energy $\emptyset$:

$$q_{st} = -\emptyset + RT \quad (57)$$

At the temperatures of the experiments of Barrer and Stuart (103) with argon sorbed by various cationic forms of synthetic faujasite, it was found that $\Delta C_p dT$ could be ignored, $\emptyset$ being the dominant contribution towards the energy of occlusion.

2.2.7. Intermolecular Forces:

The potential energy of occluded molecules, may be separated into terms corresponding to dispersion, repulsion, polarization and quadrupole effects etc.,

$$\emptyset = \emptyset_D + \emptyset_R + \emptyset_P + \emptyset_Q \quad (58)$$

However for the rare gases such as krypton, $\emptyset_Q = 0$.

Polarization Energy:

When a gas molecule comes within the external electrostatic field F , of a polarizing ion such as Na^+ , within the zeolite lattice, its electrons and nucleus experience a relative displacement, i.e. a dipole is induced. The magnitude of the induced dipole depends on the polarizability of the molecule, and the field F :

$$\mu = \alpha F \quad (59)$$

The energy of interaction between the induced dipole

and the electric field is then given by:

$$\phi_p = \int_0^F \mu \cdot dF = \frac{\alpha F^2}{2} = \frac{\alpha e^2}{2r^4} \quad (60)$$

The field F arises due to the cationic charge, and also the charge on the anionic framework, hence the polarizing field due to the cations becomes much reduced by counteracting fields of other charge centres. Barrer and Stuart (103) found this applied to the Na^+ , K^+ and Ba^{++} faujasites, i.e. the ion induced dipoles in the occluded argon molecules were almost negligible, and consequently the polarization energies were effectively zero. The isosteric heats for the Li^+ , Ca^{++} and Sr^{++} faujasites all showed marked initial decreases; this is indicative of the greater polarizing power of these ions. Since in this work, we are only interested in the sorption of rare gases by a zeolite containing only the Na^+ ion, the ϕ_p term will be ignored. Therefore:

$$\phi = \phi_D + \phi_R \quad (61)$$

Although the effects due to polarization energy may be ignored, the Na^+ ions do contribute to the dispersion and repulsion energy terms. This raises the question as to the number of Na^+ ions present in the lattice and their positions. As in section 1.0., it is found that there are four Na^+ ions per supercage in NaX (hydrated), which are situated close to the

hexagonal six-oxygen windows of the sodalite cages. These positions were determined by the three dimensional Fourier electron density analysis carried out by Broussard and Shoemaker (10). However similar studies of the dehydrated zeolite failed to locate the Na^+ ions in these positions. They are nevertheless, for the purpose of the following calculations assumed to occupy these positions.

Dispersion Forces:

London (106) first introduced the concept of dispersion forces; he employed a quantum mechanical approach to show that these forces adequately explain the non-ideal behaviour of gases and vapours. Debye (111) and Keesom (112) had previously attempted to explain this behaviour in terms of dipole and quadrupole interactions etc., but although they were relevant in cases of highly polar molecules, they failed to explain the condensation of the rare gases and the persistence of Van de Waal's forces at high temperatures. London and Eisenschitz (113) obtained the following expression for the interaction energy of two spherical molecules, the dispersion energy being assumed to arise simply from dipole-dipole interactions between the correlated electron rotations of the adjacent molecules:

$$\phi = -\frac{A}{r^6} \quad (62)$$

where A is the dispersion energy constant dependent on parameters such as polarizabilities (see below), and r is the distance in cm., between the molecules or atoms. If dipole-quadrupole interactions etc. are included,

$$\phi_D = -\frac{A}{r^6} - \frac{A'}{r^8} - \frac{A''}{r^{10}} \dots\dots\dots (63)$$

However the first term only, need be considered. Dispersion (and repulsion) forces are additive and independent of temperature. Calculations of the dispersion forces between an occluded molecule and the numerous atoms constituting the adsorbent lattice involves laborious summations. To simplify this, one energy term is obtained from an integration over the whole lattice for which the structural characteristics of the solid must be accurately known. However it has been shown by Axilrod and Teller (114,115) that non-additivity may occur depending on the geometry of the system. Errors of up to 30% are thus to be expected in calculations of dispersion energies.

Repulsion forces:

If the electron clouds of two approaching ions or molecules overlap, powerful intermolecular forces will exist. If pairwise combination of the electrons occurs in accordance with the Pauli Exclusion Principle, then chemical reaction results. However if the electrons cannot be paired, repulsion forces exist, and when these

balance the dispersion forces also present, the potential energy of the system is at a minimum. Lennard-Jones (116) derived the expression: $\phi_R = B/r^m$ (64) where B = repulsion energy constant, and Orr, from quantum mechanical considerations gave the following relationship for this repulsive term: $\phi_R = k.e^{-B/r}$ (65)

Lennard-Jones combined the effects of dispersion and repulsion to give the 6:12 potential energy function:

$$\phi = -\frac{A}{r^6} + \frac{B}{r^{12}} \quad (66)$$

Differentiation with respect to r , gives, when $\frac{d\phi}{dr}=0$

$$\frac{6A}{r^7} = \frac{12B}{r^{13}}$$

so when $r = r_e$, the equilibrium separation, $B = \frac{Ar_e^6}{2}$

$$\therefore \phi_T = \phi_D + \phi_R = -A \left(\frac{1}{r^6} - \frac{r_e^6}{2r^{12}} \right) \quad (67)$$

For like molecules, when $r = r_e$, $\phi = -A/2r_e^6$, and this relationship allows calculation of a theoretical value of the molecule-molecule interaction energy for the sorbate, which may be compared with the experimental value, (see section 4.2.5.).

2.2.8. Formulation of the Constant "A":

The value of the potential energy of occluded molecules is thus seen from the above to involve a constant "A". This may be expressed in various ways:

(a) LONDON expression: (105,113)

$$A = \frac{3}{2} \alpha_1 \cdot \alpha_2 \cdot \frac{h\nu_1 \cdot h\nu_2}{h\nu_1 + h\nu_2} \quad (68)$$

where α_1 and α_2 are the polarizabilities of the interacting molecules or ions, and $h\nu_1$, $h\nu_2$ are the characteristic energies. Since these energies are difficult to obtain experimentally, and approximate to the ionization potentials E , the London expression may also be written as:

$$A = \frac{3}{2} \alpha_1 \cdot \alpha_2 \cdot \frac{E_1 \cdot E_2}{E_1 + E_2} \quad (69)$$

(b) KIRKWOOD MULLER expression: (117)

$$A = 6mc^2 \cdot \frac{\alpha_1 \cdot \alpha_2}{\frac{\alpha_1}{\chi_1} + \frac{\alpha_2}{\chi_2}} \quad (70)$$

where m = electronic mass (g.); c = velocity of light;
 α = molecular polarizability; χ = diamagnetic susceptibility (cgs/mole).

(c) SLATER KIRKWOOD expression: (118)

$$A = \frac{3}{4\pi} \frac{eh}{m^2} \cdot \frac{\alpha_1 \cdot \alpha_2}{\left(\frac{\alpha_1}{n_1}\right)^{\frac{1}{2}} \left(\frac{\alpha_2}{n_2}\right)^{\frac{1}{2}}} \quad (71)$$

where e = electronic charge; h = planck's constant;
 m = electronic mass; α = molecular polarizability and
 n = no. of outer electrons of atomic structure.

Comparisons and reasons for choice of expression
used in this work:

In the second London expression, the use of ionization potentials assumes that attraction between molecules arises from the optical electrons only; since others exist and contribute towards the interaction energies, this London expression will consequently yield energies which are generally too small. On the other hand, the Kirkwood Muller expression gives energies which are usually too high; it leads to a maximum in the dispersion energy term. The Slater Kirkwood expression invariably gives results between the other two, and involves an uncertain factor in the somewhat arbitrary choice of n , (34). Consequently only the London and Kirkwood Muller expressions have been employed in this work; previous studies concerning the intermolecular forces have shown that the Kirkwood-Muller expression is usually the most suitable (34,119).

2.3.NEUTRON IRRADIATION.Theoretical Discussion of the Production of Lattice Damage of NaX by Neutron Irradiation:

(for a summary of symbols used in this section, see end of section 2.3.2.).

2.3.1. Energy Transfer:

When a fast neutron passes through a crystal lattice, it loses energy by suffering elastic collisions with the lattice atoms, i.e. collisions of the simple hard sphere type. If the displacement energy of the lattice atom is E_d (for calculation purposes, this is usually taken as 25 eV) and if it receives a greater energy E as a result of a collision, then it will be displaced from its normal lattice site taking its electron cloud with it. This displaced atom is known as a 'knocked-on' atom or just 'knock-on', and the process forming it is called the primary process. The 'knock-on' may then come to rest in a non-equilibrium position, hence an interstitial atom as well as a vacant lattice site result from a collision. If however the excess energy E , transferred to the atom, is greater than $2E_d$, it will become a new projectile. Initially, knock-on atoms cause damage by ionization and electronic excitation; when their energy has fallen below the limiting energy for ionization, they

suffer elastic collisions with lattice atoms, causing further displacements. These secondary collisions, in turn, result in new projectiles leading to tertiary collisions and so on, until the projectile atom possesses insufficient energy to actually displace another lattice atom. This displacement 'cascade' accounts for most of the defects produced during the bombardment with fast neutrons, i.e. more lattice atoms are displaced as a result of the cascades, than from the primary processes in which each neutron is involved. It should be made clear however, that even so, this only accounts for 10 - 20% of the total damage arising from neutron irradiation; the remaining 80 - 90% of damage arises from ionization effects due to the passage of atoms and ions throughout the lattice. (ref. 148. p. 96).

The essential feature of the aforementioned hard sphere collisions is that the probability of transferring energy E , during a collision, is independent of E , provided that $E_{\max}$ is greater than or equal to E (which must be positive). $E_{\max}$ is here defined as the maximum amount of energy that can be transferred to a lattice atom by a direct head-on collision from a neutron. If a projectile atom in a monatomic solid possesses energy E (greater than $2E_d$) then collision with another lattice atom will result

in two projectile atoms with energies $E/2$, which will in turn (if $E/2$ is greater than $2E_d$) lead to a total of four projectile atoms of energy $E/4$, and so on. This argument only holds for direct head-on collisions between elastic atoms; in glancing blows, E approaches zero. The above process continues until E/n is less than E_d when the projectile atom will have insufficient energy to displace another, or just enough, when it will promptly fall into the resulting vacancy. For solids containing more than just one type of atom, and also when the bombarding particle is a neutron or heavy charged particle, the above process differs only in the respect that when any two colliding particles possess different masses, their resultant energies will also differ, according to the law of conservation of momentum.

The fast neutrons ejected during the fission of the U^{235} atom, range in energy between 0.5 and 15 MeV, the average for the purposes of calculation being taken invariably as 1 -2 MeV. (Neutrons with energies less than 0.5 MeV are called epithermal, and if less than 0.05 eV, they are slow or thermal neutrons). For the calculations to be found later in this work, the fast neutron energy will be taken as 1 MeV. The fission neutron energy spectrum exists as a consequence of the position of the target material within the reactor, e.g.

the core, reflector, rabbit tube etc., also the degree to which the moderator has 'thermalized' the fast neutrons. The errors involved from the use of an average neutron energy of 1 MeV, are less than those arising from other stages in the calculations.

The maximum amount of energy that can be transferred in a nuclear collision, in this case, when a bombarding neutron of mass N and energy E , makes a direct head-on collision with a lattice atom of mass M , is given by:

$$E_{\max} = \frac{4EMN}{(M+N)^2} \quad (72)$$

which may be approximated on the atomic weight scale, since $N = 1$, to:

$$E_{\max} = \frac{4EM}{(M+1)^2} \approx \frac{4E}{M} \quad (73)$$

The average amount of energy transferred in such a collision is:

$$\bar{E} = \frac{E_{\max}}{2} = \frac{2EM}{(M+1)^2} \approx \frac{2E}{M} \quad (74)$$

The fraction of the total energy of the neutron that is transferred on average to a lattice atom, is therefore:

$$\frac{\bar{E}}{E} = \frac{2M}{(M+1)^2} \approx \frac{2}{M} \quad (75)$$

Consequently the smaller the lattice atom, the greater the energy transferred to it in a collision. For a silicon atom this fraction is ca. 1/15 th. and for the oxygen atom, it is ca. 1/10 th. of the neutron energy.

In general then, it is found that for atoms such as aluminium, oxygen and silicon, approximately

10 - 20% of the neutron energy appears as lattice energy (spikes, vacancies, interstitials) and approx. 80 - 90% in the form of excitation and ionization.

2.3.2. Number of Displaced Atoms:

During a displacement cascade, new projectile atoms will only be produced if the bombarding particle transfers energy in excess of E_d . Therefore the number of displacements should be:

$$N_d = \frac{E_{\max}}{4E_d} = \frac{\bar{E}}{2E_d} \quad (76)$$

where $\bar{E}$ is the average energy transferred to a knock-on. Seitz (40) considers this an overestimation and suggests instead:

$$N_d = (E'/E_d)^{\frac{1}{2}} \quad (77)$$

where E' is the average energy of all the primary knock-ons. No accurate experimental determination of the number of atoms displaced by incident radiation are available, but rough estimates have been made in a few instances, e.g. by changes in electrical resistivity of metals (120), changes in density (36), and changes in the intensities of X-ray (120) and paramagnetic absorption lines (36). Levy and Dienes (121) studied the effects of fast neutrons on alpha-alumina, by means of changes in optical properties, i.e. the growth of several absorption bands as a function of radiation dose. In order to employ such measurements, however,

it is necessary to separate the effects due to ionization from the effects due to displacements. This was found to be possible as colouration due to ionization attained saturation at a very low exposure. Calculations of the number of displaced atoms gave an overestimate of the actual number found by experiment, but the figure was of the same order of magnitude, as is the case for similar calculations for metals (121). With graphite, the theoretical estimates exceed experimental figures by only a factor of two, which is better than for most other materials; for quartz, there is a factor of 5. It is to be expected that the experimental results should be less than theoretical, because the theory makes no allowance for replacements e.g. combination of vacant lattice sites and interstitial atoms (36,120). Primak (122) has conducted several experiments with calibrated fluxes in an attempt to relate the number of displacements, i.e. damage, to the flux. It is obviously necessary to possess a fairly precise knowledge of the behaviour of atoms within a bombarded material in order to determine quantitatively the extent of damage arising from irradiation.

Dienes and Vincyard (121) showed that the no. of primary atoms displaced per unit volume by a bombarding neutron, is given by:

$$N_p = \phi \cdot t \cdot n \cdot c_d \cdot \quad (78)$$

where $\phi.t$ = instantaneous neutron flux, multiplied by time; n = no. of atoms per unit volume of target material; and c_d = displacement cross section of the lattice atom.

Since each primary knock-on produces many more displacements, N_p corresponds to only a fraction of the total no. of displacements:

$$N_d = N_p \cdot \bar{v} \quad (79)$$

where $\bar{v}$ = average no. of displacements per knock-on, which is given by:

$$\bar{v} = \frac{\bar{E}}{2E_d} = \frac{2EMN}{(M+N)^2} \cdot \frac{f}{2E_d} = \frac{EMf}{(M+1)^2} \cdot \frac{1}{E_d} \quad (80)$$

(see below for summary of symbols)

$$\therefore N_d = \phi.t.n.c_d \cdot \frac{E.M.f.}{(M+1)^2.E_d} \quad (81)$$

This expression thus allows calculation of an approx. no. of lattice atoms displaced by a given integrated neutron flux, although no allowance is made for the numerous replacements which may occur. Various estimates have been made of the %no. of displacements (vide section 4.3.1.) in an attempt to explain, at least, semi-quantitatively, the observed effects of neutron irradiation of NaX.

Summary of Symbols used in Sections 2.3.1. and 2.3.2.

E_d = displacement energy of lattice atom (ca. 25eV).

E_{max} = maximum amount of energy that may be transferred to a lattice atom in a direct head-on

collision by a bombarding neutron.

$\bar{E}$ = average energy transferred in neutron-lattice atom collisions (for glancing blows E approaches zero). $\bar{E} = E_{\max}/2$

E = average energy of bombarding neutrons (1 MeV).

M = atomic weight of lattice atom.

N = " " " neutron = 1.

N_p = no. of lattice atoms displaced by neutrons in primary collisions only.

N_d = total no. of displaced atoms; $N_d = N_p \cdot \bar{v}$ (79)

$\bar{v}$ = average no. of atoms displaced by each knock-on atom; $\bar{v} = \bar{E}/2E_d$ (80)

$\phi.t$ = total neutron flux (neutrons/cm².)

σ_d = displacement cross section of lattice atom.

n = no. of lattice atoms per unit volume of target.

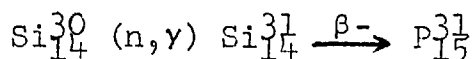
f = factor allowing for anisotropy and inelasticity in fast neutron scattering (taken as $2/3$).

2.3.3. Thermal Neutrons:

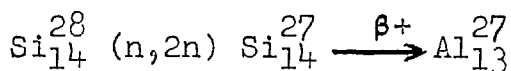
Although thermal neutrons do not cause damage by displacing lattice atoms, or by ionization, they do alter the atomic nuclei by neutron capture. The mechanisms by which nuclear transmutations take place will not be given here, but several reactions will be discussed.

The principle isotope of silicon is Si_{14}^{28}

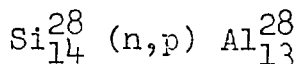
where 14 = atomic no. and 28 = atomic wt.; neutron capture produces the stable Si_{14}^{29} which likewise may be transmuted to Si_{14}^{30} . This isotope exists to the extent of 3% in the natural element and is the only Si isotope which will undergo an (n, γ) transmutation to form an unstable radionuclide. The reaction is described by:



The unstable Si_{14}^{31} promptly decays by beta emission to form a stable phosphorus isotope. The half life of the silicon isotope is only 2.65 hours, so decay is complete within a day. Since the activity of silicon so produced is very low, the advantages of silica ampoules for containing samples is obvious. The stable and most abundant isotope of Si can also undergo an (n, 2n) reaction forming the unstable Si_{14}^{27} , which decays by positron emission to form stable aluminium:

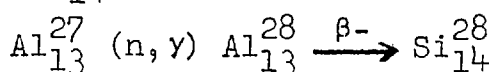


It can also undergo an (n, p) reaction to form aluminium:



However these two reactions are of little importance compared with the (n, γ) reaction of Si_{14}^{30} .

The chief isotope of aluminium is Al_{13}^{27} ; this may suffer an (n, γ) transmutation to form the unstable isotope Al_{13}^{28} which decays by beta emission to form the stable silicon atom Si_{14}^{28} :

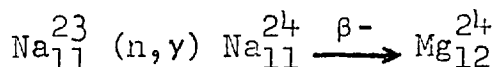


Since the half life of Al_{13}^{28} is only 2.3 mins., any activity so produced will have completely decayed within one hour. This activity is to be expected from all irradiations of samples contained in aluminium irradiation cans, upon removal of the sample from the reactor.

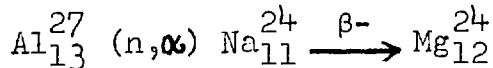
Oxygen - 16 undergoes neutron capture to form O_8^{17} which in turn may form O_8^{18} , both of which are stable. However O_8^{18} may suffer an (n, γ) reaction to form the unstable O_8^{19} which will decay within one day to stable fluorine:

$$\text{O}_8^{18} (n, \gamma) \text{O}_8^{19} \xrightarrow{\beta^-} \text{F}_9^{19}$$

The sodium cations present in NaX are of the stable isotope Na_{11}^{23} ; They may suffer an (n, γ) reaction to form unstable Na_{11}^{24} which decays by beta emission to form stable magnesium:



Since the half life is 15 hours, this activity is negligible within one week. Magnesium may also be produced by :



Summarizing, any activity resulting from a nuclear transmutation with aluminium should be 'dead' within one hour, from silicon and oxygen within one day, and from sodium, within one week. If the zeolite sample is still appreciably active after one week, the activity must arise from the decay of an impurity atom. In the case of cations, this could be K, Rb, Cs, or Ca, (vide section 4.3.4).

2.3.4. Calculation of Specific Activity:

Specific activity S, may be defined as the amount of activity produced per unit weight of the irradiated element, expressed as curies per gm. of target element. S is given by the expression (123):

$$S = \frac{0.6 \phi c (1 - \exp.-0.693t/T)}{3.7 \times 10^{10} A} \quad (82)$$

where ϕ = effective thermal neutron flux (n/cm²/sec).

c = excitation cross section of target (barns).

t = irradiation time (same units as T).

T = half life of unstable radionuclide produced.

A = atomic weight of target element.

($3.7 \cdot 10^{10}$) = no. of disintegrations per second from one gm. of pure radium = 1 curie.

This equation is only approximate; it takes no account of burn up of the target element or of possible further neutron capture reactions and transmutations. However an approximate estimate of the specific activity can be calculated.

By use of the following expression (124), it is possible to calculate the weight of radio-isotope produced as a result of thermal neutron capture:

$$M = 7.7 \cdot 10^{-9} \cdot A \cdot T \cdot S. \quad (83)$$

(where A = at. wt. of target element, T = half life of decaying nuclide in days, S = specific activity, c/gm.).

Various calculations will be found in section 4.3.3.

PART 3EXPERIMENTAL.

<u>SECTION</u>	<u>PAGE</u>
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3.3. <u>NEUTRON IRRADIATION</u>	140

3.1.CATION EXCHANGE.3.1.1. CATION EXCHANGERS.(a) Preparation of Zeolites.

The sample of "Linde Molecular Sieve -13X" used throughout, was supplied in the form of a fine white powder (approx. 200 mesh). It was washed several times with hot distilled water in order to remove any hydrolytic decomposition products (18) or excess alkali resulting from its synthesis in aqueous alkaline solution. The pH of the final washing was 8, further washing will not decrease this value without causing some damage to the material. The sample was then dried in an air oven between 110 - 120°C in order that it could be sieved through a 200 mesh sieve. The resulting powder was kept in a desiccator over a saturated solution of ammonium chloride in order to achieve a constant water content. The sample of synthetic mordenite, i.e. Zeolon (Na⁺ form), was sieved only and stored as above.

(b) Analysis of Zeolites.

At all times, chemicals of the highest purity available were used, i.e. AnalaR reagents. The method of analysis used, is that described by Vogel (125) and Meier (126) for aluminosilicates.

Water content: A sample (.05 to 0.5 g.), was weighed into a platinum crucible and ignited over a Meker

burner to constant weight. Two hours heating was usually sufficient.

Silica content: NaX and mordenite both appeared difficultly soluble in concentrated hydrochloric acid. Portions were therefore weighed out into evaporating dishes and treated as follows :-

20 ml. concentrated HCl were added and left overnight; the acid was then evaporated to dryness, the residue heated in an air oven at $110 - 120^{\circ}$ C. for two hours to dehydrate the silica, so rendering it as insoluble as possible. Acid was again added and the procedure repeated in all, five or six times. The last addition of HCl was followed by heating on a water bath with occasional stirring for several hours, adding five times the volume of water, and filtering hot through a Whatman No.41 ashless filter paper. The residue was washed with warm 1:20 HCl and then thoroughly with hot water until free from all chlorides (test with AgNO_3). The combined washings were evaporated to dryness, heated at 120° C. for 1 hour and redissolved in dilute HCl and filtered through another ashless filter paper. This was washed with warm 1:100 HCl and then hot water. Both filter papers were then ignited in a platinum crucible to constant weight; the difference in weight was due to SiO_2 . This weight was checked by adding to the residue in the crucible, 1 cc. of water, 5 drops of concentrated sulphuric acid, and 5 drops

of HF and then evaporating to dryness under an infra-red lamp. The loss in weight was due to SiO_2 (evaporated off as SiF_4 & H_2O).

Alumina content: The combined washings from the above treatment were made more acid with HCl, boiled, methyl orange added and sufficient 1:1 NH_4OH to just make the solution alkaline. It was boiled for several minutes and filtered hot. The gelatinous residue was thoroughly washed with 2% NH_4Cl solution, and the filter paper and residue then ignited to constant weight. The increase in weight of the crucible is the weight of Al_2O_3 .

Sodium content: This may be determined by difference knowing the % amounts of H_2O , SiO_2 and Al_2O_3 in a sample, but radiochemical analysis was also employed. For this purpose, Na^{22}Cl solution from the Radiochemical centre, Amersham, was employed. An N/10 solution of NaCl was prepared containing a negligible weight of the radioactive tracer. 20 cc. of this solution were then equilibrated with approx. 0.5 gm. of the zeolite, by rotating in a sealed pyrex tube in an oven at 30°C . for 2 days. By comparison of the count rate for the stock and exchange solutions, the % Na could be determined. (For details of counting technique - see section 3.1.4.)

The results of the analyses of NaX and mordenite

are given in section 4.1.1.

3.1.2. Exchanging Cations.

NaX was exchanged with Cs^+ , Ba^{++} and UO_2^{++} (uranyl) ions, and mordenite with Cs^+ and Ba^{++} .

These latter two ions were obtained from the Radiochemical centre, Amersham, as Cs^{137}Cl and $\text{Ba}^{133}\text{Cl}_2$ solutions of very high specific activity. Large volumes of decinormal solution of these salts, with count rates of approximately 2000 counts/minute, were then prepared.

The uranyl ion employed was AnalaR grade uranyl nitrate or acetate (hydrated). Exchanges were conducted in aqueous solution, but the system $\text{NaX}/\text{UO}_2^{++}/\text{ethanol}$ was also briefly studied, as at the higher concentrations of aqueous uranyl nitrate, the zeolite partially dissolved.

3.1.3. Exchange technique.

Portions of the zeolite were weighed out into dry pyrex tubes which had previously been boiled in distilled water for several hours to remove alkali. 15 or 20 cc. of exchange solution were added to the tubes, which were sealed and then rotated in an oven at $27 - 30^\circ\text{C}$. for 2 - 3 days. This was found to be sufficient for all systems studied. The exchanged zeolite was then filtered off, and the weight of Ba^{++} , Cs^+ or UO_2^{++} ion determined by analysis, Ba^{++} and Cs^+ as in the following section, and UO_2^{++} as in section 3.1.5.

3.1.4. Radioactive Counting Technique.

Cs^{137} ($t_{\frac{1}{2}} = 30$ years) and Ba^{133} ($t_{\frac{1}{2}} = 7.5$ years) were both determined by a counting technique. The equipment employed consisted of a halogen quenched liquid Geiger - Müller counter tube, type M 6 H with operating voltage 360 - 400 volts. The counts were recorded on an Ekco automatic scalar type N530F in conjunction with a probe unit of dead time 300 μsecs . The counter tube had a capacity of 10 - 15 cc . and was filled to the same mark each time.

The number of counts recorded on this scalar unit were all corrected for the background count (i.e. water, with a count rate of approximately 14 counts/minute), and also corrected for the dead time by means of the equation :-

$$N_T = \frac{N_O}{1 - t \cdot N_O} \quad (84)$$

where N_T = true count rate.
 N_O = observed count rate,
 t = dead time (mins.)

The solutions were usually counted for three successive periods of 1 kilosecond to obtain an average count. Between counting each solution, the G.M. tube was thoroughly washed to remove contamination. To show that all activity had been removed, a background count was made each time. This was also the technique adopted in analyzing the zeolites for Na^+ . (Section 3.1.1.)

3.1.5. Analysis for Uranyl Ion:

It was found that by exchange with NaX, the uranium decay series was upset, presumably by Na^+ ions in the zeolite being replaced by uni- or divalent ions which are members of the uranium decay series. It appears that NaX has a greater affinity for some of the daughter elements in the decay series, than it has for the uranyl ions. Therefore the count rate of the solution after exchange equilibrium had been attained, was not a measure of the uranyl concentration. The count rate of this solution increased with time, secular equilibrium not being achieved even after six months. Consequently, alternative methods were sought for the determination of uranium.

(a) Precipitation as Ammonium Di-uranate (127):

The solution containing uranyl nitrate and sodium nitrate was passed through a cellulose column using nitric-acid-conditioned-ether as eluate; this was designed to remove impurity cations. The ether was carefully evaporated off and the uranium precipitated as ammonium di-uranate, filtered and ignited to constant weight as U_3O_8 . Trial runs with solutions of known concentrations were made and this procedure found to be unnecessary. The uranium containing solutions were diluted to 250 cc., a small amount of ashless No. 42 Whatman filter paper pulp added, and the solution boiled with stirring. 1:1 ammonia was added using methyl red as indicator, until just alkaline. The solution was boiled for a further 5 minutes with vigorous stirring, the

uranium precipitating out as ammonium di-uranate. It was left on a water bath for one hour, and then filtered hot, through an ashless filter paper, and washed with an aqueous solution containing 10g. NH_4NO_3 and 20cc. 0.88 NH_4OH per litre. The filtrate may be tested for complete precipitation with a 3% solution of potassium ferrocyanide, which forms a dark brown complex with uranium (128). Care had to be taken at this stage to avoid peptisation, which did occur during approximately one third of the analyses carried out. However, boiling the solution sufficiently to reduce its volume by half, or redissolving in nitric acid followed by reprecipitation with ammonia, resulted in fairly reproducible results. The residue and filter paper were ignited to constant weight in a muffle furnace at 900°C , and the uranium weighed as U_3O_8 .

(b) Absorptiometric Analysis of Uranium:

The Hilger & Watts "Spekker", i.e. photoelectric absorptiometer, was employed for the determination of low concentrations of uranium in aqueous solution; dark blue filters (no. 1) and the 2cm. cells were used. The procedure adopted (129) consisted of adding the following reagents in the order given, to a solution of uranyl nitrate containing 0.05 - 2 mg. uranium: 5cc. N/10 sodium carbonate, 1cc. N/10 sodium hydroxide, and 1cc. "20-volume" hydrogen peroxide; the solution was made up to 25cc. with distilled water. All reagents used were of AnalaR quality, and the volume strength of the H_2O_2 was checked by titration with KMnO_4 and dilute

H_2SO_4 . The 'blank' solution required for this method was prepared with the above reagents. Numerous precautions had to be taken to ensure reproducibility of results, e.g. each solution had to be made up separately and the optical density measured on the Spekker immediately; the same cells were employed every time for the test and blank solutions, to ensure that the respective path lengths were identical; the test solution had to be prepared very carefully employing a micropipette for the uranium solutions; and it was necessary to ensure that no bubbles were sticking to the cell walls during measurements. A calibration curve was plotted, of measured optical density vs. uranyl nitrate concentration.

Due to the dissolution of the NaX in the higher concentrations of uranyl nitrate required for some of the exchange experiments (aluminium was actually detected in the uranyl solutions using the quinalizarin spot test, ref. 128), these exchanges were conducted in ethyl alcohol solution instead of aqueous solution. However practical difficulties were then encountered due to leakage of the solutions from the ground glass joints of the exchange tubes. It was found necessary to completely seal the pyrex glass tubes in an oxy-coal gas flame. In order to facilitate the ease of sealing in the presence of alcohol vapour the neck of the tube was constricted after addition of the zeolite sample. Mixing this alcoholic solution after exchange with the necessary ingredients for the absorptiomet-

-ric analysis, resulted in the formation of numerous bubbles which collected on the cell walls. Since these would have affected the measured optical density, the exchanged solutions were evaporated to dryness and the uranyl nitrate redissolved in water.

3.1.6. X-Ray Studies:

These studies were employed (a) to determine whether any decomposition of the zeolite samples resulted from exchange with the ions Cs^+ , Ba^{++} , and uranyl UO_2^{++} ; and (b) to determine whether the neutron irradiation of samples resulted in any structural change in the zeolite lattice. The equipment consisted of a 'Nonius' Guinier camera employing Cu K alpha radiation applied at 40KV. Four specimens were simultaneously exposed; they were mounted side by side in a flat aluminium frame and the powder was evenly spread between two layers of "sellotape". The exposure time was of the order of 12 hours.

3.2.GAS ADSORPTION.Introduction.

Isotherms have been constructed for the system NaX/krypton over the temperature range + 25°C to minus 150°C, and NaX/argon, between + 25°C and -100°C, and also at 90°K. Pressure readings ranged from less than 0.03 cms.Hg. measured with a Mcleod gauge, up to 55 cms.Hg. employing a standard mercury manometer. Temperature measurements were usually made with vapour pressure thermometers, and controlled by standard thermostat equipment. Detailed descriptions now follow of the various aspects of this sorption work, i.e. preparation of adsorbents, adsorbates, volumetric sorption apparatus, vapour pressure thermometers etc.

3.2.1. Preparation of the Adsorbents.

All samples of zeolite were kept in a desiccator containing a saturated solution of ammonium chloride. Approximately 1 gm. of the moist powder was transferred to a weighed sorption cell, whose volume had been determined with mercury. The neck of the sample cell was wiped free of powder with a pipe cleaner, and the cell reweighed to obtain the weight of zeolite used. Simultaneously, two portions of the zeolite were weighed out into platinum crucibles for a % H₂O determination. A plug of glass wool was placed in the

neck of the cell to prevent powder from being sucked into the sorption system during outgassing, and knowing its weight, an estimate of the volume of the gas that would then fill the remaining free space, could be made. The cell was then glass-blown onto the sorption apparatus and the sample outgassed, i.e. freed of physically adsorbed water vapor, as below. It is necessary to employ a standard outgassing procedure as it has been found by Papée (130) that some of the water vapour sorbed on silica and alumina is very strongly chemisorbed, and can only be removed by a near sintering process. To achieve the same surface conditions and adsorbent properties each time, strict adherence to an outgassing process should be maintained, as successive treatments might well remove successive quantities of chemisorbed water, so altering the adsorbent capacities for adsorbate.

Standard Outgassing Procedure:

- (1) the sample is pumped free of air and moisture using only the rotary oil pump, for several hours.
- (2) the mercury diffusion pump is switched on and the pumping continued for several hours more, achieving a pressure of better than 10^{-4} mm.Hg.
- (3) the sample cell is then enclosed in a furnace and the temperature slowly raised to ca. 100° C. and maintained thus overnight. Operations (1), (2)

- and (3) involve a period of about 24 hours.
- (4) during the second day, the temperature is slowly increased to 360°C. (ca. 20°C. per hour) under a vacuum of 10^{-5} to 10^{-6} mm.Hg. It is maintained thus for 24 hours, after which it is allowed to cool.

This procedure has been found to be sufficient to remove all traces of physically adsorbed water vapour from the lattice, but without damaging it in the process. One sample of NaX was outgassed for periods of 24, 20, 12, 12, & 24 hours, with sorption of argon at 90° K, (and runs at various other temperatures) between each, in order to check the reproducibility, in preparing the surface of the adsorbents.

Samples of NaX which were to be irradiated, were outgassed under the above conditions and sealed in silica ampoules. After irradiation, the samples has to be re-exposed to the atmosphere in order to fill the sorption cell. In breaking open the silica ampoule, traces of silica might have been left in the powder, so the irradiated material was firstly sieved (200 mesh) and then stored in the ammonium chloride desiccator for several days. It was consequently necessary to completely re-outgas irradiated samples. The exception to this rule was sample 7 (NaX₇^{**}); this sample was contained in two small silica ampoules, which were broken open inside a perfectly dry glove-box. The ((for asterisk notations of NaX, see Appendix).

zeolite powder was transferred to the adsorption sample cells without sieving or equilibrating with water vapour; this procedure, resulting in a smaller loss of material, was considered necessary, as each ampoule contained less than 0.1 gm. NaX.

To remove traces of adsorbate between sorption runs, the samples were usually heated to over 100°C for about one hour, under high vacuum.

3.2.2. Gas Adsorbates.

Argon, krypton and oxygen were employed for the sorption work and helium for the initial calibration of doser volumes etc. All were supplied in litre bulbs, equipped with a break-seal, from the British Oxygen Co., Ltd. The purity specifications were :

Helium	-	spectrally pure;
Argon	-	spectrally pure;
Krypton	-	99 - 100% (balance xenon);
Oxygen	-	pure.

3.2.3. Volumetric Sorption Apparatus.

A standard volumetric system was constructed and employed for all the sorption work. It consisted of a calibrated doser volume (ca. 25 cc.) from which radiated the supply gas line, Mcleod gauge, manometer, gas burette, sorption cell, and two outlets to the high vacuum pumping system. The Mcleod gauge and manometer were also connected to the low vacuum system. The separate items will now be described in more detail:-

(1) Pumping system.

This is shown schematically in figure 7. The mercury diffusion pump operates in conjunction with a rotary oil backing pump. The latter alone is capable of achieving a pressure of 10^{-3} - 10^{-4} mm.Hg, but together the moisture free system may be pumped down to 10^{-6} mm.Hg pressure in approximately 30 minutes. The oil trap prevents oil from being sucked into the system in the event of a power failure. The cold trap, a dewar flask filled with liquid nitrogen, prevents any condensible material from contaminating the mercury and oil pumps. All taps were of large bore (6-8 mm.) to ensure a good pumping rate, and greased with Apiezon grease type L, the most suitable for high vacuum systems operated at room temperature.

(2) Manometer: (see figure 9)

This was constructed of wide bore tubing (1 cm.) in order to reduce the meniscus depression effects. Menisci corrections (131) were applied on all occasions. The manometer read pressures in the range 0.2 to 55 cm. of Hg. The fixed mark (MM, see figure 9) was obtained by affixing a very thin strand of wire to the tube with 'sellotape'. Mercury column heights were measured with a cathetometer reading to 0.001 cm.

(3) McLeod Gauge: (see figure 9)

Total capacity of ca. 245 cc., capable of

FIGURE 7 PUMPING SYSTEM

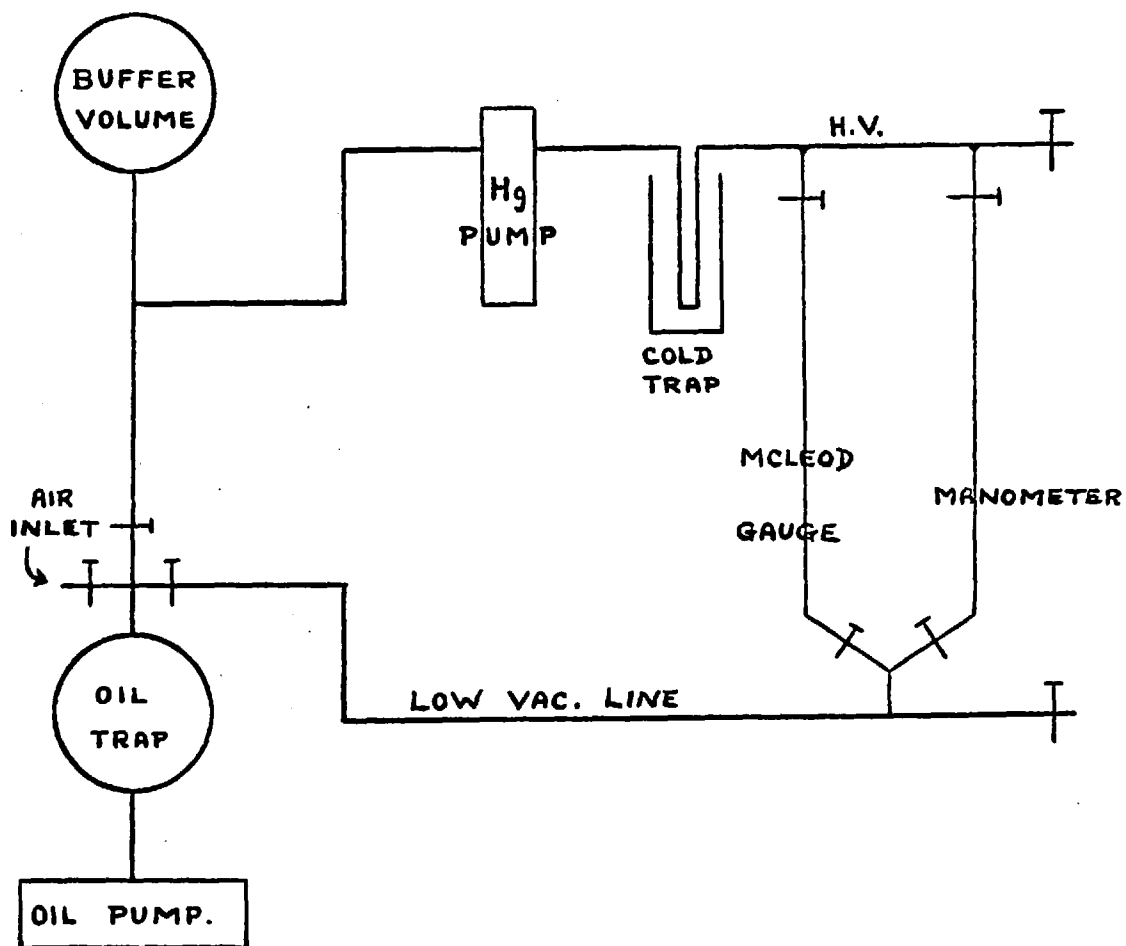
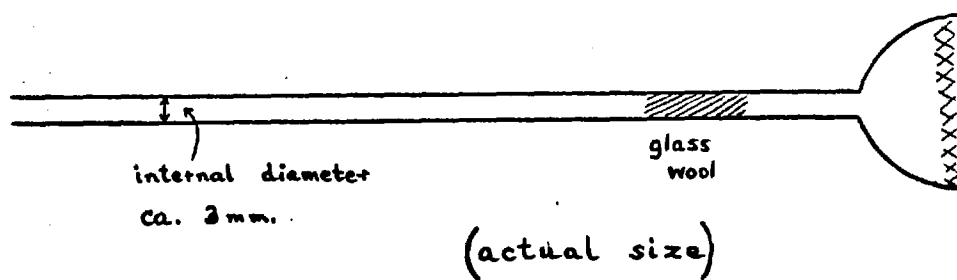


FIGURE 8 SORPTION CELL



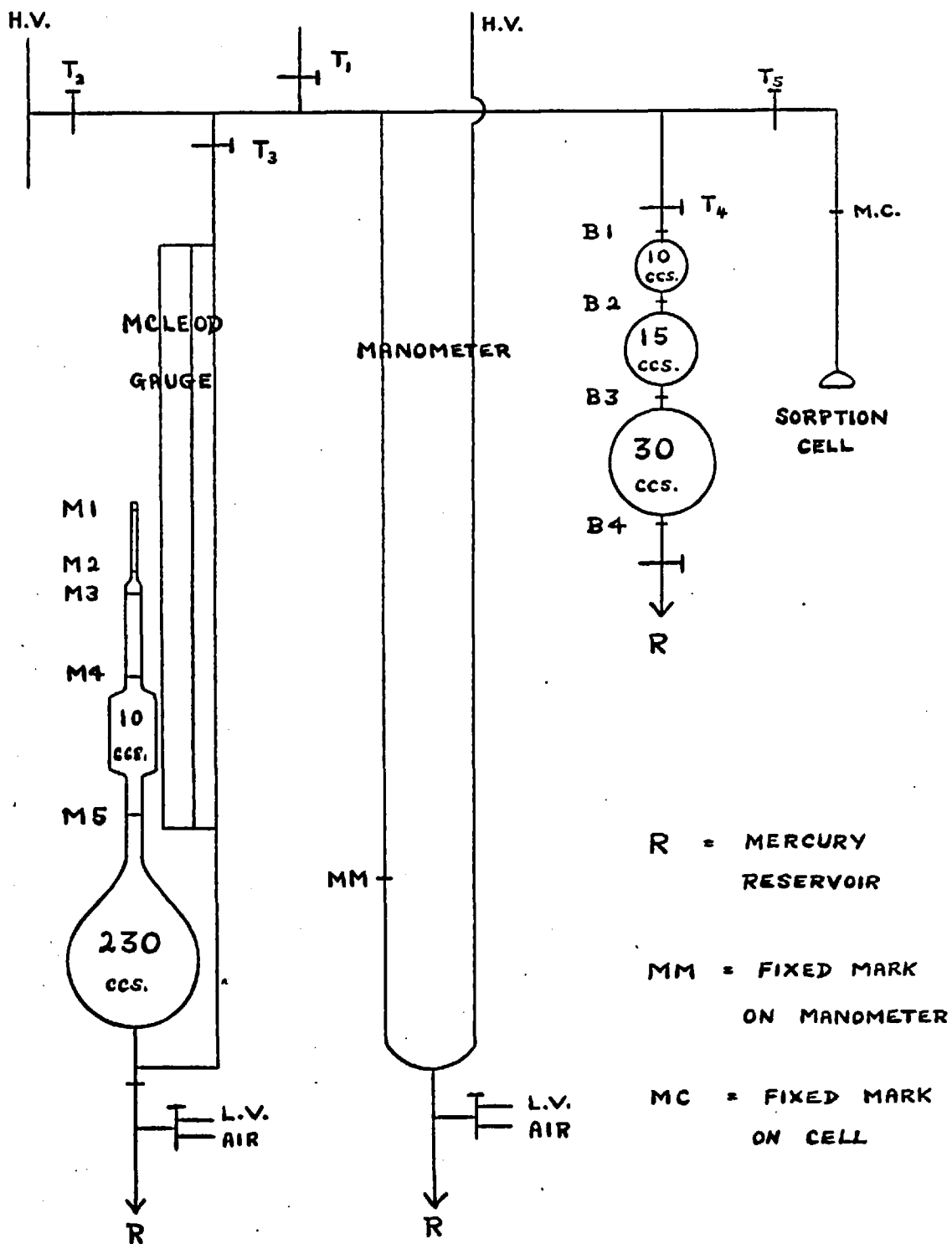
measuring pressures better than 10^{-6} mm.Hg, but only required in this sorption work to measure pressures in the range 0.03 to 0.3 cm.Hg. Five calibration marks were made on the gauge by laying two strips of 'sellotape' very close together and painting over the gap with black paint. Removing the 'sellotape' left a very fine line which was easily visible with the cathetometer. The gauge was calibrated before attachment to the system by filling to the marks with mercury, and weighing. A very long thin capillary was used to transfer mercury to the capillary section of the McLeod gauge. It was weighed before and after each addition or subtraction of mercury, and the quantity of mercury itself was also weighed. Uniform bore 1 mm. and 4 mms. Veridia tubing was used for those tubes in which mercury columns were to be measured.

(4) Gas Burette: (see figure 9)

This consisted of 3 bulbs of capacities, ca. 10, 15, and 30 mls. respectively. These volumes were determined before the gas burette was attached to the system by filling with mercury to previously made fixed marks (B1-B4) and weighing. The weight of mercury added each time was also taken.

Care must be taken during calibrations with mercury since frequently the meniscus in calibration is facing in the opposite direction to the meniscus in an actual

FIGURE 9 VOLUMETRIC SORPTION APPARATUS



reading. Although the correction is small, it is undoubtedly significant in calibrating the small volumes of the Mcleod gauge. Corrections were thus made according to Jnanananda (132).

(5) Doser Volume: (see figure 9)

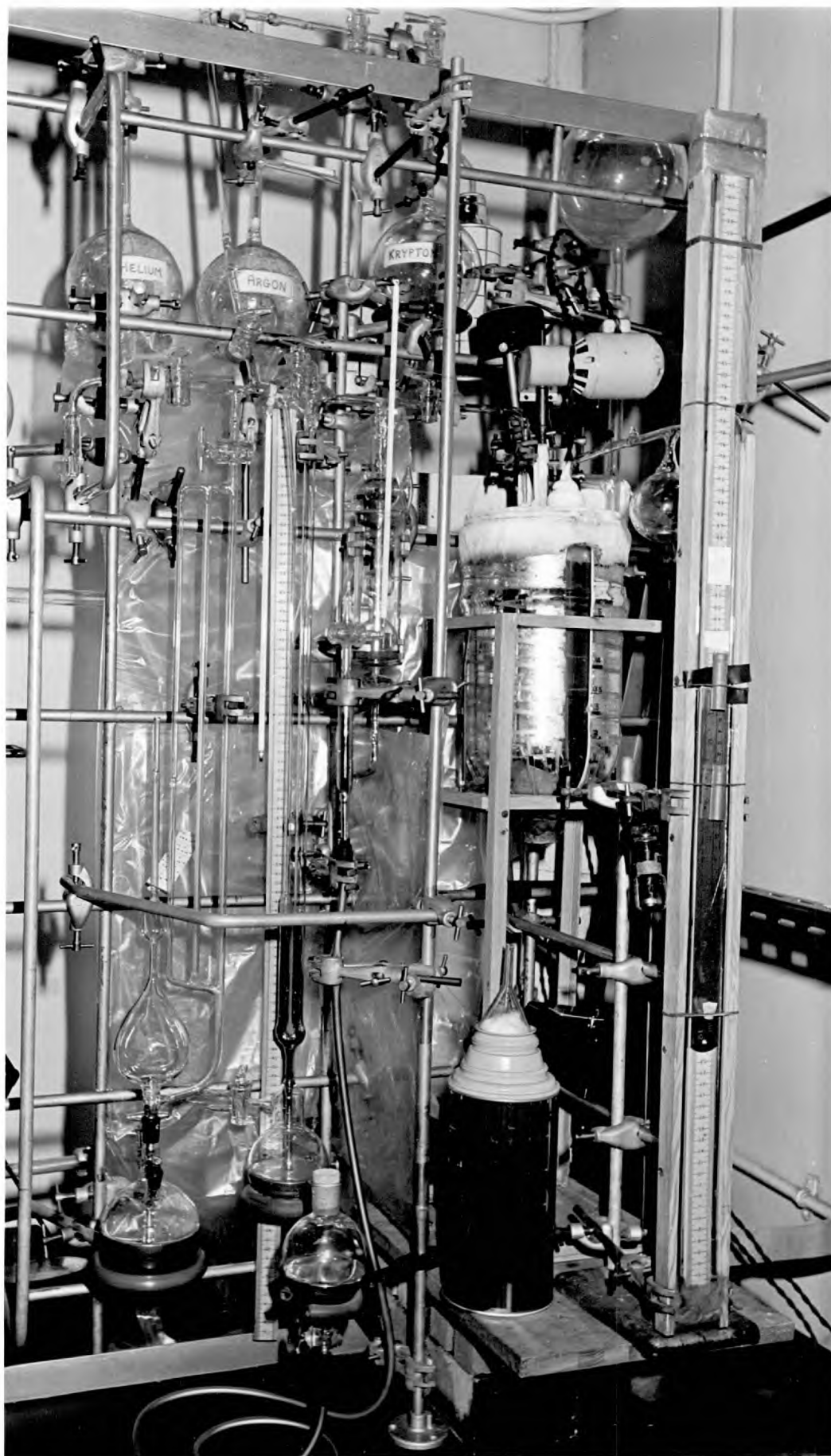
The unknown capacity of the doser volume was determined by calibration with helium gas at room temperature and was found to be about 25 cc. Pressures were taken with the manometer corresponding to the four different heights of mercury in the gas burette, and the doser volume then calculated using the expression :-

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

The ideality of helium gas was assumed. Room temperature was maintained to within $\pm 0.05^\circ\text{C}$ throughout these measurements to minimize errors. The unknown doser volume, shown on figure 9, is the volume confined between taps T1 to T5, and mark MM.

(6) Gas Line:

The litre bulbs of spectrally pure helium, argon, krypton and oxygen, were attached to the gas line, each being equipped with a 4 mm. tap, magnetic break seal, and in the case of argon, krypton and oxygen, a side arm. For argon, this contained pellets of Linde Molecular Sieve 5A. After thorough outgassing, this



acted as an adsorbent when cooled to 78°K , and allowed the argon used in an experiment to be reclaimed. Krypton and oxygen were easily frozen out into an empty side arm with liquid nitrogen, but the helium used for calibration had to be pumped away after use, because it could not easily be liquefied.

(7) Sorption Cell: (see figure 8)

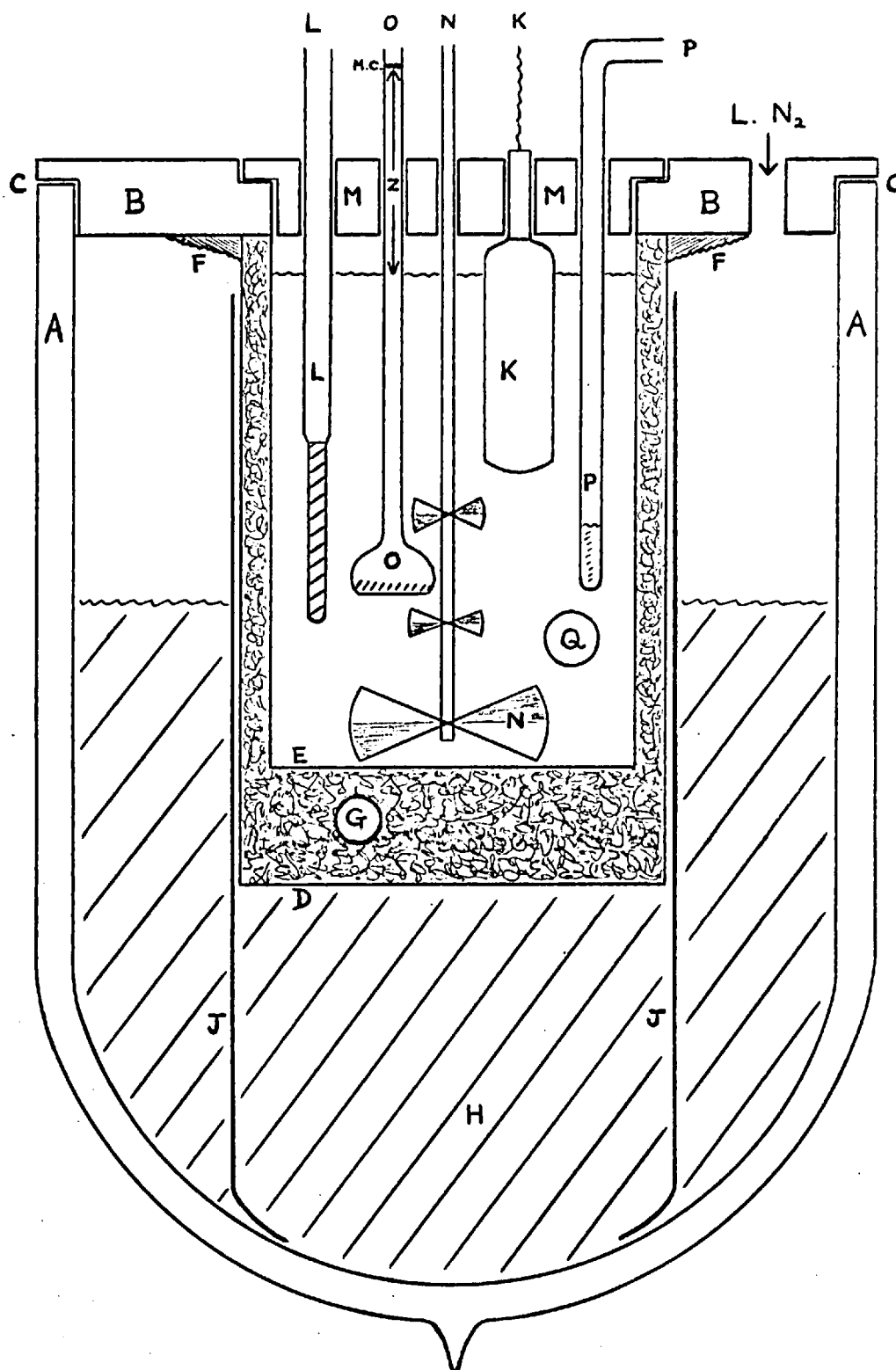
The volume of the tube between tap T_5 and the mark MC (see figure 9), at which point cells were glassblown onto, and broken off the sorption apparatus, was calibrated with helium gas in the usual way. The dimensions of the cell are shown in figure 8. The actual volume of the cell prior to the introduction of the adsorbent was determined from the weight of mercury required to fill it. The free volume of the cell was then obtained by subtracting the volume of adsorbent, and plug of glass wool, from the total volume of the cell.

3.2.4. Cryostat Bath: (see figure 11)

The cryostat bath used over the temperature range, -150° to 0°C , consisted of a large strip-window Dewar vessel (A) (180 x 250 mm.). It was fitted with a perspex lid (B) sealed to the Dewar around its rim with plasticine (C). Two beakers (D & E), the inner one (E) of 600 ccs. capacity, were fixed to the perspex lid with a glue (F) prepared by dissolving perspex turnings

FIGURE II

CRYOSTAT APPARATUS



(for alphabetical notations - see text)

in chloroform and adding red lead powder. This was very hard when dry, was insoluble in the bath liquids employed (Q), and formed a seal to prevent the bath liquid from distilling over into the liquid nitrogen coolant. It also withstood the mechanical strains set up by the unequal contractions of materials upon cooling. The space between the beakers (G) was lagged with aluminium foil and asbestos wool; this was to produce a temperature gradient between the bath liquid and coolant.

Since the liquid nitrogen (H) evaporated at the rate of approximately 1 pint/hour, it was necessary, for a constant temperature, to frequently top-up the system to a level depending on the temperature of the sorption run. However, this proved inconvenient overnight during long sorption runs, so the outer beaker was sheathed in several layers of copper foil (J), which extended from within one inch from the top, down to the bottom of the Dewar vessel. It thus remained in contact with liquid nitrogen for approximately $5\frac{1}{2}$ hours and, being a good heat conductor, tended to simulate the conditions of a constant level of liquid nitrogen. Removal of heat from the bath was exactly compensated by a 15 watt light bulb (K), operating in conjunction with a conventional thermostating device, namely, a "Sunvic" T S 7 bimetallic spiral (L), which operated a

hot wire relay. The perspex lid (B) was recessed in its centre, and contained two semicircular removable lids (M) with several holes apiece. These allowed entry of the various items required in the cryostat bath, i.e. three propellered metal stirrer (N), sorption cell (O), bimetallic strip (L), vapour pressure thermometer (P) and 15 watt heating bulb (K), all of which were positioned relative to one another as in figure 11. The heating bulb was wrapped in aluminium foil to prevent heating of the bimetallic strip, or cell, or vapour pressure thermometer by radiation. Although good temperature control was obtainable using this system ($\pm 0.03^{\circ}\text{C}$) with the bimetallic spiral control set at its most sensitive position, slow temperature drifts were occasionally observed which were corrected by manual adjustment of the control. Presumably these were due to mechanical wear of the spiral, since they are designed and marketed for use in the range 0° to 360°C . However, they were considered satisfactory even at -150°C .

Although the hardened perspex glue withstood the mechanical strain set up by the cooling of various parts of the cryostat, occasional cracks appeared; these were simply filled with more perspex glue to prevent escape of cold nitrogen vapour which tended to upset the temperature equilibrium during a sorption run.

3.2.5. Bath Liquids:

For the argon adsorption runs at 90.19°K , liquid oxygen was used as bath liquid, contained in a Dewar vessel. Carbon dioxide and water vapour condensed out and frozen by the liquid oxygen were assumed to have no effect on this temperature.

For all the adsorption runs between the temperatures 0°C and -100°C , petroleum ether (boiling range 40°C - 60°C) was found to be perfectly satisfactory. However, since it solidified in the region of -110°C , temperatures below this required the use of isopentane as bath liquid. (B.pt = $+28^{\circ}\text{C}$, fr.pt. = -158°C .) It is recommended for use near its freezing point as it does not become viscous. Since isopentane and petroleum ether are both highly inflammable liquids, suitable precautions were taken, e.g. absence of naked flames in the vicinity, the motor driving the stirrer was of the spark-free type, and liquid oxygen was never employed as the coolant, only liquid nitrogen.

Due to the relatively rapid evaporation rate of petroleum ether and isopentane at 0°C , water containing dissolved salt was used as bath liquid at this temperature. The cryostat bath was still employed with either a very small amount of liquid nitrogen as coolant ($\frac{1}{4}$ pint) or solid carbon dioxide in acetone. For the runs at 25°C , an 800 mls. beaker containing

water was satisfactory, the room temperature acting as coolant, and a neon indicator lamp as heater.

3.2.6. Temperature Measurement, Control & Accuracy:

For the sorption runs at 0°C and 25°C , a mercury in glass total immersion thermometer was used (0 to 50°C). For all other temperatures, -40° , -70° , -90° , -100° , -120° , -130° , -140° , 150°C ., vapour pressure thermometers were employed (for constructional details, see next section). The types employed, their ranges and temperatures at which used, are shown below :-

<u>Thermometer</u>	<u>Range</u> ($^{\circ}\text{C}$)	<u>Temps: at which</u> <u>used.</u> ($^{\circ}\text{C}$)
NH_3	-33 to -73	-40 -70
CO_2	-73 to -100	-90 -100
C_2H_4	-100 to -150	-120 -130 -140 -150

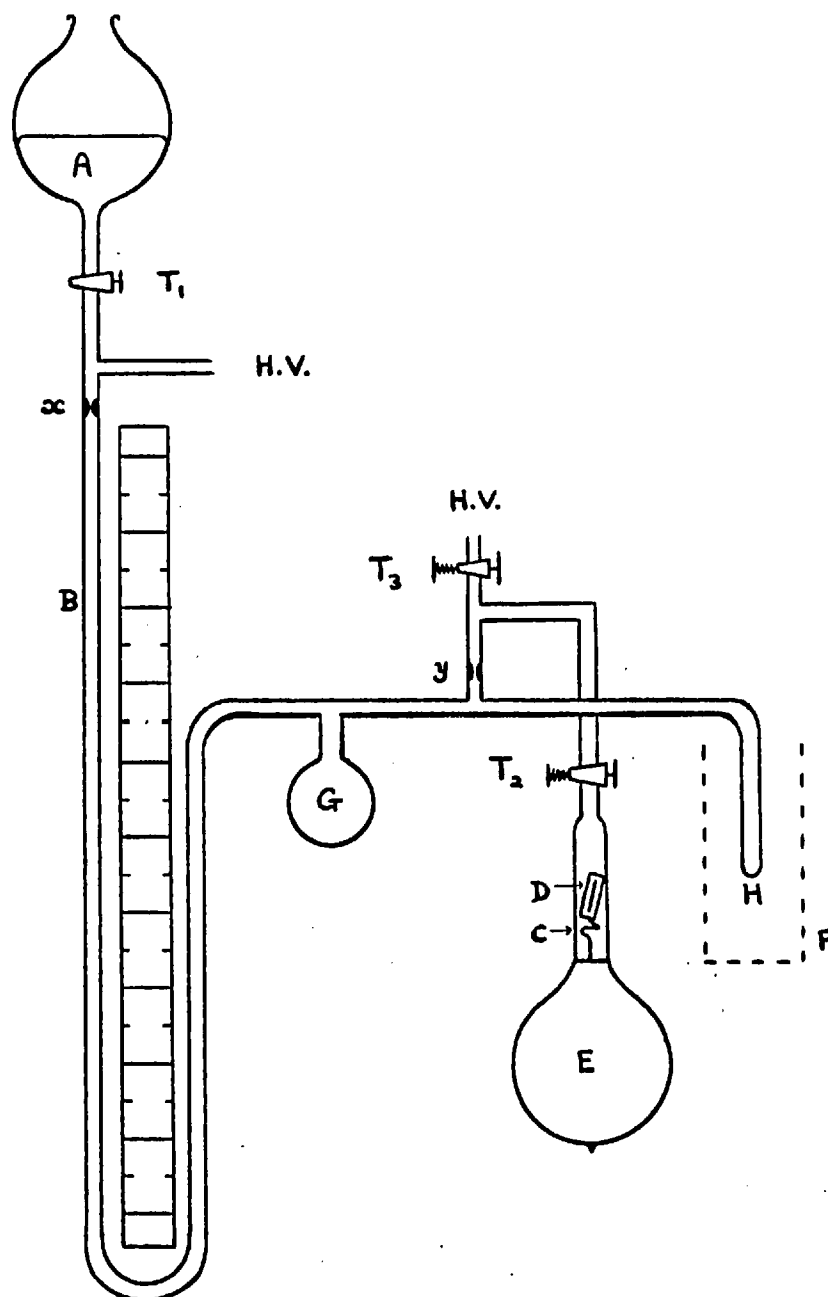
Standard tables (133,134) of vapour pressures and corresponding temperatures were used.

The temperature, when employing vapour pressure thermometers, was controlled to better than $\pm 0.05^{\circ}\text{C}$, the mercury menisci being viewed with a cathetometer to avoid parallax errors; the mercury in glass thermometers were accurate to within $\pm .005^{\circ}\text{C}$.

3.2.7. Vapour Pressure Thermometers - Construction:

The apparatus as shown in figure 12 was attached to a high vacuum pumping system (H.V.) and pumped for several days, flaming the glass tubing periodically. Tap T_1 was then carefully opened and mercury from the reservoir (A) slowly admitted to the U-tube (B) until a height of approximately 55 cms. was attained on both sides, the system still being under vacuum. The mercury was then gently boiled in situ by carefully flaming the U-tube so as to free entrained bubbles and dissolved air. When a pressure of 10^{-6} was attained and maintained thus overnight, the spring loaded tap T_2 , was closed, and the internal seal (C) to the bulb of ethylene (E) (99.9% purity, supplied by N.C.L.) broken with the magnetic weight (D). Tap T_3 (also spring loaded) to the high vacuum pumping system, was closed and T_2 opened. This resulted in a pressure of approximately 60 cm.Hg. A liquid oxygen cold trap (F) was placed around tube (H) for about eight seconds and tap T_2 immediately closed. Removal of the cold trap allowed the ethylene to evaporate so forming a pressure of approximately 88 cms.Hg. Upon sealing off at the constrictions x and y, performed when all the ethylene had been frozen out in tube (H), the gas previously occupying the tubing between y, T_3 and T_2 when released into the thermometer resulted in a final pressure of

FIGURE 12 **VAPOUR PRESSURE THERMOMETER.**



(for alphabetical notations - see text)

about 91 cm.Hg.

The vertical columns of the U-tube were of 7mm. bore Veridia tubing for accurate pressure readings, the height differences being measured with a steel rule calibrated in 0.5 mms. divisions, and viewed with a cathetometer. For the lowest temperatures (-150°C), the height difference is only 1.49 cm., so a cathetometer was used on these occasions to actually measure the height difference.

The purpose of the bulb (G) - capacity 100 cc., is to increase the volume of ethylene so that upon cooling, liquefaction occurs and not just a mere contraction of the gas. The CO_2 vapour pressure thermometer was constructed in an identical manner, the gas being obtained from a cylinder; it was purified by repeated fractional distillations between liquid oxygen and nitrogen cold traps.

3.2.8. Procedure for construction of Adsorption Isotherms:

Isotherms in the temperature range 25°C to -100°C did not require the use of the McLeod gauge. At lower temperatures however, it was found advantageous to employ the extra volume resulting from use of the McLeod gauge, in order to introduce a sufficiently large initial dose of gas to the sample. After serving this purpose, the tap to the McLeod gauge was usually

closed, the volume of gas so removed from the system being subtracted from the total. The chief use of the Mcleod gauge was, of course, for the very low pressure measurements. The method of use adopted was as follows; when equilibrium was achieved, a point decided upon when the mercury meniscus of the manometer as viewed through the cathetometer did not move for at least ten minutes, and at least thirty minutes after the last addition of gas, the distance between the mercury meniscus and the fixed mark of the manometer (MM, see figure 9) was determined with the cathetometer. The tap to the sample being closed, as it was when all pressure readings were made, the mercury in the Mcleod gauge was raised until it reached one of the fixed marks (M1 to M5), the height of the adjacent column exceeding the former by at least 10 cm. This height difference was accurately measured with the cathetometer which was also used to determine the barely readable pressure in the manometer. These two pressures were added (p_1) and using the expression $p_1v_1 = p_2v_2$ (ideality of gas assumed, at constant temp.), the actual pressure (p_2), of the system was calculated. (v_1 = volume to chosen mark of Mcleod gauge, and (v_2) = total volume of Mcleod gauge, i.e. the volume of gas enclosed when the Hg level is raised initially. The range of pressures thus measured was

ca. 0.03 cm. to 0.5 cm. Hg.

At -150°C , as many as eight consecutive pressure readings were taken with the McLeod gauge up to 0.5 cm. Hg, at which point, the tap to the gauge was closed and succeeding pressures (up to ca. 3 cm. Hg.) determined with the manometer. However, after such a series of pressure measurements, which took between 1 and 2 days, it was considered that any cumulative errors so far incurred would be magnified in the isotheric heat curves which were to be calculated from these isotherms. Since the region of pressures, 1 mm. to 3 cm. proved to be the most important in this respect, this region was invariably repeated. For the temperature -140°C , only a few pressure measurements were made with the McLeod gauge, and at even higher temperatures, (-130°C and -120°C), pressure measurements could be made directly with the manometer, only using the McLeod gauge to supply a large enough initial dose to the sample.

Further doses had to be added between each pressure reading until a value of ca. 5 cm. Hg. was attained, at which point, the gas burette became operative. By raising the mercury reservoir, attached to the gas burette by means of a flexible polythene tube, the level of mercury could be raised (or lowered) to any of the fixed and calibrated marks of the gas

burette. The function of the gas burette was therefore simply to avoid having to add a new dose between successive readings in the high pressure range.

Desorption points were obtained by simply opening the taps to the gas reservoir, and allowing a certain amount of gas to be withdrawn from the doser volume, the exact amount being calculated by measuring the pressure of gas in the doser volume before and after the removal.

The room temperature was maintained as near constant as possible throughout the pressure readings, especially when using the Mcleod gauge, and a correction was made for the temperature of the gas between the room temperature section of the apparatus, and the gas in the sorption cell itself, (See length Z in figure 11).

3.2.9. Corrections for Thermal Transpiration:

Since the temperature of the sample in the cryostat and that of the volumetric system, differed by as much as 175°C . during some sorption runs, and the diameter of the neck of the sample tube over which this difference existed was only of the order of 2 mm., it was found necessary to apply corrections for thermal transpiration. This allowance must be made because the pressure in the sorption cell is actually less than in the rest of the sorption system. The true equilibrium pressure ($p_{\text{tmm.Hg}}$) in the sample cell, was

shown by Liang (135) to be :

$$p_t = p_m \left(1 - \frac{1 - (T_1/T_2)^{\frac{1}{2}}}{\alpha_{He} \phi_g^2 p_m^2 D^2 + \beta_{He} \phi_g p_m D + 1} \right)$$

where p_m = measured pressure (mm. Hg)
 T_1 = temperature of sample ($^{\circ}$ K)
 T_2 = " " volumetric sorption system ($^{\circ}$ K)
 D = internal diameter of tube over which thermal gradient occurs (mm.)
 α_{He} = constant for reference gas (136) (= He = 2.52)
 β_{He} = $7.68(1 - (T_1/T_2)^{\frac{1}{2}})$
 ϕ_g = pressure shifting factor of adsorbate ($\phi_A = 2.93$) ($\phi_{Kr} = 3.84$).

Although the correction is very small (of the order of 1 - 2%), it is considered significant enough to apply for the low pressure (McLeod) readings, as in the argon/ 90° K and krypton/ -150° C systems.

3.2.10. Sorption of Argon:

Sorption runs for the system NaX/argon were conducted at the following temperatures: -100° , -70° , -40° , 0° , $+25^{\circ}$ C, and for purposes of comparison of saturation capacities between the standard and irradiated samples, 90.19° K.

It was initially considered that the system NaX/argon, would provide data for isosteric heat curves over a wide range of θ . Since the boiling point of argon is -186° C, isotherms at temperatures below 100° K would have been necessary to obtain values of θ as high as 0.9. The experimental difficulties encountered in maintaining such low temperatures are considerable, so

the change was made to sorption of krypton; this gas has a boiling point of -153°C , hence sorption at temperatures as low as -150°C would provide data up to a degree of saturation of ca. $\theta = 0.95$.

3.2.11. Sorption of Krypton:

Various comparatively low temperature sorption runs were conducted with the system NaX/Krypton to attempt to establish the value of the isosteric heat of adsorption on the most energetic sorption sites; these were at the following temperatures :-

-100, -90, -70, -40, 0, + 25°C .

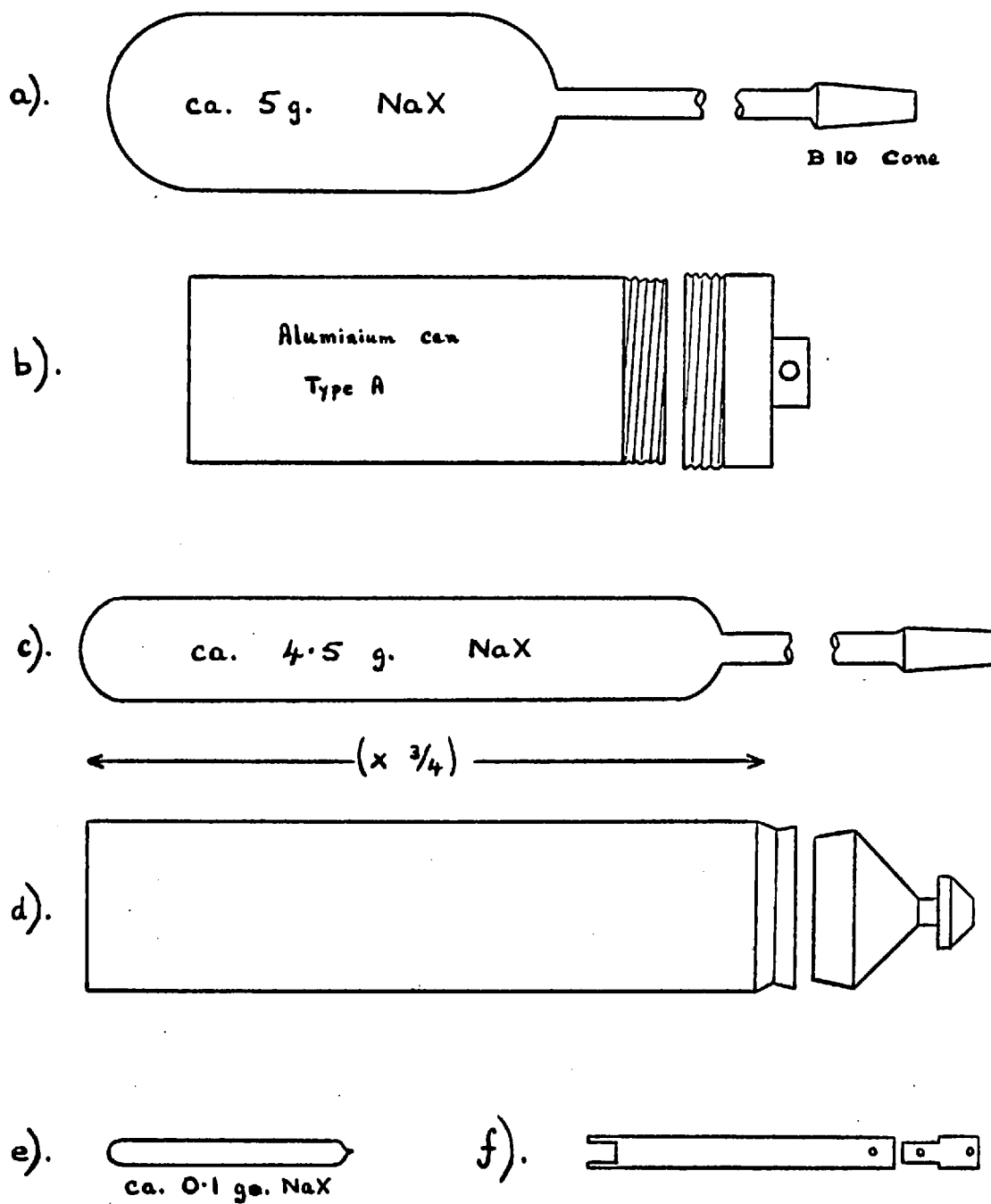
However, most attention was given to the sorption runs in the temperature range - 120° to - 150°C , since these provided the data to which the various limiting isotherm models could be applied. Great care was necessary in constructing these isotherms in order that accurate isosteric heat data could be calculated. The most significant portion of each isotherm (-120 to -150°C) was in the pressure range 1 - 10 cm.Hg, hence for each isotherm, this was usually repeated. The Mcleod gauge was employed to measure all pressures less than 0.3 cms.Hg, the manometer being used for higher pressures. The isotherms were constructed up to as high a pressure as possible with this apparatus, in order to reduce the errors in the calculation of saturation capacities, (See section 4.2.4.). The sorption runs at 25°C were used to compare the effects of radiation.

3.3.NEUTRON IRRADIATION.3.3.1. Preparation of Samples for Irradiation:

Approximately 5g. of NaX were sealed into silica ampoules. The first two samples were not dehydrated; they contained structural water, about 25% by weight, which appeared during irradiation, to be radiolytically decomposed, as upon unsealing the ampoules, a slight pressure was observed. It was estimated to be between one and two atmospheres and considered to be due to the presence of hydrogen and oxygen. Subsequent samples were therefore dehydrated at 350°C under a vacuum of 10^{-6} mm.Hg. (see standard outgassing procedure, vide section 3.2.1.). They were sealed under vacuum and thermally cycled between room temperature and 120°C for two days.

The silica ampoules used were of the dimensions shown in fig. 13a, and these were contained in standard A.W.R.E. aluminium irradiation cans of the type shown in 13b. Later samples, irradiated in the core of "Herald", required the use of silica ampoules of the dimensions shown in fig. 13c, with corresponding irradiation cans, 13d. All the silica ampoules were constructed with long necks and B 10 ground silica cones, in order that they could be fitted directly to the outgassing system. After outgassing they were sealed off at the base of the neck.

Further samples could not be irradiated at Aldermaston due to a 'shut-down' of "Herald". Facilities

FIGURE 13AMPOULES AND IRRADIATION CANS

(actual sizes)

were available however at Harwell in the "Pluto" reactor. Only very small irradiation cans were used, see figs. 13e and 13f, and in these the zeolite powder was tightly packed into thin walled silica ampoules. The powder, which had been thoroughly outgassed, was transferred to the silica ampoules in a dry box. These were attached to the pumping system by means of a short length of polythene tubing, evacuated down to about 1 mm.Hg pressure to facilitate their sealing which was then carried out, ensuring that the resulting ampoule fitted into the aluminium can. Each ampoule contained approx. 0.1g. of dehydrated powder, and in all six samples were prepared. These were suspended in the "Pluto" reactor in 2 groups of 3, in alternate positions with 3 dosimeters containing nickel wire.

3.3.2. Details of Neutron Irradiations:

Each of the 9 samples irradiated will now be discussed in as much relevant detail as supplied by the reactor groups of the U.K.A.E.A.

In-pile irradiations obviously include the effects of fast neutron bombardment, and at the same time effects due to slow neutrons and gamma rays. A considerable loss in the total flux results if an attempt is made to absorb the slow neutrons, and anyway in the separation of fissile material and radioactive materials in general by ion exchange, the exchanger would be subject to all types of radiation simultaneously. However an attempt was made initially to absorb thermal neutrons by cladding the ampoules

with cadmium foil, but this became impracticable when the samples were placed in the reactor core, for two reasons: (a) the cadmium would attain too high a temperature, and (b) the amount of cadmium would have affected the neutron flux by too great a degree for reactor safety regulations.

Upon removal from the reactor, all samples were allowed to 'cool' over a period of one week, this being sufficient for all the expected activities to have decayed to an inappreciable level. All samples were however monitored upon return, with a Dynatron Monitor unit, type 1021 C, (see section 4.3.).

The following notations have been employed throughout to describe the samples of NaX: superscript [✱] refers to irradiated but undamaged samples, and superscript ^{✱✱} refers to damaged samples, i.e. those which were observed to suffer a loss in sorptive capacity (section 4.2). The standard samples are denoted by the superscript ⁰.

SAMPLE 1: (NaX₁[✱]) This was irradiated in the fast flux of "Herald" at Aldermaston for 5 days. Measurement of the fast flux in the G2C beam plug showed it to be approx. 8.1×10^{10} n/cm²./sec. and consequently for a 5 day irradiation period, the integrated neutron flux was 3.5×10^{16} n/cm², averaged over the fission neutron spectrum. The dose measurements were made employing the S_{16}^{32} (n,p) P_{15}^{32} and Ni_{28}^{58} (n,p) Co_{27}^{58} transmutations; a nickel wire included with the samples agreed with the dosimetry measurements. This was one of the samples which had not been outgassed prior

to the irradiation, and which subsequently 'exploded' upon unsealing.

SAMPLE 2: (NaX_2^{H}) The procedure was identical with that for sample 1. The irradiation time was 15 days, resulting in a total integrated neutron flux of approx. $1.1 \times 10^{17} \text{n/cm}^2$.

SAMPLE 3: (NaX_3^{H}) All samples from no. 3 onwards were outgassed before irradiation, by the procedure given in section 3.2.1. This sample was irradiated in "Bepo" at Harwell, to a total dose of approx. $1.1 \times 10^{18} \text{n/cm}^2$.

SAMPLE 4: (NaX_4^{H}) Samples 4, 5 and 6 were all irradiated in "Herald" at Aldermaston, in the reflector or core. Sample 4 received a dose of $6.2 \pm 0.6 \times 10^{17} \text{n/cm}^2$, in the reflector.

SAMPLE 5: (NaX_5^{H}) This sample was irradiated to a total dose of $6.0 \pm 0.6 \times 10^{18} \text{n/cm}^2$, in the reactor core.

SAMPLE 6: (NaX_6^{H}) This sample was irradiated to a total dose of approx. $7 \times 10^{19} \text{n/cm}^2$, also in the core.

SAMPLE 7: (NaX_7^{H}) Samples 7, 8 and 9 were all irradiated simultaneously in "Pluto". Facilities were only available for the irradiation of very small quantities of sample, approx. 0.1g. of zeolite per ampoule, of which there were six. The two ampoules receiving the largest doses, approx. 1.75 and $1.98 \times 10^{19} \text{n/cm}^2$. were mixed and constituted sample 7. The dose was taken as the average, $1.9 \times 10^{19} \text{n/cm}^2$.

SAMPLE 8: (NaX_8^{H}) This sample resulted from mixing

the contents of the two ampoules irradiated to doses of 1.24 and $1.32 \times 10^{19} \text{n/cm}^2$, the average dose being taken as $1.3 \times 10^{19} \text{n/cm}^2$. Due to the small amounts of zeolite irradiated, it was considered best for this sample to be employed entirely for cation exchange studies, hence no sorption data is available for this sample.

SAMPLE 9: (NaX_9^{XX}) Unfortunately one of the six ampoules was crushed, either upon removal from the reactor or during transit. Sample 9 therefore consisted only of the sample irradiated to a dose of $6.6 \times 10^{18} \text{n/cm}^2$. Since there was such a small amount of zeolite, and since also the previous samples, numbers 6, 7 and 8 had been irradiated to higher doses, sample 9 was not therefore used for sorption or cation exchange experiments.

PART 4

RESULTS AND DISCUSSION.

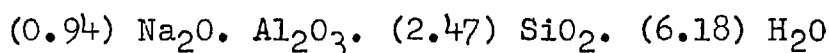
<u>SECTION</u>	<u>PAGE</u>
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4.3. <u>NEUTRON IRRADIATION</u>	233

4.1.CATION EXCHANGE4.1.1. Results of Analyses: NaX.

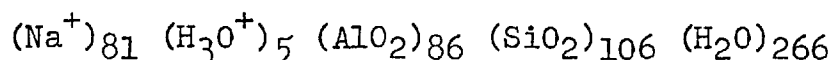
The samples of zeolite employed for analysis were obtained from the stock supply equilibrated with water vapour over a saturated solution of ammonium chloride, at room temp. The method of analysis has been described in section 3.1.1. Four analyses were carried out, the percentage weights of the constituents listed below being the average of these values. The % Na₂O was determined twice by difference and twice by the radiochemical method (vide section 3.1.4.).

<u>Na₂O</u>	<u>Al₂O₃</u>	<u>SiO₂</u>	<u>H₂O</u>
13.8%	24.3%	35.4%	26.6%

The oxide formula of NaX may therefore be written as:-



Electroneutrality within the framework of the zeolite is achieved by the presence of a counter-ion, in this case Na⁺, for every aluminium atom. There should therefore be an equal number of Na⁺ ions and aluminium atoms; the above formula shows the deficiency of Na⁺ ions in this sample, a deficiency which is assumed to be made up by the presence of an appropriate number of hydronium ions (H₃O⁺), (see section 1.0.). The formula may then be written as:-



which gives the ratio of SiO₂ to Al₂O₃ as 106 to 86; this is within the specified limits for the zeolite type "X". A table of the various ratios of constituents of different

samples of NaX, employed by other workers, is given in section 1.0. The above formula is the unit cell formula of NaX; there are thus 86 cations occupying 8 supercages, 8 sodalite cages and 16 interconnecting hexagonal prisms. The discussion in section 1.0. describes the positions or sites occupied by these cations within the lattice. Reference will only be made here to the 16 Na^+ ions per unit cell which occupy the hexagonal prisms; they enter these prisms via the sodalite cages through 6-membered oxygen rings of free diameter 2.2 Å, the small diameter of the sodium ions making this possible. However, ions as large as Cs^+ , Ba^{++} , and UO_2^{++} cannot pass through these windows and hence will not be able to exchange with these particular Na^+ ions. This fact therefore imposes a maximum of 81% ($=70/86$) on the degree of ion exchange possible in NaX, a maximum not achieved by any of the systems studied (see section 4.1.7.).

X-ray powder photographs of several partially exchanged forms of NaX were identical to those for the standard synthetic sample, thus indicating that no damage resulted from exchange in mildly acid solutions.

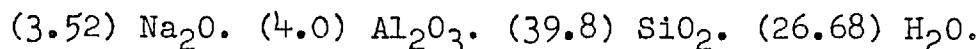
Results of Analyses of Mordenite:

Although this sample is referred to as mordenite, it is in fact the synthetic counterpart of the naturally occurring mineral. It is known commercially as "Zeolon", (Na^+ form). The bulk sample was stored over a saturated solution of NH_4Cl at room temperature, and the methods of

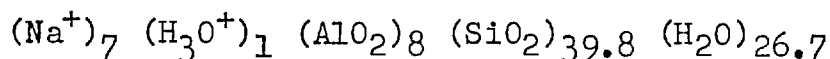
analysis are described in section 3.1.1. Two samples were analyzed and the average results are expressed as % weights:

$\frac{\text{Na}_2\text{O}}{6.3\%}$	$\frac{\text{Al}_2\text{O}_3}{11.8\%}$	$\frac{\text{SiO}_2}{68.9\%}$	$\frac{\text{H}_2\text{O}}{13.9\%}$
-------------------------------------	--	-------------------------------	-------------------------------------

The oxide formula may therefore be written as:



The cation deficiency, as with NaX, was assumed to be counterbalanced by the presence of hydronium ions. The formula may also therefore be written:



The high $\text{SiO}_2 / \text{Al}_2\text{O}_3$ ratio of 10 : 1 is partly responsible for the high stability of mordenite compared with other zeolites.

Of the 8 sodium ions per unit cell, only 4 have been definitely located (13), the others being assumed to be randomly distributed within the large channels of the lattice. Those which have been located, lie in the windows (free diameter 2.8 Å) of the channels of about 4 Å diameter, which connect the wider channels (6.6 Å). Complete ion-exchange should therefore be possible with any univalent cation of diameter not exceeding 4 Å; cations larger than this are unable to replace these 4 Na^+ ions, thus imposing a maximum exchange of 50% on systems involving such large ions.

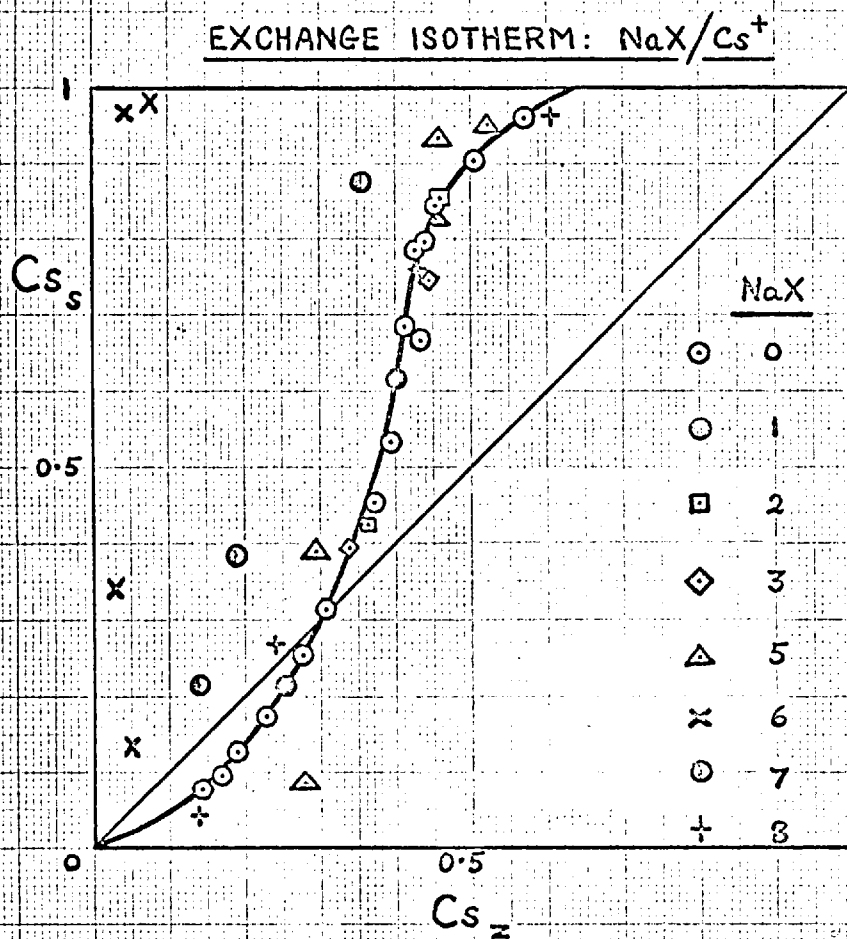
X-ray powder photographs of the standard synthetic sample and several partially exchanged (with Cs^+ and Ba^{++}) forms of mordenite, were identical, indicating no decomp-

osition resulting from the exchange in mildly acid solutions. Due to the high silica to alumina ratio (10 : 1), mordenite is very much more stable than NaX (ratio: 2.5 : 1).

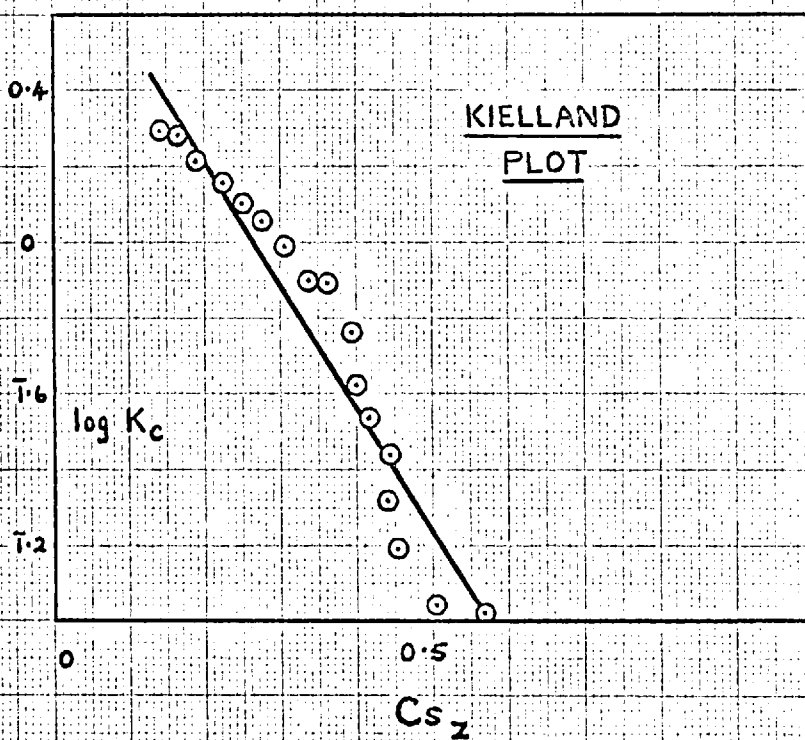
4.1.2. The NaX / Cs⁺ Exchange System:

Figure 14 a shows the exchange isotherm constructed for this system, by exchanging varying weights of NaX with aliquots of caesium chloride solution of known concentration. The Cs⁺ tracer ion was determined by the counting technique (vide section 3.1.4.). The terms Cs_s and Cs_z, represent the equivalent fractions of Cs⁺ ion in the solution and exchanger phase respectively. The isotherm is initially convex to the Cs_z axis (abscissa) indicating that the zeolite displays a greater affinity for the Cs⁺ ion. However the reverse applies beyond Cs_z = 0.3.

Complete exchange was not possible even with high concentrations of CsCl solutions, exchanged over a period of weeks. Obviously then, not all of the sodium ions in the NaX lattice can be replaced by the relatively large Cs⁺ ions. Maximum exchange corresponds to between 60 and 65% of the total number of cations per unit cell. Previous work with a different sample of NaX resulted in 58% exchange (8). It is interesting to attempt an explanation concerning the remaining 35 - 40% of the Na⁺ ions. These non-exchangeable cations are not confined to the 16 Na⁺ ions per unit cell, occupying the small hexagonal prisms, because out of the total of 86 cations per unit cell, this only accounts for 19%.



FIGURE

14 a

FIGURE

14 b

It must be assumed then that some of the Na^+ ions lying in the sodalite cage windows are also non-exchangeable; (see also section 4.1.7.).

Figure 14 b shows the linear Kielland plot of $\log K_c$ vs. Cs_Z from which a value of K_a , the thermodynamic equilibrium constant, is obtainable when $\text{Cs}_Z = 0.5$; (see below). K_c was calculated from the expression (no. 18) given on page 63. The ratio $\gamma_B / \gamma_A = \gamma_s$ used in this expression, was found to be constant, 1.02, for all the equilibrium molalities of these experiments (see p. 61). Using the expression:

$$\log K_a = \log K_c + C(1 - 2A_Z) \quad (17)$$

when $A_Z (= \text{Cs}_Z) = 0.5$, then $\log K_a = \log K_{c\frac{1}{2}}$

$$\therefore K_a = K_{c\frac{1}{2}} = 0.173$$

The standard free energy of exchange $-\Delta G^\circ$ is given by:

$$\begin{aligned} \Delta G^\circ &= - \frac{RT \cdot \ln K_a}{z_A \cdot z_B} \\ &= 1.04 \text{ k.cal./g.equivalent} \end{aligned}$$

The activity coefficients of the components in the exchanger phase are given by the Kielland relationships:

$$\begin{aligned} \log f_{AZ} &= C \cdot B_Z^2 = C \cdot \text{Na}_Z^2 \\ \log f_{BZ} &= C \cdot A_Z^2 = C \cdot \text{Cs}_Z^2 \end{aligned} \quad (16)$$

C being obtained from the slope of the Kielland plot, which equals $2C$;

$$\begin{aligned} \therefore \log f_{\text{CsX}} &= -1.6 \text{ Na}_Z^2 \\ \text{and } \log f_{\text{NaX}} &= -1.6 \text{ Cs}_Z^2 \end{aligned}$$

EXCHANGE ISOTHERM: MORDENITE / CS^+

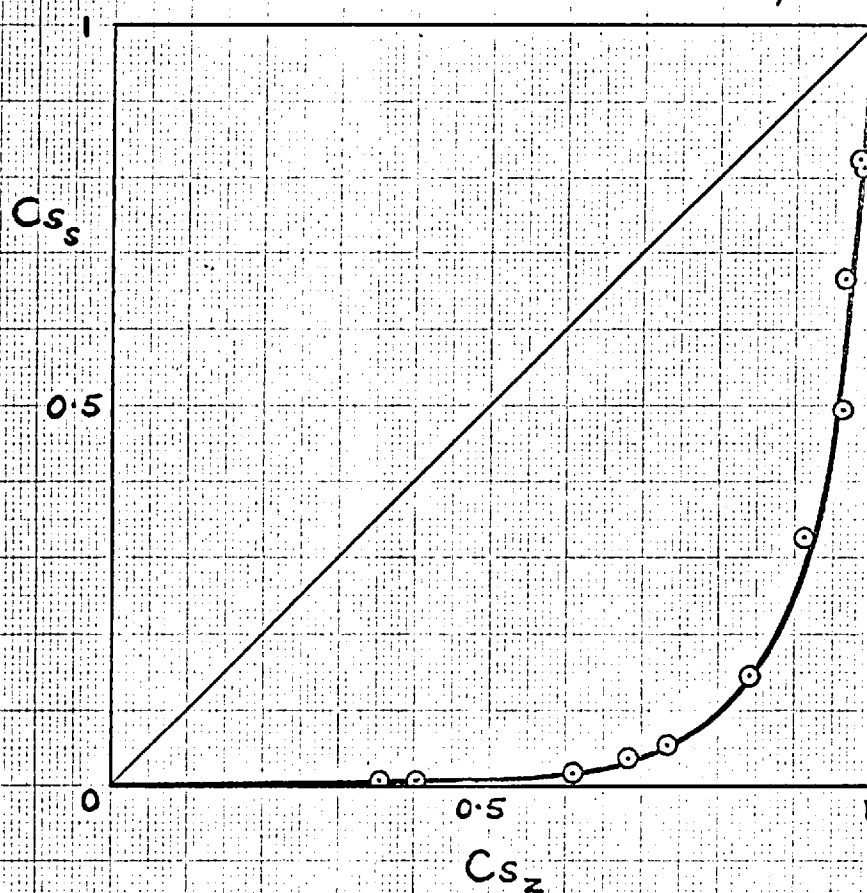


FIGURE
15 a

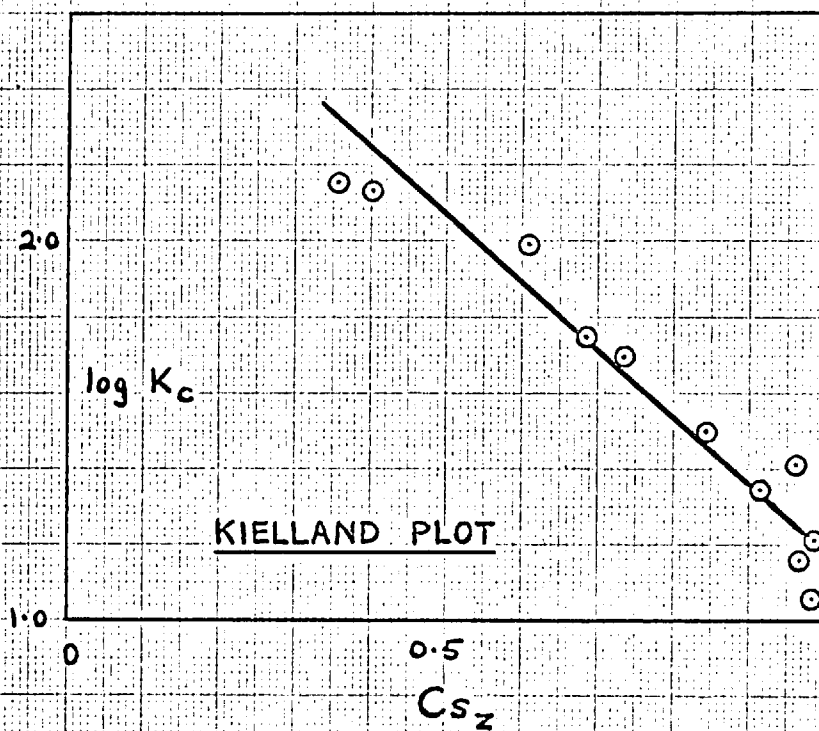


FIGURE
15 b

4.1.3. The Mordenite / Cs^+ Exchange System:

Figure 15 a shows the exchange isotherm constructed for this system. Complete exchange of Cs^+ ion for Na^+ is possible, and from the shape of the curve, it is obvious that mordenite exhibits a very strong selectivity for the Cs^+ ion, (see also section 4.1.7.).

Figure 15 b shows the linear Kielland plot of $\log K_c$ vs. Cs_Z , K_c being calculated from equation 18. When $A_Z = \text{Cs}_Z = 0.5$, the thermodynamic equilibrium constant K_a is calculated from equation 17, whence $K_a = 117.5$. The standard free energy $\Delta G^\circ = -2.83 \text{ k.cal. /g. equ.}$ The activity coefficients of the components in the exchanger phase are given by:

$$\begin{aligned}\log f_{\text{CsZ}} &= -0.89 \text{Na}_Z^2 \\ \log f_{\text{NaZ}} &= -0.89 \text{Cs}_Z^2\end{aligned}\tag{16}$$

4.1.4. The NaX / Ba^{++} Exchange System:

Figure 16 a shows the exchange isotherm constructed for this system. Complete exchange is impossible, the maximum achieved after several weeks of exchange and percolation amounting to only 74%. Initially the zeolite exhibits a very strong selectivity for the Ba^{++} ion, as illustrated by the rectangular nature of the isotherm.

Since maximum exchange corresponds to 74%, i.e. only 74% of the sodium ions in the NaX lattice are exchangeable by Ba^{++} ions, the zeolite at this stage of exchange must be regarded as the pure form of " BaX_2 "; the fact that

EXCHANGE ISOTHERM: $\text{NaX}/\text{Ba}^{++}$

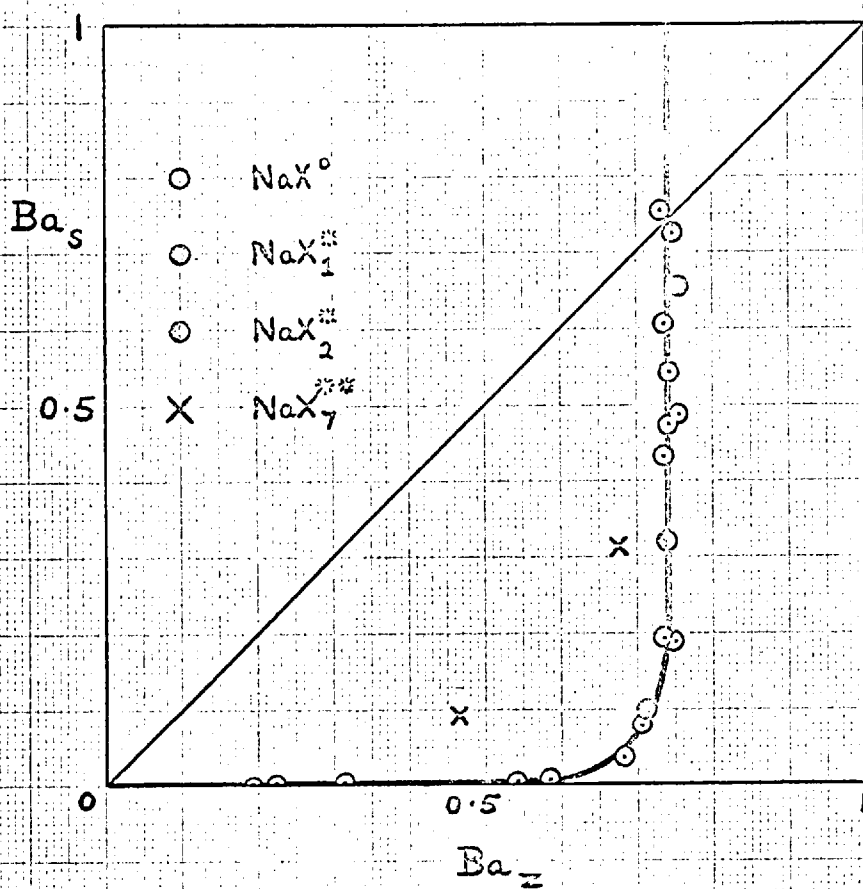


FIGURE
16 a

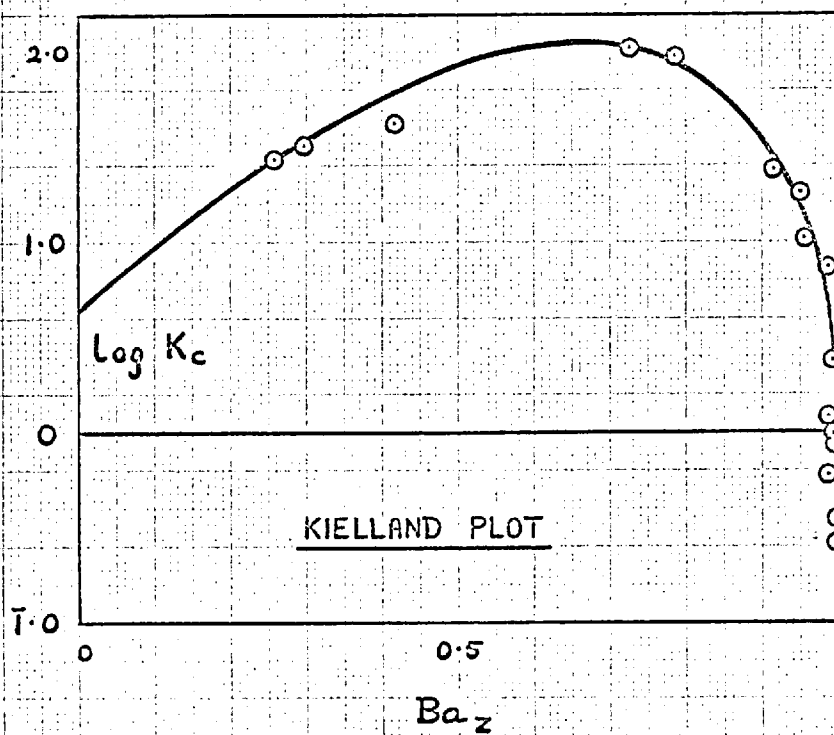


FIGURE
16 b

some Na^+ ions still occupy sites in the lattice will be ignored. Consequently, the exchange isotherm could be 'converted' to represent a maximum exchange of 100% by multiplying all the experimental Ba_Z values by $1/0.74$, i.e. the reciprocal of the observed maximum exchange. This practise was adopted by Ward (7). However, it is considered more appropriate here to display the exchange isotherm exactly as observed, and only make the above corrections in order to calculate the value of K_a etc.

Figure 16 b shows the Kielland plot of $\log K_c$ vs. Ba_Z . Since to calculate the value of K_a , the thermodynamic equilibrium constant, we require to solve the integral in expression 21 on p. 66, the values of $A_Z = \text{Ba}_Z$ determined experimentally have accordingly been 'adjusted' so that the curve cuts both vertical axes, i.e. when $A_Z = 0$ and 1. Calculation of K_c requires the use of the Glueckauf expressions (eq. 12 and 13) as shown in section 2.1.3., p. 62. Graphical integration then gives:

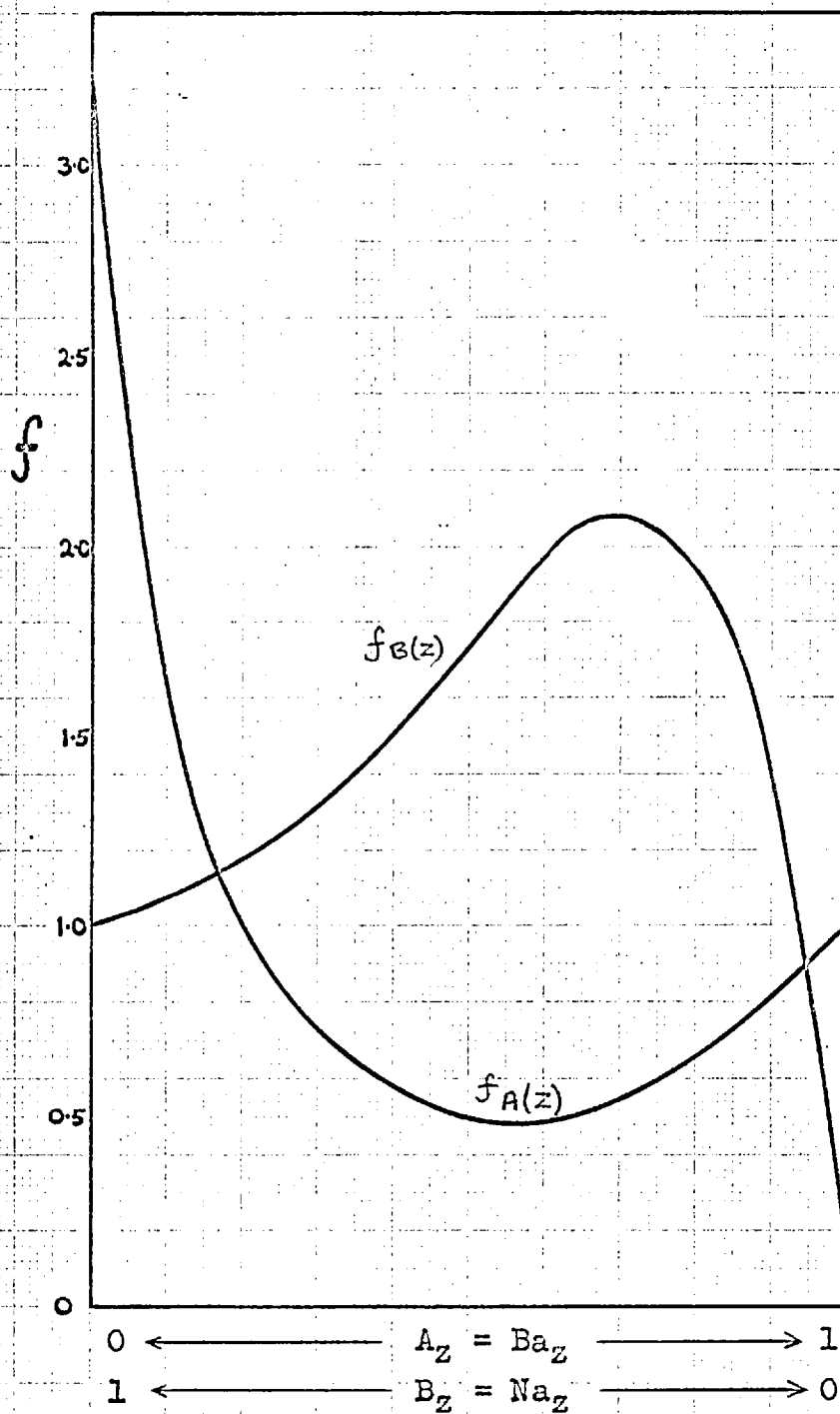
$$\begin{aligned}\ln K_a &= z_B - z_A + (1.59 \times 2.303) \\ &= 2.67 \\ \therefore K_a &= 14.4\end{aligned}$$

The standard free energy of exchange is then:

$$\Delta G^\circ = - \frac{RT \ln K_a}{z_A \cdot z_B} = -0.79 \text{ k.cal./g.equ.}$$

The activity coefficients in the exchanger phase were evaluated using the expressions 19 and 20, p. 65. As shown in figure 16 c, the activity coefficient of the

VARIATION OF ACTIVITY COEFFICIENTS
OF PURE COMPONENTS A(Z) and B(Z),
IN THE MIXED EXCHANGER PHASE.



FIGURE

16 c

Equivalent Cation Fraction

pure component A(Z), passes from unity, corresponding to $A_Z = 1$, through a minimum at $A_Z = 0.55$; and the activity coefficient for pure B(Z) passes from unity, corresponding to $B_Z = 1$, through a maximum at $B_Z = 0.3$. (As defined earlier, the pure form of the zeolite, i.e. $A(Z)_{Z_A}$, corresponds to NaX with 74% of the Na^+ ions replaced by Ba^{++} .) If the exchange equilibrium measurements were conducted in solutions of infinite dilution, then the exchangers would be in their standard states. Therefore in eq. 19 and 20, $f_{A(Z)}$ may be replaced by $f_{A(Z)}^0$.

4.1.5. The Mordenite / Ba^{++} Exchange System:

Figure 17 a shows the exchange isotherm constructed for this system. Complete exchange is impossible, the maximum achieved after several weeks of percolation amounting to approx. 72%. This isotherm is very similar in shape to that obtained for the NaX / Ba^{++} system, but the discussion in section 4.1.7. shows this to be purely coincidental, as the structures of NaX and Mordenite are significantly different.

Figure 17 b shows the Kielland plot of $\log K_c$ vs. Ba_Z , which like that for NaX / Ba^{++} has been 'adjusted' so as to cut both vertical axes, i.e. when $A_Z = 0$ and 1. Each experimental value of Ba_Z was multiplied by the reciprocal of the value of maximum exchange, i.e. $1/0.72$. Graphical integration then gives the values: $K_a = 1.14$ (21) and $\Delta G^0 = -77 \text{ cal./g.equ.}$

EXCHANGE ISOTHERM: MORDENITE / Ba^{++}

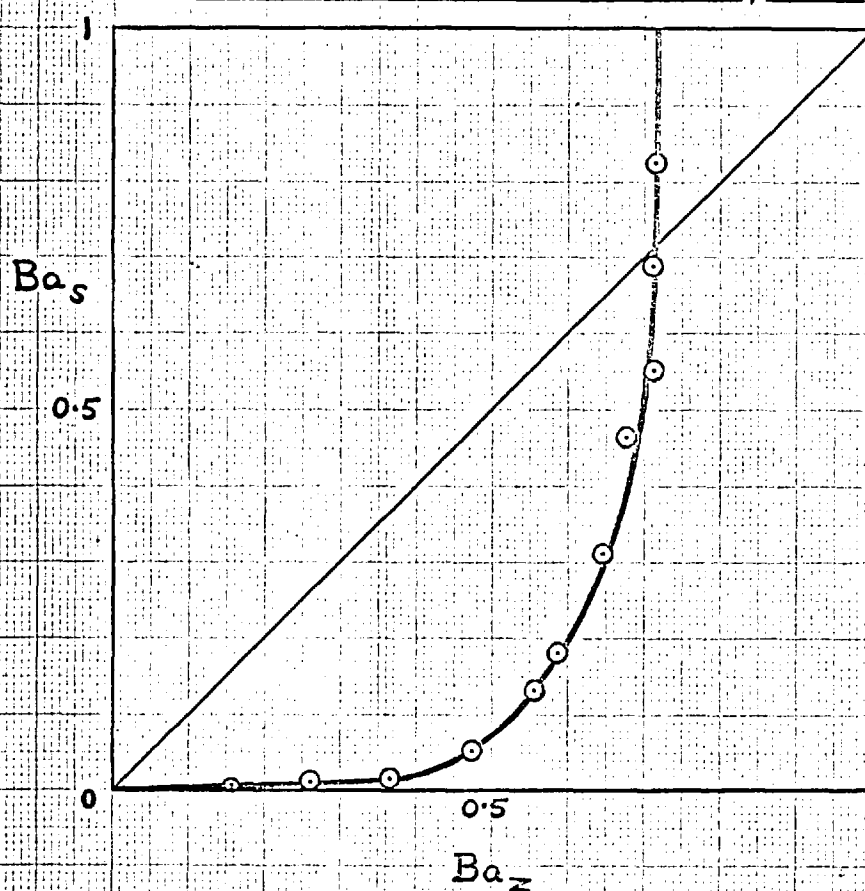


FIGURE
17 a

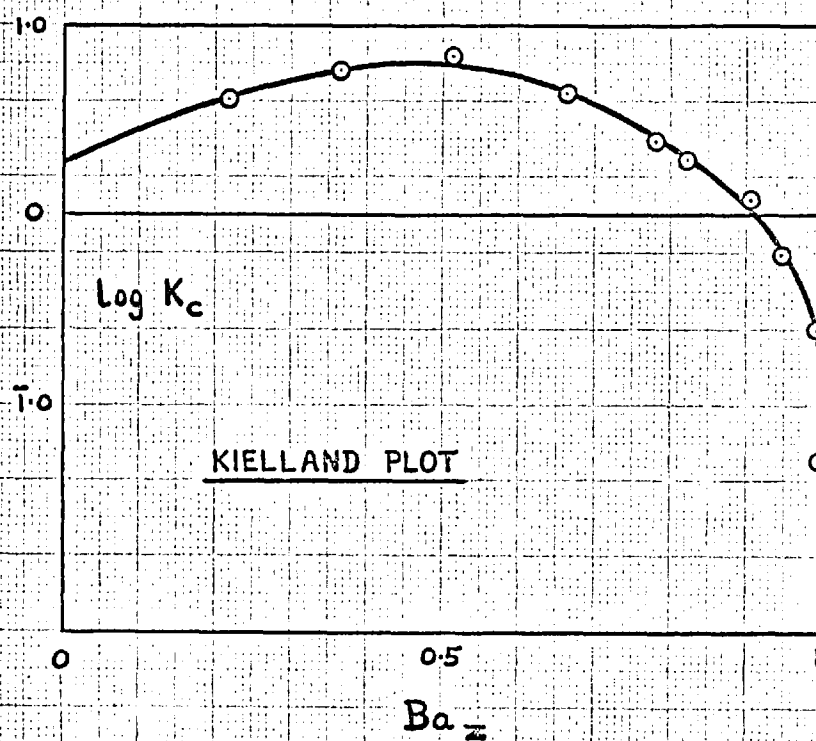


FIGURE
17 b

KIELLAND PLOT

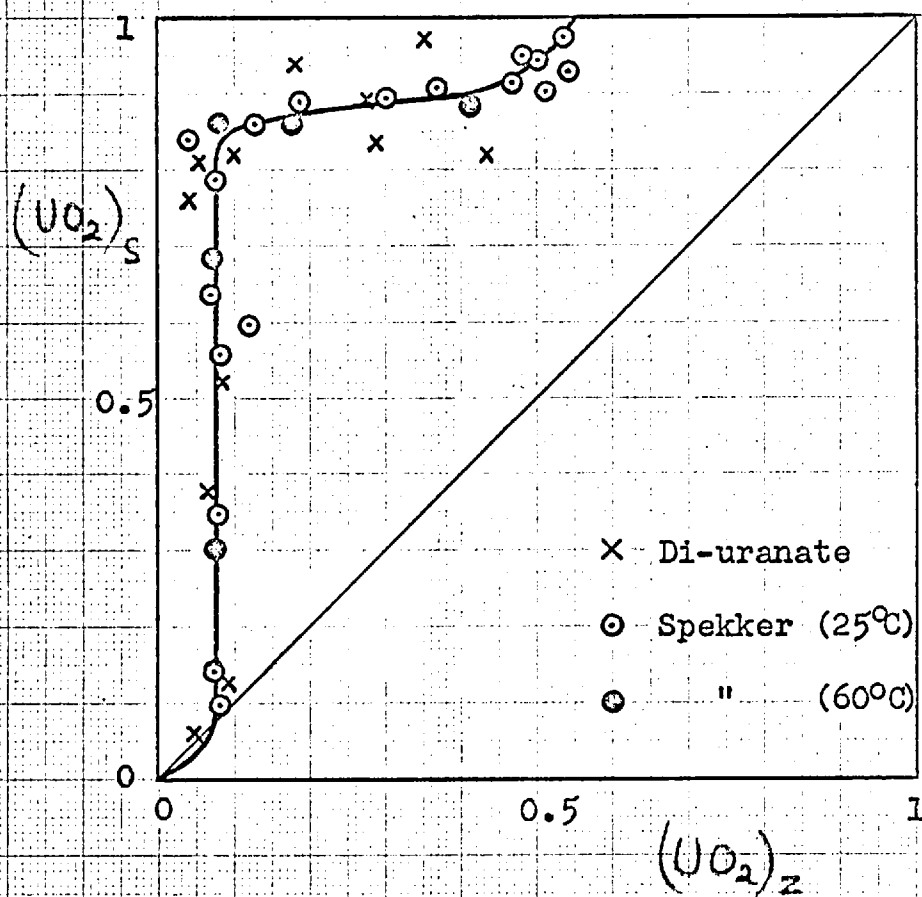
4.1.6. The NaX / UO_2^{++} Exchange System:

This system was studied to determine the selectivity shown by NaX for such a large ion as the uranyl ion, and because such a study should be useful from the point of view of the separation of fission product mixtures which contain uranium.

The curve shown in figure 18 (crosses) represents the isotherm constructed for the NaX / UO_2^{++} system in aq. solution. Initially the exchanger displays a much greater affinity for the Na^+ ion, little uptake of UO_2^{++} occurring until the equilibrium equivalent fraction of UO_2^{++} in the solution phase exceeds 0.8. In the upper region of this isotherm, a large scatter is observed in the experimental points; this is because the relatively high concentrations of uranyl ion, required to push the exchange towards the uranyl form of the exchanger, necessitated the use of uranyl nitrate solutions of low pH, between 5 and 2. Several exchanges with such acidic solutions (pH = 2), resulted in almost completely clear solutions after exchange, indicating that the zeolite had been decomposed, (NaX is only stable in solutions of pH 5-14). Partial decomposition was suspected at lower concentrations and spot tests for aluminium (quinalizarin spot test, ref.128) often confirmed this. X-ray powder photographs of several partially exchanged forms of the zeolite (i.e. $\text{Na.UO}_2\text{.X}$) revealed that they were almost completely devoid of any crystalline material, i.e. they were amorphous in nature.

FIGURE 18

EXCHANGE ISOTHERM: $\text{NaX}/\text{UO}_2^{++}$



The exchange isotherm is therefore incomplete, and not very reproducible beyond a value of $(\text{UO}_2^{++})_s$ of 0.8, as the exchanger was always susceptible to breakdown.

To overcome the problem of the acidity of the solution, exchanges were conducted in alcoholic (ethanol) instead of aqueous solution; the zeolite was then found to be stable at all concentrations. The method of analysis for the uranyl ion was also changed at this stage, from the precipitation as ammonium di-uranate to the absorptiometric method employing the "Spekker" (vide section 3.1.5.). In figure 18, the open circles represent the isotherm obtained for the NaX / UO_2^{++} system in ethanol, at 27°C. Several exchanges were conducted at 60°C (full circles), but little effect was observed from this temp. increase, indicating negligible heats of ion exchange. The scatter of experimental points observed when employing the Spekker method of analysis, is partly explained by the errors introduced upon development of the intense yellow peruranate colour. This is achieved by the addition of H_2O_2 to the solution of uranyl nitrate, already made alkaline with Na_2CO_3 . The presence of traces of NaHCO_3 , resulting from the reaction of Na_2CO_3 with the uranium solution, or introduced as an impurity with the Na_2CO_3 , causes a diminution in the intensity of the yellow colour, due to the formation of colourless uranyl tricarbonates. This results in the experimental points being slightly displaced from the true isotherm, towards lower $(\text{UO}_2)_s$ and

higher $(\text{UO}_2)_2$ values.

As explained in section 4.1.1., maximum exchange cannot exceed 81% for ions larger than 2.5 Å in diameter. The experimental maximum for this system lies between 50 and 60%. According to Sidgwick (146), the uranyl ion probably consists of a resonance hybrid of the linear forms $(\text{O} = \text{U} = \text{O})^{++}$, $(\text{O} = \text{U} \rightarrow \text{O})^{++}$ and $(\text{O} \leftarrow \text{U} \rightarrow \text{O})^{++}$, with a length of between 4.2 Å (theor.) and 3.18 Å (expt.), (c.f. diameters of Cs^+ and Ba^{++} are 3.4 and 2.8 Å respectively). Since the uranyl ion is larger than Ba^{++} , it is not surprising that the maximum exchange is appreciably less than that observed for barium exchange of NaX.

4.1.7. General Discussion of Cation Exchange Results:

An attempt is given here, to explain the maximum degrees of exchange observed for the systems studied. In the NaX / Cs^+ system, maximum exchange results in the replacement of between 60 and 65% of the Na^+ by Cs^+ ions, whereas with Ba^{++} , 74% is the maximum. As previously explained (vide sections 1.0. and 4.1.2.) 19% of the Na^+ ions in the NaX lattice are located inside the small hexagonal prisms, which form the interconnecting links between the sodalite cages. The Cs^+ and Ba^{++} ions are too large to pass through the cage windows (2.2 Å free diameter), which provide access for the Na^+ ions to these prisms, hence complete exchange is impossible. The remaining non-exchangeable Na^+ ions therefore amount to 17% for Cs^+ ,

(= 100 - 19 - 64%), and 7% for Ba^{++} (= 100 - 19 - 74%) and also 26% for UO_2^{++} (= 100 - 19 - 55%). The unit cell of NaX contains 86 cations distributed as follows: each of the hexagonal prisms contains one ion; the 8 sodalite cages have 4 windows (facing into the supercages) in each of which 'sits' a Na^+ ion, thus accounting for 32 cations; the remaining 38 are randomly distributed throughout the supercages, amounting on average to 4.75 cations per cage. A Cs^+ ion, on entering a supercage, readily exchanges with a Na^+ ion, either one which is randomly moving about, or one 'sitting' in a window. Assuming the 4.75 cations per cage are exchanged first, we have then accounted for 4.75 out of the total of 10.75 per cage, i.e. 44%. If a Cs^+ ion then replaces a Na^+ ion in a sodalite cage window, since it is much larger than the Na^+ ion, it is reasonable to assume that it does not 'sit' so deeply in the window, i.e. it is displaced towards the supercage. A slight charge redistribution therefore occurs throughout the anionic framework of the lattice, to counteract this displaced positive charge. The net result is that the remaining Na^+ ions in cage windows are attracted more strongly by the lattice. It is nevertheless possible for the Cs^+ ion to replace one more Na^+ ion, after which further exchange is prohibited, simply because the remaining 2 Na^+ ions are too firmly attracted by the lattice. This explanation then accounts for 6.75 out of the total of 10.75 cations per supercage, i.e. 63%, as observed experimentally.

To explain the maximum of 74% exchange observed in the NaX / Ba^{++} system, we must assume that the randomly distributed cations and those in the cage windows are equally exchangeable by Ba^{++} ions. Since a Ba^{++} ion is divalent, it must replace 2 Na^+ ions, thus suggesting that it occupies an intermediate position in the lattice between 2 sodalite cage windows. If all 4 Na^+ ions on these windows are replaced in this way, subsequent exchange will occur with those Na^+ ions not located in definite sites. On average this will leave 0.75 positive charges per supercage. This explanation thus accounts for 8 out of the 10.75 ions per cage, i.e. 74%, as observed experimentally.

For the NaX / UO_2^{++} system, since the uranyl ion is much larger than Ba^{++} and may experience some steric hindrance as it is a large linear ion, it is quite possible that only 2 of the 4 Na^+ ions in cage windows, are exchanged by one UO_2^{++} ion. If further exchange occurs between 4 randomly distributed Na^+ ions and 2 UO_2^{++} ions, then the fraction of ions exchanged equals $6/10.75 = 56\%$, as observed experimentally.

The situation is somewhat different in mordenite; since 4 of the 8 cations per unit cell, are randomly distributed within the channels, these can easily be replaced by any ion small enough to diffuse ^{through} the same channels, e.g. Cs^+ , Ba^{++} . The other 4 Na^+ ions per unit cell, which have been definitely located (13), lie in the $2.8 \text{ \AA}$ windows in the $4.0 \text{ \AA}$ channels. They should all therefore be replaceable

by the Cs^+ ion to give 100% exchange, as was in fact observed. Ba^{++} exchange on the other hand, leads to the problem as to how one Ba^{++} ion can replace 2 Na^+ ions which effectively lie in neighbouring channels. Obviously a re-distribution of the anionic charge on the framework must occur if Ba^{++} ions are assumed to occupy the same sites as do the Na^+ ions. However, if we assume the Ba^{++} ions to be located in between 2 sites previously occupied by Na^+ ions, then 100% exchange should be possible; (this is quite reasonable an assumption as the distance between 2 sites is of the order of $3 \text{ \AA}$). The experimentally observed maximum was only 72%, suggesting that this simple explanation is insufficient. The Ba^{++} ions might well occupy different sites altogether; it is also possible that stacking faults (see p. 16) tend to trap individual cations, thus restricting exchange by divalent ions, but at the same time allowing complete exchange by univalent ions. Similar work with different ions, both uni- and divalent, is helping to clarify these problems (12).

4.1.8. Effects of Neutron Irradiation on the Cation Exchange Properties of NaX:

As previously mentioned in section 3.2.10. and discussed more fully in section 4.2.1., the initial expt. conducted with the irradiated specimens of NaX, consisted of the sorption of argon at 90°K . Absence of any changes in the gas sorptive properties of the zeolite due to

irradiation, was not assumed to infer the absence of any effects to the cation exchange properties. For example, movement of the cations within the zeolite lattice might have no appreciable effect on the gas sorptive properties whereas the cation exchange properties could be markedly altered. Consequently, irradiated samples were subject to various exchange experiments regardless of whether or not they displayed a change in sorptive properties.

Figures 14 a and 16 a show the exchange isotherms for the systems NaX / Cs^+ and NaX / Ba^{++} respectively. Several exchange experiments were conducted on each of the samples, numbers 1, 2 and 3, and the results are shown on these graphs. It may be concluded therefore, since they all lie on the plots for the standard sample, that either the cation exchange properties of NaX are unaffected by neutron doses up to 5×10^{17} neutrons/cm²., or that any effect lies within the experimental error. All samples irradiated to neutron doses in excess of the above value, were found to be appreciably radioactive upon return from the reactor unit, activity which did not decay completely even after several months (see also section 4.3.). Percolation with saturated NaCl solutions for several days failed to remove more than just a fraction of this activity. The following procedure was therefore adopted; the percolated samples were washed free of chloride, dried and then equilibrated with water vapour over saturated NH_4Cl aq. for several days. They were then exchanged with highly active,

equivalent quantities of Na^{22}Cl solution for 3 days at 30°C ; the resultant samples were likewise washed, dried and then equilibrated with water vapour. Samples of these materials were then exchanged in the normal way with inactive CsCl (or BaCl_2), determining the resultant Na^+ ion concentration in solution by the liquid counting technique (section 3.1.4). The results of these experiments, conducted with each of the damaged samples (damaged as far as gas sorptive properties were concerned), will now be discussed, taking the zeolites in order of increasing neutron dose. The experimental scatter observed for these experiments, figs. 14 a and 16 a, result chiefly from the use of extremely small quantities of zeolite, of the order of 30 - 50 mg. per exchange, together with extremely dilute solutions.

NaX_5^{**} : ($6 \times 10^{18}\text{n/cm}^2$): the 5 experimental points shown in fig. 14 a, lie sufficiently close to the isotherm for the standard sample, for it to be assumed that for this sample, the cation exchange capacity has not been appreciably affected.

NaX_8^{**} : ($1.3 \times 10^{19}\text{n/cm}^2$): four exchanges were conducted with Cs^+ ions (see fig. 14 a). Very great care was taken with these experiments, using between 40 - 50 mg. of NaX for each. Within experimental error, the points are almost coincident with the isotherm for the standard sample.

NaX_7^{**} : ($1.9 \times 10^{19}\text{n/cm}^2$): the total weight of this sample was approx. 0.18g. It was employed for all the gas sorption studies described in section 4.2., and when these were

complete, it was prepared as above for the cation exchange studies. Due to the small initial amount of sample, only 3 exchanges were conducted with Cs^+ (and 2 with Ba^{++} , see fig. 16 a), using approx. 30 mg. for each. All 3 points are well displaced from the isotherm for NaX^0 , in a direction suggesting a decrease in exchange capacity of the zeolite at all concentrations. The 2 points from the Ba^{++} exchange confirmed this, but they differed appreciably in their displacements from the standard isotherm, suggesting experimental error.

NaX_6^{XX} : ($7 \times 10^{19}\text{n/cm}^2$): it was found possible to exchange the Na^+ ions in this sample with Na^{22} ions, up to about 80% i.e. most, though not all, of the Na^+ ions are replaceable by an equally small ion. However exchange with Cs^+ was found to be practically non-existent, as shown in fig. 14 a. This result was rather to be expected in the light of the evidence concerning the destruction to the lattice of this sample, i.e. complete loss in sorptive capacity, and X-ray studies showing it to be amorphous.

In conclusion then, no definite effects to the zeolite were observed up to and including a neutron dose of $1.3 \times 10^{19}\text{n/cm}^2$. Sample 7 displayed a distinct decrease in exchange capacity, but still functioned efficiently as a cation exchanger, as indeed it still functioned as a gas adsorbent. Only a dose of the order of $5 \times 10^{19}\text{n/cm}^2$ would render the zeolite useless for these purposes. It may thus be concluded that NaX is far more resistant towards the **damaging effects of radiation** than its organic counterparts.

4.2.GAS ADSORPTION.4.2.1. Preliminary Sorption Experiments with the Irradiated Samples:

The most obvious means of determining whether any damage has been sustained by a zeolite lattice, in respect of its gas sorptive properties, is to sorb as large a volume of gas as possible and compare this with the corresponding volume sorbed by an unirradiated sample under the same conditions. It was found that sorption of argon at the temperature of liquid oxygen (90°K) was an appropriate system for this purpose; approximately 230cc. of argon (STP)/g.NaX (dehydrated) are sorbed at a pressure of approximately 50 cm.Hg.

Two samples of the unirradiated zeolite were employed in order to obtain an accurate isotherm for comparison with the results for the irradiated specimens. The first, NaX_1^{O} , was outgassed by the standard procedure (vide section 3.2.1.), followed by further outgassing periods of 20, 12 and 12 hours. It was then opened to the atmosphere for one day, and re-outgassed by the standard procedure. Between each of these outgassing periods, a sorption run with argon at 90°K was conducted. The results of these five runs are shown in figure 19, together with the results obtained for the second standard sample, NaX_2^{O} . The single curve drawn through these points is employed for comparison purposes with

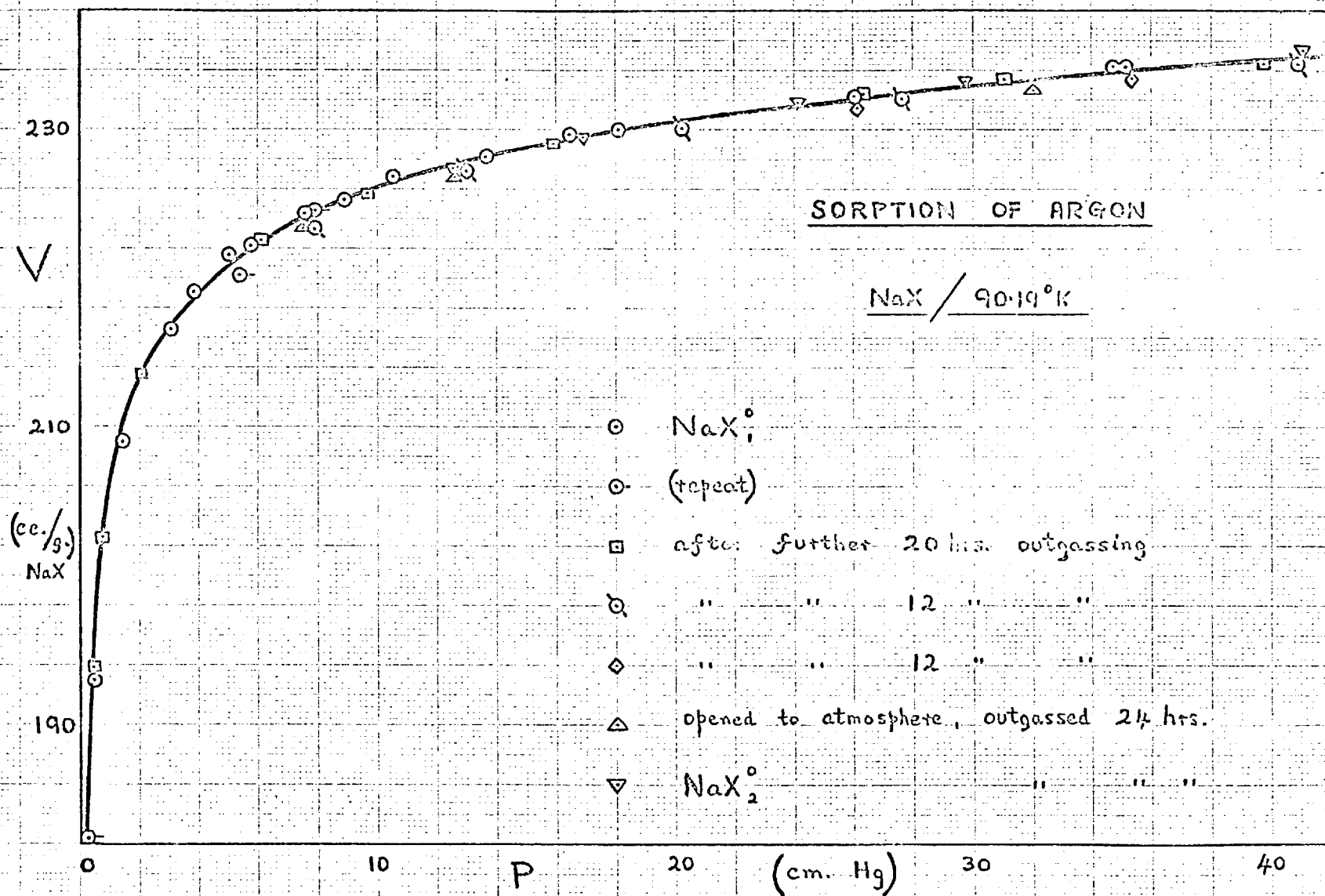


FIGURE 19

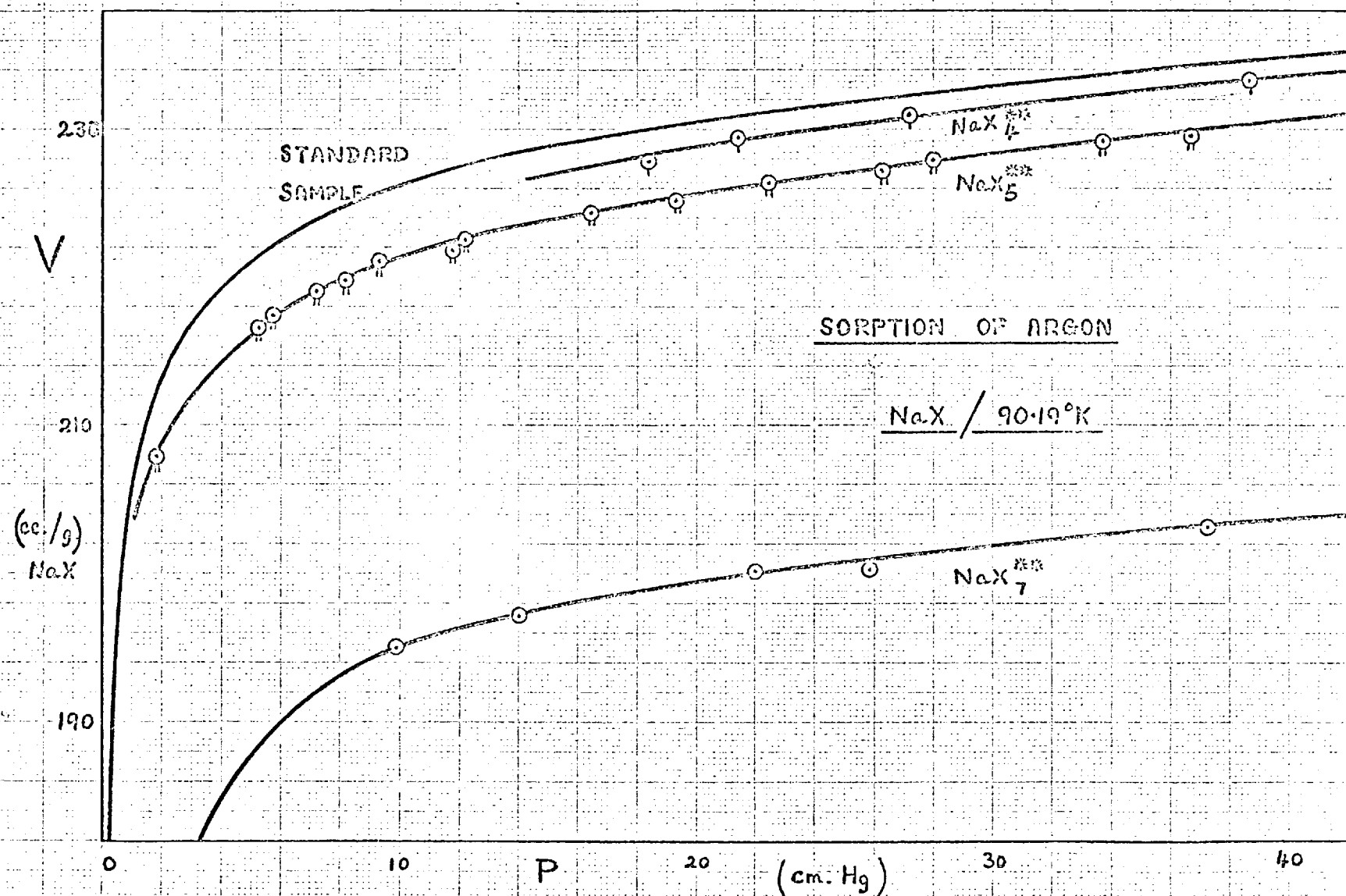


FIGURE 20

the isotherms constructed for the irradiated samples, (see figure 20). The scale of amount sorbed (ordinate) is greatly enlarged to show the excellent reproducibility.

It is feasible that irradiation of the zeolite might affect the most energetic sorption sites only, i.e. those with which the sorbed molecules initially interact. Such an effect might not be shown by the relatively high pressure readings of the previously mentioned system, i.e. argon at 90°K . Consequently, test sorption runs were also conducted on the irradiated samples, with krypton at $+25^{\circ}\text{C}$. Here the volume of gas adsorbed, even at 50 cm. Hg pressure, only just exceeded 7 cc.(STP)/g.NaX. Figure 21 shows the results obtained for all samples so tested; it will be noted that although distinct decreases in sorptive capacity were found for argon sorbed on NaX_5^{XX} and NaX_7^{XX} at 90°K , there appeared to be no observable difference between their krypton/ 25°C isotherms and that for the standard sample. This suggests that the radiation induced damage does not include any observable effect on the most energetic sorption sites, where sorption obeys Henry's law.

When radiation effects were observed by sorption of argon at 90°K (NaX_5^{XX} and NaX_7^{XX}), the samples were further subjected to sorption runs with krypton, in the temperature range, -120°C to -150°C . From these results were obtained the isosteric heat data discussed in section 4.2.4.

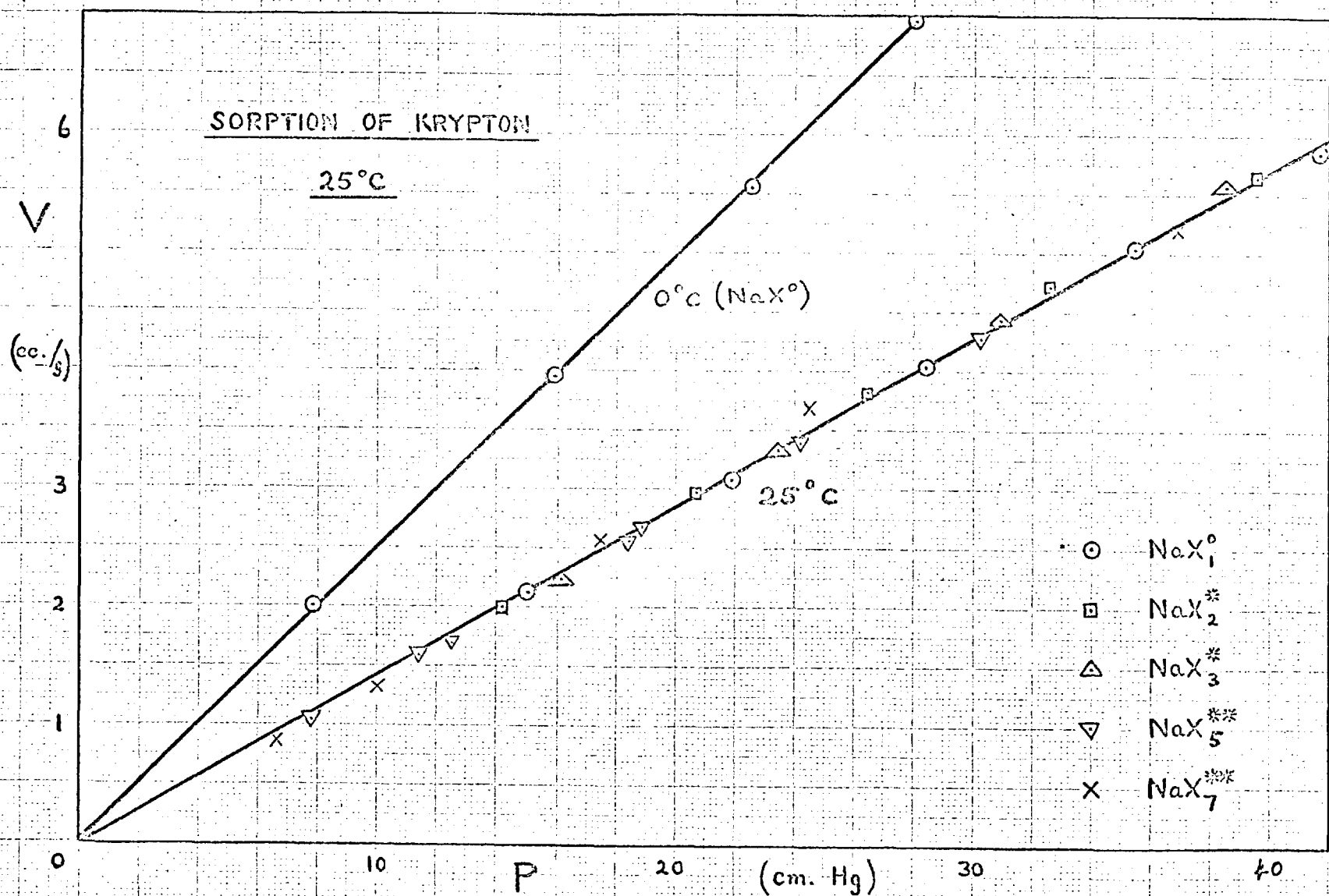
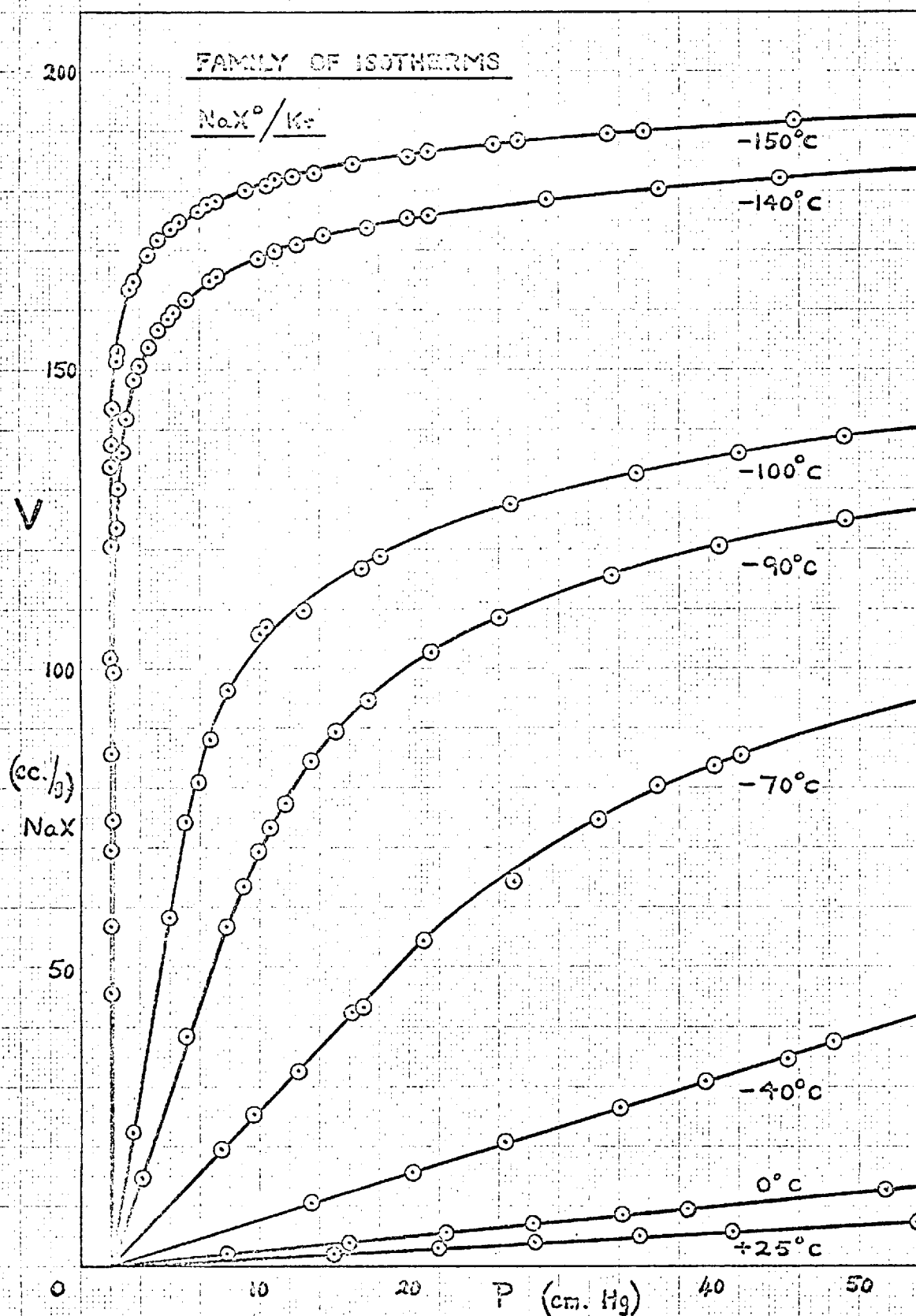


FIGURE 21

FIGURE 22



4.2.2. Occlusion of Krypton by NaX:

Figure 22 shows the family of isotherms obtained for the system, krypton sorbed by NaX^0 , over the temperature range -150°C to $+25^\circ\text{C}$. The isotherms at the temperatures 25° , 0° and -40°C are straight lines up to approximately one atmosphere pressure and thus obey Henry's law of adsorption:

$$V = k.p.$$

Below -40°C , all isotherms constructed for the krypton/ NaX^0 system were found to be linear up to between 50 and 80 cc. adsorbed (STP) after which they gradually curved towards the abscissa; equal increments in pressure lead to progressively smaller increments in volume sorbed. The low temperature isotherms were 'rectangular' in shape corresponding to type I of the Brunauer (31) classification, i.e. unimolecular adsorption. The plots shown in figure 22 are typical of all the isotherms constructed, all of which were found to be free of hysteresis i.e. desorption points coincided with sorption points.

In figure 23A, the isotherms at temperatures -120 to -150°C , have been shown for both NaX^0 and NaX_7^{xx} . To avoid confusion, only the -140°C isotherms have been shown in figure 23B for the samples NaX_2^{x} , NaX_5^{xx} and NaX_7^{xx} .

4.2.3. Saturation Capacities of NaX for Krypton.

Some of the methods of determining saturation capacities, i.e. the volumes of gas required to

FIGURE 23 A

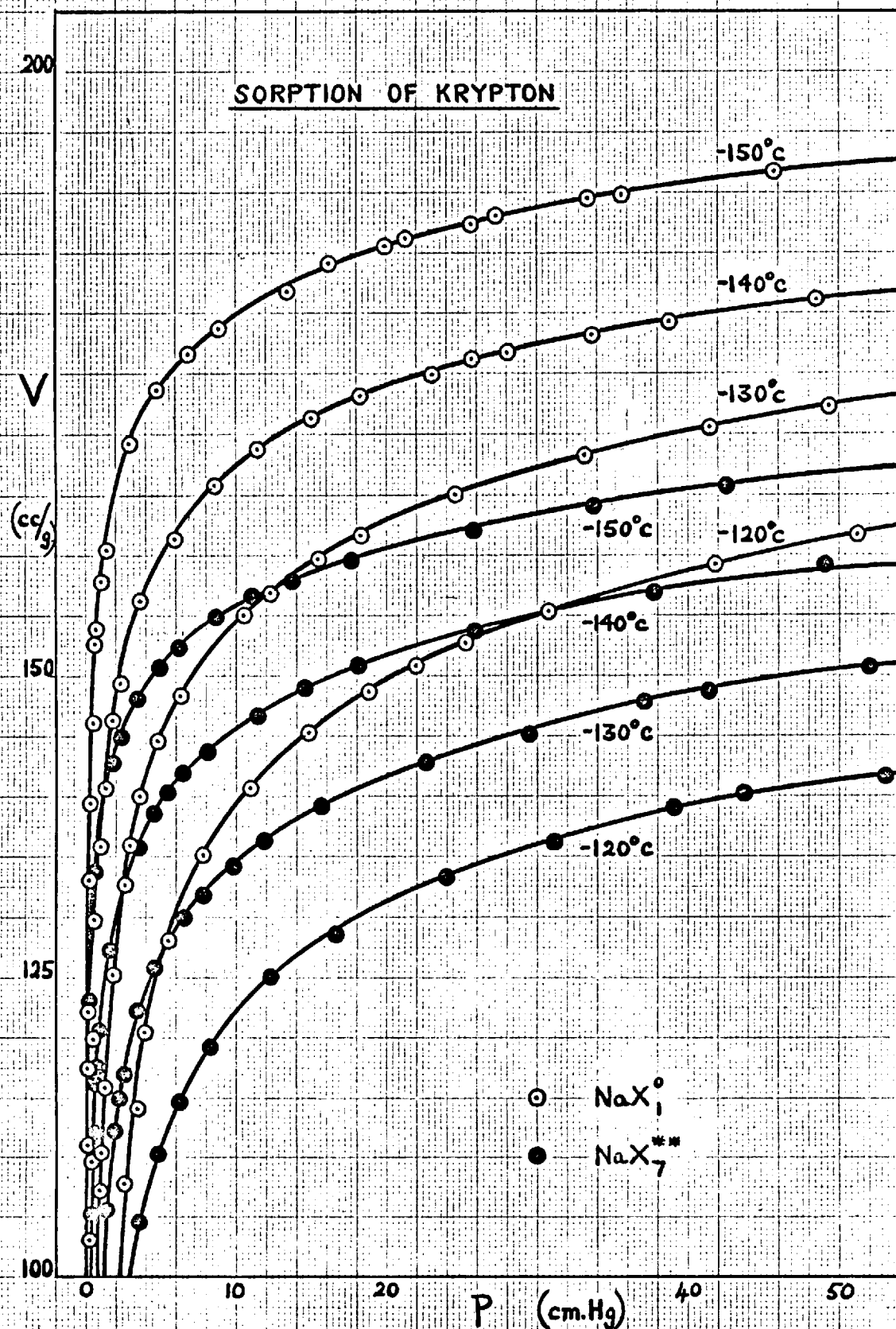
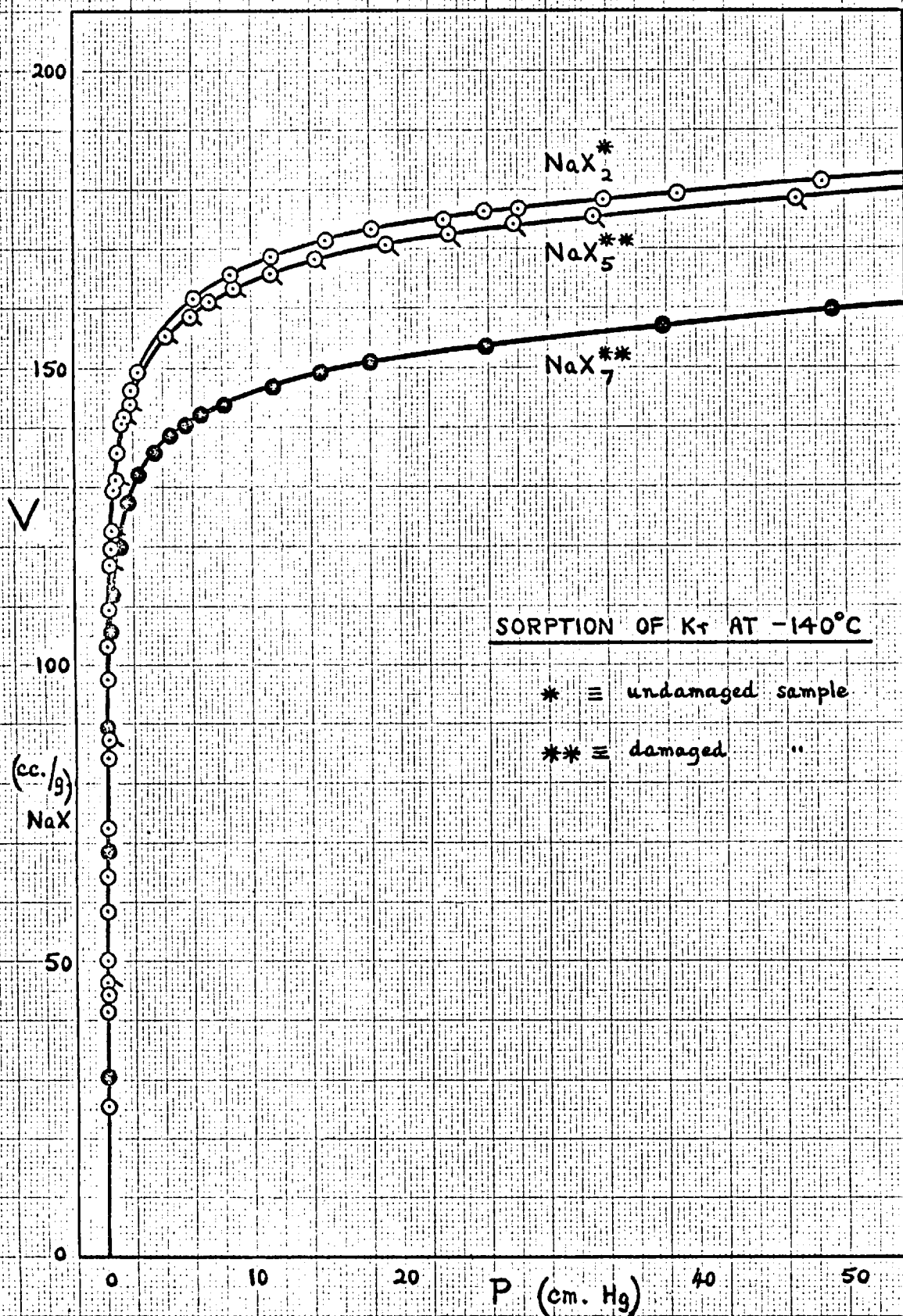


FIGURE 23·B



completely saturate the intracrystalline volume, are described here, together with the reasons for their applicability or otherwise to the sorption of krypton by NaX:-

(a) extrapolation of the rectangular isotherms as far as the saturation vapour pressures p_0 , for each temperature, when a direct reading of V_{sat} is possible on the ordinate axis. However, for krypton at -150°C this involves an extrapolation from approximately 50 cm.Hg. pressure up to 96 cm.Hg., and even larger at the higher temperatures. Such an extrapolation incurs too great an error, hence this method was not used.

(b) extrapolation of the linear portion of a graph of $\log p$ vs. $\log V$.

(The above two methods apply chiefly to systems for which experimental results are obtainable to within several cm.Hg. pressure of the saturation vapour pressure of the adsorbate.)

(c) comparison with the volume of water required to saturate the intracrystalline pore space. This method is open to question as it assumes that the water and krypton molecules both occupy the same cavities and channels.

(d) for the isotherms constructed between the temperatures -120°C and -150°C , plots of (p/V) vs. (p) give straight lines at low pressures (in accordance with the Langmuir isotherm) which become very gentle curves at higher pressures. From the limiting slopes of these

plots in the high pressure region, values of saturation volumes may be obtained. Since the curvature of these plots is barely discernable, a reliable value of V_{sat} is easily calculated. The results so obtained are tabulated below, both for the irradiated and unirradiated samples.

Saturation Capacities for standard & damaged samples. (cc. Kr (STP)/g. dehydrated NaX)

Temp. (°C)	NaX ⁰	NaX ₂ ^X	Average for NaX ⁰	NaX ₅ ^{XX}	NaX ₆ ^{XX} (a)	NaX ₇ ^{XX}
-150	198.5	-	198.5	195.0	0	173.6
-140	190.2	189.8	190.0	186.3	0	166.2
-130	-	182.1	182.1	178.5	0	158.6
-120	-	173.8	173.8	170.7	0	151.0
(a) - see text.						

Since the second irradiated sample NaX₂^X, was found to be undamaged, i.e. no change in sorptive capacity for argon at 90°K, the saturation capacities at all temperatures should be identical with those for the standard unirradiated sample. Column 4 of the above table was therefore obtained from the isotherms using NaX⁰ and NaX₂^X as sorbents. The % losses in saturation capacities are shown in the following table. With reference to note (a) in these two tables, sorption of argon by NaX₆^{XX} at 90°K amounted to only 1.5 cc. of gas at 50 cm.Hg. pressure, whereas the standard sample sorbed 230 cc. argon under the same conditions. The 'isotherm' was found to

be non-reproducible, even if several hours were allowed for "equilibrium" to be attained before each pressure reading was taken. Since krypton is a larger atom than argon, no attempt was made to measure the sorption of krypton in this sample, hence the saturation capacities for this sample have been listed above as zero; consequently the % loss in saturation capacity is 100%.

Percentage Losses in Saturation Capacity for
Krypton resulting from radiation damage.

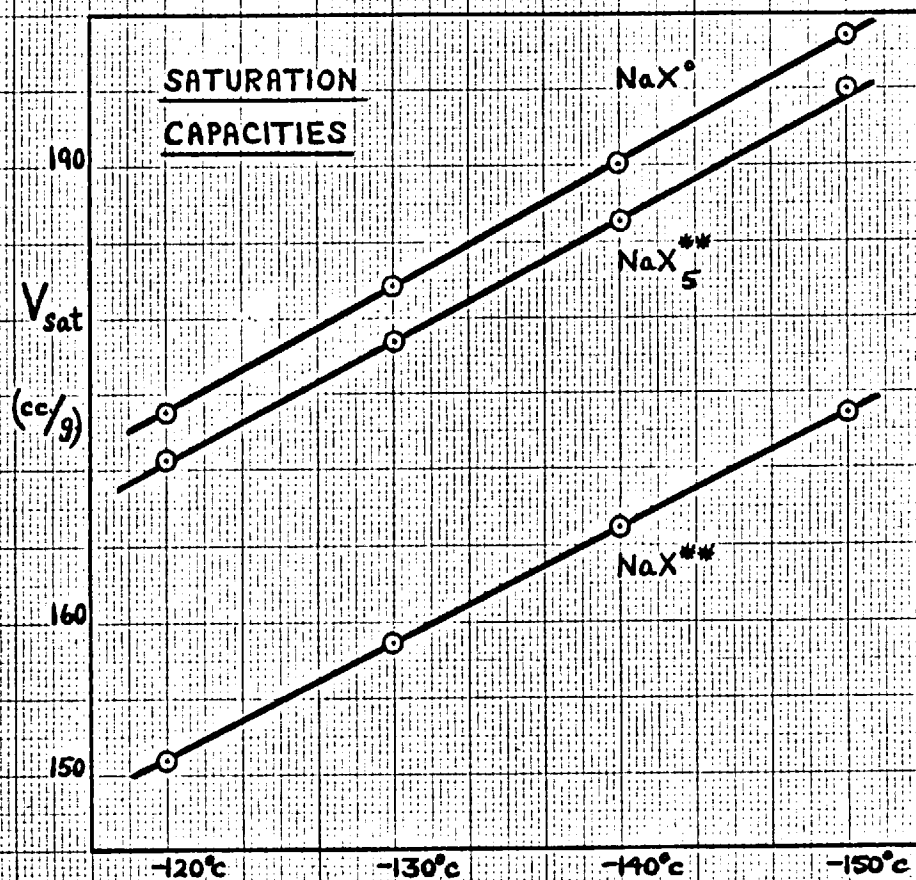
Temp. (°C)	<u>Irradiated & damaged samples of NaX^{3X}</u>		
	No.5	No.6 (a)	No.7
-150	1.8%	100	12.5%
-140	1.9%	100	12.5%
-130	2.0%	100	12.9%
-120	1.8%	100	13.1%
(a) - see text.			

The oxygen molecule is smaller than argon ($2.8 \text{ \AA}$ as opposed to $3.84 \text{ \AA}$), but, even so, only 4 cc. oxygen were sorbed at 90°K and 50 cm.Hg. pressure. For the above reasons, it is concluded that sample 6 suffered some form of lattice collapse as a result of the integrated neutron flux of approx. 7×10^{19} neutrons/cm². (More detailed discussion given in section 4.3.4.) An X-ray photograph of this sample showed not a single line, thus indicating an amorphous material.

Variation of Saturation Capacities with Temp.

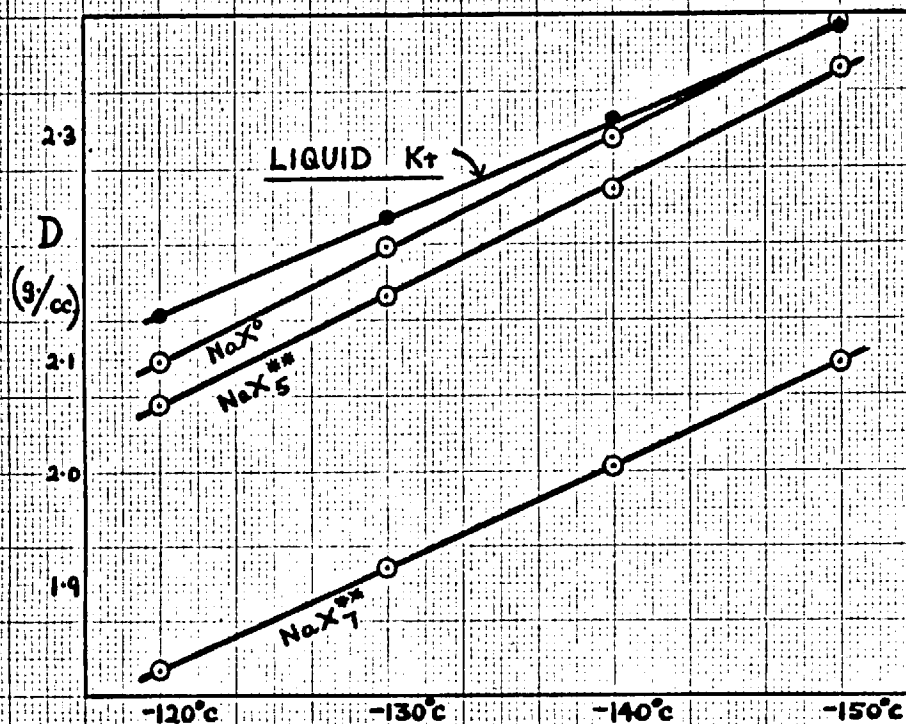
It was seen from the table on page 179 that the saturation capacities of NaX for krypton decreased with increasing temperature. This is shown for the standard sample and for the damaged samples, numbers 5 & 7 in Fig. 24 A.

The intracrystalline volume of NaX^{O} may be expressed as 0.31cc./g.(anhyd.)NaX, (see following section); at the saturation vapour pressure of krypton at -150°C , this volume is occupied by 198.5 cc.krypton (STP); since 1 g. mole occupies 22.4 litres at STP, calculation shows that the density of the sorbed krypton is 2.395 g./cc. as opposed to the tabulated value of 2.390 g./cc. (138). Figure 24B shows the plot of tabulated liquid krypton densities at various temperatures, (full circles). The calculated densities of sorbed krypton gas are also shown (open circles), using for all three samples, the value of 0.31 cc./g. NaX^{O} as the intracrystalline volume. Since the saturation capacities of krypton in the damaged samples is less than for the standard sample, it is reasonable to assume that the intracrystalline volume will be proportionately less. Using values of 0.305 and 0.27 cc./g.NaX for NaX_5^{XX} and NaX_7^{XX} respectively (i.e. 0.31 x ratio of saturation capacities of standard and damaged sample at -150°C), the plots of sorbed krypton density vs. temperature, are then found to be coincident with the



FIGURE

24 A



FIGURE

24 B

plot for NaX^{O} . Since these density plots are almost parallel to that for the liquid krypton densities, it may be concluded that at saturation, sorbed krypton approximates to the state of a bulk fluid, both in the standard and damaged samples.

Number of Krypton molecules occluded per supercage.

The intracrystalline pore volume of NaX is 0.53 cc./cc. anhydrous NaX. This volume is made up of the constituent volumes of the three types of cages, in the following percentages:-

supercages: 81%

sodalite cages: 14%

hexagonal interconnecting prisms: 5%

The free diameter of the 6-membered oxygen windows in the sodalite cage is $2.2\text{\AA}$, access to the hexagonal prisms being via these cages, and the diameter of the krypton molecule is $3.94\text{\AA}$. Consequently krypton is assumed to occupy the supercages only. The 'effective' intracrystalline volume is therefore 81% of 0.53 cc, i.e. 0.43 cc./cc. NaX. If the density of anhydrous NaX is taken as 1.4 g./cc. calculated by summing the weights of the atoms constituting one unit cell, of edge length $25\text{\AA}$, then 0.43 cc./cc. NaX is equivalent to 0.31 cc./g. anhydrous NaX. This volume may also be calculated as follows: at the saturation vapour pressure of krypton at -150°C (i.e. 96 cm.Hg), one g. NaX sorbs 198.5 cc. (STP) gas. Since one mole (i.e. 83.8g.) occupies 22.4 litres at

STP., 198.5 cc. is equivalent to 0.74 g. of krypton. The density of liquid krypton (adsorbed gas is assumed at saturation to possess the properties of bulk fluid) at -150°C , is 2.390 g./cc. therefore $0.74 \text{ g.} \equiv 0.31 \text{ cc.}$ krypton at STP. sorbed by one g. anhydrous NaX, as previously calculated. From the weights of the constituent atoms in a unit cell, the number of unit cells/g. zeolite, and also the number of supercages, can be calculated (each unit cell contains 8 supercages, vide section 1.0.); there are in fact 3.64×10^{20} supercages /g. anhydrous NaX. Therefore the number of krypton molecules per supercage at saturation is -

$$\frac{\text{weight of krypton sorbed/g. NaX}}{3.64 \times 10^{20}} \times \frac{N_0}{M}$$

- where N_0 is the Avogadro Number. This number of molecules is temperature dependent; the results for the standard sample, and for the irradiated sample number 7, are given below:

Number of Krypton Molecules Occupying
One Supercage of NaX at Saturation.

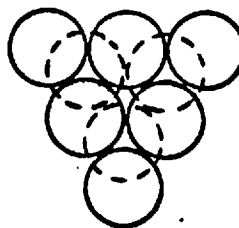
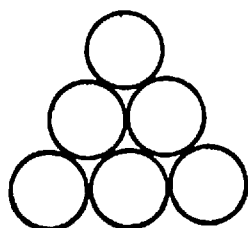
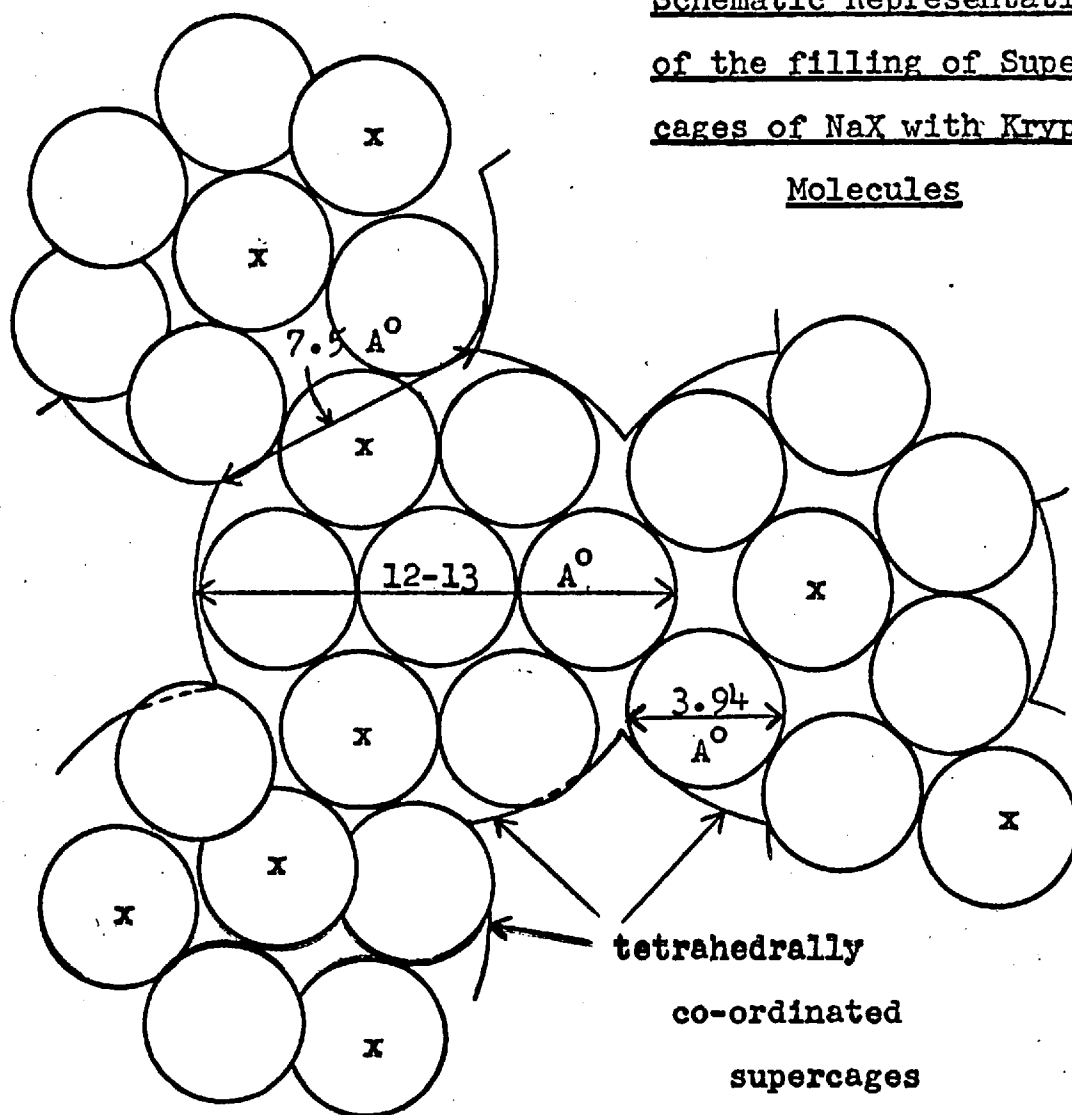
Temp. ($^{\circ}\text{C}$)	-150	-140	-130	-120
NaX ⁰	14.7	14.0	13.4	12.8
NaX ₇ ^{irr}	12.8	12.3	11.7	11.2

Assuming the krypton molecule, and the supercage of NaX to be both spherical in shape, then at -150°C the 14.7 molecules occupying one supercage, may, to a

first approximation, be assumed to ^{be} hexagonally close-packed, in which case there will only be one molecule not actually touching the cage walls, surrounded by 12 molecules which are touching them. However, each supercage 'possesses' 4 windows of free diameter ca. $7.5 \text{ \AA}$, which means a reduction in the surface area of the cage walls and a consequent increase in the number of molecules not touching them. The ratio of molecules touching the walls to those which do not, then equals about 9 to 5, instead of 12 to 1 as above. These numbers 9 and 5 are estimated from figure 25, remembering that at saturation there are 14 - 15 molecules of krypton filling the supercage, and that a molecule in one cage has as its neighbours, some of those in adjoining cages. Figure 25 is a schematic representation of the manner in which krypton molecules are believed to fill the cavities in NaX. Several points should be mentioned in connection with this diagram:-

- (a) it is a two dimensional representation of a three dimensional model; the supercages are tetrahedrally disposed and not equilaterally as shown.
- (b) the curved lines denoting the supercage walls actually represent the peripheries of framework oxygen atoms.
- (c) molecules denoted "x" do not touch cage walls at all.
- (d) overlap between sorbed molecules is possible in such a diagram, as those shown do not all necessarily lie in exactly the same plane; overlap with the cage walls is also possible, i.e. by molecules 'sitting' in cage windows.

Schematic Representation
of the filling of Super-
cages of NaX with Krypton
Molecules



hexagonal close-packing
of 'hard spheres'.

4.2.4. Isosteric Heats of Occlusion of Krypton in NaX.

Isosteric heats of adsorption for the system Kr/NaX have been measured from zero coverage up to approx. $\theta = 0.95$. As shown in section 2.2.3., the isosteric heat is given by the Clausius - Clapeyron equation, (eq.22). Integrating between the limits T_1 and T_2 , corresponding to pressures p_1 and p_2 , then:

$$2.303. \log p_1/p_2 = \frac{\Delta H}{R} \left\{ \frac{1}{T_1} - \frac{1}{T_2} \right\} \quad (25a)$$

The values of $\log p$ required for this expression were interpolated from graphs of $\log p$ vs. V , the amount sorbed (see figure 26). Plotting values of ΔH so obtained, vs. V , or θ (where θ in this instance must be taken as the average of the saturation capacities at T_1 and T_2), gives the variation of the isosteric heat with degree of saturation. Since from four isotherms, six plots of ΔH may be obtained, an 'average' plot should provide a fairly accurate illustration of the change in ΔH with θ . Figure 27 shows this 'average' plot; no experimental points are shown, because such a plot results from readings taken directly from the 'smoothed' $\log p$ vs. V curves (figure 26), drawn on a large scale. The plots for the damaged sample, NaX_7^{**} , are also shown in fig.26; at low pressures, they are coincident with the plots for the standard sample. The vertical arrows in fig. 27 denote the maximum errors for these values of ΔH . The interesting features in this plot include:-

(1) the initial constancy of ΔH , around 4 kcal/mole,

FIGURE 26

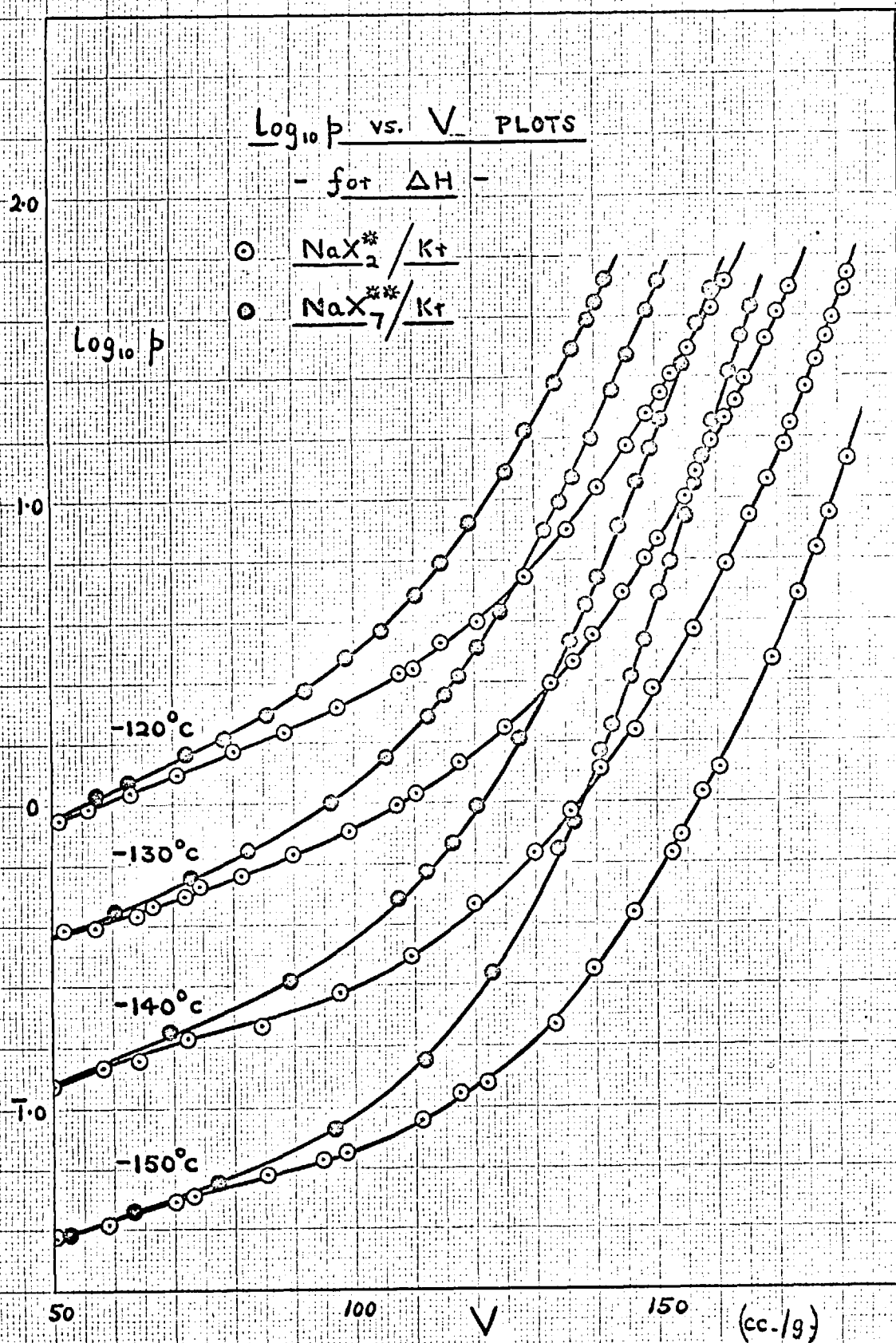
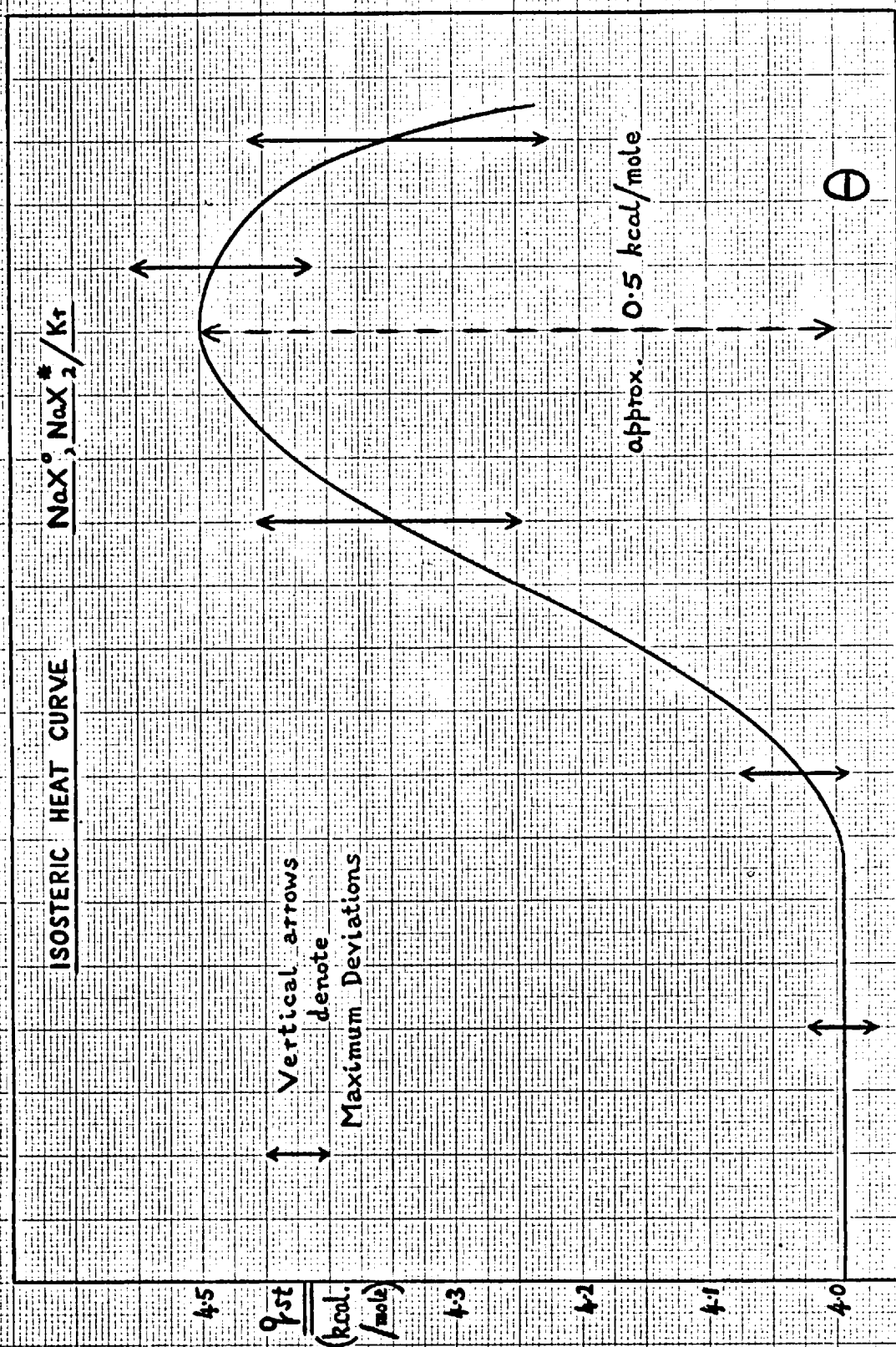


FIGURE 27



in the region $0 < \theta < 0.35$.

(2) the steady increase of ΔH from $\theta = 0.35$ up to $\theta = 0.75$, at which point it attains a maximum.

(3) the height of the maximum (above the value of ΔH when $\theta = 0$), which is about 500 cal/mole.

(4) the rapid fall in ΔH , from this maximum at $\theta = 0.75$ up to $\theta = 1$.

Each of these points will now be discussed in more detail.

If it is assumed that krypton molecules are firstly adsorbed on or near to the sodalite cage windows which are tetrahedrally disposed in the supercage, this will result in 4 molecules being sorbed (per supercage) with a constant heat of adsorption. This corresponds to $\theta = 4/14.7$, i.e. ca. 0.3, as was observed experimentally. These 4 molecules per cage are too far apart to interact with each other, but subsequent krypton molecules are then sorbed quite close to them, giving rise to an increasing sorbate molecule - molecule interaction energy. The actual krypton framework interaction energy may be less than that for the molecules previously sorbed but the net result is an increase in ΔH at $\theta = 0.3$ to 0.35. This is supported by the fact that there was occasionally observed a slight decrease in ΔH just preceeding the steep rise up ^{to} the maximum. The maximum at $\theta = 0.7$ to 0.75 corresponds to between 10 and 11 molecules sorbed per cage. If sorbed molecules are assumed to be separated by their equilibrium distances,

then the isosteric heat would increase linearly for all values of θ up to saturation, however, a maximum was observed. Kington et.al. (83, 108, 142, 144) also observed maxima in the plots of ΔH vs. θ for the gases, argon, oxygen and carbon dioxide sorbed on chabazite. The heights of these maxima (above the minimum observed values of ΔH) were 150-200, 300, and 700-800 cal/mole. respectively, and they were concluded to arise from mutual interactions between sorbed molecules. Kington was able to explain the actual packing of sorbed molecules into the two types of cavities, the explanation agreeing well with the experimental results. However, chabazite has since been shown to possess only one type of cavity(147); even so, the rise in ΔH may be explained by the mutual interactions of sorbed molecules.

As shown in the previous section, by considering the actual packing of molecules into the inter-connecting supercages, there are about 9 molecules touching the supercage walls, for every 5 or 6 molecules separated from the walls. The latter molecules are thus sorbed with a decreased ΔH , since they are somewhat removed from the proximity of the oxygen atoms constituting the cage walls. Thus the maximum in the ΔH vs θ curve, according to this argument, represents the point where the cage walls are completely covered with krypton molecules and should therefore occur at $\theta = \text{ca. } 0.65$. The experimental maximum occurs at $\theta = 0.75$, so this

slightly greater value of θ probably represents a more efficient packing of the sorbate molecules.

Figure 28 shows the 'average' ΔH vs. V curves obtained for NaX_5^{XX} and NaX_7^{XX} together with the 'average' curve for the standard sample, for comparison. Within experimental error, the curves are identical. Various assumptions may thus be made; since the sorption of argon at 90°K and krypton over the temperature range -120 to -150°C , showed there to be a distinct decrease in the saturation capacities (approx. 2% for NaX_5^{XX} and approx. 13% for NaX_7^{XX}) it may be assumed that a certain amount of damage resulted from the neutron irradiation (the nature of this damage will also be discussed in section 4.3.4.). However, as no appreciable change was observed in the isosteric heat curve, it must be assumed that either:

- (a) any effect was lost within the experimental error;
- (b) that the whole lattice contracted, resulting in the same number of supercages but each having a somewhat smaller volume. This might have been expected to lead to a slight change in the ΔH vs. θ curve but, even with a 13% loss in sorptive capacity, this change may have been too small to detect;
- (c) that complete destruction of some supercages occurred, leaving others intact, i.e. their might be amorphous regions present in the otherwise unaltered lattice. This would result in no change in the ΔH vs. θ

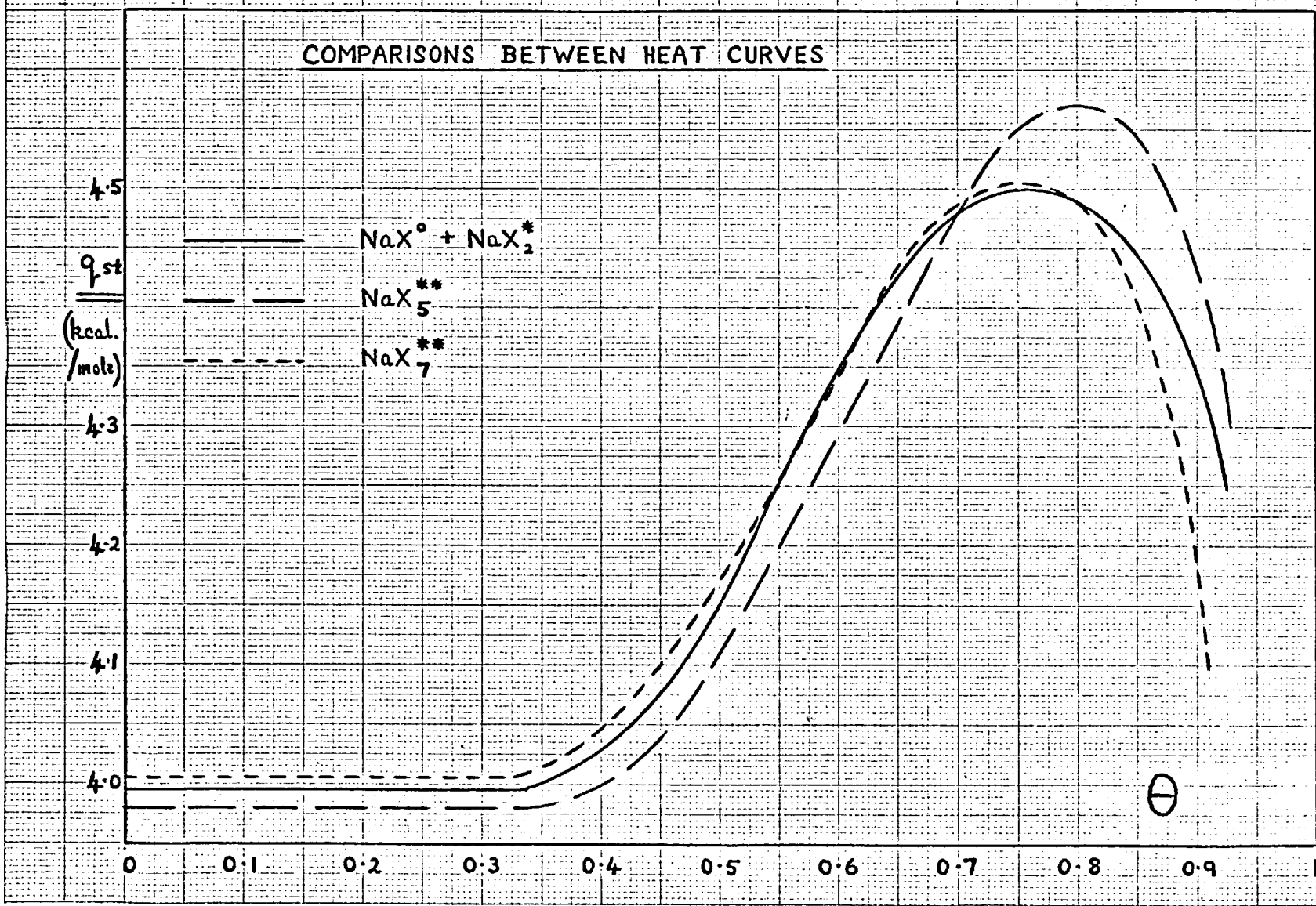


FIGURE 28

curve if no sorption occurred in the amorphous regions. Sample 6 was rendered completely amorphous by the heavy neutron dose of $7 \times 10^{19} \text{ n/cm}^2$ and, as a result, sorbed only a few cc. of gas. It can thus be concluded that any amorphous regions will not sorb appreciable volumes of gas and therefore as previously indicated, we would not really expect to observe any change in the heat curves.

It is appropriate at this point to discuss the information interpreted from the X-ray powder photographs of the irradiated zeolite samples. Sample 6 ($7 \times 10^{19} \text{ n/cm}^2$) as already mentioned resulted in not a single line in the photograph; there was simply a uniformly diffuse background, indicating that the sample was completely amorphous. Sample 7 ($1.9 \times 10^{19} \text{ n/cm}^2$; 13% loss in sorptive capacity) displayed some interesting features:

- (i) all four of the zeolite samples mounted in the aluminium frame (see section 3.1.6.) were of even thickness, and yet sample 7, the only damaged sample, possessed a distinctly more diffuse background suggesting that at least part of the material was amorphous.
- (ii) all of the visible lines (at least 30) were noticeably displaced in a direction indicating a decrease in lattice dimensions, i.e. a lattice contraction.

(iii) every line was not only displaced but also noticeably broadened, indicating disorder in the lattice, e.g. distortions resulting from interstitials and vacancies, etc. The X-ray data may thus be said to provide support for both (b) and (c) above. No other irradiated specimen resulted in observable differences in the X-ray pattern, from that of the standard sample.

It should also be noted here that if a lattice contraction occurred, the ratio of surface to volume of a supercage would increase. This would mean a greater ratio of sorbed molecules touching the cage walls to those not touching, hence the ΔH peak should be observed at a higher value of θ . No such change in θ was observed, but this might be expected, as any change would be a small one and probably be lost in the experimental error of the ΔH vs. θ curve.

Variation of Heat of Occlusion with Temperature.

The isotherms constructed for the system NaX/krypton, over the temperature range $+25^{\circ}\text{C}$ to -100°C , were employed to determine if there was any effect of temperature on the isosteric heat and, if not, to establish the value of ΔH in the range $\theta = 0$ to 0.3 for the very low temperature studies. The table below shows the values of ΔH obtained from various pairs of these isotherms; there does appear to be a slight change in ΔH with temperature, the heat of sorption increasing

as the temperature decreases. The high temperature isotherm data (+25 to -100°C) could not therefore be employed to establish the value of ΔH over the range $\theta = 0$ to 0.3 for the low temperature (-120 to -150°C) data.

Temps. of 2 isotherms (°C)		ΔH (kcal/mole)	Temps of 2 isotherms (°C)		ΔH (kcal/mole)
+25	0	3.7	-100	-120	4.0
0	-40	3.7	-120	-130)	4.0 (see fig. 27).
-40	-70	3.8	-120	-140)	
-40	-90	3.8	-120	-150)	
-70	-90	3.9	-130	-140)	
-70	-100	4.0	-130	-150)	
-90	-100	4.0	-140	-150)	

4.2.5. Comparison of Isotherm Data with Ideal Models of the Sorbed State:

Since the simple isotherm expression $p = k\theta$, i.e. Henry's law, does not fit over very extensive ranges of θ , other isotherm models have been applied to the data. The two main types of sorption possible, localized and mobile, were described in section 2.2.4.; each represents an extreme case and the experimental results may not agree with one or the other over the whole range of coverage. The various limiting isotherm models will now be discussed.

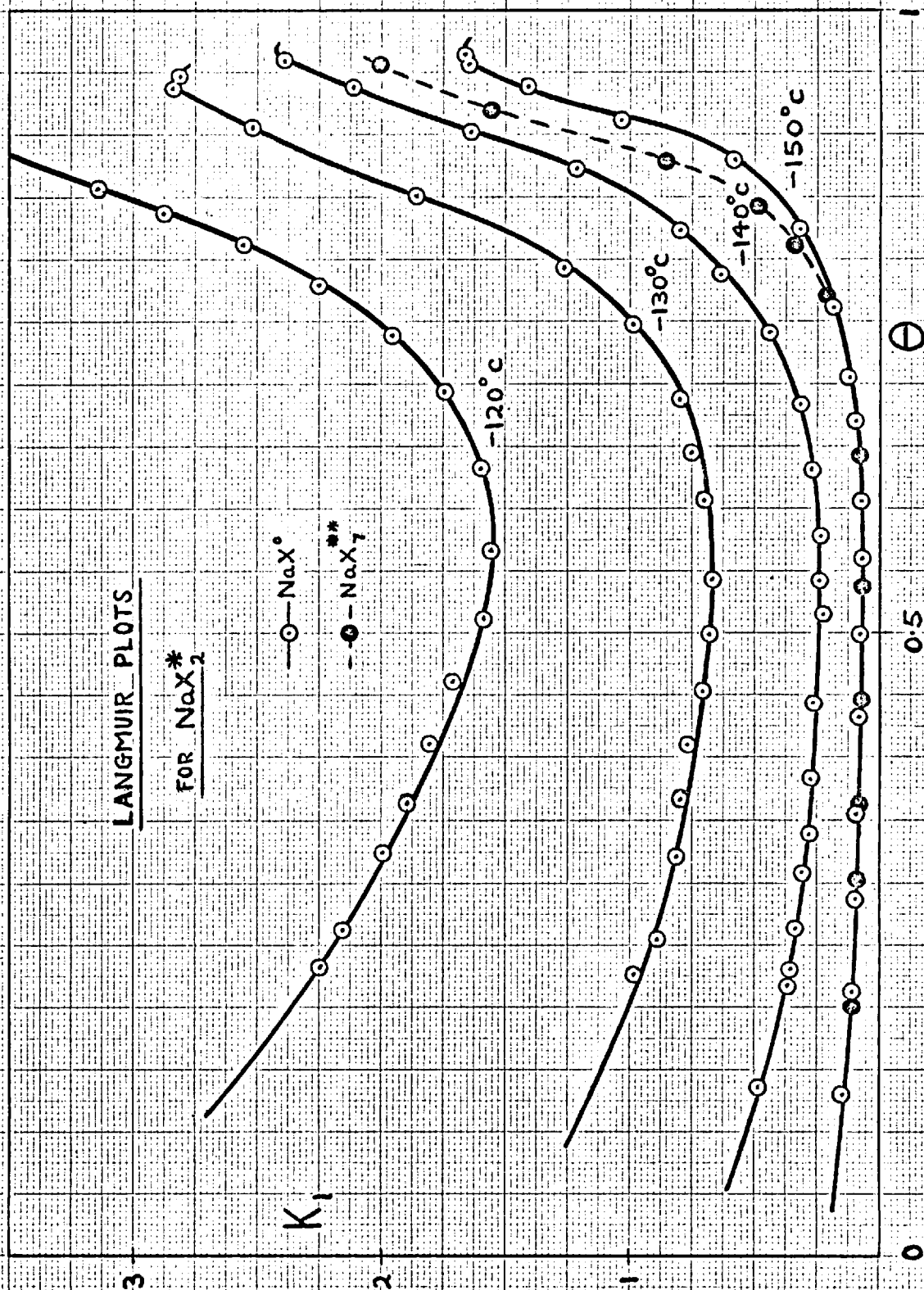
Localized Sorption without mutual interactions between sorbed molecules:

The following expression was derived by Langmuir (93):

$$K_1 = p \frac{(1-\theta)}{\theta} \quad (26)$$

where p = equilibrium pressure and θ = degree of saturation. For an isotherm model to be appropriate, the isotherm constant K , must be independent of θ over the range $\theta = 0$ to 1. Figure 29 shows the plots of K_1 vs. θ for the isotherms conducted at temperatures -120 to 150°C . It is seen that this simple isotherm model for localized sorption applies best at -150°C , where K_1 is fairly constant up to $\theta = 0.7$. The isosteric heat data in the previous section shows, however, that there is an increase in ΔH resulting from sorbed molecule-molecule interactions, which are not allowed for in Langmuir model; consequently, the constancy of K_1 up to $\theta = 0.7$ must be the result of cancellations from two competing factors. Between $\theta = 0.7$ and 0.95 , K_1 rises very rapidly to a maximum before decreasing again. The saturation vapour pressure of krypton at -150°C is too high to allow the obtainment of data beyond $\theta = 0.95$. However, since the decrease in K_1 at this high coverage is attributed to capillary condensation and multilayer formation on the zeolite surfaces, it is not relevant to this discussion of intracrystalline sorption, although the increase in K_1 up to the maximum is. A pronounced

FIGURE 29



increase in K_1 has previously been observed by Barrer & Reucroft (32), Barrer & Stuart (33), and others; the only explanation given for the increase in K_1 , in terms of the Langmuir equation, is that of an endothermal molecule-molecule interaction energy. Since such interactions are always associated with an exothermal energy, the explanation must lie elsewhere, i.e. in changes of entropy, either thermal or configurational (see later in this section). This assumes that the energy of sorption between sorbate and sorbent remains constant up to $\theta = 1$;

in section 4.2.4., it is shown that beyond $\theta = 0.75$ sorbed molecules were not touching the cage walls, but were completely surrounded by other sorbate molecules; this led to a rapid decrease in ΔH which corresponds with the rapid increase in K_1 .

Mobile Sorption without interactions between mutually sorbed molecules:

The following expression was derived from the Volmer equation of state (91):-

$$K_4 = p \frac{(1-\theta)}{\theta} \exp \left(\frac{-\theta}{(1-\theta)} \right) \quad (34)$$

In figure 30, it is seen that K_4 decreases over the entire range of θ , and hence this model is also inadequate.

Isotherm models in which allowance is made for mutual sorbate molecule interactions:

Any isotherm model which allows for sorbate molecule interactions should be more realistic for the

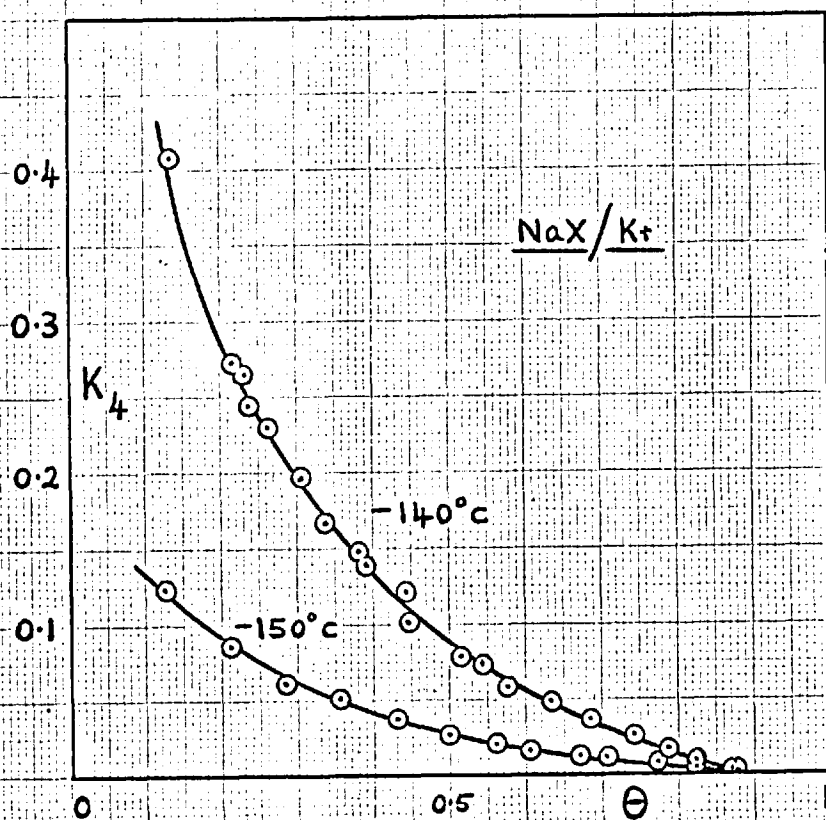


FIGURE
30

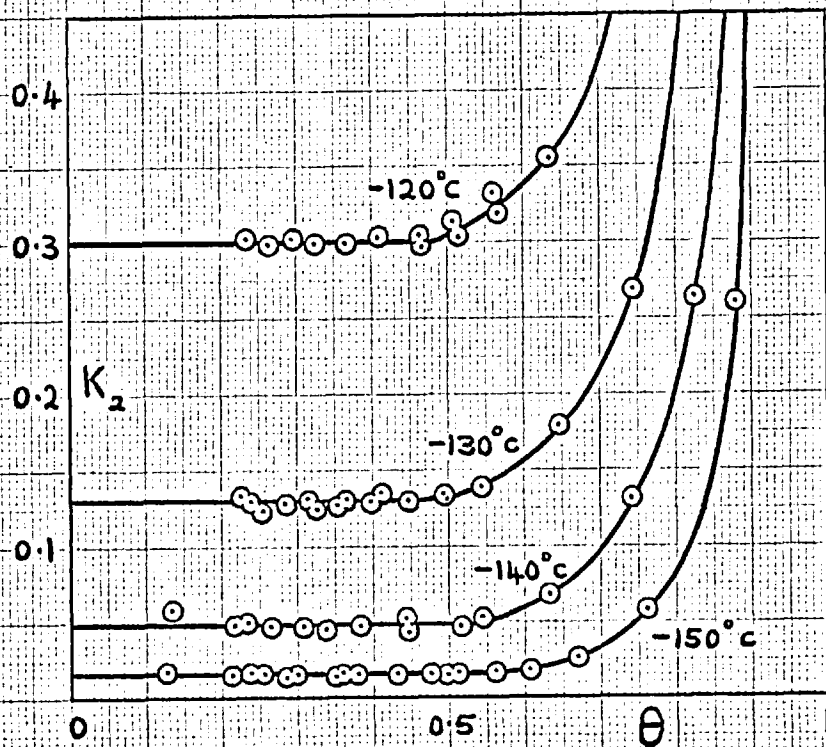


FIGURE
31

system studied, since in the confined interspaces of NaX, sorbed molecules are certain to exert their attractive forces towards each other. This is in fact, well illustrated by the isosteric heat curve.

Localized Sorption with Interactions:

The simple Langmuir expression for localized sorption may be adapted to allow for sorbate molecule interactions by the addition of an exponential term containing the interaction energy, $2w$, between two sorbed molecules; (N.B. $2w$ is negative because it is an energy of attraction).

$$K_2 = \frac{p(1-\theta)}{\theta} \cdot \frac{\exp(-\frac{2w\theta}{RT})}{RT} \quad (28)$$

In figure 31 are shown the plots of K_2 vs. θ for the temperature range -120 to -150°C . In each case, K_2 is constant up to approx. $\theta = 0.5$, after which there is a rapid increase. Although K_2 provides a better explanation than K_1 for the sorption of krypton by NaX, by being constant up to $\theta = 0.5$ at the various temperatures studied, it is nevertheless unsatisfactory above this value of θ . It should be noted however, that since this model is valid up to $\theta = 0.5$, it does explain the interactions between sorbed molecules up to a point, i.e. from the ΔH vs. θ plots, it is apparent that these interactions become significant well before $\theta = 0.5$, at $\theta = 0.35$.

Barrer & Reucroft (32) introduced a second exponential term into the expression for K_2 , i.e.

$$K_6 = p \frac{(1-\theta)}{\theta} \cdot \exp \left(\frac{-2w\theta}{RT} \right) \cdot \exp f(\theta) \quad (28a)$$

where the first exponential term has its usual significance (see above), and the second exponential term allows for the "freezing" of the sorbate molecules as they gradually lose thermal entropy by filling the intracrystalline pore space. For the system, carbon tetrafluoride sorbed by NaX, they obtained an expression which satisfactorily explained the isotherm data up to ca. $\theta = 1$. However, the values used in the $\exp.f(\theta)$ term were purely arbitrary and hence it has no real significance.

Determination of the Experimental value of the Molecule-molecule Interaction Energy (2w):

Barrer & Reucroft (32) showed that an experimental value of $2w$ could be obtained from the isotherm model K_2 . Equation (28) may be written:

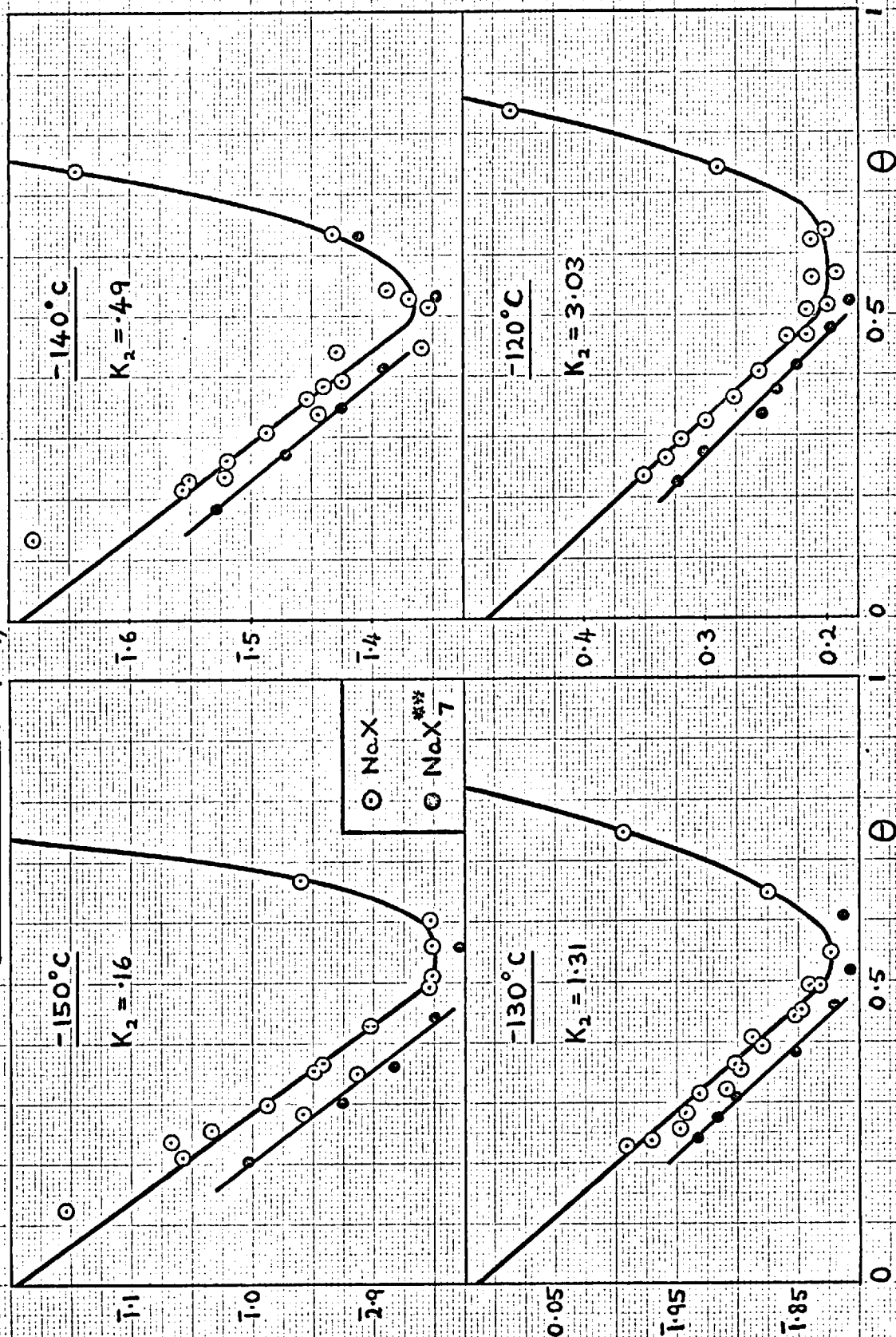
$$\log p \frac{(1-\theta)}{\theta} = \theta \cdot \frac{2w \log_{10} e}{RT} + \log K_2 \quad (28c)$$

By plotting $\log p \frac{(1-\theta)}{\theta}$ vs. θ , we obtain in the range of validity of this isotherm expression, straight lines of negative slope equal to $\frac{2w \log_{10} e}{RT}$, from which values of

$2w$ are obtainable. Figure 32 shows these plots, with linear portions up to $\theta = 0.5$, (open circles represent NaX^{O} and full circles, NaX^{XX}). Extrapolation to the

FIGURE 32

PLOTS OF $\frac{\log p(1-\theta)}{\theta}$ vs. θ (for "2W")



ordinate axis gives the logarithm of the isotherm constant K_2 . The slope of these plots changes from negative to positive around $\theta = 0.5$; this must not, however, be assumed to mean that the attractive forces existing between two krypton molecules becomes a repulsive force beyond a figure of approximately seven krypton molecules per supercage (total capacity = 14-15 molecules), but rather that the isotherm model is unsatisfactory beyond this value of θ . The following table shows the values of $(2w)$ so obtained :-

(2w): Values of Molecule-Molecule Interaction Energy:

(obtained from figure 32) (cal/mole).

Temp. ($^{\circ}\text{C}$)	-150	-140	-130	-120	Average.
NaX^{O}	-397	-404	-363	-374	-384
$\text{NaX}_{7}^{\text{XX}}$	-362	-361	-342	-352	-354

The average values of -384 and -354 cal/mole for NaX^{O} and $\text{NaX}_{7}^{\text{XX}}$ respectively are used for calculations throughout this work. The theoretical values of $2w$ calculated with the London and Kirkwood Muller expressions, assuming the 6:12 interaction, are -200 and -560 cal/mole respectively.

The difference between the experimental figures, -384 and -354 cal/mole, for $2w$, may be the result of experimental error; however, it could possibly be explained as follows. From the X-ray data previously

discussed in section 4.2.4., it is believed that there has been a slight lattice contraction in the sample NaX^{HH}_7 . The sorption results confirm this by showing that the number of krypton molecules that fill the supercage at saturation, is less than for NaX^{O} under identical conditions. The decrease in sorptive capacity could also be explained however, by the complete destruction of some supercages, by small regions of the lattice being rendered amorphous, in which case the reduction in the number of sorbate molecules filling a supercage would not be as large as previously indicated (4.2.4). Sorbate molecules might therefore be more closely packed in the damaged zeolite, in which case the mutual repulsion energy would increase giving a net decrease (numerical) in the total interaction energy, as shown above.

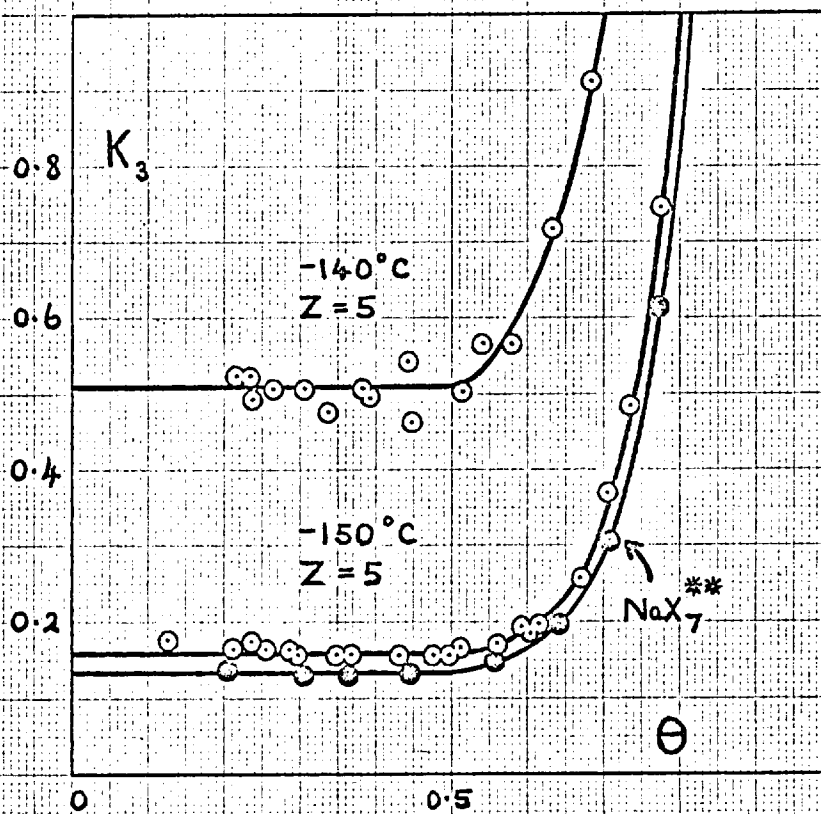
Localized Sorption with Interactions, allowance being made for changes in Configurational Entropy.

The isotherm model K_3 is expressed as follows:

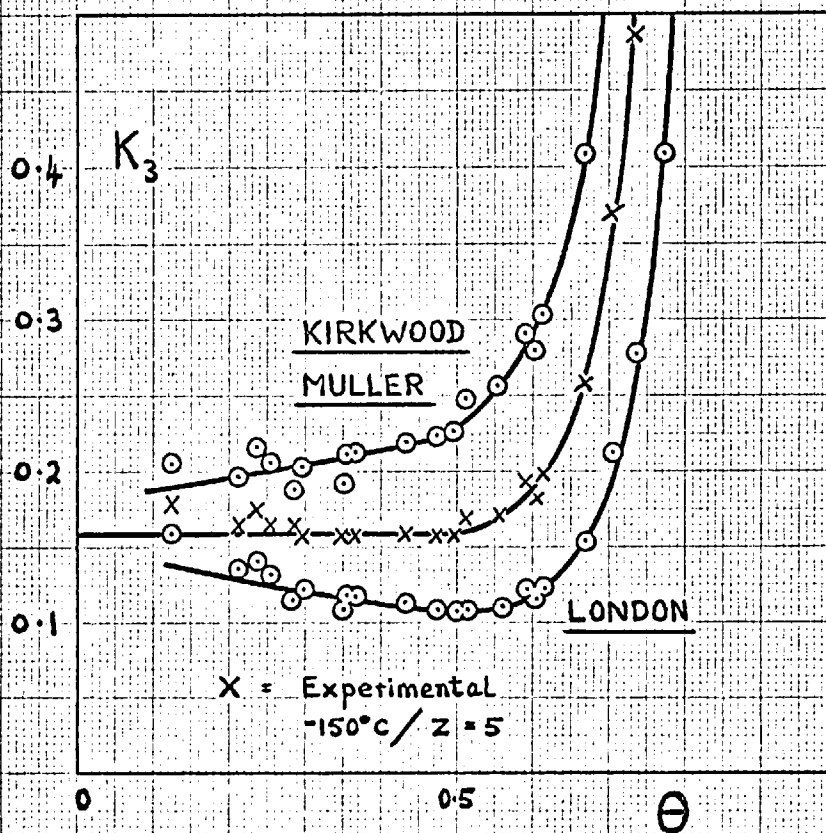
$$K_3 = \frac{p(1-\theta)}{\theta} \cdot \frac{(\beta+1-2\theta)^z}{(2-2\theta)} \quad (31)$$

where
$$\beta = \left(\frac{1-4\theta(1-\theta) \left(1 - \exp\left(\frac{-2w}{zkT}\right) \right) }{1} \right)^{\frac{1}{2}} \quad (32)$$

The value of $2w$ employed was -384 cal/mole obtained as shown above. The term z is defined as the coordination number of a molecule when sorbed on a sorption site, i.e. the number of nearest neighbour sorbate molecules also



FIGURE

33

FIGURE

34

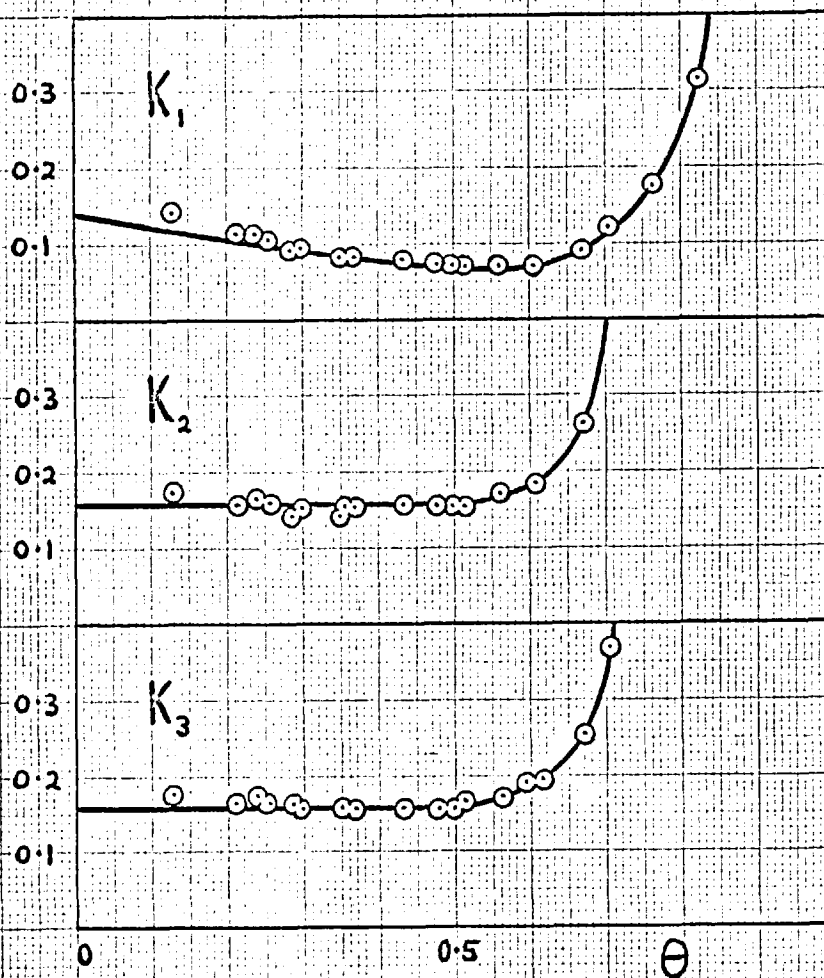
sorbed on sorption sites; hence it excludes any molecules not sorbed on the cage walls. From the discussion given in section 4.2.3. concerning the filling of the sorbent cages with sorbate molecules, z is taken as 4. K_3 appears to be insensitive anyway, to changes in z , as the plots using $z = 3, 4$ and 5 are practically coincident. Figure 33 shows that K_3 is constant up to $\theta = 0.5$, after which a rapid decrease is observed; figure 34 shows the plots of K_3 employing the London & Kirkwood-Muller values of $2w$ compared with the plot using the experimental $2w$. For the sake of comparison, all three localized models are shown together in figure 35. It thus appears that changes of configurational entropy (allowed for in model K_3) are also unable to satisfactorily explain the increase in the isotherm constant beyond $\theta = 0.5$. The deviations from the Langmuir localized model can only therefore be attributed to changes in thermal entropy.

Mobile Sorption with Interactions:

The following expression was derived by Hill from the Van der Waals' equation of state (91):-

$$K_5 = \frac{p(1-\theta)}{\theta} \cdot \frac{\exp\left(\frac{-\theta}{(1-\theta)} + \alpha\theta\right)}{(1-\theta)} \quad (35)$$

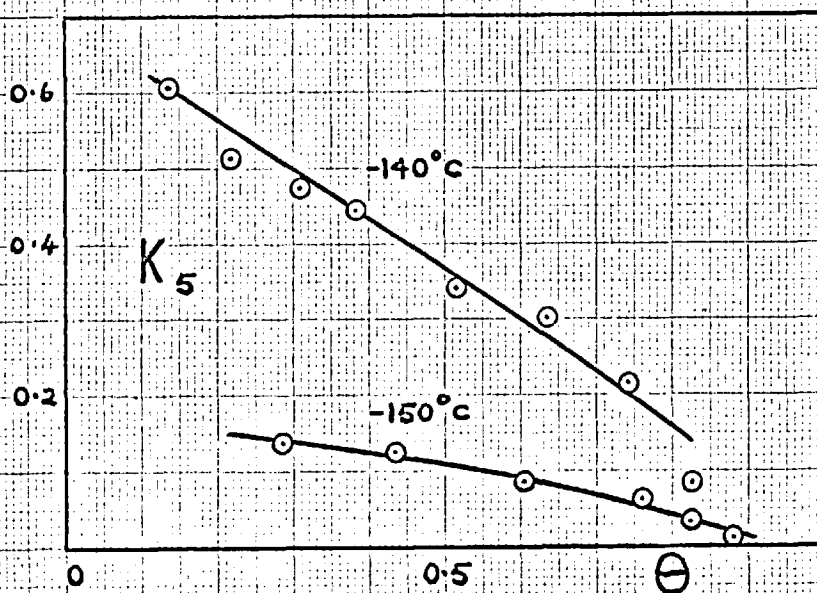
where $\alpha = \frac{2a}{bKT}$, a and b being the two dimensional Van der Waals' constants for the adsorbate. (These are related to the three dimensional constants by expressions given by Hill (91).) Fig. 36 shows that



FIGURE

35

Comparisons between Localized Models (-150°C)



FIGURE

36

the plots of K_5 vs. θ decrease steadily with θ . This could have one of several explanations :-

- (a) the thermal entropy increases for the more tightly packed molecules, which is most unlikely;
- (b) the Van der Waals' equation of state employed in the derivation could be inadequate for this system. (This has already been shown to be partially responsible, ref.137).
- (c) the system is not one of mobile sorption at all.

We may therefore conclude from the above discussion that sorption of Kr by NaX at low temperatures (-150°C etc.) is localized. The Langmuir model gives a value of the isotherm constant which is almost independent of θ up to $\theta = 0.7$, but in not allowing for molecule-molecule interactions, appears somewhat unlikely to be the appropriate model even so. Consideration of these interactions, i.e. in the K_2 and K_3 models, gives isotherm constants independent of θ up to $\theta = 0.5$ for all temperatures, after which rapid increases are observed.

It should also be emphasised at this point that even if one of the ideal models does provide a constant value for K , over whole or part of the range of θ , it should not necessarily be assumed that the particular model adequately explains the sorption process occurring; constancy of K may be purely coincidental over part of the range of coverage. It has already been noted by Barrer et.al.(27) and Young (66)

that a far more rigorous test concerns thermodynamical functions such as entropy, in particular the thermal entropy. In order to adequately explain the experimental data, the thermal entropy must satisfy certain criteria (67):

- (a) it must be positive, with reasonable physical magnitudes, and
- (b) independent of θ .

Consequently a discussion will now follow concerning the entropy functions associated with the isotherm models already discussed.

4.2.6. Entropy of Occlusion of krypton by NaX:

Localized Sorption:

As was shown in the theoretical section (2.2.5.), the entropy of adsorbate may be expressed as follows:-

$$\bar{S}_s = \bar{S}_{th} + \bar{S}_c \quad (41)$$

representing the differential molar entropy of sorbed gas, thermal and configurational entropy terms respectively. This simple expression is, however, confined to systems of localized sorption, where the sorbate possesses no degrees of translational freedom. The configurational entropy is related to θ by the expression:

$$\bar{S}_c = R \ln \frac{(1-\theta)}{\theta} \quad (42)$$

and the molar entropy of the gas in the sorbed phase, at equilibrium pressure p and temperature T , is given by:-

$$\bar{S}_s = \frac{\Delta H}{T} + R \ln \left(\frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{kT}{p} + \frac{5R}{2} \right) \quad (40)$$

Both of these expressions contain known constants, e.g. R , k , h etc., and experimentally obtainable functions such as θ and ΔH . Consequently a value of $\bar{S}_{th}$ may be calculated from equation 41 for any value of θ , at any temperature, if the isotherm data is available to provide p and ΔH . Figure 37 shows the plots of the differential entropy functions, $\bar{S}_s$, $\bar{S}_c$ and $\bar{S}_{th}$, corresponding to the isotherm models K_1 and K_2 for the temperature -150°C . Both $\bar{S}_s$ and $\bar{S}_c$ decrease with increasing θ , but at unequal rates, consequently $\bar{S}_{th}$ (K_1 K_2) is not constant. As explained in the previous section, we should expect there to be mutual sorbate molecule interactions in the system studied. However, the isotherm model which allows for these, but at the same time does not allow for configurational entropy changes (i.e. K_2), gives an identical plot for $\bar{S}_{th}$ as K_1 .

The isotherm model which does not allow for configurational entropy changes (i.e. K_3) requires the use of the equation 43. Using the experimentally obtained value of $2w$ and the co-ordination number $z = 4$ (see earlier), the thermal entropy was calculated for the temperature -150°C . Figure 37 shows that $\bar{S}_s$ and $\bar{S}_c$ (K_3) decrease steadily at approximately the same rate, so that $\bar{S}_{th}$ (K_3) is reasonably constant. It is

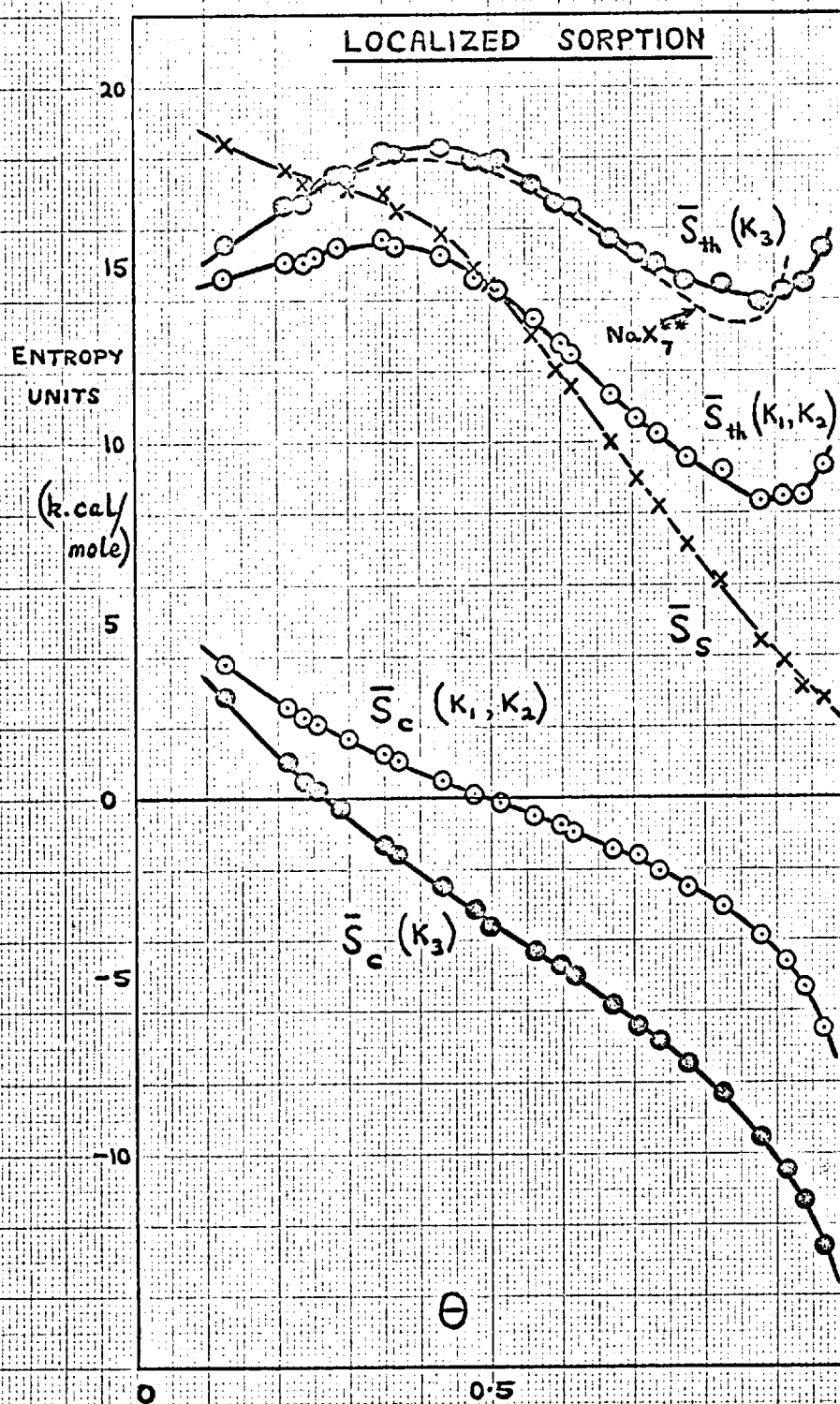


FIGURE
37

in fact more nearly constant than the thermal entropy corresponding to models K_1 and K_2 .

Mobile Sorption:

For such systems, $\bar{S}_s$ is again given by equation (40); it is the same for all types of adsorption because it is a constant for a given gas at any temperature. Instead of changes of configurational entropy, however, we must now think in terms of the translational degrees of freedom possessed by the sorbed phase;

$$\bar{S}_s = {}_1\bar{S}_T + \bar{S}_{th}' \quad (47)$$

$$\text{and} \quad \bar{S}_s = {}_2\bar{S}_T + \bar{S}_{th}'' \quad (48)$$

where $\bar{S}_{th}'$ and $\bar{S}_{th}''$ are the residual thermal entropies, and ${}_1\bar{S}_T$ and ${}_2\bar{S}_T$ have been defined by equations 49 and 50 in section 2.2.5. Fig. 38 shows the plots of $\bar{S}_s$, ${}_1\bar{S}_T$ and ${}_2\bar{S}_T$, and the thermal entropies $\bar{S}_{th}'$ and $\bar{S}_{th}''$. Although the latter are not constant, they vary by only ± 1.5 entropy units over the range $\theta = 0$ to $\theta = 0.8$, compared to variations of ± 2 and ± 3.5 entropy units respectively for the localized models (K_3) and (K_1, K_2). On this basis the mobile sorption model provides as good an explanation of the experimental results as any. There appears to be little difference in the constancy of $\bar{S}_{th}$ when considering one or two degrees of translational freedom; however, one of the criteria of the thermal entropy (67) states that it must be positive and of reasonable physical magnitudes. Since $\bar{S}_{th}'$ is greater than $\bar{S}_{th}''$ (8-9

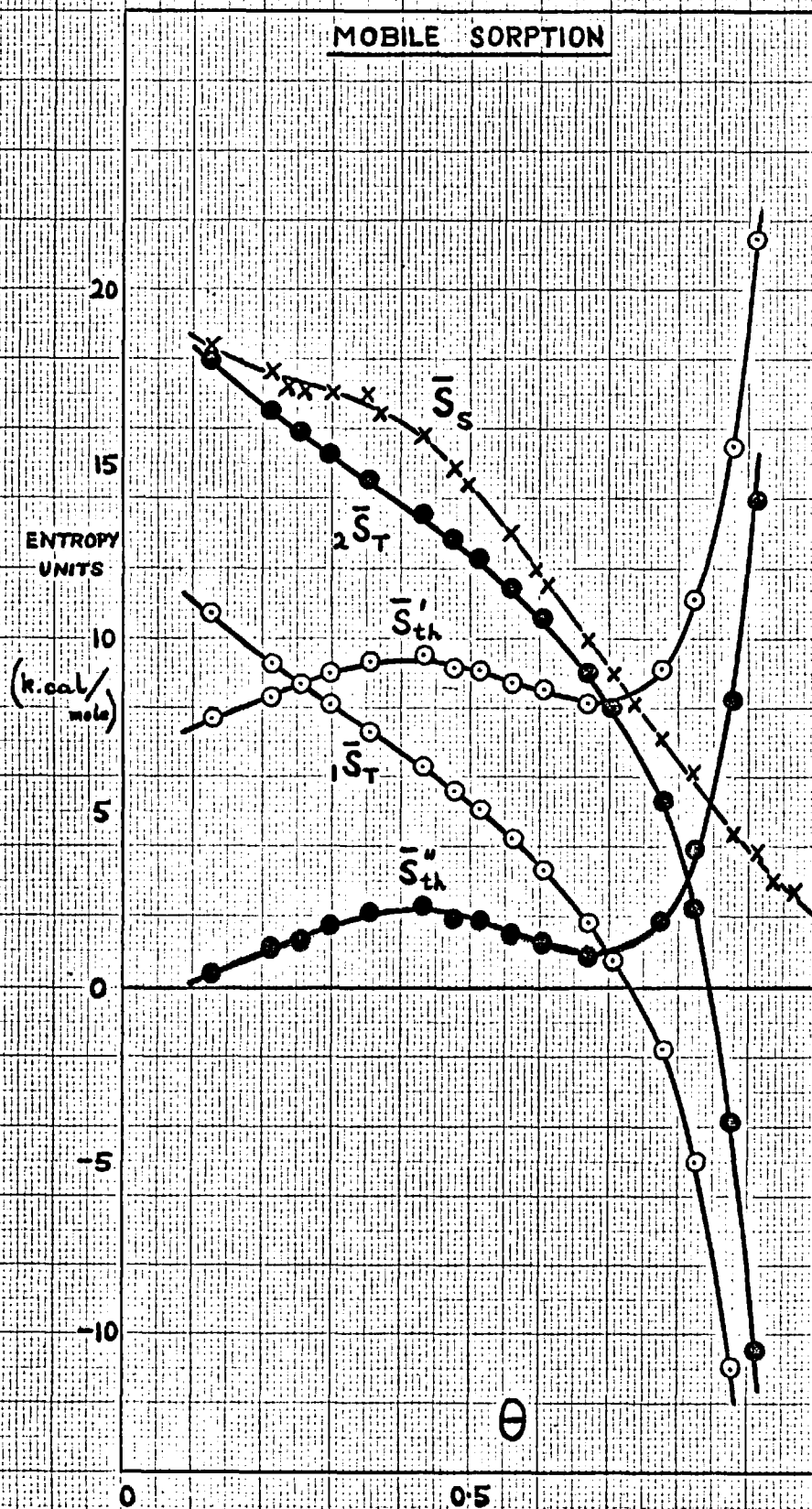


FIGURE
38

cal/deg.mole as opposed to 1-2 cal/deg.mole), mobile sorption with one degree of translational freedom is the most appropriate model. In conclusion then, of the localised models, K_3 proves to be the most appropriate. Considering both the constancy of this isotherm model, and the fairly constant value of thermal entropy over a wide range of Θ , this model is considered to best explain the sorption of krypton by NaX.

The isotherm data compiled for sample no. 7, (NaX_7^{XX}), was employed to determine if neutron irradiation resulted in any change in the isotherm model, and corresponding entropy functions, previously found to explain the sorption of krypton by the standard sample. The plot for the simple Langmuir model was coincident with that for NaX^0 , up to $\Theta = 0.7$, after which it increased more rapidly (see figure 29). The plot for K_3 vs. Θ was slightly below that for NaX^0 but still constant only up to $\Theta = 0.5$; this reduction is partly caused by the observed reduction in the experimental value of the molecule-molecule interaction energy, $2w$, from -384 cal/mole for NaX^0 to -354 cal/mole for NaX_7^{XX} ; (this value was calculated from the plots, full circles, in figure 32). In figure 37, the dotted curve almost coincident with $\bar{S}_{\text{th}} (K_3)$, is that obtained for the damaged sample, NaX_7^{XX} . The close similarity in the results for NaX^0 and NaX_7^{XX} thus indicate that although a loss in sorptive capacity was observed, the sorption of krypton by the

damaged zeolite still agreed best with the ideal model of localized sorption, with mutually sorbed molecule interactions and allowance being made for changes in configurational entropy.

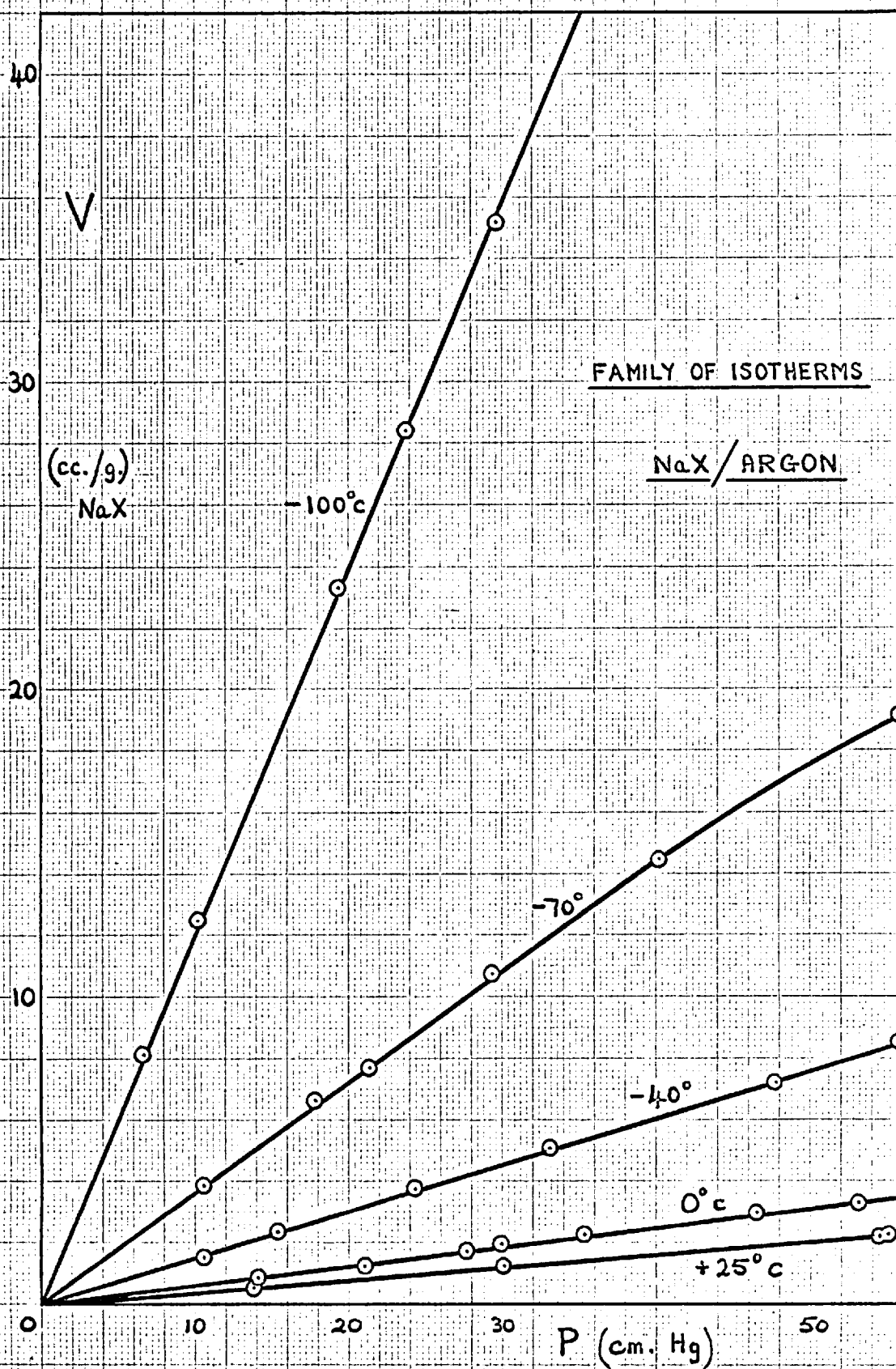
It is hoped that further work on the neutron irradiation of zeolites and the subsequent thermodynamical analysis as outlined in this work, will lead to more positive results. In the case of NaX, neutron doses greater than 1.9×10^{19} n/cm² will be required to cause further damage to the lattice framework and, at the same time, to affect the sorption sites. This dose may well be very critical as too high a dose will simply render the zeolite amorphous.

4.2.7. Occlusion of Argon by NaX.

Isotherms for the system NaX/argon were constructed in the temperature range + 25°C to -100°C, and also at the temperature of liquid oxygen 90.19°K. Figure 39 shows the family of isotherms obtained for the higher temperatures; the plots are linear at the temperatures + 25°C, 0°C and -40°C, but those at -70 and -100°C. eventually curve towards the pressure axis as the pressure increases.

The sorption of argon by NaX at 90.19°K has already been discussed in section 4.2.1. All irradiated samples were initially examined by means of this sorption experiment.

FIGURE 39



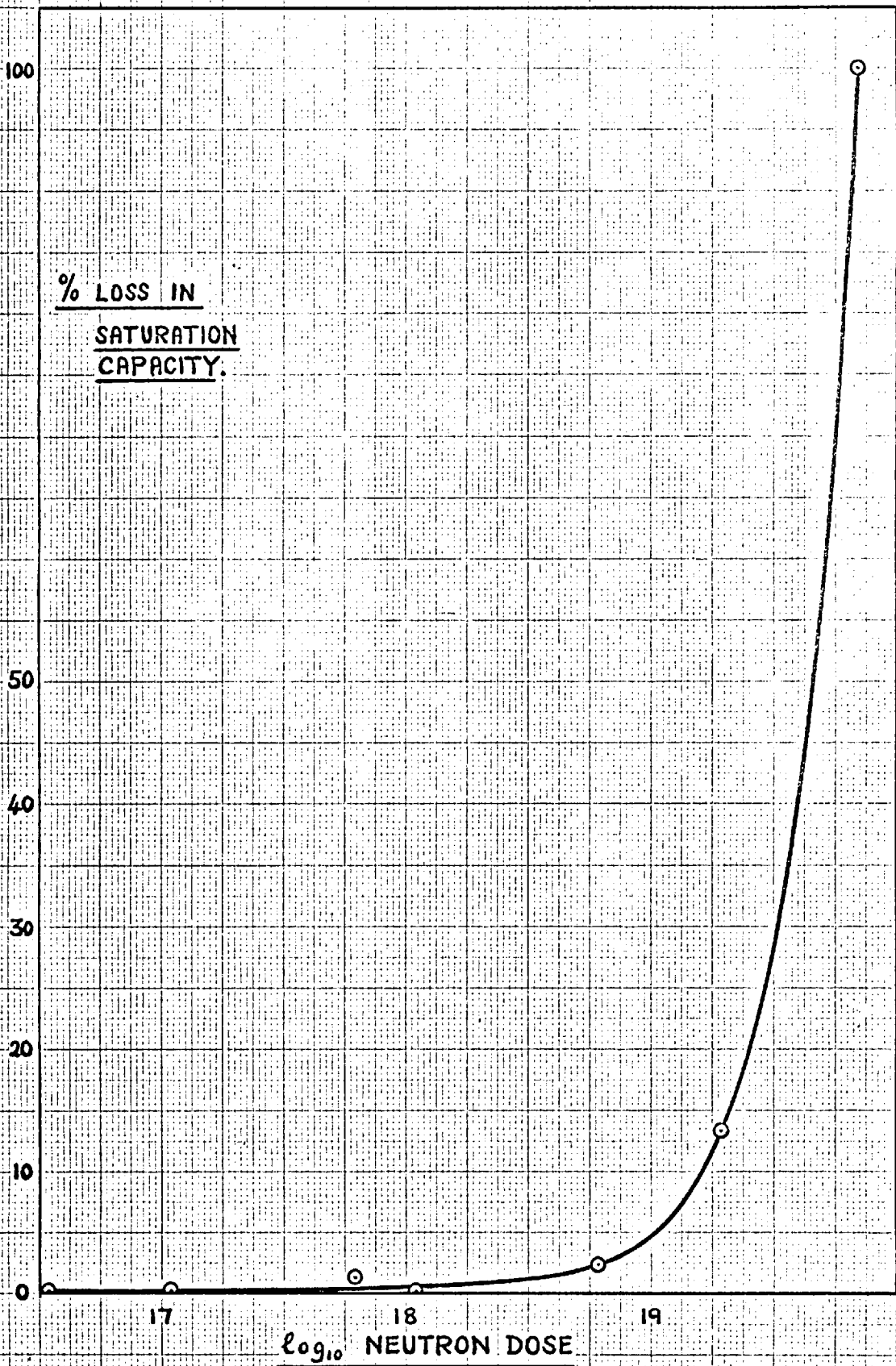
Saturation Capacities:

Section 4.2.1. does not however, include the saturation capacities of the samples of unirradiated and damaged samples. These were calculated in the same manner as for krypton sorption at -150°C etc., i.e. by plotting p/V vs. p and using the limiting slope in the high pressure region to calculate a value of V_{sat} . The values obtained are tabulated below together with the % capacity losses :-

Sample.	Saturation Capacity.	% Loss in Capacity.
NaX_0^{O} NaX_1^{H} NaX_2^{H} NaX_3^{H}	244.6	-
NaX_4^{HH}	241.9	1.1
NaX_5^{HH}	238.8	2.4
NaX_6^{HH}	(less than 10)	(100)
NaX_7^{HH}	212.0	13.3

The 13.3% loss in sorptive capacity of the sample NaX_7^{HH} for argon may be compared to the 12.8% loss in capacity for krypton, and the 2.4% loss in capacity for argon by NaX_5^{HH} may be compared to the 1.9% loss in capacity for krypton. (The figures quoted for krypton are the average %'s obtained from the -120 to -150°C isotherms). A plot of (% loss in capacity for argon) vs. (the log. of neutron dose) is given in figure 40. The steep rise in this curve indicates that damage rapidly becomes extensive when the integrated neutron dose exceeds 10^{19} n/cm^2 .

FIGURE 40



4.2.8. Heats of Occlusion of Argon in NaX.

The isosteric heats of occlusion were calculated for the pairs of isotherms, $0^{\circ}/25^{\circ}$, $-40^{\circ}/-70^{\circ}$, $-40^{\circ}/-100^{\circ}$ and $-70^{\circ}/-100^{\circ}\text{C}$, and found to be 2.7, 2.75, 2.75 and 2.8 k.cal./mole respectively. These results show there to be a slight temperature dependence in the isosteric heats, the heat evolved increasing, the lower the temperature of the experiment. The same effect was observed with krypton sorption (vide section 4.2.4.).

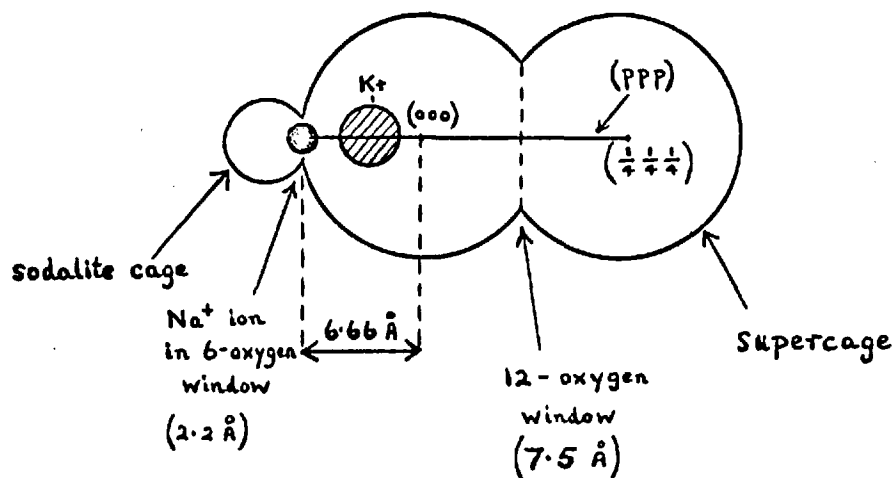
4.2.9. Intermolecular Forces.

As previously discussed (vide section 2.2.7.) only dispersion and repulsion forces between the adsorbate and adsorbent atoms need be considered for the system, krypton sorbed on NaX. Polarization, dipole-dipole interactions etc. are either negligible or non-existent, (see page 89), therefore :

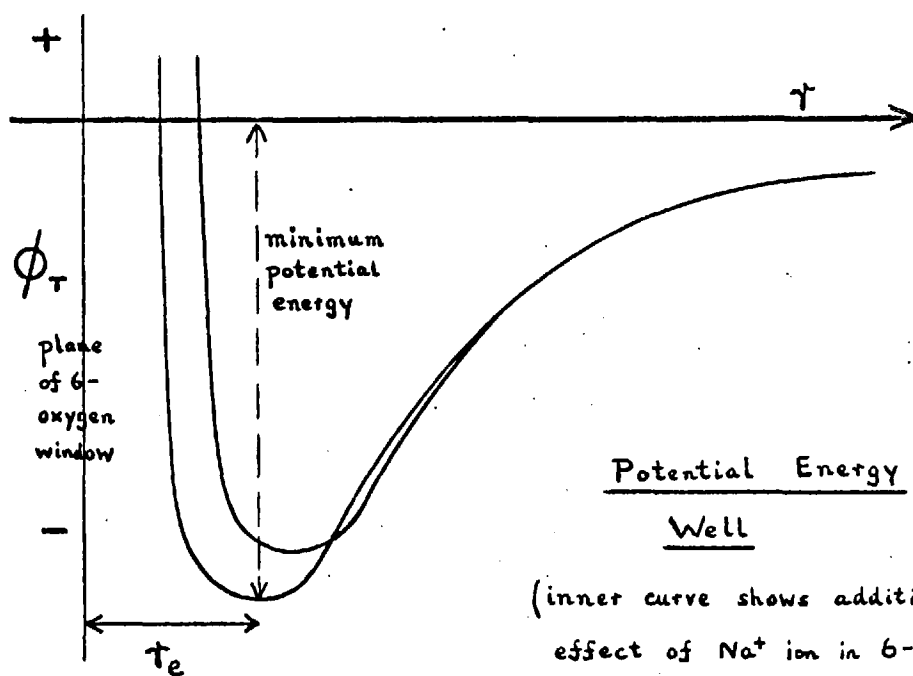
$$\phi_T = \phi_D + \phi_R \quad (61)$$

The main contribution to the dispersion energy arises from the numerous oxygen atoms of the zeolite lattice. The relatively small number of aluminium and silicon atoms are screened by these oxygen atoms, so their contribution towards the dispersion energy interactions, is negligible. However, the contributions from the cations located within the lattice cannot be ignored, although it is sometimes difficult to locate their precise positions, if indeed they occupy definite sites.

The Lennard-Jones 6-12 potential energy function (116), equation 66, page 92, relates these dispersion and repulsion energies to r , the distance separating the lattice atom and guest molecule, and r_e , this distance at equilibrium, which, to a first approximation is the sum of the radii of the two interacting atoms. The constant A is given by either the London expression (refs.105,113,) number 69, page 93, or the Kirkwood-Muller expression (ref.117), number 70, page 93. The Slater-Kirkwood expression (ref.118), number 71, page 93, will be ignored throughout this discussion as this value of A lies between the above two values. The values of A calculated from these expressions, for the interaction between framework oxygen and krypton, and between two krypton molecules are given later in this section. The Kr - O interactions involve a very laborious series of summations in order to account for all the oxygen atoms (constituting a "supercage"), with which the krypton atom reacts. Figure 41 schematically illustrates the outline of a supercage with a hexagonal window of six oxygen atoms on the left hand side opening into a sodalite cage, and a twelve oxygen window opening into another supercage on the right hand side; (each supercage has four adjacent supercages and four adjacent sodalite cages tetrahedrally disposed, but, for the sake of clarity, only one of each has been shown). For the purpose of these calculations, the krypton 'probe'

FIGURE 41

Schematic Representation of Kr probe molecule moving along (PPP) axis towards Na⁺ ion and Sodalite cage.

FIGURE 42

(inner curve shows additional effect of Na⁺ ion in 6-oxygen window).

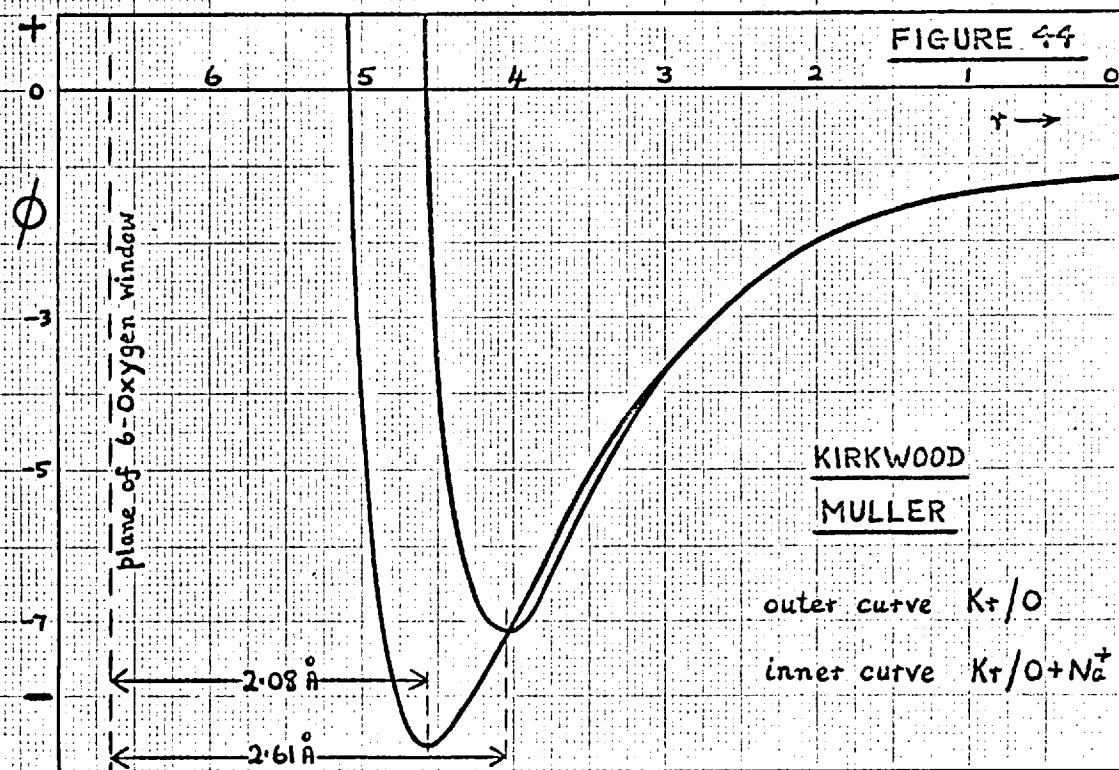
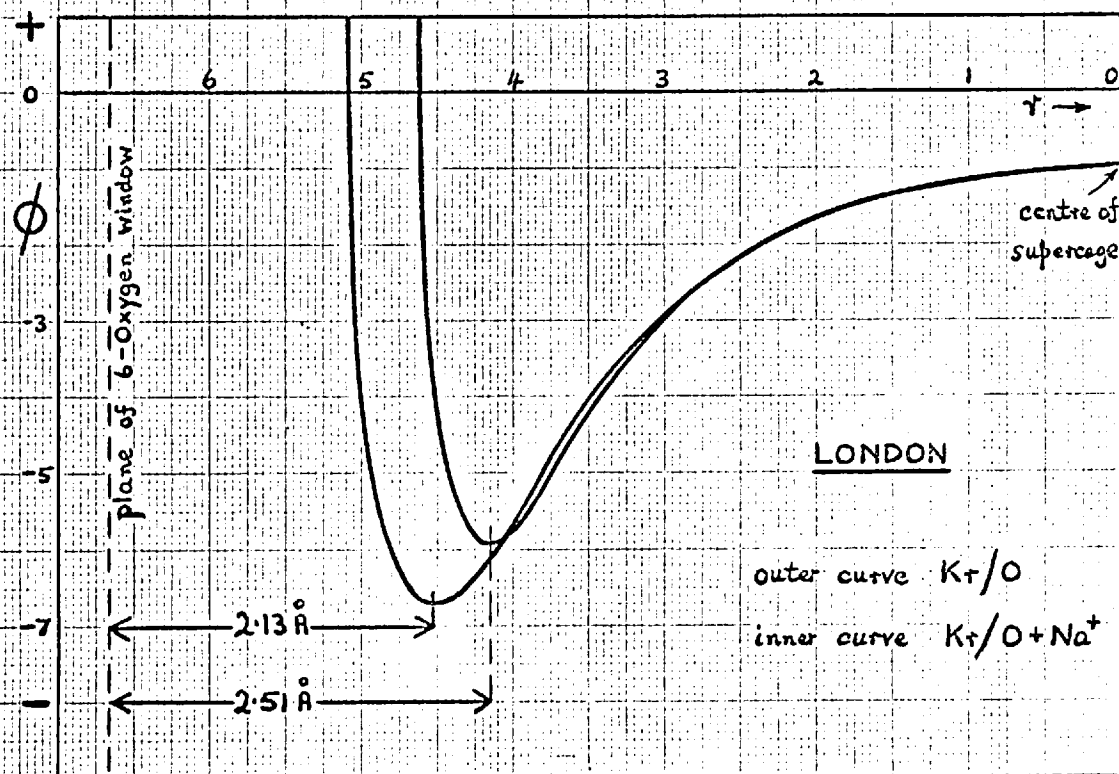
molecule is assumed to travel along the axis joining the centres of two supercages, towards the 6-oxygen ring of the adjacent sodalite cage. If the centre of one supercage is taken as the origin, then the centre of the adjoining supercage is given the co-ordinates $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, and the co-ordinates of any point on this line may be denoted by (ppp), where p denotes variable parameter. This proves extremely convenient as it allows relatively easy calculation of r^2 , i.e. the square of the distance between a krypton molecule on this axis to any framework oxygen, and consequently r^6 and r^{12} also, the reciprocals of which are required in the Lennard-Jones equation.

The positions of the framework oxygens were determined by three dimensional Fourier electron density analysis by Broussard and Shoemaker (10) and the values of $1/r^6$ and $1/r^{12}$ computed by Crawford and Kerr (140).

The question then arises as to whether or not, we are justified in making these summations. Barrer & Stuart (145) integrated the Lennard-Jones equation over the volume of a clathrate compound outside the given cavity; this could likewise be done with a zeolite, but would only account for a fraction of the total interaction energy, over 90% being due to the oxygen atoms 'lining' the supercage walls. It can be shown in any case, that interactions between atoms further apart than $2r_e$ may be regarded as negligible. Consequently, the above summations will be regarded as sufficient for

the calculation of the total interaction energy ϕ_T . Plotting ϕ_T vs. distance of krypton probe molecule from the origin, results in a potential energy curve of the form shown in fig. 42, which also illustrates the effect of including the interaction between the krypton molecule and the Na^+ ion; this is assumed to lie in the plane of the 6-oxygen ring (see later). As might be expected now that an additional atom is considered, the distance between the Kr molecule and the sodalite cage window increases, so the potential energy minimum decreases (numerically). The following table shows the dispersion energy constants for the interacting pairs (Kr - O), (Kr - Kr) and (Kr - Na^+); and also the minimum potential energies of the Kr-sodalite cage window interactions, calculated using these values in expression, no. 67, p. 92. Two values of potential energy are given, the first, when assuming the Na^+ is absent from the window, and the second, assuming it occupies the same position as it does in the hydrated zeolite; the corresponding equilibrium separations between the probe molecule and the window are also quoted; the ϕ_T and r_e values are all taken from figures 43 and 44, which show the potential energy curves due to the interactions between the probe molecule and framework oxygen atoms alone, and also when considering the presence of the Na^+ ion. The dotted vertical line represents the plane of the 6-oxygen window and the abscissa corresponds to the (ppp) axis along which the probe molecule is moving.

FIGURE 43



POTENTIAL ENERGY WELLS

	London	Kirkwood Muller	units
<u>Dispersion Energy</u>			
<u>Constants:</u>			
(Kr - O)	2.303×10^{-42}	2.875×10^{-42}	} cal. cm ⁶ ./ mole.
(Kr - Kr)	1.489×10^{-42}	4.201×10^{-42}	
(Kr - Na ⁺)	0.176×10^{-42}	0.421×10^{-42}	
<u>Minimum Potential</u>			
<u>Energies:</u>			
without Na ⁺	6.70	8.65	} k.cal. /mole.
with Na ⁺	5.90	7.15	
<u>Equilibrium (Kr - O)</u>			
<u>Separations:</u>			
without Na ⁺	2.13	2.08	} Å
with Na ⁺	2.51	2.61	

When the probe molecule reaches its equilibrium position, it is preferentially occupying a position at which its potential energy is a minimum, and since the energy wells are relatively deep and narrow, the molecule will tend to remain in this sorbed position (corresponding to localized sorption). The greater the depth of the well, the greater the forces of localized sorption. As can be seen from the above figures, the net effect of the Na⁺ ion in the sodalite cage window, is to reduce by about 10 - 15%, the interaction energy between the framework oxygen atoms and the Kr molecule. Since the cations actually contribute very little to the total dispersion

energy, this 10 -15% reduction in energy is explained by the Na^+ ion displacing the probe molecule; moving it further towards the centre of the supercage, hence reducing the interactions with the framework oxygen atoms. The position of the Na^+ ion in the dehydrated lattice is not known for certain; upon dehydration, it is fairly reasonable to suppose that it is drawn slightly further into the sodalite cage, thus reducing the $\text{Kr} - \text{Na}^+$ interaction. This results in an increase in the depth of the potential energy well; the two curves in fig. 43 (or 44) thus represent the extreme values of ϕ_T , the inner curve assuming the Na^+ ion occupies the same position as in the hydrated lattice, and the outer curve assuming the complete absence of this ion from the vicinity of the window.

If the first 4 krypton molecules are preferentially sorbed on the sodalite cage windows, then these sites must be energetically more favourable than the remaining sites in the supercage. The difference cannot be large however, otherwise a decrease would have been observed in the ΔH vs. θ plot (fig.27), instead of the pronounced peak. It is in fact possible that the peak represents the net result of an increase due to molecule-molecule interactions, plus a decrease due to $\text{Kr} - \text{O}$ interactions (reduced by the presence of Na^+ ions in cage windows).

It was assumed in section 4.2.3., that the adsorbed krypton molecules would only occupy the supercages in NaX . This arises from the fact that the Kr atom

has a diameter of 3.94 Å, and the free diameter of the sodalite cage window is 2.2 Å. The potential energy plot shows that if the Kr probe molecule approaches as close as 1.5 Å to the window, then the repulsion energy term would be of the order of 100 kcal./mole. Hence it is extremely unlikely that the Kr molecule could enter a sodalite cage.

4.2.10. Interpretation of Isothermic Heats in Terms of Intermolecular Forces:

Since the energy of sorption is the difference between the sum of the heat contents of the separated adsorbate and adsorbent, and the enthalpy of the sorbed phase, it should be possible to explain this exothermal sorption process in terms of intermolecular forces, i.e. the forces of interaction between the adsorbent lattice atoms and the adsorbate molecules.

As previously shown in section 2.2.6., the isothermic heat may be directly related to the potential energy, by the approximation:

$$\emptyset = -q_{st} + RT \quad (57)$$

where $\emptyset$, q_{st} and R are expressed in cal/mole of adsorbate. From figs. 43 and 44 of the previous section, the maximum values of $\emptyset_T$ are seen to be approx. 7 and 9 k.cal./mole (London and Kirkwood Muller respectively), for Kr sorbed on the sodalite cage windows; for Kr sorbed on different sites in the supercage, $\emptyset_T$ will be slightly less. The

isosteric heat curve, fig.27 of section 4.2.4., shows that when q_{st} is independent of the amount sorbed (up to $\Theta=0.3$) $q_{st} = 4$ k.cal/mole. Since the term RT only amounts to approx. 0.25 k.cal/mole, the agreement is not very good. Barrer & Wasilewski (34) observed a value of q_{st} (+ RT) of 16 k.cal/mole for the sorption of iodine by NaX, which agreed very well with the calculated maximum value of $\phi_T = \phi_D + \phi_R$ of 15.1 k.cal/mole.

Up to now, we have only been concerned with the sorbate-lattice interactions. An attempt to explain the peak of the isosteric heat curve (fig. 27) will now be presented; it is considered to be due to sorbate-sorbate interactions.

The partial molar energy of the sorbed gas, $\bar{E}_s$, may be expressed in terms of the molar energy and the number of molecules actually sorbed:

$$\bar{E}_s = \tilde{E}_s + n_s \left[\frac{\partial \tilde{E}_s}{\partial n_s} \right]_{P,T,n_a} \quad (84)$$

The molar energy is given by:

$$\tilde{E}_s = \tilde{E}_{Kr-L} + \tilde{E}_{Kr-Kr} \quad (85)$$

these two terms representing the contributions towards the molar energy of the sorbed phase, from the Kr - lattice and Kr - Kr interactions respectively. If it is assumed that $\tilde{E}_{Kr-L}$ is independent of Θ for all values (i.e. $q_{st_{Kr-L}} = - \phi_{Kr-L} + RT$), substitution of equations 84 and 85 into the expression for the isosteric heat at temp. T ,

$$\text{i.e.} \quad q_{st} = \tilde{E}_g - \bar{E}_s + RT \quad (51)$$

$$= \tilde{E}_g - \tilde{E}_s - n_s \left[\frac{\partial \tilde{E}_s}{\partial n_s} \right]_{P,T,n_a} + RT \quad (52)$$

$$\therefore q_{st} = \tilde{E}_g - \tilde{E}_{Kr-L} + \tilde{E}_{Kr-Kr} + n_s \left[\frac{\partial \tilde{E}_{Kr-Kr}}{\partial n_s} \right] + RT \quad (86)$$

Considering the simple model of localized sorption with interactions, $\tilde{E}_{Kr-Kr}$ may be expressed as $\frac{1}{2} \cdot 2w \cdot \theta \cdot z$, where $2w$ is the interaction energy between a pair of sorbed molecules (see sections 2.2.4. and 4.2.5.) and has the value -384 cal/mole; θ is the degree of saturation, i.e. a fraction of n_s ; and z is the co-ordination number of a sorbed molecule = 4. Since $\tilde{E}_{Kr-Kr} = \frac{1}{2} \cdot 2w \cdot \theta \cdot z$ and θ is a fraction of n_s ,

$$n_s \left[\frac{\partial \tilde{E}_{Kr-Kr}}{\partial n_s} \right] = \frac{1}{2} \cdot 2w \cdot \theta \cdot z \quad (87)$$

Substitution in (86) gives:

$$\begin{aligned} q_{st} &= \tilde{E}_g - \tilde{E}_{Kr-L} + \frac{1}{2} \cdot 2w \cdot \theta \cdot z + \frac{1}{2} \cdot 2w \cdot \theta \cdot z + RT \\ &= \tilde{E}_g - \tilde{E}_{Kr-L} + 2w \cdot \theta \cdot z + RT \end{aligned} \quad (88)$$

This relationship shows that q_{st} should increase linearly with θ as soon as the sorbed molecules are sufficiently close as to interact. This was in fact observed experimentally in the range $0.35 < \theta < 0.725$. The difference in q_{st} corresponding to these two values of θ , is given by the only variable term in equ. 88, namely $2w \cdot \theta \cdot z$.

Thus, the calculated height of the isosteric heat peak is:

$$(2w \cdot \theta \cdot z)_{q_{\max}} - (2w \cdot \theta \cdot z)_{q_{\min}}$$

$$\begin{aligned}
 &= (0.384 \times 0.75 \times 4) - (0.384 \times 0.35 \times 4) \\
 &= 0.61 \text{ k.cal/mole}
 \end{aligned}$$

which is to be compared with the experimental figure of 0.5 ± 0.05 k.cal/mole. For the system, iodine sorbed on NaX, Barrer & Wasilewski (34) calculated a peak height of 4.6 k.cal/mole, the experimental value being 3.7 k.cal/mol. For iodine sorbed on zeolite "5A" and chabazite, the theoretical values were also higher than the experimental. They tentatively concluded that the sorbed iodine molecules were not lying exactly parallel to each other inside the crystal lattice, and therefore the calculated value was a maximum. The krypton molecules in NaX may well be separated by less than the sum of their Van de Waals radii, in which case, $2w$ would be less (numerically). From a potential energy curve (e.g. fig. 42), it can be seen that a very small decrease in the equilibrium separation of two sorbed molecules would result in a large numerical decrease in ϕ . It was assumed earlier that $E_{\text{Kr-L}}$, the molar energy of interaction between sorbate and lattice, was independent of θ . This is not strictly true; in section 4.2.9., it was considered that there was an enhanced energy of interaction between the 4 sodalite cage windows per supercage and the first 4 molecules of krypton sorbed, subsequent molecules being sorbed on other sites with slightly lower heats of adsorption. This effectively means an increase in the height of the isosteric heat peak; the experimental value then agrees more closely with the theoretical value.

Taking into account the assumptions and approximations made in calculating intermolecular forces, it may be concluded that the experimentally observed isosteric heats may be explained in terms of:-

- (a) surface homogeneity up to $\theta = 0.3$ to $.35$, when the heat of adsorption results entirely from sorbate - lattice interactions, and after which the theory assumes $q_{st_{Kr-L}}$ to remain constant, p. 229.
- (b) after $\theta = 0.3$, mutual interactions between sorbed molecules become significant, producing a peak in the isosteric heat curve, the height of which is less than, but of the same order as the theoretically calculated value of 0.61 k.cal/mole.

4.3.NEUTRON IRRADIATION.Some Miscellaneous Observations:

The effects of neutron irradiation of NaX in respect of its cation exchange properties have already been discussed in section 4.1.8., and as regards gas adsorption, in section 4.2.3. for krypton and section 4.2.7. for argon. This section includes some miscellaneous observations and some simple calculations for the damage arising from fast neutron bombardment, and for the nuclear transmutations due to thermal neutrons.

Gas evolution: The first two samples of zeolite were found upon unsealing of the silica ampoule, to possess an appreciable gas pressure. Since the zeolite had not been outgassed, it consisted of over 25% by weight of water. The pressure observed was therefore assumed to be due to hydrogen and oxygen, resulting from the radiolytic decomposition of some of this water. At much higher radiation doses, the pressure build-up might have caused mechanical failure of the silica ampoules during irradiation, and consequently succeeding samples were always completely outgassed before sealing, (vide section 3.2.1.).

Colouration of Samples: Only the sample irradiated to a dose of $7 \times 10^{19} \text{ n/cm}^2$ exhibited any colour effect; it assumed a very pale tinge of cream. Colour changes have frequently been observed in quartz and silica (36,

52) and in fact this was found to be the case with the silica ampoules. The ampoule irradiated to a dose of 3.5×10^{16} n/cm² was a pronounced purple in colour, and the second ampoule (dose = 1.1×10^{17} n/cm²) was even darker in colour. For progressively high doses however, the colour intensity steadily decreased until sample 5, (dose = 6×10^{18} n/cm²), for which the ampoule was quite colourless. In contrast, the ampoule irradiated to a dose of 7×10^{19} n/cm² was again tinted slightly purple. The colour is bleached upon heating in a bunsen flame, i.e. the radiation produced defects are annealed out.

Remaining Activity in Zeolite Samples after Irradiations:

As explained in section 2.3.3., all the activities resulting from nuclear transmutations of Al, Si, O & Na⁺ will have decayed to an inappreciable level within one week. However, the samples, nos. 4 to 9, were found to be appreciably active upon return from the reactor unit. With samples 6, 7 and 8, this activity was only partially decreased by exchange with saturated sodium chloride solutions, even at 100°C. This meant that either the active cations were trapped within a partially collapsed lattice, or that the activity was not in fact due to exchangeable cations. A portion of sample 6 (dose = 7×10^{19} n/cm²) was dissolved in concentrated hydrochloric acid, the insoluble silica being filtered off. This solution was then counted regularly in the Geiger-Muller liquid counter over a period of several months,

in order to determine the half life of the active element, and hence its identity. Initially the half life appeared, from the plot of log count rate vs. time, to be approximately 22 days. However, such a plot should be a straight line; in fact it was found to be a very gentle curve convex to the abscissa, inferring the presence of more than one activity. Counting over a long period would therefore be necessary to identify the half lives, since even for 2 active isotopes, one must almost completely decay before the second one can be positively identified. The count rate was recorded every week for several months, so that at least an estimate could be made of the half lives of these impurity atoms. The longer lived isotope appeared to possess a half life of the order of 2-3 years, corresponding to one of the chief possibilities (vide section 2.3.3.) namely, caesium - 134 . Assuming this to be so, it was then possible to determine the half life of the shorter lived isotope which was found to be less than 20 days; this was most likely to be rubidium - 86 . Thus by the liquid counting technique, it was possible over a period of several months, to state with a fair degree of certainty, that the impurity atoms were Rb^{86} and Cs^{134} , resulting presumably from (n, γ) transmutations of Rb^{85} and Cs^{133} .

A more convenient method of determining the

identity of these activities is by gamma-spectroscopy. For this purpose, the above solution was employed and the intensities of the γ -rays determined by means of a scintillation counter. By comparison with standard cobalt - 60 and caesium - 137 sources, with known γ -energies of 1.17 and 1.33 MeV, and 661 KeV respectively, two maxima were found in the plot of count rate vs. voltage (see figure 45) corresponding to γ -energies of 0.8 and 1.08 MeV. The latter corresponds to Rb^{86} , hence confirming the existence of Rb^{85} as an impurity atom in NaX. Although the peak corresponding to a γ -energy of 0.8 MeV might well be partly due to the presence of Cs^{134} (γ -energies of 0.6 and 0.8), the height of the peak suggests it is chiefly caused by Compton scattering; consequently, this observation cannot really be considered as proof of the existence of Cs^{133} as an impurity in NaX.

4.3.1. Calculation of Energy Transfer during Fast Neutron Bombardment and the Number of Atoms displaced:

The neutrons emitted from the fission of a U^{235} atom range in energy from 0.5 to 15 MeV, the average for the purposes of calculation usually being taken as 1 - 2 MeV. The value of 1 MeV will be used here.

The maximum amount of energy that may be transferred to an element of atomic mass M , in an elastic collision, by a neutron of mass $N = 1$, and energy

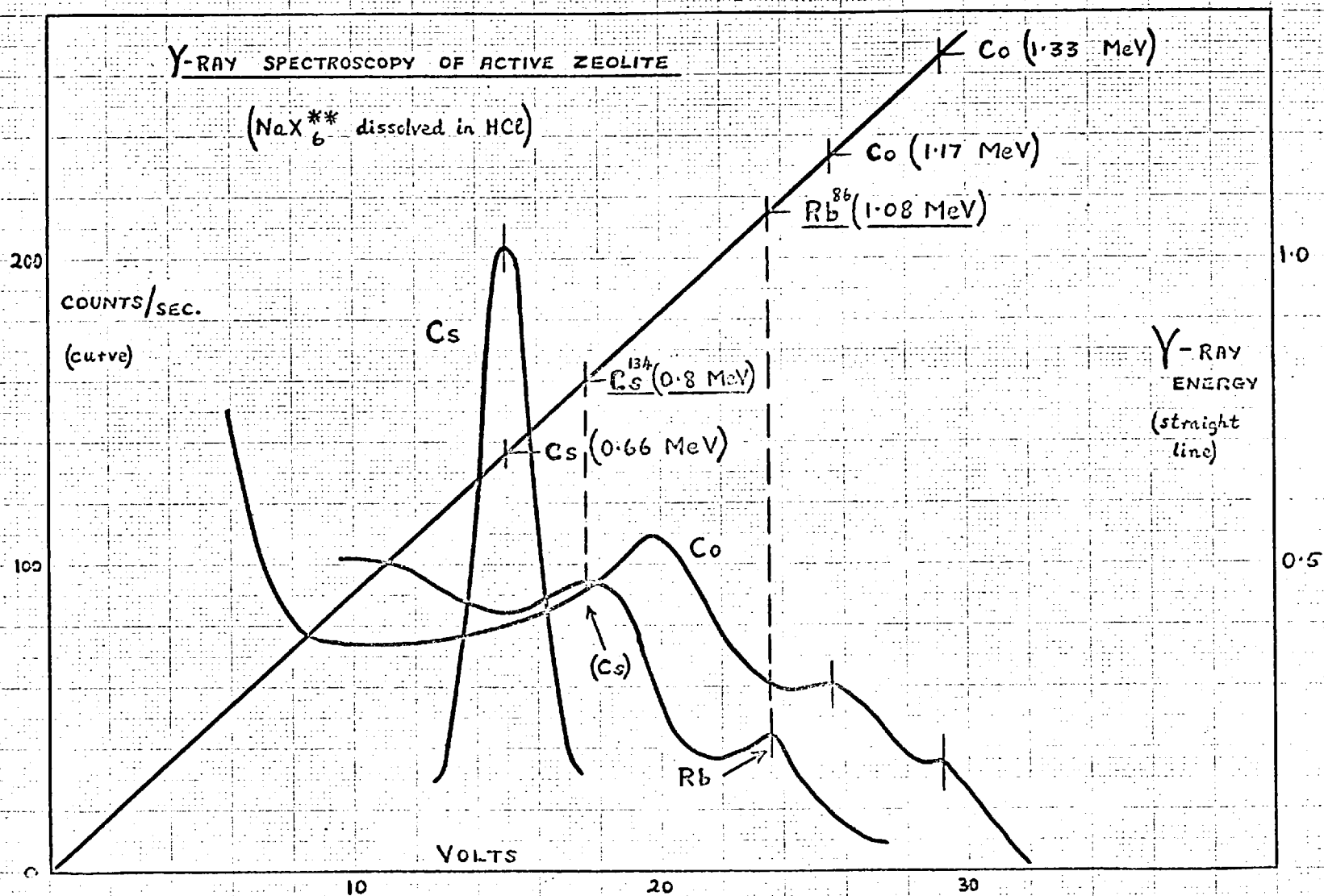


FIGURE 4.5

E , is given by :-

$$E_{\max} = \frac{4EMN}{(M+N)^2} \quad (72)$$

which approximates to:- $\frac{4EM}{(M+1)^2}$ or $\frac{4E}{M}$ (73)

For a silicon atom this is approximately 0.1 MeV, i.e. one tenth of the incident neutron energy. This applies to a direct head on collision between the neutron and lattice atom; in glancing collisions, the energy transferred would be correspondingly less. The average energy transferred is $\bar{E} = E_{\max}/2 = 0.05$ MeV, which is considerably larger than the displacement energy of an atom, usually taken as 25 eV. Consequently, as long as the bombarding neutron still possesses energy in excess of $M/2 \times 25$ eV, it will continue to displace lattice atoms upon collision. The number of primary collisions resulting in displacements due to each bombarding neutron, may therefore be expressed as :-

$$\begin{aligned} N_d &= \frac{E_{\max}}{4 E_d} = \frac{\bar{E}}{2E_d} = \frac{0.05 \text{ MeV}}{2 \times 25 \text{ eV}} \quad (76) \\ &= 1000 \text{ displacements.} \end{aligned}$$

According to previous calculations (vide section 2.3.3.), this estimate is of the order of five times too large, i.e. approximately 200 primary displacements occur per incident neutron. These 200 projectile atoms resulting from every fast neutron, travel throughout the lattice causing ionisation and excitation until they come to

rest as interstitial atoms or fall into a vacant lattice site.

The expression derived by Dienes & Vineyard (121) may also be employed to calculate the number of displacements, in this case within a specific volume of the target material: $N_p = \phi \cdot t \cdot n \cdot c_d$ (78)

where N_p = number of primary displaced atoms.

$\phi \cdot t$ = total integrated fast neutron flux.

n = no. of atoms per unit weight of bombarded material.

c_d = displacement cross section of target element.

As shown in 2.3.2.:
$$N_d = \frac{N_p \cdot E.M.f.}{E_d \cdot (M+N)^2} \quad (80)$$

The following table gives the values of n for NaX, the cross sections of the lattice atoms and the number of displacements (corrected for replacements by dividing by 5) corresponding to the two neutron doses of 6×10^{18} and 7×10^{19} n/cm². (NaX₅^{xx} and NaX₆^{xx} respectively).

Percentage Number of Displaced Atoms
resulting from Neutron Bombardment.

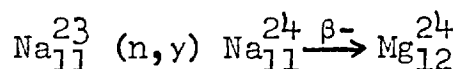
Atom	No. of atoms /g. NaX ($\times 10^{21}$)	Cross Section (barns)	$N_d (\times 10^{20})$ (corr ^d) (7×10^{19})	% No. of atoms displaced	% No. of displaced atoms ₁₈ (6×10^{18})
Si	4.8	4.7	2.8	6%	0.5%
Al	3.9	2.6	1.3	3%	0.3%
Na ⁺	3.7	3.7	2.0	5%	0.4%
O	17.6	8.0	52	30%	2.5%

These calculations show therefore, that a total neutron dose of 7×10^{19} n/cm² displaced approximately 45% of all the atoms present in the sample of NaX, even allowing for replacements. With such a large proportion of atoms removed from their normal lattice sites, it is to be expected that the lattice would suffer a major collapse, and consequently lose its sorptive properties. Sample 5 was observed to have lost approximately 2% of its sorptive capacity, which is qualitatively supported by the above calculation, where a total of about 4% of the lattice atoms have been displaced. The expression of Dienes & Vineyard (121) thus appears to provide a good estimate of the amount of damage to be expected in a zeolite for a given fast neutron dose.

4.3.2. Calculation of Specific Activities resulting from the irradiation of NaX with slow neutrons.

The yield or specific activity of an element is given by equation 82, section 2.3.4., page 105. Anhydrous NaX contains approximately 14% by weight of Na²³, and each sample tube contained approximately 0.1 g. NaX, hence the specific activity per ampoule approximated to 1 curie. Similar calculations for the Al₁₃²⁸, Si₁₄³¹ and O₈¹⁹ atoms give the following specific activities per ampoule respectively: 0.3 curies, 0.2 mc and 3 μ c, all of which completely decay within one day.

4.3.3. Calculation of Yield of Mg from Na decay:



The actual weight of magnesium produced in a sample by the β -decay of the unstable Na^{24} , may be calculated as follows:

$$\text{Mass (of Mg)} = 7.7 \times 10^{-9} \cdot \text{A.T.S.} \quad (83)$$

where A, T, & S are defined in section 2.3.4., whence the mass of magnesium equals $8.8 \times 10^{-7} \text{ g./g. anhydrous NaX}$. Since the replacement of Na^+ ions by the divalent Mg^{++} ions, is bound to affect the sorptive properties of the zeolite, it is interesting to make the above calculation. However, the yield of magnesium is so small that it is extremely unlikely that the isosteric heat curves would show the slightest change. Much heavier thermal neutron doses would be necessary to produce any appreciable effect; and they would have to be pure thermal neutrons, otherwise excessive physical damage would also result from the fast neutron bombardment.

4.3.4. Discussion of the form in which structural damage to a zeolite is manifested.

Crawford & Wittels (51) assumed that the lattice vacancies and interstitials resulting from the neutron irradiation of quartz, were almost entirely due to oxygen atoms. This assumption arises because the displacement cross sections of the oxygen and silicon atoms are 8.0 and 4.7 barns respectively; because there

are more O atoms than Si atoms per unit volume; and because more energy is required to displace a Si atom. This latter reason arises from the fact that each Si atom is covalently bonded to four O atoms, whereas each O atom is joined to only two neighbouring atoms. The same applies to the structure of NaX, the cross sections of Al and Na^+ being 3.9 and 3.7 barns respectively, and where the oxygen atoms outnumber the others by about 4 to 1 in each case. It is therefore to be expected that a high percentage number of displaced oxygen atoms, will result in a collapse of the lattice, i.e. partial collapse throughout, or, in the other extreme, complete collapse within small regions.

Appreciable damage to quartz occurs at a slightly higher dose than for NaX, i.e. approximately 2×10^{20} as opposed to $7 \times 10^{19} \text{ n/cm}^2$; this might be expected as the quartz lattice is more compact than the very open lattice of NaX (0.53 void space). Collapse of a zeolite lattice is thus easier to comprehend than a similar occurrence in quartz. Density measurements showed there to be a distinct increase in density for the completely damaged sample ($7 \times 10^{19} \text{ n/cm}^2$), from approximately 2.0 g/cc. of hydrated NaX to 2.4 g/cc., representing a 20% increase. This is greater, but of the same order, as the density increase observed for vitreous silica. Primak (52) suggested that the displaced atoms in vitreous silica lodge in the cavities

within the lattice, so permitting a general relaxation of the structure into a more compact arrangement, thus increasing the density.

Work by Levy & Kammerer (58) on the neutron irradiation of diamond, led Dienes & Vineyard (121) to make the tentative conclusion that in diamond, a drastic collapse of the crystal lattice occurs rather suddenly at high exposures. This might be said to have been observed with NaX, see figure 40.

Two other facts are worthy of mention here; firstly, Simon (56) observed a decrease in the Si-O-Si bond angle (from 142° to 138°) in silica, upon neutron irradiation, which would be expected upon relaxation of a lattice; and secondly, irradiation of coesite, a high density silica (3.01 g/cc), with a neutron dose sufficient to reduce quartz and vitreous silica to a common amorphous phase, had no observable effect. This suggests that the more dense and compact the structure, the less the structural effects.

It has frequently been observed that annealing of damage is possible simply by heating the sample. Primak & Szymanski (55) found that vitreous silica could be gradually annealed at 300°C and Primak et al. (141) found that diamond was annealed above 100°C . The silica ampoules containing the zeolite samples were coloured purple by the neutron irradiation, but heating the ampoules in a bunsen flame bleached them. The irradiated

zeolite samples were heated to 350°C for 24 hours before sorption measurements were made; it must be hoped that annealing of any structural damage did not take place.

It was hoped that neutron irradiation of NaX would have resulted in measurable changes in the isosteric heats etc. (see section 4.2.2.), in order that an analysis in terms of thermodynamical properties could have been made. However, doses in excess of $2 \times 10^{19} \text{ n/cm}^2$ will be necessary for this purpose, although too great an excess will lead to a general structural collapse as was observed for sample 6 (dose of $7 \times 10^{19} \text{ n/cm}^2$). It is also considered that even more accurate isotherms are desirable for the obtainment of accurate isosteric heat curves.

APPENDIXES

SUMMARY OF EFFECTS OF
NEUTRON IRRADIATION OF LINDE MOLECULAR SIEVE 13-X

<u>Sample</u> <u>of NaX</u>	<u>Dose</u> (n/cm ²)	<u>Cation</u> <u>Exchange</u>	<u>Capacity Loss</u>		<u>X-rays</u>
			<u>%A</u>	<u>%Kr</u>	
NaX ₁ ^x	3.5x10 ¹⁶	p.165	)	no damage	-
NaX ₂ ^x	1.1x10 ¹⁷	p.165			-
NaX ₃ ^x	1.1x10 ¹⁸	p.165			-
NaX ₄ ^{xx}	6.2x10 ¹⁷	-	1.1	-	-
NaX ₅ ^{xx}	6.0x10 ¹⁸	p.167	2.4	1.9	-
NaX ₆ ^{xx}	7.0x10 ¹⁹	p.168	(100)	(100)	p.194
NaX ₇ ^{xx}	1.9x10 ¹⁹	p.167	13.3	12.8	p.194
NaX ₈ ^{xx}	1.3x10 ¹⁹	p.167	-	-	-
NaX ₉ ^{xx}	6.6x10 ¹⁸	p.145	-	-	-

NaX Sample Notations:

Superscript ^x denotes irradiated but undamaged sample.

Superscript ^{xx} denotes irradiated and damaged sample (as observed by sorption).

Superscript ^o denotes standard sample.

Subscript numbers equal order of irradiation.

APPENDIX ACATION EXCHANGE:

NaX / Cs⁺ Exchange System: (27°C): Figure 14 a.

Standard Sample:Irradiated Samples:

<u>A_s=Cs_s</u>	<u>A_z=Cs_z</u>	<u>Sample</u>	<u>Initial</u>	<u>A_s=Cs_s</u>	<u>A_z=Cs_z</u>
			<u>Molality</u>		
.960	.570				
.903	.505				
.843	.454	<u>NaX^{xx}₁</u>	(unless	.616	.401
.793	.440		other-	.211	.251
.786	.426		wise		
.682	.413	<u>NaX^{xx}₂</u>	stated,	.852	.460
.679	.416			.427	.363
.666	.433		m=0.05)		
.532	.394	<u>NaX^{xx}₃</u>		.745	.444
.453	.371			.393	.338
.314	.306				
.253	.276	<u>NaX^{xx}₅</u>	.025	.951	.520
.172	.227		.025	.934	.459
.126	.189		.00625	.823	.451
.096	.167		.00125	.389	.295
.082	.146		.00625	.084	.280
.078	.142	<u>NaX^{xx}₆</u>	.008	.983	.078
			.004	.966	.044
			.002	.340	.030
			.00032	.131	.051
<u>NaX / UO₂⁺⁺ System:</u>					
(fig.18) (25°C)					
.973	.535	<u>NaX^{xx}₇</u>	.025	.874	.354
.950	.480		.00125	.382	.190
.942	.501		.00125	.216	.140
.930	.541				
.912	.468	<u>NaX^{xx}₈</u>	.025	.961	.602
.908	.369		.004	.760	.430
.902	.512		.00064	.268	.240
.892	.301		.00032	.041	.139
.890	.188				
.860	.128				
.840	.040	<u>NaX/UO₂⁺⁺ (cont.):</u>			(di-uranate)
.788	.074		(60°C)	.82	.42
.638	.069			.821	.100
.598	.120	.882	.411	.810	.052
.560	.081	.861	.080	.760	.044
.349	.079	.859	.076	.522	.085
.141	.071	.682	.071	.375	.065
.099	.081	.301	.074	.125	.092
				.062	.048

NaX / Ba⁺⁺ Exchange System:

(27°C) (fig.16a)

<u>Initial</u> <u>Molality</u> <u>of BaCl₂.</u>	<u>Ba_s</u>	<u>Ba_z</u>
.025	.754	.731
.0332	.727	.748
.0332	.604	.736
.025	.542	.741
.0332	.489	.760
.0332	.490	.758
.025	.475	.742
.025	.431	.736
.0332	.193	.736
.025	.191	.750
.0332	.080	.708
.025	.039	.682
.025	.0053	.584
.0332	.005	.540
.025	.0023	.311
.025	.0017	.222
.025	.0016	.192

<u>NaX₁^H</u>		
.025	.656	.756
.025	.099	.712

<u>NaX₂^X</u>		
.025	.320	.740

<u>NaX₇^{XX}</u>	(fig.16a)	
.025	.312	.678
.0125	.092	.467

Mordenite / Cs⁺ System:

(27°C) (fig.15a)

<u>Initial</u> <u>Molality</u> <u>of CsCl.</u>	<u>Cs_s</u>	<u>Cs_z</u>
.04709	.822	.981
.04709	.815	.986
.04709	.668	.966
.04709	.494	.961
.04709	.329	.914
.05	.146	.841
.03767	.052	.733
.0157	.036	.684
.05	.016	.610
.05	.005	.401
.01256	.004	.357

Mordenite / Ba⁺⁺ System:

(27°C) (fig.17a)

.025	.826	.715
"	.691	.711
"	.552	.712
"	.463	.676
"	.313	.647
"	.180	.587
"	.132	.557
"	.053	.473
"	.019	.365
"	.012	.261
"	.008	.156

APPENDIX BGAS ADSORPTION.ISOTHERM DATA

P = equilibrium pressure (cm.Hg).

V = volume of gas adsorbed at equilibrium

(cc.S.T.P./g.anhydrous NaX).

List of Isotherm Data in Appendix B.

<u>Page</u>	<u>Adsorbents</u>	<u>Adsorbates</u>	<u>Temperatures</u> (°C)
249	NaX ₁ ^O	Argon	+25, 0, -40, -70, -100
250	NaX ₁ ^O NaX ₂ ^O	"	90.19°K
251	NaX ₂ ^H NaX ₃ ^H NaX ₄ ^H	"	"
	NaX ₅ ^H NaX ₇ ^H		
252	NaX ₁ ^O NaX ₂ ^H NaX ₃ ^H	Krypton	25°C
	NaX ₅ ^H NaX ₇ ^H		
253	NaX ₁ ^O	"	0, -40, -70, -90, -100
254	NaX ₁ ^O	"	-150, -140
256	NaX ₂ ^H	"	-150, -140
257	NaX ₂ ^H	"	-130, -120
258	NaX ₅ ^H	"	-150, -140
259	NaX ₅ ^H	"	-130, -120
260	NaX ₇ ^H	"	-150, -140
261	NaX ₇ ^H	"	-130, -120

NaX₁⁰/ARGON (see figure 39)

25°C

V	P
0.292	7.458
0.817	19.209
1.121	27.047
1.688	40.287
2.107	51.669
1.555	37.135
0.591	13.865
1.287	30.088
2.260	55.087
2.236	54.508

0°C

V	P
0.833	14.095
1.274	20.964
1.737	27.672
2.248	35.429
2.988	46.503
1.968	29.926
3.371	53.217

-70°C

3.868	10.688
6.634	17.942
7.778	21.457
10.762	29.289
14.497	40.234
19.282	54.436

-40°C

8.281	56.142
7.262	47.825
5.045	33.154
3.767	24.346
2.378	15.361
1.571	10.615

-100°C

8.167	6.714
12.443	10.233
23.378	19.349
28.436	23.842
35.240	29.646
47.413	41.274
57.166	51.665

NaX₁^O/ARGON (see figure 19)

(Outgassed 24hrs. at 350°C)

		V	P
		222.535	6.091
		225.819	9.612
		229.099	15.897
		232.341	26.357
		233.425	31.021
		234.486	39.749
		237.171	52.793
		(Further 12hrs. outgassing)	
		223.433	7.928
		227.221	13.069
		230.121	20.249
		232.072	27.645
		234.569	40.906
		(Further 12hrs. outgassing)	
		223.867	7.748
		227.384	13.083
		231.737	26.063
		233.717	35.359
		236.297	51.688
		(Sample opened to atmosphere, re-outgassed 24hrs)	
		223.309	7.526
		226.840	12.604
		232.749	31.979
		234.936	44.667
		(Second sample NaX ₂ ^O , outgassed 24hrs. at 350°C).	
		227.507	12.524
		229.594	16.911
		231.886	24.123
		233.292	29.766
		235.443	41.150
		236.974	50.790
		(Further 24hrs. outgassing)	
		41.894	0.019
		115.880	0.049
		193.811	0.441
		202.664	0.784
		202.651	0.792
		213.576	2.056
		(contd. in next column)	

NaX (all irradiated samples)/ARGON/90.19°K (figure 20)

NaX₂^{XX}

V	P
223.391	8.656
227.279	15.093
229.634	20.159
231.553	27.031
232.901	33.322
234.133	39.673
236.176	54.493
228.041	14.809
222.481	6.596
209.231	1.548
218.454	4.520
221.160	6.462
224.282	9.337
226.164	11.900
228.232	16.058
232.056	28.122
234.336	38.303
235.785	46.964
236.674	53.194
232.245	27.565

NaX₃^{XX}

220.852	5.434
221.955	6.184
225.201	9.651
228.169	14.970
230.663	22.190
232.710	30.546
234.281	38.262
235.617	46.508

NaX₄^{XX}

V	P
227.730	18.407
229.397	21.426
230.821	27.158
233.251	38.665
234.989	49.188

NaX₅^{XX}

V	P
221.720	11.804
225.126	19.288
227.137	26.251
229.467	36.724
231.329	46.506
222.443	12.198
219.720	8.189
216.423	5.226

207.800	1.873
217.347	5.769
218.959	7.191
220.901	9.320
224.373	16.440
226.392	22.516
227.948	28.044
229.197	33.688
231.127	42.853
232.498	52.002

NaX₇^{XX}

V	P
200.147	25.860
203.193	37.250
205.489	48.117
205.995	54.764
200.166	21.998
197.172	14.040
194.907	9.901

NaX (all samples)/KRYPTON/25°C. (figure 21)

NaX⁰

NaX^{HH}₅

V

P

V

P

2.116
3.073
4.036
5.032
5.850
7.640

15.067
21.869
28.401
35.423
41.650
55.759

1.689
2.555
3.377
4.270

12.586
18.443
24.161
30.265

1.044
1.588
2.676
4.369
6.458

7.823
11.435
18.862
31.011
45.573

NaX^{HH}₂

2.004
2.963
3.814
4.709
1.987
5.649
7.460

14.256
20.728
26.444
32.575
14.125
39.527
54.215

NaX^{HH}₇

0.857
1.318
2.559
3.269
5.189
7.044

6.652
10.030
17.490
24.436
36.824
49.124

NaX^{HH}₃

2.234
3.326
4.443
5.569

16.147
23.461
30.892
38.453

NaX₁^O/KRYPTON/various temperatures. (figure 22).

0°C.

V	P
12.564	51.837
9.542	38.466
8.433	34.209
7.049	28.299
5.548	22.517
3.945	15.917
2.001	7.870

-90°C

V	P
14.958	2.145
38.193	5.188
56.786	7.796
63.404	8.883
69.135	9.934
73.274	10.775
77.239	11.702
84.099	13.465
89.388	15.186
94.736	17.354
102.490	21.504
108.730	26.080
115.700	33.594
120.548	40.778
124.683	49.165

-40°C

43.590	58.563
37.145	48.385
34.929	45.304
30.890	39.856
26.530	34.114
20.525	26.512
15.612	20.268
10.298	13.527

-100°C

22.079	1.613
58.072	4.060
109.881	13.084
116.987	16.905
118.890	18.176
127.409	26.832
132.606	35.208
136.054	42.113
138.622	49.121
106.969	10.448
105.727	10.106
96.119	7.908
88.037	6.709
80.660	5.904
74.212	5.184

-70°C

19.430	7.510
25.270	9.653
44.305	16.870
54.212	20.993
66.406	27.087
74.705	32.580
80.137	36.541
83.413	40.310
32.697	12.605
42.261	16.347
85.289	42.131

NaX₁⁰/KRYPTON./(-150, -140°C) (figure 22).

-150°C

V	P
56.684	0.037
85.525	0.060
120.167	0.108
151.253	0.556
164.517	1.714
169.016	2.652
173.310	4.127
176.350	5.913
178.094	7.208
180.072	9.102
182.321	12.197
184.252	16.245
186.185	21.257
188.045	27.260
189.516	33.357
184.299	16.297
163.291	1.458
174.516	4.755
176.149	5.749
177.863	7.104
180.914	10.619
182.800	13.696
184.417	16.802
185.591	19.867
187.400	25.670
189.752	35.644
191.608	45.718
69.501	0.044
101.643	0.073
133.509	0.170
137.291	0.225
143.259	0.317
152.931	0.619
162.942	1.386
171.502	3.268
177.779	6.602
181.775	11.048

-140°C

V	P
175.573	21.305
182.000	44.712
180.213	36.672
178.354	29.172
168.341	10.052
168.414	9.923
170.929	12.531
173.892	17.181
45.240	0.104
74.589	0.172
99.312	0.246
123.153	0.478
148.182	1.811
153.578	2.697
156.261	3.318
159.243	4.268
161.322	5.113
165.161	7.165
68.651	0.161
100.274	0.261
130.069	0.642
136.134	0.857
141.720	1.169
150.312	2.053
158.423	3.896
164.866	6.797
169.791	11.014
172.365	14.377
175.453	19.755

NaX₂^H /KRYPTON/(-150, -140°C). (figure 23 A).

-150°C

V	P
25.423	0.021
47.265	0.036
70.390	0.049
94.740	0.067
117.448	0.110
139.462	0.280
157.919	1.070
42.098	0.031
50.594	0.037
59.073	0.041
73.314	0.051
85.630	0.060
98.849	0.071
111.065	0.090
122.118	0.120
133.015	0.184
139.994	0.291
146.171	0.429
153.788	0.768
157.781	1.073
152.628	0.680
160.268	1.288
169.185	2.972
173.512	4.802
176.624	6.895
178.673	8.844
181.790	13.373

-140°C

V	P
25.758	0.075
44.115	0.108
64.395	0.143
84.209	0.215
103.039	0.290
41.641	0.101
50.068	0.118
58.451	0.137
72.539	0.171
84.826	0.184
97.758	0.239
109.618	0.315
119.892	0.466
129.768	0.688
135.889	0.931
140.773	1.272
146.486	1.899
149.548	2.344
146.647	1.733
156.339	3.699
161.505	6.016
165.679	8.631
166.530	9.281
168.661	11.450
171.315	15.054
173.081	18.228
176.171	25.771
165.646	8.703
172.369	17.369
174.943	23.114
176.605	28.044
178.166	33.758
179.283	38.784
181.094	48.437
181.960	54.705

NaX_2^{H} /KRYPTON/(-130, -120°C). (figure 23 A).

-130°C

V	P
43.684	0.296
51.308	0.345
58.649	0.384
66.633	0.460
74.571	0.538
82.576	0.584
90.608	0.671
99.134	0.796
107.109	0.954
115.957	1.247
125.213	1.763
132.722	2.504
41.213	0.286
46.270	0.302
52.086	0.381
57.244	0.391
64.239	0.430
72.045	0.497
81.520	0.578
90.073	0.677
90.079	0.683
99.211	0.803
110.301	1.075
117.388	1.362
136.054	2.898
139.917	3.617
144.588	4.886
148.283	6.330
150.224	7.320
155.039	10.576
156.875	12.307
159.741	15.552
161.590	18.264
163.184	20.851
164.950	24.520
168.193	33.209
170.504	41.530
172.249	49.377

-120°C

V	P
40.591	0.685
45.549	0.764
51.301	0.878
56.351	0.959
63.212	1.082
70.872	1.242
80.124	1.468
88.442	1.715
97.207	2.077
107.768	2.676
114.171	3.378
80.894	1.434
89.066	1.669
98.181	2.029
109.893	2.752
120.476	3.953
128.159	5.496
135.111	7.886
140.767	10.951
145.284	14.788
148.799	18.830
150.884	21.978
152.791	25.233
155.412	30.778
159.183	41.845
161.643	51.189

$\text{NaX}_5^{\text{HH}} / \text{KRYPTON} / (-150^\circ, -140^\circ\text{C})$ (figure 23 B)

-150°C

V	P
147.640	0.555
151.803	0.773
156.948	1.181
162.708	1.983
164.530	2.409
165.385	2.624
167.714	3.301
168.690	3.696
170.061	4.359
171.632	5.134
174.810	7.383
174.759	7.386
176.841	9.698
180.519	15.824
184.420	27.153
186.638	37.031
188.346	46.949
189.214	53.734
34.409	0.029
51.066	0.041
72.340	0.054
95.347	0.073
116.822	0.114
125.898	0.157
133.670	0.231
142.786	0.390

-140°C

V	P
131.308	0.793
141.860	1.467
149.302	2.551
155.281	4.211
158.692	5.855
161.108	7.152
163.310	8.793
165.923	11.315
168.192	14.273
170.855	19.014
172.761	23.293
174.187	27.727
175.649	33.184
178.642	46.708
179.835	55.876
119.013	0.475
118.502	0.463
117.907	0.455
119.715	0.480
122.814	0.552
127.737	0.681
137.371	1.140
144.292	1.803
146.047	2.038
46.374	0.110
66.664	0.159
87.231	0.229
114.761	0.397
124.781	0.576
122.327	0.527

$\text{NaX}_5^{\text{HH}}/\text{KRYPTON}/(-130, -120^\circ\text{C})$ (no figure)

-130°C

V	P
169.596	52.971
166.555	38.761
165.682	35.432
163.761	29.680
161.450	24.125
158.020	17.986
156.610	15.953
154.649	13.597
151.717	10.758
150.423	9.677
149.186	8.892
145.225	6.666
143.292	5.803
140.129	4.707
138.854	4.354
135.613	3.543
143.624	5.762
139.719	4.472
135.022	3.317
131.159	2.678
127.865	2.260
124.992	1.968
68.866	0.489
76.374	0.545
84.314	0.621
91.758	0.713
99.715	0.843
107.693	1.049
115.703	1.332
123.631	1.825
130.692	2.591
95.467	0.788
105.467	0.981
123.475	1.812
135.390	3.347
142.206	5.140
146.692	7.053
150.632	9.505

-120°C

V	P
125.632	5.589
128.035	6.285
130.498	7.202
135.226	9.340
138.406	11.397
140.358	12.919
143.983	16.267
146.140	19.082
148.127	21.939
150.395	26.083
154.478	35.690
157.319	44.862
158.983	51.879
58.814	1.007
63.994	1.100
69.552	1.212
76.638	1.386
84.774	1.614
92.873	1.894
101.825	2.359
110.428	3.027
118.385	4.056
125.794	5.608

$\text{NaX}_7^{\text{H}_2\text{O}} / \text{KRYPTON} / (-150, -140^\circ\text{C})$ (figure 23 A).

-150°C

V	P
35.592	0.026
52.425	0.036
63.033	0.044
77.441	0.057
96.871	0.085
111.465	0.144
122.949	0.275
135.675	0.773
133.653	0.697
136.161	0.869
140.921	1.479
142.802	1.816
144.958	2.315
145.956	2.625
148.125	3.457
150.781	4.891
152.438	6.235
154.939	8.730
156.647	11.140
157.997	13.722
159.571	17.763
162.092	25.868
164.082	33.869
165.860	42.678

-140°C

V	P
30.851	0.077
45.202	0.111
68.708	0.173
69.386	0.176
89.207	0.259
105.240	0.445
107.038	0.480
111.964	0.596
117.614	0.809
120.582	0.981
116.276	0.737
127.473	1.613
132.131	2.435
135.745	3.427
138.656	4.517
140.429	5.532
142.060	6.485
143.884	8.137
146.980	11.474
149.091	14.670
150.896	18.074
153.615	25.907
156.910	37.806
159.181	49.159
159.283	55.492
159.213	49.202

$\text{NaX}_7^{\text{xx}}/\text{KRYPTON}/(-130, -120^\circ\text{C})$ (figure 23 A).

-130°C

V	P
43.884	0.316
38.273	0.272
49.424	0.363
60.608	0.439
73.122	0.567
82.220	0.693
96.129	1.001
105.617	1.418
112.207	1.925
115.099	2.253
116.935	2.495
118.311	2.718
122.438	3.588
125.925	4.625
130.051	6.455
117.415	2.634
120.614	3.265
124.383	4.251
128.196	5.766
131.798	7.862
134.203	9.752
136.328	11.870
139.226	15.704
142.937	22.631
145.592	29.572
147.901	37.217
148.752	41.407
150.717	52.077
150.953	58.994
150.857	52.050

-120°C

V	P
51.196	0.922
57.262	1.064
62.809	1.183
72.393	1.455
78.635	1.653
85.899	1.977
92.188	2.368
98.900	2.990
104.594	3.707
104.568	3.711
110.109	4.827
114.658	6.239
119.392	8.344
125.061	12.332
128.695	16.679
133.295	24.003
136.372	31.220
139.085	39.162
140.320	43.882
141.747	53.115
34.491	0.623
40.877	0.747

APPENDIX CINTERMOLECULAR FORCE DATA

<u>Atom</u> <u>or Ion</u>	<u>Radius</u> (Å)	<u>Molecular</u> <u>Polarizability</u> (cm ³ /molecule)	<u>Diamagnetic</u> <u>Susceptibility</u> (cm ³ /molecule)	<u>Ionisation</u> <u>Potential</u> (eV)
Kr	1.97 ⁽¹⁾	24.8x10 ⁻²⁵ ⁽⁴⁾	-47.85x10 ⁻³⁰ ⁽⁵⁾	14.0 ⁽⁶⁾
O	1.40 ⁽²⁾	39.0x10 ⁻²⁵ ⁽²⁾	-20.92x10 ⁻³⁰ ⁽³⁾	13.55 ⁽⁷⁾
Na ⁺	0.98 ⁽³⁾	1.9x10 ⁻²⁵ ⁽²⁾	-6.95x10 ⁻³⁰ ⁽³⁾	47.3 ⁽⁸⁾

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Conversion Factors:⁽⁸⁾

$$(\text{ eV / mole }) \times (23.054) = (\text{ k.cal / mole })$$

$$(\text{ ergs / molecule }) \times (N_0 / J) = \text{ cal/mole . }$$

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