

PREPARATION AND PROPERTIES
OF
SOME NEW ZEOLITES

By

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ABSTRACT

The hydrothermal crystallisation of hydrous gels of composition $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2$ ($3 \leq n \leq 9.5$) and $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2$ ($7 \leq n \leq 9.0$) has been studied between 100° and 400°C . The crystals produced included strontium ferrierite and three barium zeolites without natural counterparts, Ba-J, Ba-K and Ba-Z. Ba-Z crystallised from gels of oxide composition $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$ and $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 8.5\text{SiO}_2$ at 300°C . It has a water content of 6.4%, which is low for a zeolite although amorphous silica may be present as well.

The sorptive characteristics of these compounds, some of their ion-exchanged forms, and a mixed sodium-potassium form of zeolite L supplied by M. Damm were investigated. The sorbates used were oxygen, nitrogen, neon, argon, krypton, xenon, carbon dioxide, methane, ethane, propane, n-butane, iso-butane, neo-pentane, benzene, thiophen, pyrrole, o-, m- and p-xylene. It was found that ferrierite treated with 0.08N HCl had the highest sorptive capacity of the ferrierites for most of the sorbates and that it readily sorbed thiophen and pyrrole. Potassium ferrierite sorbed only oxygen, neon and carbon dioxide. Ba-K and Ba-Z sorbed oxygen slowly and it seemed that this sorption was diffusion controlled.

Isosteric heats have been measured for the sorption

of oxygen and neon in strontium ferrierite and for the sorption of methane, ethane, propane, n-butane, iso-butane and neo-pentane in zeolite L. It was found that q_{st} for the n-paraffins obeyed the equation $q_{st} = 4.8 + 2.2 (n-1)$, where n is the number of carbon atoms. The isosteric heats for propane, n-butane, iso-butane and neo-pentane showed maxima as the degree of pore filling increased, and this was attributed to sorbate-sorbate molecule interactions.

Some isotherm data for methane, ethane and propane was interpreted in terms of a localised model. No satisfactory isotherm model was found for any of the other systems studied. Empirical isotherm equations based on a virial equation of state for the sorbed phase were calculated and isotherm equilibrium constants were derived from these.

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INTRODUCTION

Work in these laboratories has been concerned with hydrothermal synthesis of the aluminosilicates of the alkali metals, and also those of calcium, strontium, barium, thallium and some substituted alkyl ammonium bases. For the most part highly reactive starting materials have been used and a number of synthetic materials have been produced, some of them without known natural counterparts. The strongly alkaline low temperature hydrothermal conditions used have favoured the production of zeolites and the study of the ion-exchange and sorptive properties of these products has formed an important part of the work.

The present work has two objectives; the first to reinvestigate the crystallisation fields of the barium and strontium zeolites with a view to finding the optimum conditions for their preparation, and the second to characterize the sorption properties of these compounds. Interest was centered on four zeolites. These were strontium ferrierite, Ba-K, Ba-J and Ba-Z. Ferrierite is a highly siliceous zeolite occurring rarely in nature and the barium zeolites have no natural counterparts.

The sorption characteristics of a fifth compound, zeolite L, a new synthetic compound, were also investigated.

Before the experimental results are presented a number of topics of general relevance to the work will be discussed.

CHAPTER 1

1.1. Zeolite Structures

Zeolites may be given the empirical oxide formula $(M^{II}, M_2^I) \cdot O \cdot Al_2O_3 \cdot nSiO_2 \cdot mH_2O$. The values of n and m may vary: M^{II} and M^I are respectively di- and monovalent cations. The ratio $(M^{II}, M_2^I)O : Al_2O_3$ is unity, which means that the structures are all based on AlO_4 or SiO_4 tetrahedra linked to each of four other tetrahedra by sharing the four apical oxygen atoms. According to an empirical rule of W. Loewenstein¹, AlO_4 tetrahedra can be joined in this way to SiO_4 tetrahedra only, never to another AlO_4 . This means that n in the oxide formula cannot be less than two in the completed aluminosilicate framework. The cations and water molecules are present in interstices of the framework. This carries a net negative charge equal to the number of Al atoms in it.

The hydrated feldspathoids sodalite, cancrinite and zeolitic gallogermanates² are closely related compounds. A summary of the seven groups of naturally occurring zeolites is shown in Tables 1 and 2.

The overall features of the aluminosilicate frameworks within the seven groups are known but the Al/Si distribution, cation positions and water molecule sites is only available for a few zeolites.

The occupancy of tetrahedral sites by silicon or

Table 1

Zeolite Type	Unit Cell Content	Approx Intra-crystalline Vol for H ₂ O cm ³ /cm ³ of zeolite	Isostructural Species
<u>Natrolite Group</u>			
Natrolite	$\text{Na}_{16}[\text{Al}_{16}\text{Si}_{24}\text{O}_{80}], 16\text{H}_2\text{O}$	•21	Mesolite
Thomsonite	$\text{Na}_4\text{Ca}_6[\text{Al}_{20}\text{Si}_{20}\text{O}_{80}], 24\text{H}_2\text{O}$	•33	Gonnardite
Edingtonite	$\text{Ba}_2[\text{Al}_4\text{Si}_6\text{O}_{20}], 8\text{H}_2\text{O}$	0•30	
<u>Chabazite Group</u>			
Gmelinite	$\text{Na}_8[\text{Al}_8\text{Si}_{16}\text{O}_{48}], 24\text{H}_2\text{O}$	•45	
Chabazite	$\text{Ca}_2[\text{Al}_4\text{Si}_8\text{O}_{24}], 13\text{H}_2\text{O}$	•46	Linde T
Erionite	$(\text{Ca etc})_{4.5}[\text{Al}_4\text{Si}_{27}\text{O}_{72}], 27\text{H}_2\text{O}$	•36	
<u>Phillipsite Group</u>			
Phillipsite	$(\text{K, Na})_{10}[\text{Al}_{16}\text{Si}_{22}\text{O}_{64}], 20\text{H}_2\text{O}$	•36	Harmotome
Barrer's P	$\text{Na}_6[\text{Al}_6\text{Si}_{10}\text{O}_{32}], 15\text{H}_2\text{O}$		Linde B
Gismondite	$\text{Ca}_4[\text{Al}_8\text{Si}_8\text{O}_{32}], 16\text{H}_2\text{O}$	•49	
<u>Heulandite Group</u>			
Heulandite	$\text{Ca}_4[\text{Al}_8\text{Si}_{28}\text{O}_{72}], 24\text{H}_2\text{O}$	•33	
Stilbite	$\text{Na}_2\text{Ca}_4[\text{Al}_{10}\text{Si}_{26}\text{O}_{72}], 28\text{H}_2\text{O}$	•37	P Chinotilolite
Brewsterite	$(\text{Sr, Ba, Ca})_2[\text{Al}_4\text{Si}_{12}\text{O}_{32}], 10\text{H}_2\text{O}$		

Table 2

Zeolite Type	Unit Cell Content	Approx Intracrystalline Vol. for H ₂ O cm ³ /cm ³ of zeolite	Isostructural species
<u>Faujasite Group</u>			
Faujasite	(Na ₂ , Ca) ₃₂ , [Al ₆₄ Si ₁₂₈ O ₃₈₄], 256H ₂ O	.54	Linde X Linde Y ZK-4
Linde A	Na ₉₆ , [Al ₉₆ Si ₉₆ O ₃₈₄], 216H ₂ O		
ZK-5	Na ₂₄ , [Al ₂₄ Si ₇₂ O ₁₉₂], 90H ₂ O		
Paulingite	(K ₂ , Ca, Na ₂) ₁₅₂ , [Al ₁₅₂ Si ₅₂₀ O ₆₇₂], (+ ~ 700H ₂ O)	.47	
<u>Analclime Group</u>			
Analclime	Na ₁₆ , [Al ₁₆ Si ₃₂ O ₉₆], 16H ₂ O	.18	Wairakite
<u>Mordenite Group</u>			
Mordenite	Na ₈ , [Al ₈ Si ₄₀ O ₉₆], 24H ₂ O	.29	
Dachiardite	Na ₅ , [Al ₅ Si ₁₉ O ₄₈], 12H ₂ O	.31	
Epistilbite	Ca ₃ , [Al ₆ Si ₁₈ O ₄₈], 16H ₂ O	.33	
Ferrierite	Na ₂ , Mg ₂ , [Al ₆ Si ₃₀ O ₇₂], 18H ₂ O	.27	
Bikitaite	Li ₂ , [Al ₂ Si ₄ O ₁₂], 2H ₂ O		

aluminium can be shown by measurement of M - O interatomic distances as Al - O distance > Si - O by $0.13 \text{ \AA}$ approximately³. Results for natrolite⁴ and gismondite⁵ show that the frameworks are partially ordered with respect to silicon and aluminium. A technique introduced by Lentz⁶ seems to identify the silica groupings within the frameworks. The zeolite is decomposed with concentrated hydrochloric acid in the presence of hexamethyldisiloxane and the resulting silicate units separated by gas chromatography are claimed to have the same structures as units occurring in the parent mineral. By this method Fischer predicted the four membered rings of silica tetrahedra in Laumonite.

The tetrahedrally sited silicon or aluminium is not disturbed during cation exchange although acid leaching removes alumina from highly siliceous zeolites without destruction of crystallinity. It is likely that the alumina tetrahedra are here replaced by tetrahedral groups of four OH's.

1.2. Cation Positions

The position of an exchangeable cation depends on the bonding with water molecules and bonding to oxygen atoms of the framework in order to balance the charge deficiency of the alumino-silicate framework. As the Si: Al ratio increases there may be an increasing tendency for the

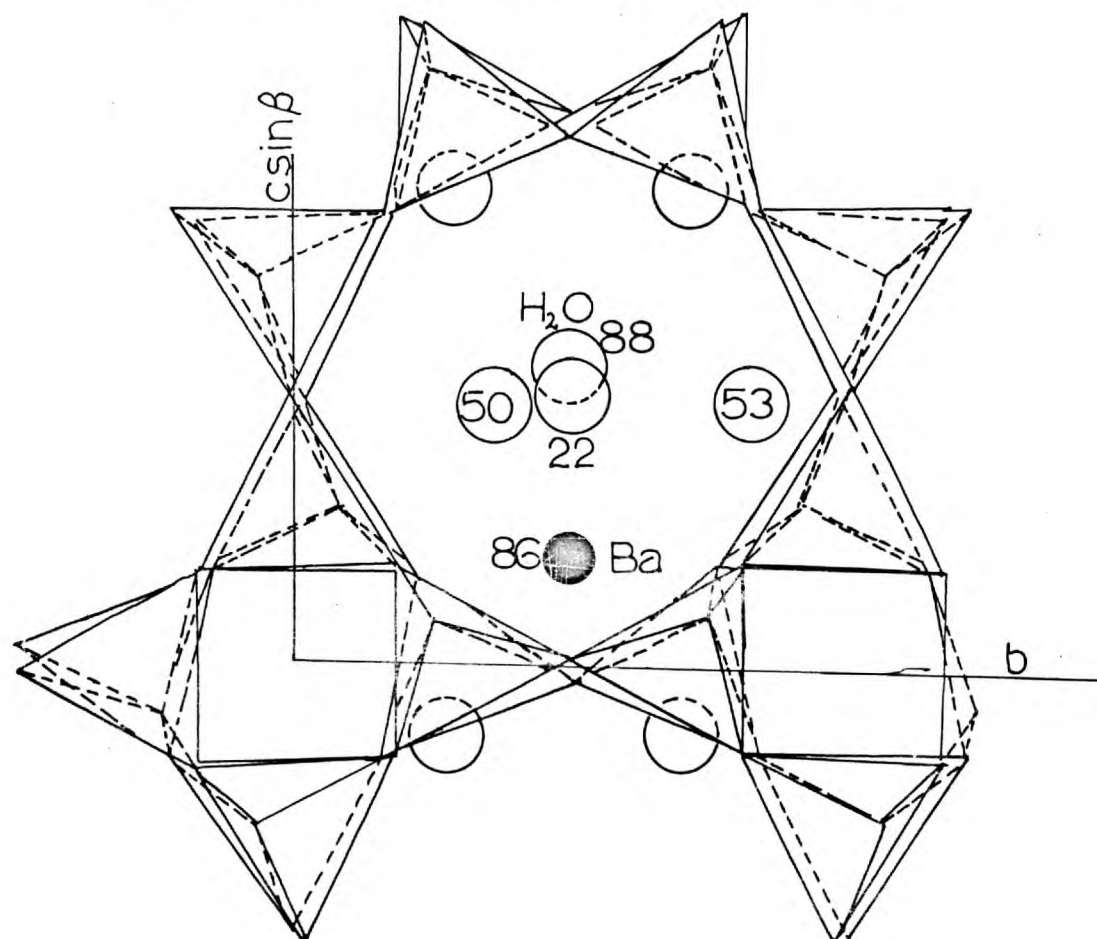
exchangeable cations to become more dissociated from the oxygen atoms of the framework, and so a greater tendency to form a brine inside the pores. Zeolite composition, degree of hydration and temperature are the main factors in determining cation position. Thermal disorder, partial occupancy of sites and crystal imperfections have limited investigations of cationic sites.

The cation site, which is fully occupied, has been identified in natrolite, gismondite and harmotome. The latter with a unit cell composition $\text{Ba}_2\text{Al}_4\text{Si}_{12}\text{O}_{32}$ has two Ba^{++} ions per unit cell⁷. Fig. (1) shows the cations in the large channels along the axis. The barium atoms are surrounded by six oxygen atoms and four water molecules. Eight of the twelve water molecules in a unit cell are bound to barium atoms, but the remainder are not, and have fixed positions in the cages.

The cation positions in large pore zeolites are not well established. There are usually several sites, some partially occupied, and it is thought that some cations are free to move through the aluminosilicate frameworks.

In the synthetic zeolites X and Y⁸ the framework consists of a tetrahedral arrangement of truncated octahedra, i.e. the octahedra are joined at the octahedral faces by hexagonal prisms. The centres of the truncated octahedra occupy the same relative positions as the carbon atoms in diamond. The cations in X and Y occupy

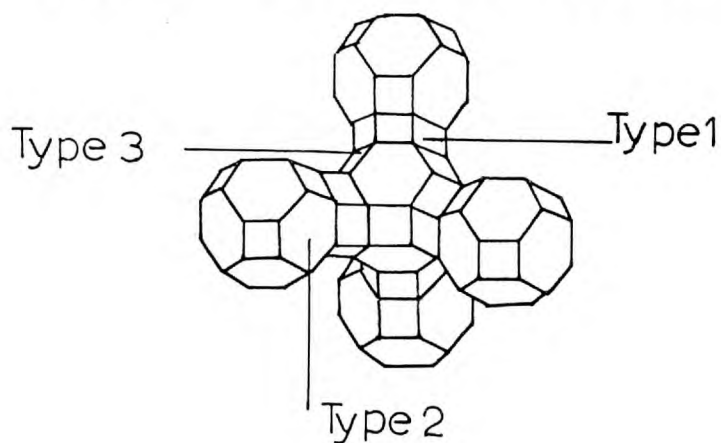
FIG1
Part of the Harmotome structure.



Nos = % of the repeat unit along a axis

FIG2

Cation Positions X&Y zeolites



three types of position, Fig. (2).

Type I in the centres of the hexagonal prism, 16 sites per unit cell.

Type II located at the single 6-rings on the 3-fold axis, 32 sites per unit cell.

Type III on the walls of the channels next to the four-membered rings, 48 sites per unit cell.

However, Broussard and Shoemaker⁹ from X-ray crystal studies on hydrated zeolite X report only two cation sites corresponding to types I - II. It has been suggested that in the hydrated zeolite, cations not located in I or II and the water molecules behave as a strong electrolyte solution, and are free to move through the framework. Electron spin resonance studies were made by Barry¹⁰ on a manganese form of 13X pre-exchanged with certain ions and concluded that the Mn^{+2} positions depended on the other ions present and dehydration. Electron spin resonance investigations on hydrated 13X pre-exchanged with Zn^{++} , Mg^{++} and Li^+ ions indicated that the Mn^{++} was in the hexagonal prisms (site I). However, 13X pre-exchanged with Na^+ , K^+ , Cd^{++} , La^{+++} and Ca^{++} , ions with a lower charge/radius ratio had no Mn^{++} in site I. Dehydration of 13X pre-exchanged with Zn^{+2} and Li^+ was accompanied in the case of the Li^+ form, by a migration of Mn^{+2} from site I; in the Zn^{+2} form the Mn^{+2} remained in site I; in the pre-exchanged calcium form the Mn^{+2}

enters the prism only after dehydration at 200°C, but at 400°C moves from site I.

1.3. Water Molecules in Zeolites

The position of the water molecules in small or narrow cavity zeolites is well defined, but in the larger pore systems the experimental data is uncertain, although it is to be expected that some cations will have appreciable water of hydration.

In the small pore zeolite Brewsterite¹¹, of unit cell composition (Sr, Ba, Ca) $\text{Al}_2\text{Si}_{16}\text{O}_{46}5\text{H}_2\text{O}$, there are two sets of intersecting channels each defined by eight-membered rings. The strontium atom lies near the intersection of the channels with five water molecules (an incomplete sphere of hydration) and four slightly more distant framework oxygen atoms. Figs. (3) and (4).

In faujasite there are 260 water molecules per unit cell; Baur¹² placed 40% of the exchangeable cations within the cuboctahedral aluminosilicate cages and 16% of the water molecules in one position within and one outside the cages. The remaining cations and water molecules were not definitely located. However, infrared studies of fully hydrated faujasite, heats of occlusion of water in faujasite, conductivity and activation energies for cations in hydrated faujasite and other evidence indicate that the water molecules and

cations in the zeolite behave similarly to an electrolyte solution and are disordered and highly mobile.

1.4. Dehydration of Zeolites

During dehydration the zeolite structure may remain stable, it may alter slightly or it may collapse. Linde A zeolite and faujasite structures change very little during dehydration, but the chabazite framework undergoes a slight modification. Hydrated chabazite¹³ has an almost circular but non-planar 8-ring aperture in comparison with the approximately rectangular planar 8-ring window in the dehydrated form. Fig. (5). The distortion is initiated by the change in position of the calcium ions and the interactions between the water molecules and the framework. The hexagonal prisms can move about the inter-prism linkages resulting in large changes of the inter-prism angle.

The dehydration behaviour of synthetic cubic and tetragonal Na-P zeolites¹⁴ and some mono- and dioatomic ion-exchanged derivatives has been studied by static, stepwise dehydration in conjunction with X-ray powder diffractometry at elevated temperatures, both under controlled conditions of water-vapour pressure. First-order collapse, or stepwise dehydration-type reactions are reported, and in most cases two, but sometimes three such reactions occur during the dehydration of a P

FIG 5

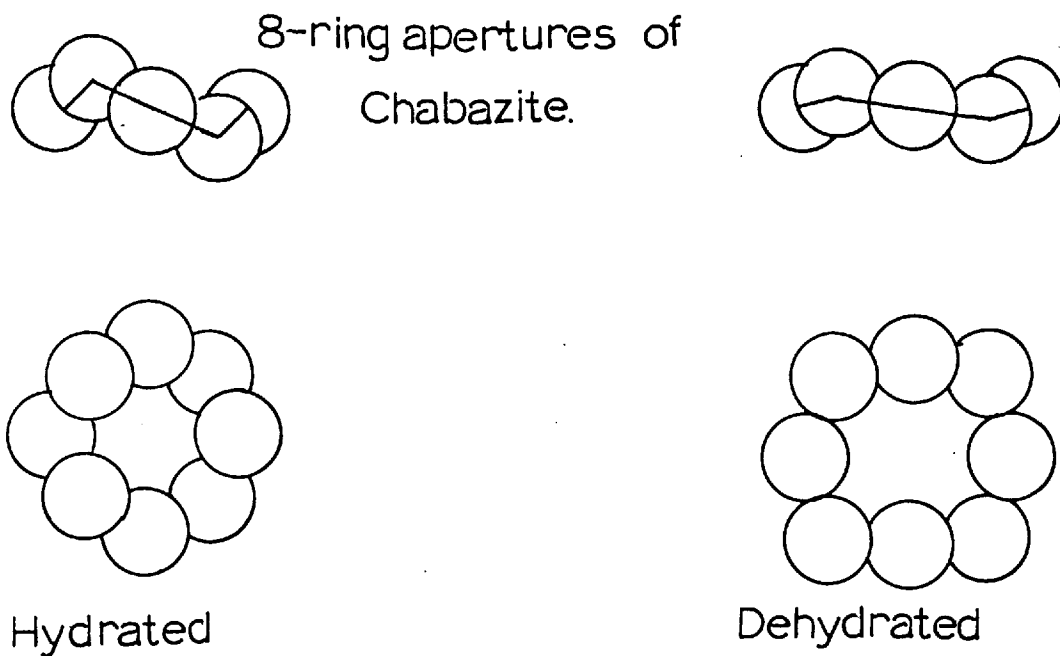
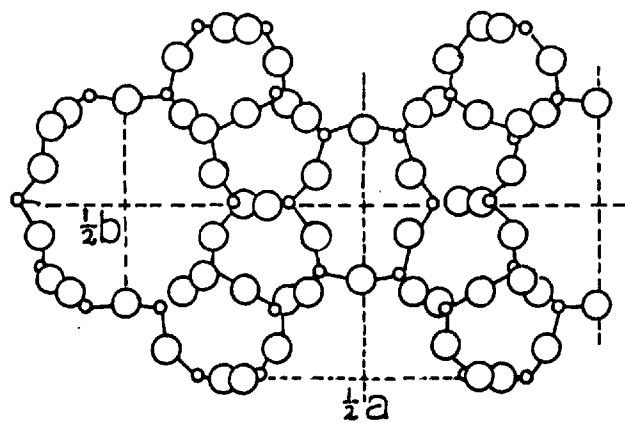


FIG 6

Ferrierite – projection along z axis.



○ oxygen.
 • Al or Si.

zeolite, for example, over a range of 0-400°C produces reversibly five distinct structural modifications. At 60°C an enantiotropic phase transition takes place, followed at higher temperatures by three separate stages of collapse with the removal of water and shrinkages of the unit cell.

Some zeolites during dehydration undergo a more complete breakdown of the lattice. Heulandite¹⁵ loses water reversibly until the final one or two molecules per unit cell and then irreversible collapse of the structure takes place.

Carter et. al.¹⁶ made infra-red studies of a series of ion-exchanged faujasites and detected residual hydroxyl groups even after dehydration at 450 - 600°C. Deuterium exchange was possible with all the hydroxyl groups, indicating their accessibility, but whether they are inside the zeolite cavities or on the crystal faces is unknown.

1.5. Structural Imperfections

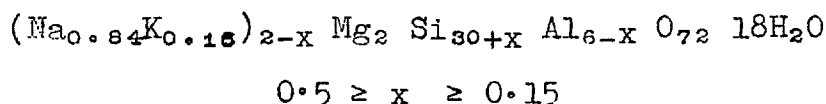
In the chabazite group of zeolites it is possible for mistakes to occur in the stacking sequence of the single or double six-membered rings. Such stacking faults are common in gmelinite¹⁷. The rather open channels parallel to C are blocked by occasional C-layers in the hexagonal AB-sequence of double six-membered rings and the effective

free diameter of the intracrystalline channels is reduced.

Twinning has been observed in most naturally occurring zeolites. Dachiardite forms octagonal groups consisting of eight individuals, with no appreciable distortion of the framework at the twin junctions. Twinning does not impair the sieve properties in contrast to faulting, but the apparent symmetry of the structure may be too high as a result. It seems probable that many zeolite structures determined represent only average structures having a higher symmetry than the true configuration.

1.6. Ferrierite Structure^{18,19}

Analysis of a naturally occurring form indicated the unit cell content to be represented by:-



The parameters of the orthorhombic unit cell were $a = 19.16 \text{ \AA}$, $b = 14.13 \text{ \AA}$, $c = 7.49 \text{ \AA}$. The framework, which is shown in Fig. (6), is composed of rings of 10, 8, 6 and 5 linked Si/AlO₄ tetrahedra, and closely resembles that found in mordenite²⁰, dachiardite²¹ and epistilbite²². There are two systems of interesting channels: (a) a system bounded by ten-membered rings running parallel to the c axis and approximately elliptical in cross section having major and minor diameters of $5.4 \text{ \AA}$ and $4.2 \text{ \AA}$, and cross sectional areas of about $18 \text{ \AA}^2$;

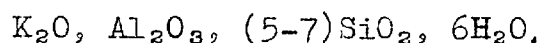
and (b) a system bounded by eight-membered rings, parallel to b; $4.7 \text{ \AA}$ by $3.7 \text{ \AA}$ in cross section and $12 \text{ \AA}^2$ in area, and leading into roughly spherical cavities with diameters of about $7 \text{ \AA}$.

These cavities contain $\text{Mg}(\text{H}_2\text{O})_6^{++}$ ions, which have two possible octahedral configurations differing by 42° about the C axis. Fig. (7). It was impossible to locate the sodium ions or the six remaining water molecules as they have no discernable crystallographic periodicity. However, it seems likely they are located within the open channels in the structure.

Vaughan¹⁸ measured M - O and O....O distances and concluded that the distribution of Al and Si sites was random and that there was the likelihood of hydrogen bonding between the water oxygen atoms O(9), and O(3) framework atoms, Fig. (8), since the O(9)....O(3) distances are $2.93 \text{ \AA}$ compared with the O....O length of $2.76 \text{ \AA}$ in ice²³.

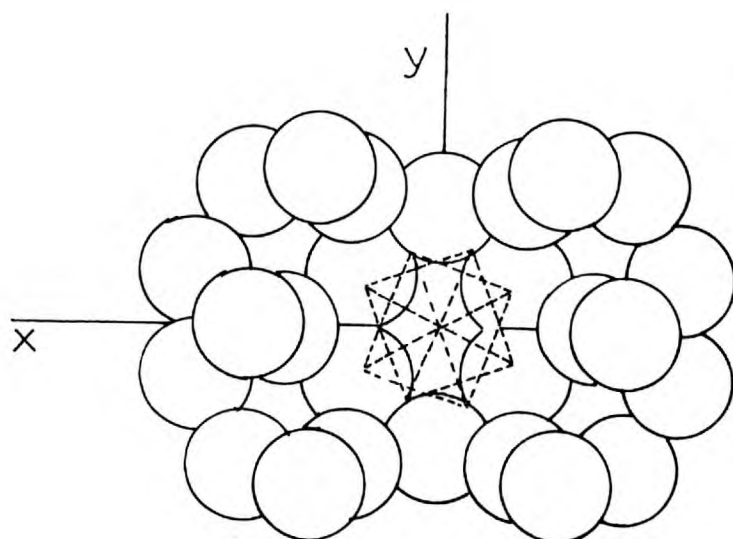
1.7 Proposed Structures of Linde L Zeolite

Chemical analysis has shown L to have a composition, expressed in terms of the constituent oxides, which corresponds with the formula



Although zeolite L may be synthesised from systems containing both sodium and potassium ions, the major

FIG 7

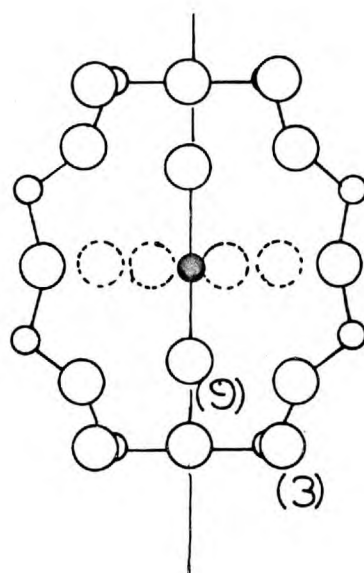


Ferrierite framework
oxygen atoms.

$\text{Mg}(\text{H}_2\text{O})_6^{2+}$ octahedron (dotted lines)

FIG8

Projection of Ferrierite along the
y axis



○ oxygen

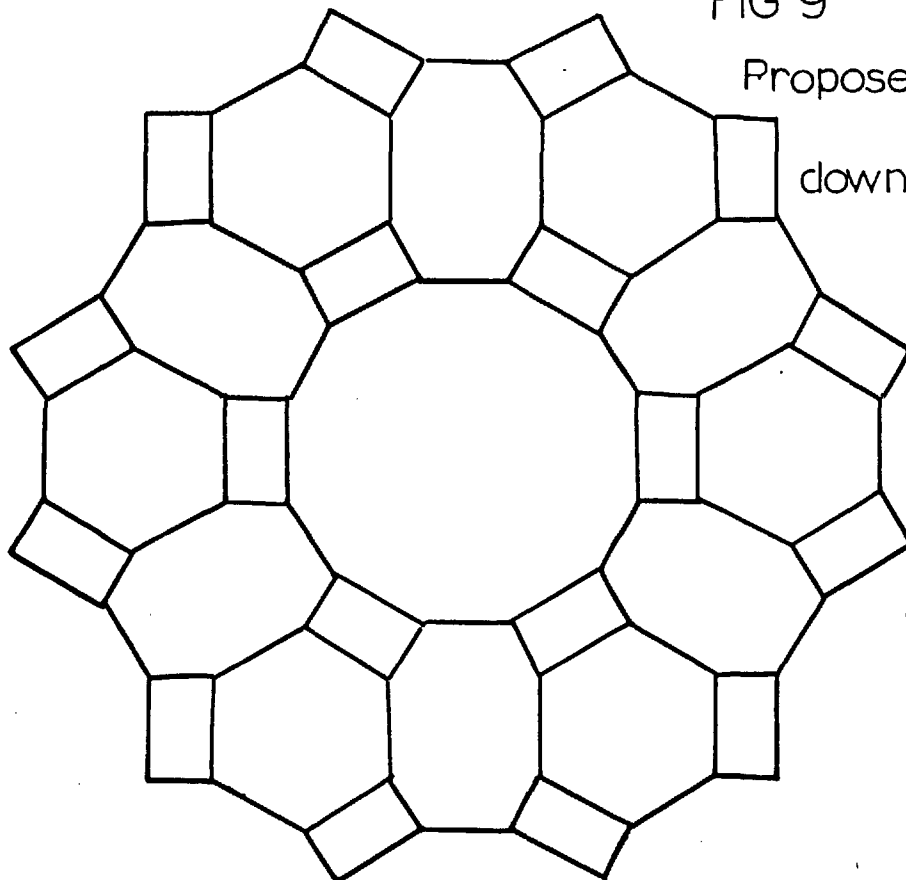
○ Al or Si

● Mg.

FIG 9

Proposed L structure.

down c axis



cation component is potassium. From powder data Breck²⁴ proposed a hexagonal unit cell with composition $K_{36} [(AlO_2)_{36}(SiO_2)_{108}] 86H_2O$ with $a = 18.4 \text{ \AA}$ and $c = 30.2 \text{ \AA}$. Breck's structure for zeolite L is produced by linking truncated octahedra in the same manner as the individual SiO_4 tetrahedra in the structure of β -tridymite, (hexagonal wurtzite structure). This structure provides for parallel channels in the direction of the c-axis, which intersect channels that run in a plane perpendicular to the c-axis at angles of 120° . The channels parallel to c would have free diameters of $7.4 \text{ \AA}$. Channels in the direction of the a axis are smaller, of $6 - 7 \text{ \AA}$ diameter. The density calculated on the proposed hexagonal cell with 96 tetrahedra is lower than the observed value.

An alternative structure has been²⁵ proposed in which cancrinite cages are stacked in columns parallel to the c-axis and interlinked by M - O - M bonds forming channels of large twelve membered rings, $7.8 \text{ \AA}$ in free diameter. The structure has a hexagonal unit cell, $a = 18.4 \text{ \AA}$, $c = 7.5 \text{ \AA}$ and has 144 tetrahedra per unit cell rather than 96 and therefore no discrepancy of densities between observed and calculated values. The twelve ringed channels in the dehydrated form seem to contain no blocking cations and are available to large sorbate molecules.

CHAPTER 2

2.1 Mineral Synthesis

The experimental techniques adopted in mineral synthesis are imitative of natural geochemical processes. However, in the laboratory it is impossible to match the great periods of time involved in the formation of most natural minerals.

2.1.1. Sintering Reactions.

In these solid state reactions²⁶ the reactants diffuse at the boundaries between adjacent phases at temperatures below the melting points of the solids concerned. Reaction rates can be measured, but are dependent on such factors as grain size, compacting pressures, intimacy of mixing and thermal and chemical histories of the reactants. The crystals are usually small, and a polycrystalline mosaic results. Numerous syntheses of minerals by sintering have been recorded although the main value of the method is its provision of quantitative information concerning reaction mechanisms.

2.1.2. Vapour-Phase Crystallisation

Good crystals of ammonium chloride can easily be grown from its vapour, and there is little doubt that many minerals could also be formed in a similar way, provided sufficiently high but controlled temperature

conditions are achieved. Frankel²⁷ produced small crystals of cassiterite (SnO_2) by volatilization. Doelter²⁸ reported the preparation of enstatite and sillimanite at very high temperatures and probably by volatilization. Gaseous SiF_4 is reported²⁹ to react with superheated water vapour to give quartz crystals.

2.1.3. Pyrolytic Crystallisation

This method, in which the crystals are grown by cooling a melt, has proved valuable for producing large single crystals³⁰. In silicate chemistry difficulties arise in growing large crystals because of the great viscosity of the melt. Nucleation sets in at a rate which at first increases and then decreases with degree of undercooling, but subsequent growth is slow in the viscous magma, and usually only small crystals result. If the cooling is too rapid the whole mass sets to a glass. The general pattern of pyrolytic crystallisation of silicate magmas has been outlined³¹. When the melting point of the desired compound is very high, the flame-fusion technique of Verneuil may be used. In the production of single crystals of corundum, a fine powder of alumina is fed through the oxygen jet of an oxy-hydrogen burner. It melts as it passes through the flame and is deposited on the molten surface of the

growing crystal beneath.

2.1.4. High Pressure Crystallisation

During crystallisation a melt is sometimes exposed simultaneously to heat and great pressure. Natural crystallisations of deep-seated igneous rocks often occur under such conditions. An imitation of pneumatolytic high-pressure conditions was made by Michel-Levy³², who obtained small crystals of feldspar by detonating explosive charges in bombs up to temperatures of 850°C. Diamond has also been prepared³³ using apparatus capable of maintaining pressures up to 100,000 atms. at temperatures between 1200 and 2400°C.

2.1.5. Hydrothermal Synthesis

In this technique the reactants, together with a considerable amount of water are heated in sealed vessels. The crystallisation temperatures may be 600°C. or more and the pressure up to at least 60,000 p.s.i. In many of the crystals the water plays a structural role in the lattice; but anhydrous crystals are also easily grown (e.g. feldspars or quartz). In general, the proportion of hydrous to anhydrous species decreases as the temperature of crystallisation is raised.

2.2. Theoretical Aspects of Hydrothermal Synthesis of Zeolites.

A naturally occurring zeolite, which has formed and existed over long periods of geologic time, and a structurally related synthetic zeolite, rapidly prepared hydrothermally can exhibit differences due to ordering and changes in chemical composition. Many of the synthesised zeolites have no natural counterparts, for example zeolite A. Some synthetic species may be metastable relative to other phases and in time could possibly change into naturally occurring forms.

2.2.1. Metastability

The stable product of a synthesis is the species which has the minimum free energy in the given physical and chemical environment. Fyfe and Verhoogen³⁴ have pointed out that the free energy of polymorphic transitions or of reactions between silicates is, in general, only of the order of a few hundred or thousand calories per mole. Consequently in crystallisations where highly reactive amorphous reactants are used metastable assemblies may form and persist. Slight impurities, surface effects and methods of preparing reagents may have a marked effect on the final products.

Entropy changes may be a major factor affecting the production of metastable species, that is, species

which have a free energy higher than the minimum for the system, but whose rate of reaction to form the stable species is extremely slow. Ostwald's step rule, or law of stages, states that the phase which is most likely to appear is not necessarily the most stable one. Two different, but not contradictory explanations have been proposed. One suggestion is that the nucleation of the form with the least surface energy will be favoured³⁵, resulting in the preferential growth of a metastable phase, which may then persist. Fyfe and Verhoogen³⁴ however, showed that the rate of nucleation for a polymorphic transition includes a term with the form $\exp\left(\frac{-\Delta S \Delta T}{2RT}\right)$, where ΔS is the entropy change in the transition and $\Delta T = T_c - T$ (T_c is the equilibrium temperature, and T the temperature at which the nucleation takes place). This indicates that the greatest rate of nucleation is obtained for the transition involving the least decrease in entropy. Therefore there is a strong tendency for a phase with a crystalline structure close to that of the reactant, or a previously formed species, to nucleate. For example, there may be several possible polymorphs between the starting materials of high free energy and entropy and the stable product with minimum free energy and low entropy. In such a case a metastable polymorph, whose formation involved a smaller change in

entropy, will often be produced in experiments of short duration. It is therefore expected that the very reactive hydrous gels used in the present work will tend to produce metastable species.

2.2.2. Nucleation

Quantitative relationships have been derived for rates of nucleation but in a hydrothermal system where we have multicomponent inhomogeneous phases there is little data on solubility and supersaturation of the species. Goldsmith³⁶ has attempted a qualitative explanation of nucleation in such a complex system by means of the concept of simplicity. This is defined by saying that the compound with the highest degree of randomness in its structure is the compound of greatest simplicity. He postulates on kinetic grounds that the structures of greatest simplicity should be those most readily nucleated in a complex random system such as we have in hydrothermal syntheses, since the greater the disorder or entropy which can be tolerated and yet produce a nucleus which can grow, the greater is the chance of this occurring by means of random fluctuations in the solution. Many substances which exist as several polymorphs tend to crystallize initially as the high temperature modification, that is the disordered form e.g. synthetic alkali feldspars. In the case of

alternative polymorphic forms the more disordered form, or the more structurally simple form, often has a smaller unit cell than the more ordered complex form and so it may be that the form with the greatest simplicity can be nucleated by a smaller embryo than the more complex one. That the high simplicity form would continue to grow and persist is probably due to the high energy barrier to transformation. This principle cannot be used to predict possible products with much certainty since other thermodynamic properties may overrule these essentially kinetic considerations. Breck³⁷ has pointed out that zeolites which have the highest structural symmetry and simplicity in terms of basic structural units, such as zeolites A, X, Y and B nucleate and crystallize more readily at low temperatures while more complex structures (i.e. those with lower simplicity) such as mordenite, ferrierite and analcime require higher temperatures.

2.2.3. Mechanism of Gel Crystallisation

Zhdanov³⁸ has studied the crystallisation of Na, K, and Na-K aluminosilicates under hydrothermal conditions. The formation of zeolite crystals occurred from the colloidal gels in which the liquid and solid phases had different composition, and the crystallisation

of a certain structural type was the result of polycondensation of hydrated silicate and aluminate ions and was not determined by the composition of the Si-O-Al network of the initial gel skeleton. The crystal formation proceeds through some quasi-equilibrium concentration of the components in the liquid phase which is reached by dissolving the gel skeleton. Edwards and Fortnum³⁹ measured the Raman spectrum of the aqueous silicate ion and detected hydroxylated species consistent with a condensation reaction in crystallisation.

Barrer⁴⁰ has suggested that it is difficult to visualise complex open structures such as zeolites being built up by the single addition of $[\text{SiO}_4]$ or $[\text{AlO}_4]$ tetrahedra. A study of the zeolites with known structures suggests that they can be regarded as built up from simple rings or polyhedral units of tetrahedra. It was therefore postulated that such secondary building units exist in anionic form in solution, and these stack together in various co-ordinations to form the different zeolitic structures. For example, if two four-membered rings join together a cubic anion results and these cubes may be stacked in eight-fold co-ordination to give Linde Sieve A. Again if three four membered rings are appropriately linked by oxygen bridges, a double six-ring anion is formed.

The chabazite type of structure contains such units.

The high anionic charges make the real existence of such complex anions unlikely. However there is no reason why full ionisation should be realized, since the oxygen atoms linked only to Al or Si may not be O^- groups but may exist partly as unionized $-OH$ groups.

2.3. Kinetics of Zeolite Formation

Domine and Quobex⁴¹ synthesised mordenite hydrothermally from $SiO_2/Al_2O_3/Na_2O$ gels, and also from an amorphous silicate-aluminate gel prepared by mixing aluminium sulphate and sodium silicate solutions. The use of the amorphous gel simplifies the study of crystallisation because there is just one starting material of homogeneous chemical composition; the influence of the type of silica and the degree of polymerisation of silicic acid on the reaction products is eliminated. The rate of mordenite formation in both types of synthesis was a function of temperature, alkalinity, and concentration of reactants. It was found that the rate of reaction was zero during a period of induction and then increased sharply to a maximum and finally decreased to zero again. The reaction rate increased with increasing pH until at $pH > 13$ the yield of mordenite decreased and

analcite began to form. Alkalinity played a catalytic role. It increased the quantity of silica in solution and accelerated the reaction. Temperature influenced only the rate of crystallisation, there was no range of temperature thermodynamically limited for producing mordenite. The overall rate of reaction can be represented by

$$V_T = K_T f([A], [B], \dots) \quad \text{§ §}$$

where K_T is a constant depending only upon the temperature, $K_T = A \exp^{-E/RT}$. E is the activation energy of the reaction. $[]$ = concentration of reactant; alkali, etc.

Activation energies can be evaluated from the slopes of the kinetic curves at different temperatures under strictly analogous synthesis conditions. Breck estimated the activation energy to be 15 kcals. per Avogadro's number of framework units for the X zeolite, 14 kcals. for the Y, and 11 kcals. for type A. Greenberg has reported an activation energy of 21.5 kcals./mole for the depolymerisation of silica in basic solution which is not much larger than the activation energy in the formation of the X zeolite.

During induction periods nucleation probably takes place, the nuclei grow to a critical size and then rapid crystallisation sets in. It seems certain that silica from the gel colloids dissolves in the liquid

phases during the induction periods as nearly always excess silica has to be used to obtain pure products. Seeding experiments have not produced any significant increase in crystal sizes.

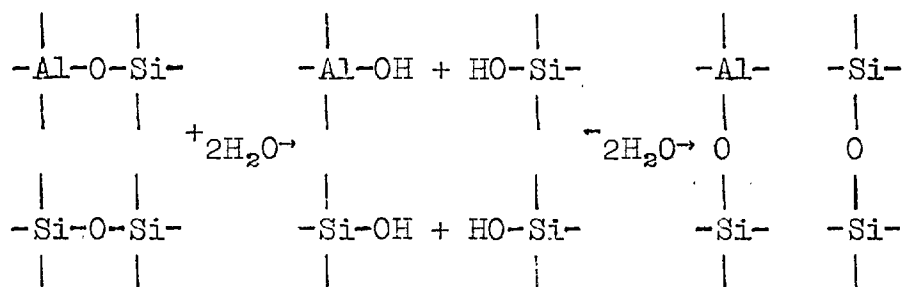
2.4. Water in Hydrothermal Crystallisations

In hydrothermal chemistry water is present as a major component of crystallising magmas. Particularly under alkaline conditions water facilitates syntheses due to the different roles it can play. These are described below.

2.4.1. Chemisorption

Water may be chemisorbed on oxide, silica and alumina surfaces, and through electron transfer can modify the normal defect structure of oxide and other lattices and so alter rates of migration of lattice units to a growing or germ nucleus.

Water may penetrate into silica and silicates producing new defects. Such penetration occurs in silicates by bond hydrolyses and subsequent reformation of bonds with new partners. This assists reorganization, nucleus formation and crystal growth.



A study of the solubility of water in silica glass by Moulson and Roberts⁴² supports the chemisorption process throughout the body of the silica since the solubility varied as the square root of the pressure of the surrounding water vapour, suggesting that the water molecule dissociated on entry with the production of two hydroxyl groups in the atomic network of the glass. The presence of the OH groups and their concentration was ascertained by infra-red absorption.

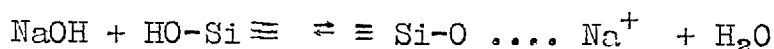
2.4.2. Bond Hydrolysis and Viscosity

The rate of nucleation of a new crystalline phase is dependent on the degree of super-cooling and the viscosity of the magma. Hydroxyl concentrations in silica phases are usually low,⁴¹ (6×10^{-3} OH groups per SiO_2 structural unit at $600^\circ\text{C}.$) but under hydrothermal conditions, i.e. in presence of a liquid water phase and high water vapour pressures, the concentrations will become much larger and the bond rearrangements due to hydrolysis will reduce the viscosity of siliceous

media. Since the viscosity increases as the super-cooling increases ($\eta = \eta_0 \exp^{E/RT}$) the rate of nucleation reaches a maximum and then decreases as the viscosity of the magma increases. The effect of bond hydrolysis is to increase the maxima in the nucleation rates and move them to lower temperatures.

2.4.3. Solvent Action of Water

In alkaline media, usually adopted in hydrothermal systems, the process of hydroxylation is accompanied by ionization:



Therefore, by the law of mass action hydrolysis may be enhanced to the extent of partial solution and so facilitates crystallisation.

2.4.4. Porous Crystal Stabilisation

Porous aluminosilicates will not form in the absence of 'guest' molecules of either a salt or water. The stabilising effect of water can be understood thermodynamically using the Gibbs-Duhem equation. Considering one mixed mole of guest molecules A and of chosen lattice forming units S of a host lattice,

N_A = mole fraction of A.

N_S = mole fraction of S.

V_1 = volume of one mixed mole at pressure P.

μ'_A = chemical potential of A.

μ''_A = chemical potential of A in melt or vapour.

μ_S = chemical potential of S.

a_A = activity of guest molecules in vapour (or melt).

p_A = water vapour pressure.

where $N_A d\mu'_A + (1-N_A)d\mu_S = V_1 dP$. (Gibbs-Duhem eqn.)

At equilibrium $d\mu''_A = d\mu'_A$, and so

$$d\mu_S = \frac{V_1 dP - N_A d\mu''_A}{(1-N_A)} \quad (1)$$

$$\Delta\mu_S = \int_0^P \frac{V_1}{1-N_A} dP - RT \int_0^{a_A} \frac{N_A}{(1-N_A)} d \ln a_A$$

If $V_m = \frac{V_1}{1-N_A}$ does not vary significantly with pressure, this gives

$$\Delta\mu_S = V_M p_A - \frac{MRT}{n} \int_0^{p_A} \frac{x}{p_A} dp_A \quad (2)$$

where M = mol.wt. of S and m of A; x is the number of grammes of guest molecules A per gramme of host lattice and V_M = volume of one mole of sorbent of molecular weight M . The first term of (2) is negligible at pressures up to one atmosphere. The second term can

be evaluated graphically using the sorption isotherm of the water. The values of $\Delta\mu_2$ can be substantial, and are always in the direction of greater stability the larger the zeolite water content. Barrer and Bratt⁴³ measured the chemical potential change of the faujasite-type framework when ammonia and water molecules were occluded. They found a large stabilization factor.

2.5. Phase Equilibria

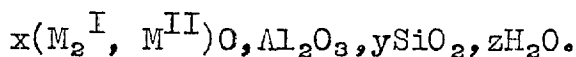
Phase equilibria in hydrothermal systems has been reviewed by Niggli and Morcy⁴⁴. Although hydrothermal systems have three or four components, consideration of simpler binary models is helpful.

In the temperature-concentration projection of the phase equilibrium diagram for a binary system, the solubility or fusion curve joins the triple points of the two components. This may or may not intersect the critical curve, i.e. the locus of all points where the critical phenomena occur for mixtures intermediate between the two pure components. If the curve is not intersected only unsaturated solutions show critical phenomena, and the two-phase line equilibrium can be studied without the appearance of critical phenomena. In the second case, intersection of the critical curve, there will be an upper and lower

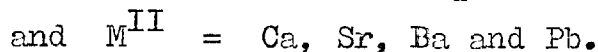
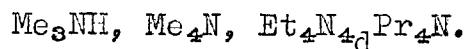
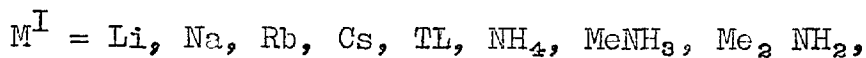
critical point at which the saturated solution will show critical phenomena. Above the upper and below the lower of these intersection points the three phases, solid, liquid and vapour may co-exist, whilst in the intermediate region solid and gaseous solutions will be the only stable phases. In the region between the two critical end points the two component system will be divariant and for a given temperature and volume, a small change in the amount of one of the components will change the pressure, and therefore the concentration of the vapour phase. As a result variations in the degree of filling of a closed vessel may influence the product formed. This is the case in most silicate or aluminosilicate and water systems. However, in the present work, the temperatures were too low for critical phenomena to occur.

2.6. Crystallisation Fields

In these laboratories hydrothermal crystallisations have been made⁴⁵⁻⁵⁵ using as parent materials hydrous gels having the oxide compositions



where



The values of x ranged from less than unity to 3 or 4, and those of y between 2 and 12. z was large compared with x or y . The temperatures ranged from less than 100° to about 450°C . The alumina was normally introduced as sodium aluminate or a freshly prepared aluminium hydroxide, and the silica as gel, sol, or, less often, as powdered silica glass. The usual degree of filling of the autoclaves with aqueous gel was about 50% of their volume.

A large number of non-zeolitic mineral type compounds were made as well as zeolitic phases belonging to the mordenite-heulandite, chabazite, analcite, natrolite, faujasite, harmotome-phillipsite, and Linde Sieve A groups. A considerable number of zeolites without known natural counterparts were also prepared. The low temperature syntheses of zeolites X and Y (structurally similar to faujasite) and zeolite L⁵⁶ have been made by the Union Carbide Corporation.

CHAPTER 3

Theoretical Aspects of Sorption

3.1 Thermodynamics of Sorption and Isotherm Models

Hill, Everett and Drain⁵⁷⁻⁶² have reviewed the thermodynamic treatments of physical adsorption. The experimental results obtained in the present work have been analysed by the methods of solution thermodynamics.

3.1.1 Summary of Symbols

The symbols used in this work are as follows:-

P = pressure.

T = temperature, °K.

Subscripts 1, 2 and g refer to sorbate, sorbent and gas respectively.

$\bar{X}$ = a partial molar derivative w.r.t. n , the number of moles of the species present.

$\tilde{X}$ = integral quantity per gram mole.

ρ = concentration ratio of sorbate to sorbent n_1/n_2 .

$\tilde{X}^0$ = integral quantity in a standard state.

$\tilde{S}_c$ = molar configurational entropy.

$\bar{S}_c$ = partial molar configurational entropy.

$\bar{S}_{th}^1$ = residual thermal entropy defined as

$$\bar{S}_{th}^1 = \bar{S}_{1-1} - \bar{S}_t.$$

$\bar{S}_{th}^{11}$ = residual thermal entropy defined as

$$\bar{S}_{th}^{11} = \bar{S}_{1-2} - \bar{S}_t.$$

${}_1\bar{S}_t$ = partial molar entropy resulting from one degree of translational freedom of the guest molecule.

t = translational degree of freedom.

ν = vibrational frequency.

k = Boltzmann's constant.

h = Planck's constant.

3.1.2 Solution Thermodynamics

The adsorbent-adsorbate system is considered as a single condensed phase of two components (binary mixture) with energy U , entropy S and volume V in equilibrium with unadsorbed gas. Using the standard methods of solution thermodynamics we can write:-

$$dU = TdS - PdV + \mu_1 dn_1 + \mu_2 dn_2 \quad (1)$$

$$dG = -SdT + VdP + \mu_1 dn_1 + \mu_2 dn_2 \quad (2)$$

and also since $\mu_1 = \mu_1(T, P, \Gamma)$

$$d\mu_1 = \left(\frac{\partial \mu_1}{\partial T} \right)_{P, \Gamma} dT + \left(\frac{\partial \mu_1}{\partial P} \right)_{T, \Gamma} dP + \left(\frac{\partial \mu_1}{\partial \Gamma} \right)_{T, P} d\Gamma \quad (3)$$

But since $\left(\frac{\partial \mu_1}{\partial T} \right)_{P, \Gamma} = -\bar{S}_1$ and $\left(\frac{\partial \mu_1}{\partial P} \right)_{T, \Gamma} = \bar{V}_1$

Equation (3) becomes:-

$$d\mu_1 = -\bar{S}_1 dT + \bar{V}_1 dP + \left(\frac{\partial \mu_1}{\partial \Gamma} \right)_{T, P} d\Gamma \quad (4)$$

For the gas we have the well known expression:-

$$d\mu_g = -\tilde{S}_g dT + \tilde{V}_g dP \quad (5)$$

At equilibrium between gas and the condensed phase,

$$d\mu_1 = d\mu_g \text{ so that}$$

$$-\bar{S}_1 dT + \bar{V}_1 dP + \left(\frac{\partial \mu_1}{\partial T} \right)_{P,T} dp = -\tilde{S}_g dT + \tilde{V}_g dP \quad (6)$$

Under ordinary experimental conditions $P = p$ and so for constant p

$$\left(\frac{\partial p}{\partial T} \right)_p = (\tilde{S}_g - \bar{S}_1) / (\tilde{V}_g - \bar{V}_1) \quad (7)$$

Using the usual approximations (a) of a perfect gas and (b) $\tilde{V}_g \gg \bar{V}_1$ we obtain,

$$\begin{aligned} \left(\frac{\partial \ln p}{\partial T} \right)_p &= (\tilde{S}_g - \bar{S}_1) / RT \\ &= (\tilde{H}_g - \bar{H}_1) / RT^2 = q_{st} / RT^2 \end{aligned} \quad (8)$$

$q_{st} = -\Delta \bar{H}_1$, is the isosteric heat of sorption.

3.1.3 Entropy of Sorption

~~Rearrangement of (8) will give us~~ ^{From equation we obtain} the entropy change

$$\Delta S = \tilde{S}_g - \bar{S}_1 = -\frac{\Delta \bar{H}_1}{T} \quad (9)$$

$\tilde{S}_g$ is the entropy of the gas at pressure p .

But

$$\tilde{S}_g = \tilde{S}_g^\circ + R \ln p^\circ / p \quad (10)$$

Combining (9) and (10) we obtain

$$\bar{S}_1 = \tilde{S}_g^\circ + R \ln p^\circ / p + \frac{\Delta \bar{H}_1}{T} \quad (11)$$

The standard pressure p° for a gas is usually taken to be 1 atm. If a correction for non ideality of the gas is required, a term Ap is subtracted from the above

expression for $\bar{S}_1$, where approximately, $A = \frac{27RT_c^3}{32P_c T^3}$

T_c and P_c are respectively the critical temperature and pressure.

3.1.4 Isosteric Heat of Adsorption

In deriving the isosteric heat of adsorption we considered the amount of sorbent n_2 , and not its surface area. Therefore, equation (8) applies regardless of whether the sorbent swells on sorption, or the area or number of sorption sites changes with temperature or pressure, or even whether an 'area' exists.

Two methods can be employed to obtain the isosteric heat of sorption from the experimental isotherm data:

(a) Equation (8) can be rearranged in the form

$$\left(\frac{\partial \ln p}{\partial 1/T} \right)_n = \frac{\Delta \bar{H}_1}{R} \quad (8i)$$

and so the isosteric heat can be evaluated from a series of plotting $\log_{10} P$ vs $1/T$ for a fixed amount adsorbed. The slope of this plot, or tangent if a curve results, multiplied by $2.303 R$ gives q_{st} .

(b) Plots of $\log_{10} p$ versus V_s (amount sorbed) can be constructed for a series of isotherms and hence $\log P_1/P_2$ corresponding to T_1 and T_2 , for a fixed amount adsorbed may be obtained; the isosteric heat is given by the integrated form of (8)

$$q_{st} = 4.57 \left(\frac{T_1 T_2}{T_1 - T_2} \right) \log_{10} P_1/P_2 \quad (8ii)$$

3.2 Thermodynamic Properties of Sorbent

These may be obtained from the isotherms. At constant T the Gibbs-Duhem relationship gives:

$$n_1 d\mu_1 + n_2 d\mu_2 = VdP \quad (12)$$

Define $N_1 = \frac{n_1}{n_1+n_2}$, $N_2 = \frac{n_2}{n_1+n_2}$ where N_1 and N_2 are

mole fractions.

Let V_x = volume of mixed mole = $\frac{V}{N_1+N_2}$, substituting

these in (12)

$$N_1 d\mu_1 + (1 - N_1) d\mu_2 = V_x dP \quad (13)$$

On rearranging

$$d\mu_2 = \frac{V_x dP}{1-N_1} - \frac{N_1 d\mu_1}{1-N_1} \quad (14)$$

At equilibrium $d\mu_1 = d\mu_g$ and assuming ideality

$$d\mu_g = RT d \ln P.$$

Substituting in (14) and integrating, assuming that there is no expansion of the zeolite lattice on sorption, we obtain

$$\Delta\mu_2 = \mu_2 - \mu_{0_2} = V_M(P - P_0) - \frac{MRT}{m} \int_{P_0}^P \frac{y}{P} dP \quad (15)$$

where y = amount adsorbed gm/gm of outgassed sorbent

m = molecular weight of sorbate

V_M = volume of one mole of sorbent of molecular weight M .

The first term of (15) is small compared to the second term which can be evaluated from the sorption

isotherm. Also from the Gibbs-Helmholtz relationship we have:

$$\frac{\partial(\mu_2 - \mu_{02})}{\partial T} = -(\bar{S}_2 - \bar{S}_{02}) = -\Delta\bar{S}_2 \quad (16)$$

$$\text{and } \left[\frac{\partial}{\partial T} \left(\frac{\Delta\mu_2}{T} \right) \right]_X = -(\bar{H}_2 - \bar{H}_{02}) = -\frac{\Delta\bar{H}_2}{T^2} \quad (17)$$

Thus the entropy and enthalpy changes of the sorbent on sorption can be found.

3.3 Half Standard Entropy of Adsorption⁶³

On rearranging and differentiating equation (11) we obtain:

$$\frac{\partial}{\partial T} (\bar{S}_1 - \tilde{S}_g^0) = \frac{\partial}{\partial T} (R \ln p^0/p) + \frac{\partial}{\partial T} \left(\frac{\Delta\bar{H}_1}{T} \right) \quad (18)$$

If $\Delta\bar{H}_1$ is independent of T, then the right hand side of equ. (18) is zero

$$\therefore \left(\frac{\partial \bar{S}_1}{\partial T} \right)_X = \left(\frac{\partial \tilde{S}_g^0}{\partial T} \right) \quad (19)$$

$\Delta\bar{S}_1 = \tilde{S}_g^0 - \bar{S}_1$ is best described as a half standard entropy.

Half Standard Integral Entropy of Adsorption

An analogous equation to (19) can be derived for the integral entropy of sorption if it is once more assumed that there is no temperature coefficient in the isosteric heat.

From the definition of $\tilde{S}_1$ we can write:

$$\tilde{S}_g^0 - \tilde{S}_1 = \tilde{S}_g^0 - \frac{1}{n_1} \int_0^{n_1} \bar{S}_1 dn_1 = -\frac{1}{n_1} \int_0^{n_1} (\bar{S}_1 - \tilde{S}_g^0) dn_1$$

$$\begin{aligned}
\therefore \frac{d}{dT} (\tilde{S}_g^o - \tilde{S}_1) &= -\frac{d}{dT} \left[\frac{1}{n_1} \int_0^{n_1} (\bar{S}_1 - \tilde{S}_g^o) dn_1 \right] \\
&= -\frac{d}{dT} \left[\frac{1}{n_1} \int_0^{n_1} (R \ln p^o/p + \frac{\Delta \bar{H}_1}{T}) dn_1 \right] \\
&= \frac{1}{n_1} \left[\int_0^{n_1} \frac{d}{dT} (R \ln p^o/p + \frac{\Delta \bar{H}_1}{T}) dn_1 \right] \quad (21)
\end{aligned}$$

If $\Delta \bar{H}_1$ is independent of temperature the right-hand side of (21) vanishes according to the Clausius-Clapeyron equation.

$$\text{i.e. } \frac{\partial}{\partial T} (\tilde{S}_g^o - \tilde{S}_1)_x = 0 \quad (22)$$

$\tilde{S}_g^o - \tilde{S}_1$ can be designated $\Delta \tilde{S}_1$ analogous to $\Delta \bar{S}_1$ above for the half standard integral entropy of sorption.

Combining (19) and (22) we have:

$$\frac{\partial \tilde{S}_g^o}{\partial T} = \left(\frac{\partial \tilde{S}_1}{\partial T} \right)_x = \left(\frac{\partial \bar{S}_1}{\partial T} \right)_x \quad (23)$$

$$\text{Also by definition } \bar{S}_1 = \tilde{S}_1 + n_1 \left(\frac{\partial \tilde{S}_1}{\partial n_1} \right) \quad (24)$$

$$\text{and } \tilde{S}_g^o - \bar{S}_1 = \Delta \bar{S}_1 \quad (19)$$

$$\tilde{S}_g^o - \tilde{S}_1 = \Delta \tilde{S}_1 \quad (25)$$

By substituting in (24) for $\bar{S}_1$ and $\tilde{S}_1$ from (19) and (25)

$$\frac{\partial \tilde{S}_1}{\partial n_1} = \frac{1}{n_1} (\Delta \tilde{S}_1 - \Delta \bar{S}_1)$$

$$\therefore \frac{\partial}{\partial T} \left[\left(\frac{\partial \tilde{S}_1}{\partial n_1} \right)_x \right] = 0$$

If the integral entropy of the sorbate is known at one temperature, then it can be obtained at any other by using

equation (22); the only requirement is that the standard entropy of the gas be known at that temperature.

3.4 Empirical Isotherm Equations

Restating equation (15), derived from the Gibbs-Duhem relationship at constant temperature,

$$\Delta\mu_2 = \int_0^P V dP - \frac{MRT}{m} \int_0^P \frac{y}{p} dP \quad (15)$$

Usually the first term on the right-hand side of the equation can be neglected. A second expression for the change in chemical potential of the sorbent during adsorption can be stated as follows:

$$\Delta\mu_2 = \int_0^{-\pi} V dP \quad (26)$$

where π is the hydrostatic pressure which would have to be applied to the zeolite/sorbed phase to raise the chemical potential of the zeolite to that of sorbate-free crystals.

Equating the two expressions, (15) and (26) for $\Delta\mu_2$ we obtain

$$\frac{MRT}{m} \int_0^P \frac{y}{p} dP = V\pi$$

Therefore,

$$\frac{\pi}{RT} = \frac{\partial}{m} \int_0^P \frac{y}{p} dP \quad (27)$$

where ∂ is the density of the zeolite crystal. Inserting C , the concentration of the sorbate in the sorbate-zeolite

solution into the denominator of (27) we obtain,

$$\frac{\pi}{CRT} = \frac{\partial}{\partial C} \int_0^P \frac{y}{p} dP$$

However π/CRT can be described by a virial equation of state:

$$\frac{\pi}{CRT} = 1 + A_1 C + A_2 C^2 + \dots + A_n C^n \quad (28)$$

i.e.

$$\frac{\partial}{\partial C} \int_0^P \frac{y}{p} dP = 1 + A_1 C + A_2 C^2 + \dots + A_n C^n$$

$$\therefore \int_0^P \frac{C}{P} dP = C + A_1 C^2 + A_2 C^3 + \dots + A_n C^{n+1} \quad (29)$$

Considering the first three terms only of the virial equation then (29) becomes

$$\int_0^P \frac{C}{P} dP = C + A_1 C^2 + A_2 C^3 \quad (30)$$

i.e.

$$\frac{dP}{P} = \left(\frac{1}{C} + 2A_1 + 3A_2 C \right) dC \quad (31)$$

Integration of (31) gives:

$$P = KC \exp(2A_1 C + \frac{3}{2} A_2 C^2) \quad (32)$$

where K is the Henry Law constant for small C. Since

$C = k_1 \theta_1$ where $k_1 = \left(\frac{\partial}{\partial m} \right) y$ sat. equation (32) may also be

written:

$$P = K_1 \theta \exp(2A'_1 \theta + \frac{3}{2} A'_2 \theta^2) \quad (33)$$

or more generally:

$$P = K_2 \theta \exp(2A'_1 \theta + \frac{3}{2} A'_2 \theta^2 + \dots + \frac{n+1}{n} A'_n \theta^n)$$

Isotherm equations can thus be obtained from any isotherm data sufficiently complete to permit the evaluation of the integral

$$\int_0^p \frac{p}{p} dP$$

3.5 Isotherm Models

Models give descriptions of idealised systems and may not be applicable to real systems. Deviations may arise from surface heterogeneities, multilayer formation, and mutual interactions between sorbed molecules. It is necessary to consider all possible isotherm models when the state of the adsorbed phase is being investigated, as often in the complete sorption process the sorption is not purely of one kind.

The following models will be considered:

- (i) Localised model
- (ii) Localised model with mutual interactions
- (iii) Mobile model
- (iv) Mobile model with mutual interactions.

3.5.1 State of the Adsorbed Molecule

A molecule when adsorbed on a surface enters the potential field associated with the surface. This field will vary according to the nature of the sorbent. Thus the adsorbate molecules may encounter potential barriers

in their motion along the surface. Two extreme cases may be considered although the actual state of the sorbed molecule may lie anywhere between the extremes.

Localized

The sorbed molecule is said to vibrate about a mean position on the surface. Localisation may be due to the molecule lacking sufficient thermal energy to overcome surface potential energy barriers or the mutual caging effect of the sorbed molecules on each other. A single molecule may not be permanently confined to a particular occlusion site on the surface. It may by diffusion or desorption/resorption occupy neighbouring sites. Although the molecule may occasionally move from one site to another, the sorption is still said to be localised.

Mobile

The average thermal energy of the molecules may be larger than the surface potential energy barrier. If so, the molecules will be able to move freely over the surface and are therefore mobile.

3.5.2 Localized Models

No Mutual Interactions

In an ideal localised model of intracrystalline sorption the molecules are assumed to be sorbed on a

three-dimensional array of energetically homogeneous sites with no interactions between neighbouring molecules. Fowler's⁶⁴ statistical-mechanical treatment of surface adsorption applied equally well to sorption on a three-dimensional array of sites and the isotherm equation, deduced originally by Langmuir⁶⁵ from a kinetic treatment of adsorption, is

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

K_L contains the ratio of the partition functions of the gaseous molecule and of the internal degrees of freedom of the sorbed molecule, including vibrations relative to its mean position; p is the equilibrium gas-phase pressure corresponding to any fraction of sites covered, θ . The theory requires that the vibrations and rotations executed by the sorbed molecules should remain unchanged by any variation in sorbate concentration, i.e. K_L should not be a function of θ and should thus be a constant at any one temperature. For purposes of testing experimental data it is usual to write (34) in the linear form

$$\frac{p}{V} = \frac{K_L}{V_{sat}} + \frac{p}{V_{sat}} \quad (35)$$

where V is the volume (S.T.P.) sorbed at pressure p and V_{sat} the volume (S.T.P.) sorbed at saturation. However, the criterion of the linearity of a plot is not easy to apply with certainty. If K_L is calculated from experi-

mental values of Θ and p for the entire concentration range and plotted as a function of Θ , then the constancy of K_L would suggest the validity of the theory. A further test of the theoretical isotherm is the reproducibility of experimental observations, especially entropy values.

3.5.3 Entropy of Localised Phase.

The entropy of a localized sorbate phase may be conveniently separated into thermal and configurational terms

$$\bar{S}_1 = \bar{S}_c + \bar{S}_{th} \quad (36)$$

The thermal entropy will include contributions from the electronic states of the molecule, vibrations about chemical bonds, rotations and restricted rotations, and vibrations about the mean position on a site. The configurational entropy arises from the number of distinguishable arrangements of m molecules on M identical sites which is given by $M!/m!(M-m)!$. If it is assumed that all these arrangements are equally probable then the entropy of the system will include a term, $k \ln M!/m!(M-m)!$, where k is the Boltzmann constant. Using Stirling's approximation the entropy term reduces to

$$-k [m \ln m/M + (M-m) \ln (M-m)/M]$$

The partial molar configurational entropy, $\bar{S}_c$, of the

adsorbed molecules is obtained by differentiation with respect to m , and multiplying by Avogadro's number

$$\bar{S}_c = R \ln \frac{1-\theta}{\theta} \quad (37)$$

where $\theta = m/M$ i.e. the coverage.

In testing the validity of the localised model the difference between the experimentally observed $\bar{S}_1$, and the value of $\bar{S}_c$ obtained from (37) is calculated. The partial molar thermal entropy must be constant independent of θ ; also it must be positive and be compatible with reasonable values of the vibrational frequency of the molecules in the intracrystalline cavities. For example, in a sorbed phase of monatomic molecules it will be essentially the entropy of the three vibrational degrees of freedom about the mean position on the site.

Assuming equipartition of entropy between these three vibrations, an average vibrational frequency may be obtained. The value to be expected has been discussed by Hill⁵⁹ and should be in the range 10^{11} to 10^{12} sec⁻¹.

Mutual Interactions

The effect of interactions between nearest neighbour molecules in a localised system has been considered by numerous workers⁶⁶⁻⁶⁹. The quasi-chemical equilibrium approach of Fowler and Guggenheim⁷⁰ for interactions between nearest neighbours only gives the isotherm

$$p = K_{LI} \left(\frac{\theta}{1-\theta} \right) \left[\frac{2(1-\theta)}{\beta+1-2\theta} \right]^z \quad (38)$$

where z is the number of nearest neighbours of any site and β is given by

$$\beta = \left\{ 1 - 4\theta(1 - \theta)[1 - \exp(-2w/zkT)] \right\}^{\frac{1}{2}}$$

$2w/z$ is the interaction energy between two adjacent molecules. It is negative for attractive interactions and may be evaluated from a knowledge of the potential energy of the two molecules concerned. z may be determined from the geometry of the three-dimensional lattice. K_{LI} contains the partition function of gaseous and sorbed molecules and is a constant independent of sorbate concentration for any given T . The isotherm is best tested by calculating K_{LI} for a series of experimental values of θ and p .

The partial molar configurational entropy is given by,

$$\bar{S}_c = R \ln \frac{1-\theta}{\theta} - zR \ln \frac{2(1-\theta)}{(\beta+1-2\theta)} + \frac{w(\beta-1+2\theta)}{T\beta} \quad (39)$$

The difference between the ideal and the non-ideal configurational entropy of a localised phase has been considered for argon in chabazite⁷¹. It was found that the maximum divergence between the ideal and the non-ideal case was 0.33 cal/mole deg. in the range $\theta = 0.1$ to 0.9.

3.5.4 Mobile Models

There are two major approaches to the treatment of these models. The first is that of statistical mechanics based on the partition function described by Fowler and Guggenheim⁷⁰, while the other proposes an equation of state as a starting point and proceeds to the sorption isotherm by the application of the Gibbs equation or by the method by Everett⁶¹.

There are three cases to be considered:

- (a) a perfect two-dimensional gas of point particles, in which the area accessible to the sorbed molecules is independent of their number, and in which no mutual interaction between sorbed molecules is allowed;
- (b) a two-dimensional gas in which the molecules have a finite cross-section, the accessible area thus being reduced by the progressive addition of molecules, no mutual interactions allowed;
- (c) a two-dimensional van der Waals gas exhibiting both a co-area and mutual interactions between sorbed molecules.

In the first case the isotherm can be represented by the following equation:

$$p = Kp\theta \quad (40)$$

Equation (40) is the Henry's Law isotherm.

The preceding model based on a two-dimensional perfect gas of point particles is oversimplified, a

more satisfactory model, the Volmer model, introduces a finite co-area for each molecule but again neglects the possibility of mutual interaction between sorbed molecules. The form of the isotherm can be represented as follows,

$$p = K_V \left(\frac{\theta}{1-\theta} \right) \exp \left(\frac{\theta}{1-\theta} \right) \quad (41)$$

where K_V is a constant for any given sorbate and temperature.

For a sorbed phase in which the molecules have a finite area and exhibit mutual interactions according to an analogue of van der Waals equation the isotherm has the form

$$p = K_{VW} \left(\frac{\theta}{1-\theta} \right) \exp \left(\frac{\theta}{1-\theta} - \alpha \theta \right) \quad (42)$$

where $\alpha = 2a'/b'kT$, a' and b' are two-dimensional van der Waals constants.

3.5.5 Entropy Functions in Mobile Models

The partial molar entropy of the sorbed phase $\bar{S}_1$, must be compatible either with one or two degrees of translational freedom (three translational degrees of freedom are not to be expected in compact frameworks such as chabazite or ferrierite). The entropy can be divided into two parts, thus:

$$\bar{S}_1 = {}_1\bar{S}_t + \bar{S}'_{th} \quad (43)$$

$$\text{and } \bar{S}_1 = {}_2\bar{S}_t + S''_{th} \quad (44)$$

${}_1 \bar{S}_t$ and ${}_2 \bar{S}_t$ are the partial molar translational entropies, resulting from one and two degrees of translational freedom of the guest molecules respectively, $\bar{S}_{th}$ and $\bar{S}'_{th}$ are the residual thermal entropies. The thermal entropies must be positive quantities and should, for the range in θ for which the sorption model is valid, be independent of θ . For models (41) and (42) ${}_1 \bar{S}_t$ and ${}_2 \bar{S}_t$ may be formulated:-

$${}_1 \bar{S}_t = R \ln \left[\frac{(2\pi mkT)^{\frac{1}{2}}}{h} \cdot L \frac{(1-\theta)}{\theta} \right] + R \left(\frac{1}{2} - \frac{\theta}{1-\theta} \right) \quad (45)$$

$${}_2 \bar{S}_t = R \ln \left[\frac{2\pi mkT}{h^2} \cdot a \frac{(1-\theta)}{\theta} \right] + R \left(1 - \frac{\theta}{1-\theta} \right) \quad (46)$$

where L = co-length of a sorbed molecule and a = co-area. Garden, Kington and Laing showed that argon occluded in chabazite at 90.19°K was in reasonable accord with the isotherm for mobile molecules without interaction. The values $\bar{S}_1 - {}_2 \bar{S}_t$ and $\bar{S}_1 - {}_1 \bar{S}_t$ were calculated, $\bar{S}'_{th}$ was a positive quantity, approximately constant over the range of validity of the model, whereas $\bar{S}''_{th}$ had a negative value. Argon, therefore, possesses one translational degree of freedom at this temperature and $\bar{S}'_{th}$ corresponds to two vibrational degrees of freedom, since rotations are not involved in the case of the molecule.

3.6 Tests of Isotherm Models

From equation (15) the following relationship for

the change in chemical potential of the sorbent was stated:

$$\Delta\mu_2 = - \frac{MRT}{m} \int_0^P \frac{y}{p} dP$$

If substitution is made for y/p in terms of θ for the ideal model equations (34) - (41) we obtain:

$$\Delta\mu_2 = \frac{RTMy}{m} \text{sat} \ln(1 - \theta) \text{ (for Langmuir's isotherm)} \quad (47)$$

and,

$$\Delta\mu_2 = -\frac{RTMy}{m} \text{sat} \frac{\theta}{1-\theta} \text{ (for Volmer's isotherm)} \quad (48)$$

$$\text{But, } \Delta\mu_2 = - V\pi \quad (26)$$

Therefore

$$\frac{\pi}{CRT} = - \frac{\ln(1-\theta)}{\theta} \text{ (Langmuir's isotherm)} \quad (49)$$

and

$$\frac{\pi}{CRT} = \frac{1}{1-\theta} \text{ (Volmer's isotherm)} \quad (50)$$

The equations derived in this section provide further tests of the degree of correspondence of any isotherm model to a real system. The tests can be applied in the following ways:

(i) $\Delta\mu_2$ can be obtained as a function of y , at various temperatures from the experimental data using equation (15); the curves so obtained can be compared with those predicted by ideal model equations such as (47), (48).

(ii) Using the equation,

$$\frac{\pi}{CRT} = \frac{\partial}{\partial C} \int_0^p \frac{y}{P} dP \quad (27)$$

plots of π/CRT against y can be constructed for various temperatures in the experimental range; these plots can be compared with the curves characteristic of the ideal models as in equations (49) and (50).

(iii) $\frac{\pi}{CRT}$ plotted against θ gives a characteristic curve independent of temperature and sorbent for ideal models. Thus if the Langmuir ideal model were valid a plot of π/CRT against θ should be identical with that of $-\frac{\ln(1-\theta)}{\theta}$ against θ , at all temperatures.

CHAPTER 4.

Physical Adsorption Forces

The movement and alignment of electrons within atoms and molecules create intermolecular attraction and repulsion forces. These can be divided into dispersion, repulsion and electrostatic forces, the latter including polarisation and electrical multipole effects.

4.1. Dispersion Forces ϕ_D

Atoms and molecules possess instantaneous dipole and multipole moments as a result of the motion of their electrons. The instantaneous moments induce in any neighbouring atom or molecule resonant moments which are in phase with those of the first atom or molecule so that there is a force of attraction between them. These forces are known as dispersion forces on account of their relationship with optical dispersion⁷².

The dispersion energy is given by the expression:-

$$\phi_D = \underbrace{-\frac{A}{r^6}}_{(a)} - \underbrace{\frac{A_1}{r^8}}_{(b)} - \underbrace{\frac{A_2}{r^{10}}}_{(c)} \quad (1)$$

- (a) Arises from fluctuating dipole/dipole coupling.
- (b) Arises from fluctuating dipole/quadrupole coupling.
- (c) Arises from fluctuating quadrupole/quadrupole coupling.

The first term is usually the only one considered in calculating the dispersion energy, the other two being ignored. Kiselev⁷³ used equation (1) to calculate heats of adsorption of various gases on graphite and estimated the dipole-quadrupole term contributed 10 per cent and the quadrupole-quadrupole term 1 per cent to the total value of the dispersion interaction.

London⁷² derived an expression for A:

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

where α_1 , α_2 are the polarizabilities of the interacting atoms or molecules, ν_1 , ν_2 are the corresponding characteristic frequencies, and h is Planck's constant. Since $h\nu_1$ and $h\nu_2$ are often approximately equal to the ionization energies of the atoms or molecules (2) can be expressed as:

$$A = \frac{3}{2} \alpha_1 \alpha_2 \frac{I_1 I_2}{I_1 + I_2} \quad (3)$$

The London expression is derived by considering the attractive force due to the optical electrons only; since other electrons present contribute to the force a modification of this approach is necessary.

4.1.1. Slater-Kirkwood Modification⁷⁴

If the total number of electrons in the outer electron shells contribute to the dispersion energy a second expression for A can be derived:

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

where e = electronic charge, m = mass of the electron and n the number of electrons in the outermost shell. This treatment neglects the inner electrons.

4.1.2. Kirkwood-Muller Modification⁷⁵

Kirkwood and Muller have derived the formula:

$$A = 6mc^2 \frac{\alpha_1 \alpha_2}{\alpha_1/\chi_1 + \alpha_2/\chi_2} \quad (5)$$

where c = velocity of light and χ = diamagnetic susceptibility.

The London formula understates the dispersion energy; it replaces the fluctuating multipoles resulting from an assembly electrons by a single electron multipole interaction. In some cases for agreement with experimental values of dispersion energy, the constant A in London's formula must contain terms corresponding to twice the ionization potential. The Slater-Kirkwood expression gives larger values for dispersion energies. However, the effective values of n , the number of electrons involved in instantaneous multipoles is much larger than the actual number of electrons in the outer shells⁷⁶. The Kirkwood-Muller approximation leads to dispersion energies which are

too high. Electron correlation is ignored, i.e. the tendency of electrons with parallel spins to avoid each other.

Casimir and Polder⁷⁷ found that if r , the distance between the atoms or molecules, was of the order of a few hundred angstrom units then the time of propagation of the electromagnetic interaction was of the same magnitude as a dipole rotation. The dipole coupling effect is lowered and the dispersion energy reduced. A formula for the dispersion energy was derived involving the retardation effect and for an identical pair of atoms is given by:

$$\phi_D = -\frac{23}{8\pi^3} \frac{\hbar c \alpha^2}{r^7} \quad (6)$$

McLachlan⁷⁸ considered dispersion energy in terms of the electric polarisability at an imaginary frequency $w = i\xi$. This polarisability refers to the dipole moment induced by an electric field with an exponential time-dependence $\exp(\xi t)$ instead of the usual oscillating field. In this form the theory allows for retardation effects and gives energies obtained by London or by Casimir and Polder.

$$\phi_D = -\frac{3\hbar}{2\pi^2 r^6} \int_0^\infty \alpha(i\xi) \beta(i\xi) d\xi \quad \text{for } r \ll \frac{\lambda}{2\pi} \quad (7)$$

where λ is the associated wavelength of the electromagnetic field, α and β are the polarisabilities of

two different atoms.

If $r \gg \frac{\lambda}{2\pi}$ e.g. $1000\text{\AA}$

$$\phi_D = \frac{23}{8\pi^2} \frac{hc}{r^7} [\alpha(o)\beta(o)] \quad (8)$$

4.1.3. Three-Body Forces

When three atoms form a triangle with the distances AC, BC both equal to r the energy is

$$\phi_{ABC} = K \frac{3h}{2\pi^2 r^9} \int_0^\infty \alpha(i\xi)\beta(i\xi)\gamma(i\xi)d\xi \quad (9)$$

where K is a numerical factor dependent on the arrangement of the three atoms: $+11/8$ for an equilateral triangle, $\frac{1}{2\sqrt{2}}$ for a right-angled one, and $-1/32$ for a linear arrangement.

The normal van der Waals attraction between two adsorbed atoms is reduced by three-body interaction forces. Everett and Barker⁷⁹ have found good experimental evidence for this effect.

4.2. Repulsive Forces ϕ_R

In accordance with the Pauli exclusion principal interpenetration of electronic clouds of atoms and molecules gives rise to repulsion forces. Wave mechanics shows that these forces vary exponentially with the distance of separation. Hirschfelder, Curtiss and Bird⁸⁰ have reviewed the derivation of these

interactions. A simple form of ϕ_R between identical inert gas atoms is given by the expression:-

$$\phi_R = B \exp.(-ar) \quad (10)$$

where B and a are positive constants and r the distance between atomic nuclei.

A further expression for the repulsive interaction can be stated as follows:-

$$\phi_R = Br^{-m} \quad (11)$$

This equation has no theoretical basis, but it can be used to interpret empirical data with values of m from nine to thirteen, twelve being the most common value. At very short distances expression (11) is less accurate; nevertheless, the mathematical simplicity of equation (11) has led to its extensive use.

4.3. Combined Dispersion and Repulsive Forces. $\phi_D + \phi_R$

Combining (11) with the dispersion energy expression, $-\frac{A}{r^6}$ and using the fact that at the equilibrium distance r_e , $\frac{d\phi}{dr} = 0$ we get

$$2B = Ar_e^6 \quad (12)$$

(when only dispersion and repulsion energy is involved)

The dispersion and repulsion expressions may then be combined to give an interaction known as the

Lennard-Jones 6-12 potential:

$$\phi = \phi_D + \phi_R = -A \left[\frac{1}{r^6} - \frac{r^6}{2r^{12}} \right] \quad (13)$$

Dispersion and repulsion forces are nearly additive and temperature independent.

4.4. Electrostatic Forces

Classical electrostatics give an expression for the potential due to a neutral distribution of positive and negative charges:

$$\phi_r = \sum_i \frac{e_i}{r_i} \quad (14)$$

where r_i is the distance of the i^{th} charge e_i from a point P. If r is the distance of point P considered from an arbitrary origin O, and S_i the distance of the i^{th} charge from O (S_i is defined by coordinates x_i , y_i and z_i such that $s_i^2 = x_i^2 + y_i^2 + z_i^2$) then $1/r_i$ can be expanded in terms of r and s_i in a Taylor series:

$$\begin{aligned} \frac{1}{r_i} &= \frac{1}{r} + x_i \frac{\partial}{\partial x} \left(\frac{1}{r} \right) + y_i \frac{\partial}{\partial y} \left(\frac{1}{r} \right) + z_i \frac{\partial}{\partial z} \left(\frac{1}{r} \right) + \\ &\frac{1}{2} \left[x_i^2 \frac{\partial^2}{\partial x^2} \left(\frac{1}{r} \right) + 2x_i y_i \frac{\partial^2}{\partial x \partial y} \left(\frac{1}{r} \right) + \dots \right] + \quad (15) \end{aligned}$$

Substituting the Taylor expansion for $1/r_i$ in (15) gives

$$\begin{aligned} \phi_r = & \sum_i \frac{e_i}{r} + \sum_i \left[e_i x_i \frac{\partial}{\partial x} \left(\frac{1}{r} \right) + e_i y_i \frac{\partial}{\partial y} \left(\frac{1}{r} \right) + e_i z_i \frac{\partial}{\partial z} \left(\frac{1}{r} \right) \right] \\ & + \frac{1}{2} \sum_i \left[e_i x_i^2 \frac{\partial^2}{\partial x^2} \left(\frac{1}{r} \right) + 2 e_i x_i y_i \frac{\partial^2}{\partial x \partial y} \left(\frac{1}{r} \right) + \dots \right] + (16) \end{aligned}$$

Equation (16) can be put into a short-hand tensor notation as follows

$$\phi_r = \frac{q}{r} + \mu_\alpha \frac{\partial}{\partial r_\alpha} \left(\frac{1}{r} \right) + \frac{1}{2} Q_{\alpha\beta} \frac{\partial}{\partial r_\alpha} \frac{\partial}{\partial r_\beta} \left(\frac{1}{r} \right) + \dots (17)$$

where the Greek subscripts denote tensor suffixes;

$q = \sum_i e_i$, $\mu_\alpha = \sum_i e_i r_{i\alpha}$ is the permanent dipole moment and $Q_{\alpha\beta} = \sum_i e_i r_{i\alpha} r_{i\beta}$, a second order tensor, is the quadrupole moment. In general, there are six

components of Q , but it is always possible to choose three principal axes such that $Q_{\alpha\beta} = 0$ if $\alpha \neq \beta$. If these principal axes make angles θ_x , θ_y , θ_z with respect to r , the equation becomes

$$\begin{aligned} \phi_r = & \frac{q}{r} - \frac{1}{r^2} \{ \mu_x \cos \theta_x + \mu_y \cos \theta_y + \mu_z \cos \theta_z \} + \\ & \frac{1}{2} r^2 \{ Q_{xx} (3 \cos^2 \theta_x - 1) + Q_{yy} (3 \cos^2 \theta_y - 1) + Q_{zz} (3 \cos^2 \theta_z - 1) \} + \\ & \dots (18) \end{aligned}$$

where μ_x , μ_y , μ_z are the components of μ along the principal axes, and Q_{xx} , Q_{yy} , Q_{zz} the principal quadrupole moments of the distribution. If Q_a and Q_b are chosen such that $Q_a = Q_{zz} - Q_{xx}$, $Q_b = Q_{zz} - Q_{yy}$ then

(18) reduces to

$$\phi_r = \frac{q}{r} - \frac{\mu \cos \theta}{r^2} - \frac{1}{2r^3} \{Q_a (3\cos^2 \theta_x - 1) + Q_b (3\cos^2 \theta_y - 1)\} \dots (19)$$

where θ is the angle between μ and r . If the charge distribution is axially symmetric about the z axis then

$$Q_a = Q_b = Q = \sum_i e_i (z_i^2 - x_i^2) = \sum_i e_i (3z_i^2 - r_i^2)$$

and

$$\phi_r = \frac{q}{r} - \frac{\mu \cos \theta}{r^2} + \frac{Q}{2r^3} (3\cos^2 \theta - 1) - \dots$$

The interaction of a system of charges with an external field is given by $E_{\text{inter}} = \sum_i e_i \phi_i$ where ϕ_i is the potential at the i^{th} charge. Choosing an arbitrary origin and expanding ϕ_i about the origin in a like manner to $1/r_1$ in a previous section the interaction can be represented as that between a series of point multipoles at the origin and the potential gradient (dipole), field gradient (quadrupole) and so on for higher multipoles.

4.4.1. Field Dipole Interactions $\phi_{F,\mu}$

The potential energy of a dipolar molecule in an electric field may be expressed as

$$\phi_{F,\mu} = -\mu F \cos \theta \quad (20)$$

where μ is the dipole moment, F the field strength, and θ the angle of the dipole to the direction of the

field. When a dipole is in the direction and sense of the field, then the potential energy is a minimum. Thermal agitation of molecules will tend to oppose the alignment of their dipoles in orientations associated with minimum potential energy. The Keesom⁸¹ average potential is

$$\phi_{F,\mu} = C \coth C + kT \quad (21)$$

where $C = - \frac{Ze\mu}{r^2}$

4.4.2. Dipole-Dipole Interactions

These interactions depend on the dipole orientations. When the dipoles are aligned along the axis joining their mid-points then a summation of Coulombic interactions gives an energy

$$\phi_{D.D.} = - \frac{2\mu_1\mu_2}{r^3} \quad (22)$$

where r is the distance between the mid-points of the dipole, μ_1, μ_2 are the dipole moments. If the dipoles are induced dipoles then equation (22) becomes

$$\phi_{D.D.} = - 2 \frac{\alpha_1 F_2 \cdot \alpha_2 F_1}{r^3} \quad (23)$$

where F_1 and F_2 are the fields due to the dipoles and α_1 and α_2 the polarisabilities. In this case $\phi_{D.D.}$ is proportional to $1/r^7$ as F_1 and F_2 include inverse square terms of r .

The general expression for the energy of interacting dipoles is as follows

$$\phi_{D.D.} = - \frac{\mu_1 \mu_2}{r^3} \left\{ 2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos (\phi_1 - \phi_2) \right\} \quad (24)$$

where θ_1 and θ_2 are the angles between the dipole axes and the line joining their centres, and $(\phi_1 - \phi_2)$ is the angle between the planes formed by the dipole axes and the line joining the centres. A Keesom average may be obtained for the average interaction of two dipoles.

Barrer and Bratt⁸² attributed the large energetic heterogeneity for water occlusion in sodium faujasite at low coverages to a field dipole interaction. They calculated the field dipole interaction at $\theta = 0$ and $\theta = 0.3$ (θ = coverage) and the difference between the values was attributed to the change in effective field strength. The decrease in field strength suggested an initial occupation by water of sites near a few exposed ions which behaved virtually as though isolated.

4.4.3. Quadrupoles

Buckingham⁸³ has reviewed quadrupoles and methods of measuring quadrupole moments. Unfortunately, several different definitions of the quadrupole and higher moments are in use, so that care is needed in applying formulae in the literature.

The moments in (18) can also be written

$$Q_{xx} = \iiint \rho(r_1) x^2 dr_1 \quad \text{etc.} \quad (25)$$

where $\rho(r_1) dr$ is the total charge within a differential volume dr_1 about the point r_1 . If $Q_{xx} = Q_{yy}$, then the quadrupole tensor is completely specified by the scalar quantity:

$$Q = (Q_{zz} - Q_{xx}) = \sum_i e_i (z_i^2 - x_i^2) \quad (26)$$

$$\text{or } Q = \iiint (r^2) (3\cos^2 \theta - 1) r^2 dr \quad (27)$$

An alternative definition introduces a factor ~~of~~ $\frac{1}{2}$ in (27). If the molecule is rotating the quadrupole is effectively reduced to about a half of its value for the non-rotating state.

An expression for the potential energy of a quadrupole in an electric field may be obtained if the following assumptions are made⁸⁴:

- (i) The quadrupole is linear.
- (ii) The gradient of each of the three components of the electric field is linear. This is true only over small distances.
- (iii) The field has cylindrical symmetry about an axis. If this axis is taken to be coincident with the principal axis of the molecule then the potential energy of the quadrupole is

$$\phi_{F.Q.} = - \frac{1}{2} \frac{dF}{dx} Q \quad (28)$$

where $\frac{dF}{dx}$ is the field gradient. If the quadrupole is orientated at an angle θ to the field,

$$\phi_{F.Q.} = \frac{1}{6} \frac{dF}{dx} Q(3\cos^2 \theta - 1) \quad (29)$$

A Keelson temperature average may be obtained, as in the case of a dipole, for its interaction with a field.

Barrer and Stuart⁸⁵ explained the preferred sorption of nitrogen as compared with argon in faujasite in terms of a quadrupole interaction. Kington and Macleod⁸⁶ demonstrated the influence of the quadrupole on the heats of sorption for carbon dioxide, carbon monoxide, nitrogen, hydrogen and oxygen in chabazite.

4.4.4. Quadrupole-Quadrupole Interactions. $\phi_{Q.Q.}$

Kington and Macleod⁸⁶ expressed this interaction as follows:

$$\begin{aligned} \phi_{Q.Q.} = \frac{3}{16} \frac{Q_1 Q_2}{r^3} & \left[1 - 5\cos^2 \theta_1 - 5\cos^2 \theta_2 + 17 \cos^2 \theta_1 \cos^2 \theta_2 \right. \\ & + 16 \sin \theta_1 \sin \theta_2 \cos \theta_1 \cos \theta_2 \cos(\phi_1 - \phi_2) + 2 \sin^2 \theta_1 \sin^2 \theta_2 \cos^2 \\ & \left. (\phi_1 - \phi_2) \right] \end{aligned} \quad (30)$$

where θ_1 and θ_2 are the angles between the quadrupole axes and the line joining their centres; $(\phi_1 - \phi_2)$ is the angle between the planes formed by the quadrupole axes and the line joining the centres, and r the distance between the centres of the quadrupoles Q_1 and

Q_2 . Kington and Macleod suggest that the absence of maxima in the differential heat curves of carbon monoxide and nitrogen may be associated with the existence of clusters in which the molecular quadruples are orientated parallel to each other and the resulting interaction energy, $\phi_{Q,Q}$, may reduce the overall interaction energy.

4.4.5. Methods of Measuring Quadrupole Moments

Molecular quadrupole moments are not easy to measure directly because it is difficult to produce sufficiently large field gradients. Most of the molecular quadrupoles so far measured have been determined indirectly.

In the presence of a strong field a gas or liquid becomes doubly refracting. Buckingham⁸⁷ measured the quadrupole of the carbon dioxide molecule by determining the **birefringence** induced in gaseous carbon dioxide by an inhomogeneous electric field. Smith and Howard⁸⁸ suggested determining molecular quadrupole moments by measuring the broadening of microwave resonance lines (notably the ammonia inversion spectrum) by foreign non-dipolar gases. Smith⁸⁹ estimated that the dipole-quadrupole interaction was dominant in determining collisions between an ammonia molecule and one whose leading multipole

was a quadrupole. However quadrupole-quadrupole interactions may be significant and so quadrupole moments deduced from pressure-broadening data are not reliable. Harrick and Ramsey⁹⁰ calculated the quadrupole moment of the hydrogen molecule from magnetic-susceptibility measurements. They utilized the fact that the diamagnetic anisotropy of an axially symmetric molecule is⁹¹

$$\chi_{zz} - \chi_{xx} = \frac{e^2}{4mc^2} \sum_i (Z_i^2 - X_i^2) - \chi_{HF} \quad (31)$$

where χ_{zz} and χ_{xx} are the molecular susceptibilities parallel and perpendicular to the axis, and the summation is over all the electrons, χ_{HF} , the high-frequency contribution to χ_{xx} . Diamagnetic anisotropies are known for a number of molecules, but the difficulties involved in measuring χ_{HF} limit the usefulness of this method in determining quadrupole moments.

4.5. Polarisation Forces. ϕ_P

When an atom or molecule is placed in an external field F , the electrons and nuclei experience a relative displacement, i.e. a dipole is induced. If the electric field is small, then the magnitude of the induced dipole is given by

$$\mu_{\text{induced}} = \alpha F \quad (32)$$

where α is the polarisability of the molecule. The energy of the induced dipole in the electric field F is given by:-

$$\phi_p = \int_0^F \mu_{\text{ind}} dF = -\frac{1}{2} \alpha F^2 \quad (33)$$

The polarisability of a molecule is directional and the quantity α is represented by a tensor. For most simple molecules the polarisability is isotropic and may be represented by a single scalar quantity. Usually, except at a very small distance from the surface, the polarisation energy is small. Lennard-Jones and Dent⁹³ demonstrated that the polarisation energy for argon approaching a heteropolar surface of alternate K^+ and Cl^- ions in potassium chloride was very small. There was nearly complete screening of the effects of positive ions by negative ions and vice-versa. Charge distributions in zeolites are different, the anionic charge being spread in smaller units on a larger number of atoms than the cationic charge. Calculation of polarisation energies for zeolite model structures show that the energy is very sensitive to the symmetry of charge distribution, but it is insufficiently reduced in some positions to account, for example, for the minor role played by polarisation in the argon-Na-faujasite system. The expression (32) is valid only for weak fields; strong fields may introduce terms in higher powers of F .

There may then be an approach to saturation of polarisation for stronger fields. This behaviour may be represented empirically by

$$\mu = \frac{2\mu_{\infty}}{\pi} \tan^{-1} \frac{F}{a} \quad (34)$$

where a is a constant equal to $2\mu_{\infty}/\pi\alpha$. As F/a becomes large, μ , according to equation (34), tends to μ_{∞} , while for small F , equation (32) is recovered. The polarisation energy is then

$$\phi_p = \frac{4\mu_{\infty}^2}{\pi^2\alpha} \ln \left[1 + \left(\frac{F}{a} \right)^2 \right]^{\frac{1}{2}} - \frac{2\mu_{\infty}F}{\pi} \tan^{-1} \frac{F}{a} \quad (35)$$

4.6. Relationship of Intermolecular Forces to the Isostatic Heat

The isosteric heat of sorption q_{st} is related to the energy of the sorbed phase as follows

$$q_{st} = \tilde{U}_g - \tilde{U}_1 + RT \quad (36)$$

$$= \tilde{U}_g - \tilde{U}_1 - n_1 \bar{U}_1 + RT \quad (37)$$

(U defined in chapter 3), n_1 = number of moles of sorbate. At 0°K only potential energy need be considered and the isosteric heat is then, neglecting zero-point energy, given by

$$q_{st}^0 = -\phi - n_1 \left(\frac{\partial \phi}{\partial n_1} \right)_{P.T.n_2} \quad (38)$$

where ϕ is the interaction energy of the sorbed molecule with the sorbent. The isosteric heat at 0°K is related to q_{st} at temperature T by the expression

$$q_{st} = q_{st}^0 - \int_0^T \Delta C_p dT \quad (39)$$

where $-\Delta C_p = (\bar{C}_g - \bar{C}_1)$ and $\bar{C}_g$ and $\bar{C}_1$ denote molar and molar differential heat capacities of the sorbate in the gas phase and in the crystal, respectively.

Orr,⁹³ using an empirical formula for the heat capacity of the sorbate, found that there was a negligible change in the heat of sorption in the temperature range 0°K-80°K. The change in q_{st} with temperature is within the experimental error and the calculated intermolecular energies may be equated directly with the heat of sorption.

4.7. Calculation of Intermolecular Forces in Sorption

The total interaction of a polarisable molecule possessing a dipole, and a quadrupole with a sorbent which has an electrostatic field and field gradient is given by

$$\phi = \phi_D + \phi_R + \phi_Q + \phi_P + \phi_{F,\mu} + \phi_{SP}. \quad (40)$$

where ϕ_{SP} is the self-potential of the sorbate molecules. This represents the molecule-molecule interaction energies in the sorbed phase.

In order to calculate the components in (40) it is necessary to know the equilibrium distance between sorbent and sorbate, the charge distribution of the sorbent and sorbate, polarisabilities of sorbates, dipole and quadrupole moments of sorbates and the field strengths of the sorbent.

Energy component terms have been evaluated for various gases sorbed in zeolite crystals. Large energetic heterogeneity at low coverages for ammonia and carbon dioxide sorption^{94,95} in synthetic near-faujasites is accounted for by large field-gradient quadrupole interactions, whereas the similar heterogeneity associated with iodine occlusion⁹⁶ is probably caused by a large polarisation energy term. The energetics of inclusion of fluorine compounds⁹⁷ in faujasite seems mainly due to combined dispersion and repulsion interaction components.

CHAPTER 5

Experimental Section

5.1 Sorption Systems

The apparatus consisted of a high vacuum pumping system, incorporating two volumetric and two independent gravimetric adsorption systems. Pyrex glass was used throughout. A general diagram of the apparatus is shown in Figure 10.

5.1.1 The Pumping System

An 'Edwards Speedivac' rotary oil pump was used to back a single stage mercury diffusion pump. The combination achieved an ultimate vacuum of 1×10^{-6} cm Hg. To enhance pumping speed at low pressures, the connections between the diffusion pump, the liquid nitrogen trap and the high vacuum line were made of glass tubing of large internal diameter (10 mm).

A buffer volume between the rotary oil pump and the diffusion pump enabled the latter to operate whilst the rotary pump was disconnected.

5.1.2 Volumetric Systems

An adsorbent bulb was connected to a mercury-in-glass manometer and a water jacketed gas burette. A 'fixed' mark was made on the manometer, this was measured

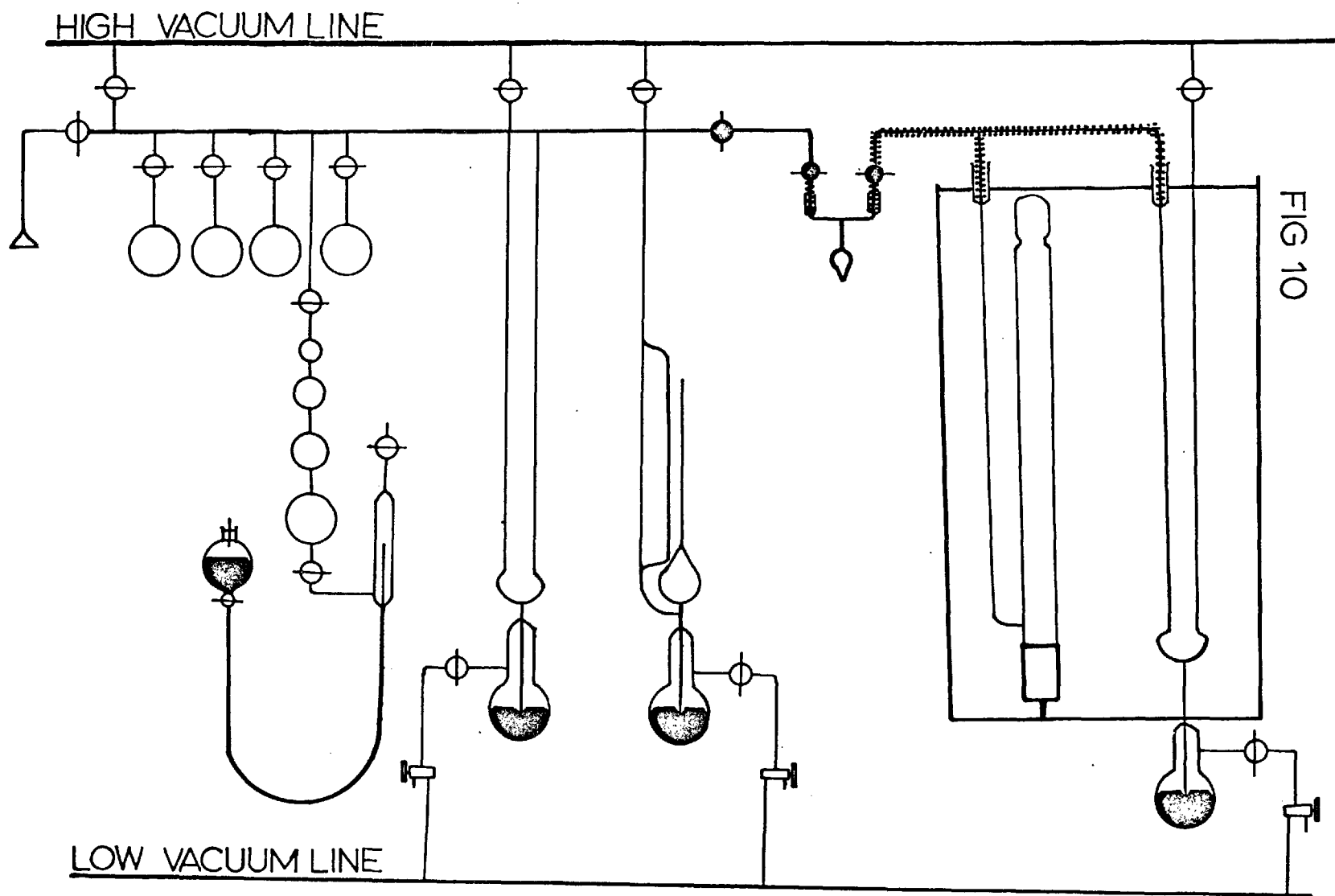


FIG 10

together with the two mercury levels for each pressure measurement using a cathetometer. The doser volumes were kept to a minimum using tubing of small diameter.

5.2 Volumetric Calibrations

5.2.1 Gas Burettes (V_B)

Each gas burette contained four bulbs having a total volume of approximately 140 ml. The bulb volumes were determined with mercury. The volumes (in ml) are given in Table 3.

Table 3.

Gas Burette	A	B
Bulb 1 (top)	9.99	10.01
Bulb 2	19.75	19.06
Bulb 3	34.47	34.46
Bulb 4	74.34	74.21
Total Volume	138.55	137.74

5.2.2 Doser Volumes (V_D)

The doser volume was defined as the volume enclosed between stopcocks T_1 , T_2 , T_3 , calibration mark M_1 on the manometer and the top of the smallest bulb of the gas

FIG11

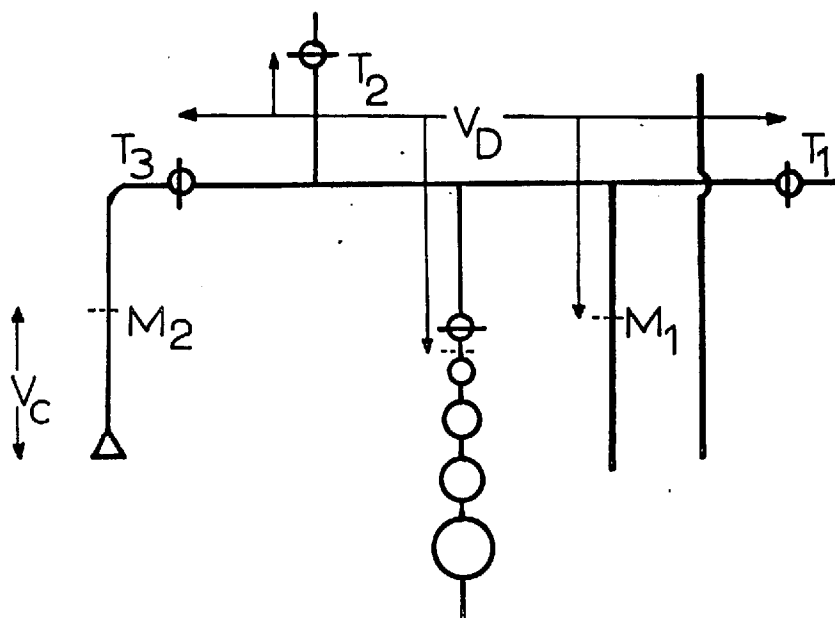
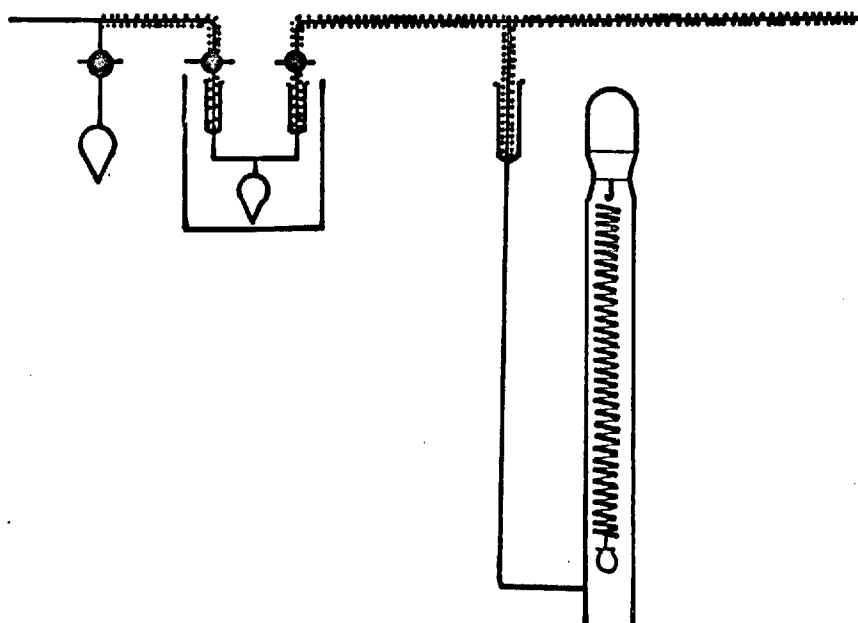


FIG12



burette (Fig. 11).

These volumes were determined with helium (ideal gas relationships were assumed) at different pressures provided by four different calibrated gas burette volumes.

Table 4.

Doser Volume System A	7.27 ccs.
Doser Volume System B	9.53 ccs.

5.2.3 Sorbent Bulb Volumes (V_G)

The volume enclosed in the sorbent chamber upto the mark M_2 was approximately 3 mls. The bulb was calibrated with mercury upto mark M_2 .

About 0.5 g of sorbent was used in each sorption cell, and a glass-wool plug inserted in the cell exit in order to prevent the transfer of sorbent to other parts of the apparatus. The volume of the sorbent was calculated from the density and mass of the sample, this volume together with that of the glass wool (ca. 0.02 cc) was subtracted from the empty cell volume.

5.2.4 Total Volume of Sorption Unit (V_T)

The doser cell volumes together with the volume between M_2 and T_3 were measured as a combined volume

(V_T) using helium gas and the usual gas laws.

5.2.5 McLeod Gauge

The gauge was used as an indicator of vacuum only. The bulb volume was ascertained before complete construction of the gauge with water. The closed capillary, 12.7 cms in length, of 1.5 mm constant-bore Veridia tubing was calibrated with mercury. An error of less than 1% was indicated in the capillary volume.

All pressures on the manometers were read correct to 0.005 cm using one cathetometer serving both volumetric systems. Corrections for capillary depression of the mercury menisci were made using the data given by Kay and Laby.

5.3 Gravimetric Systems

A modification of the McBain-Bakr⁹⁸ silica spring method was used. A diagram of the apparatus is shown in Fig. 12.

5.3.1 Balance Cases

The pyrex balance case tubes had internal diameters of 5 cms. The B.45 standard joints at the top of the cases were greased with Apiezon T grease. The silica springs were suspended within the cases from hooked, weighted glass bobs held in constrictions in the upper

end of the balance cases. The sorbents were contained in small pyrex glass buckets, of 0.2 - 0.3 gm in weight, hooked on the lower end of the springs.

Balance Case Thermostat Tank

The tank consisted of a steel frame, three sides of asbestos insulated copper and two of plate glass. The latter were held in place by rectangular rubber gaskets. Two manometers were connected through the base of the thermostat to mercury reservoirs. The manometer arms were of 10 mm 'Veridia' precision bore tubing; one arm being connected to the gas line and the other, through a stopcock to the high vacuum line. The sorbate inlet line was wound with asbestos covered heating wire in order to prevent the formation of cold spots. The heating wire was carried below the level of the water, in the thermostat, by means of inscals.

The temperature of the thermostat was controlled to within $\pm 0.1^{\circ}\text{C}$ with a Sunvic bimetallic strip and hot wire relay. The thermostat was heated to 1°C below the required temperature by an immersion heater in the base of the tank and controlled by a Variac transformer upto a maximum of 1 kilowatt. Fine temperature control was achieved with a 250 watt 'Red-red' heater connected to the relay. Water in the tank was agitated by a pulley system of motor driven copper stirrers and evaporation

was minimised by floating a little Silicone fluid on the surface of the water.

5.3.2 Sorbate Storage Reservoir

The sorbate storage reservoir consisted of a pear shaped glass bulb of approximately 10 ml capacity. A greaseless stopcock connected the reservoir to the manometer and balance case and through another greaseless stopcock to the sorbate distillation train.

5.3.3 Sorbate Reservoir Thermostat

The storage reservoirs were immersed to half way up the inscals (Fig. 12) in water filled 4 litre beakers. Temperature control was achieved with Sunvic bimetallic strip/hot wire relay systems. The heaters were 250 watt radiation bulbs connected to the relays.

5.3.4 Sorbate Distillation Train

Purification of liquid sorbates was effected by distillation under vacuum from conically shaped bulbs into the sorbate reservoirs. The assembly was connected through a cold trap to the high vacuum line. The conical bulbs were attached to the system by means of standard joints which facilitated the introduction or removal of liquid sorbates from the whole gravimetric system.

5.3.5 Silica Springs

Silica Springs were supplied by Thermal Syndicate Limited. The maximum loading for each spring was 1 gm. Springs with sensitivities of 23 cms/gm or 38 cms/gm were used. Calibrations were made by measuring the spring length after a small glass weight had been suspended from the spring. Five weights were used (0.2, 0.3, 0.4, 0.6, 0.8 gm approximately) for calibration at five temperatures in the range 25 - 60°C. It was not found necessary to make any buoyancy correction as such a correction was negligible. The maximum change in length of any one spring over the specified temperature range for a certain weight did not exceed $\pm .003$ cms. This affects the sensitivity by .01%, and was therefore negligible.

After a series of occlusion isotherms the sorbents were outgassed and the spring extensions remeasured. The sensitivities remained the same.

5.3.6 Temperature Measurement

All temperatures were read with mercury-in-glass thermometers, supplied by Sugden Powell Limited, which had been calibrated against a standard thermometer certified by the National Physical Laboratory.

5.3.7 Cathetometer

A one meter cathetometer, supplied by Precision Industries Limited, was used in the measurement of spring lengths and pressures.

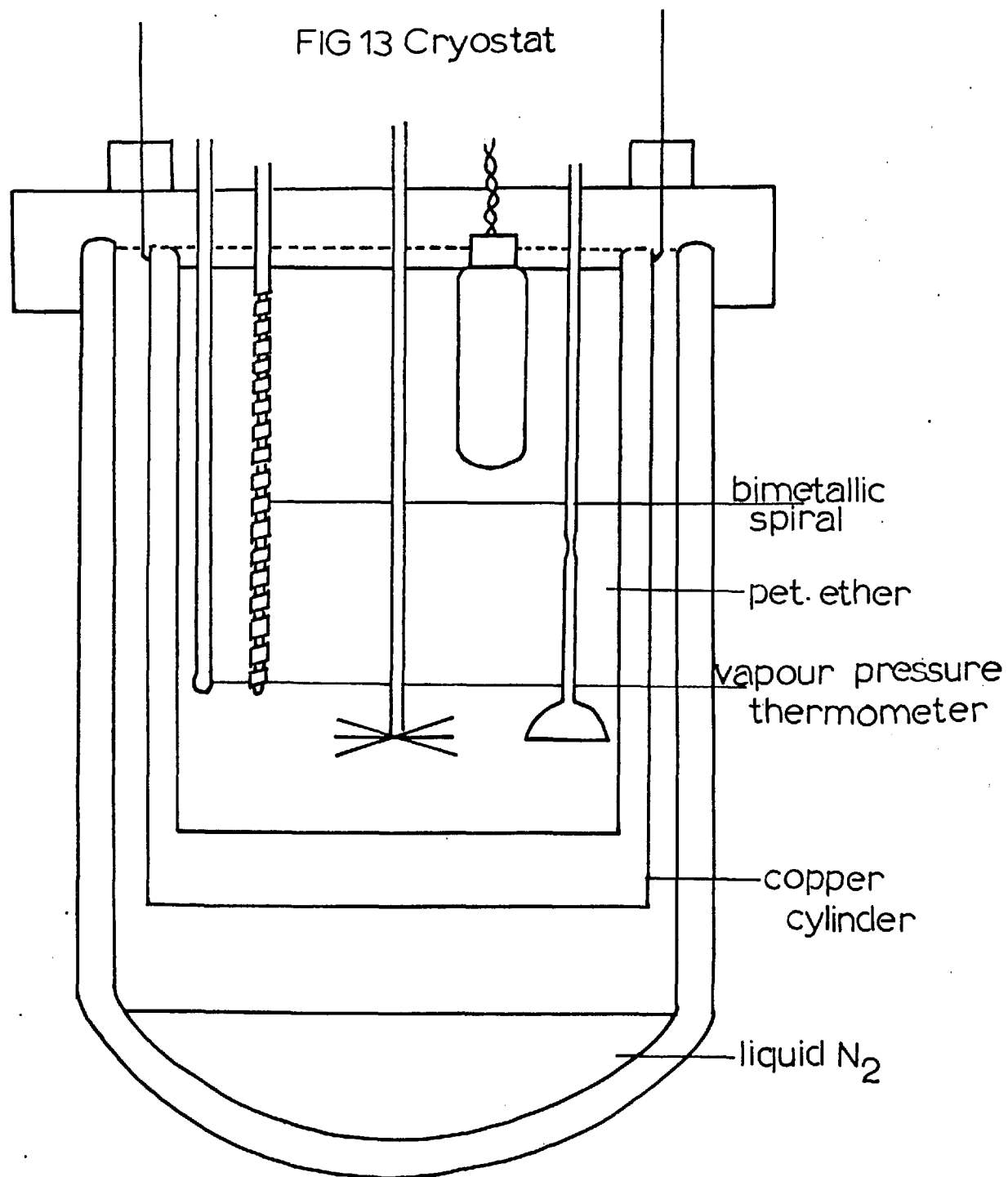
5.4 Temperature Control of Sorbent Baths

By a suitable choice of thermostating technique the range - 120°C to + 210°C was achieved.

5.4.1 Range - 120°C to 0°C

A cryostat shown in Fig. 13 was found satisfactory. An 600 ml beaker containing petroleum ether was lagged with aluminium foil and asbestos wool and encased in a copper cylinder. Glass rods attached to the cylinder enabled the latter's height to be adjusted. The whole was surrounded by a large Dewar vessel into which the refrigerant liquid, nitrogen, was poured. Removal of heat from the bath was compensated by a conventional thermostating device, i.e. a 'Sunvic' T.S. 7 bimetallic spiral operating a 15 watt heater via a hot wire relay. Distillation of petroleum ether into the Dewar was minimised by fitting a perspex cover to the beaker.

By adjustment of the height of the beaker and the level of the liquid nitrogen in the Dewar, the above range of temperature was obtained for periods upto twelve hours.



Even temperature distribution throughout the bath was ensured by using a high speed stirrer. The temperature was recorded with a vapour pressure thermometer. It was possible to maintain the temperature of the bath to $\pm 0.1^{\circ}\text{C}$ of the required value.

5.4.2 Range + 25°C to + 210°C

A 500 ml beaker lagged with asbestos rope containing MS 710 silicone oil was used. A 100 watt heater connected to the mains via a Variac transformer maintained the bath at the approximate temperature, fine control was achieved with a bimetallic spiral in conjunction with a 25 watt heater and Sunvic relay. The stirring arrangement and possible temperature control was as in the cryostat bath.

The water thermostat tank used in the gravimetric systems is described elsewhere.

5.5 Temperature Measurement

The temperature of the petroleum ether in the cryostat was measured with vapour pressure thermometers. A sulphur dioxide thermometer was used in the range -10°C to -40°C , an ammonia thermometer in the range -40°C to -70°C , a carbon dioxide thermometer in the range -75°C to -90°C and an ethylene thermometer in the range -90°C to -120°C . The construction of these

thermometers will now be briefly outlined.

The apparatus shown in Fig. 14 was attached to the high vacuum line and pumped out overnight. Tap T_2 was then carefully opened and mercury from the reservoir slowly admitted to the U-tube until a height of approximately 55 cms. was attained on both sides. The mercury was carefully boiled in situ to remove air bubbles and when finally a good vacuum was obtained the constrictions (H) and (G) were completely sealed.

Carefully purified gas was frozen from (L) into (C) which was cooled in liquid nitrogen and the constriction (F) was sealed off. The condensate in (C) was allowed to evaporate and enter the thermometer through the spring loaded tap T_1 . Tap T_1 was closed when a pressure of approximately 100 cm. Hg had built up in (O), and (C) was again cooled in liquid nitrogen. The construction of the thermometer was completed by sealing off the constriction (F) while (D) was cooled in liquid nitrogen. The purpose of the bulb (B), capacity 100 cm³ was to increase the volume of the gas in the thermometer so that on cooling, liquefaction occurs and not just thermal contraction of the gas.

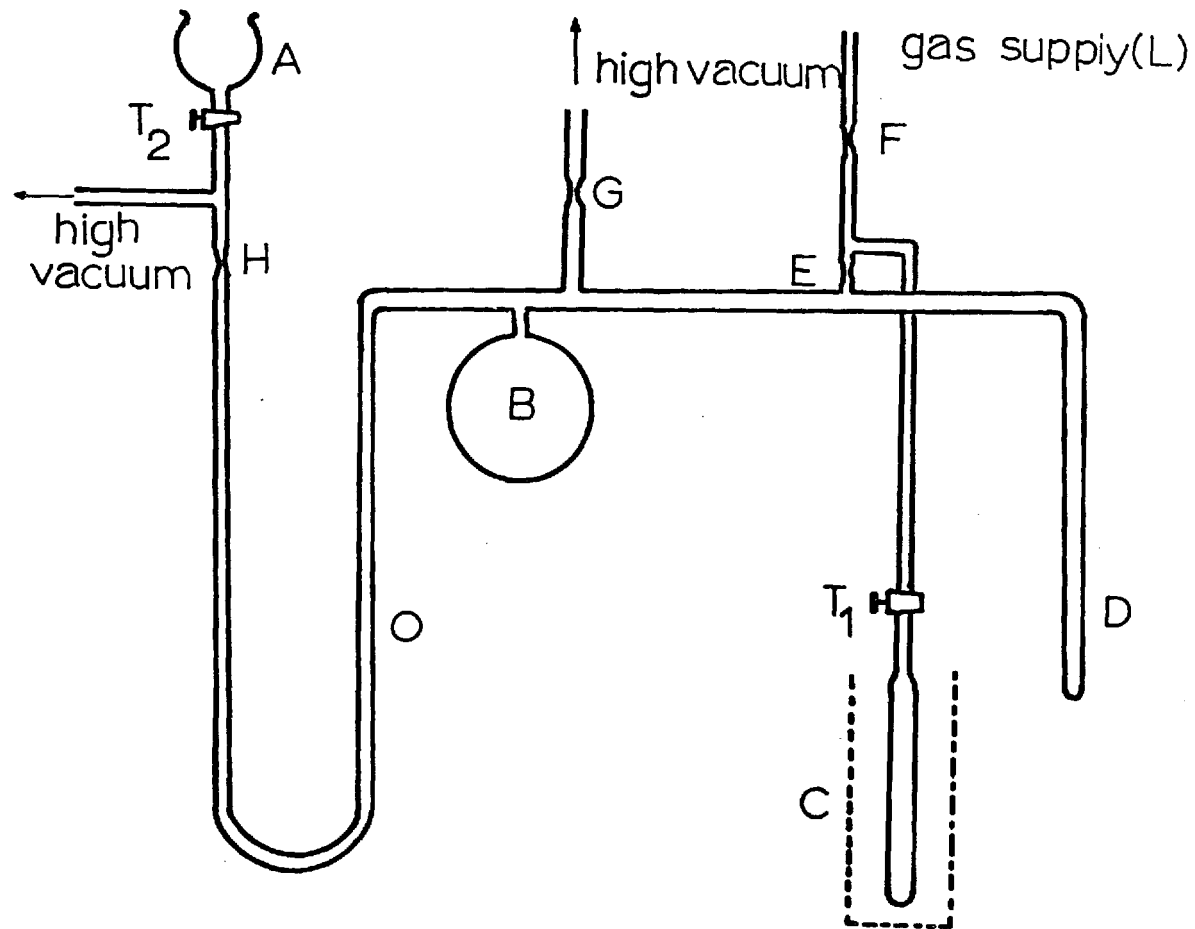


FIG 14

Construction of vapour pressure thermometers

5.6 Sorbents and their Preparation for Occlusion

5.6.1 Sorbents

Investigation of the sorption properties of the following sorbents was made.

- (i) Strontium, Calcium, Lithium, Sodium, Potassium and Hydrogen forms of Ferrierite.
- (ii) Barium and CalciumJ.
- (iii) Barium K and Z.
- (iv) Mixed Sodium Potassium form of Zeolite L.

5.6.2 Preparation of Sorbents

Gravimetric Systems

The hydrated sorbent, sieved through a 200 mesh sieve, was placed in a glass bucket (total weight approximately 0.6 gm) and hooked onto the silica spring which was, in turn, suspended from the weighted glass bob and placed within the balance case. The system was evacuated slowly to prevent loss of sorbent from the bucket. Outgassing was carried out at room temperature overnight. An electric furnace, in series with a Variac transformer, was then placed around the balance case. The temperature was increased at two hourly intervals until the furnace reached 345°C. These conditions were maintained for twenty-four hours.

Volumetric Systems

The sorbent was placed in the sorption cell and glassblown onto the doser part of the unit. The furnaces employed and outgassing techniques used were identical to those described for the spring balance systems.

X-ray examination revealed that no detectable crystal breakdown or recrystallization occurred during outgassing of any of the sorbents.

5.7 Sorbates

The sorbates were supplied in 1 and $\frac{1}{2}$ litre ampoules. The National Physical Laboratory examined the purity of the hydrocarbons using mass spectrometry, gas chromatography and freezing-point techniques. The most probable impurities were specified.

Table 5

Sorbate	Impurity
Methane	Ethane
Ethane	Methane
Propane	Ethane
n Butane	.03% iso-butane
Iso-Butane	Butane
Neo-Pentane	Unspecified

The liquid sorbates were all AnalaR grade, supplied by British Drug Houses Limited, and distilled under vacuum into the sorbate reservoirs. Thiophen, Pyrrole, Benzene, o-Xylene, m-Xylene and p-Xylene were used.

Sorbates Used.

Table 6

Sorbate	Purity	Suppliers
Oxygen	Spectrally pure	British Oxygen Co. Ltd.
Nitrogen	Spectrally pure	British Oxygen Co. Ltd.
Neon	Spectrally pure	British Oxygen Co. Ltd.
Argon	Spectrally pure	British Oxygen Co. Ltd.
Krypton	99-100% Balance Xenon	British Oxygen Co. Ltd.
Xenon	99-100% Balance Krypton	British Oxygen Co. Ltd.
Carbon Dioxide	Spectrally pure	British Oxygen Co. Ltd.
Methane	99.9 moles per cent.	National Physical Lab.
Ethane	99.9 moles per cent.	National Physical Lab.
Propane	99.9 moles per cent.	National Physical Lab.
n-Butane	99.97 moles per cent.	National Physical Lab.
Iso-Butane	99.97 moles per cent.	National Physical Lab.
Neo-Pentane	99.88 moles per cent	National Physical Lab.

5.8 Hydrothermal Crystallisations

5.8.1 Chemicals

(a) Alkalis The strontium used was in the form of strontium hydroxide octahydrate (recrystallised) supplied by Messrs. Hopkins and Williams. The barium used was B.D.H. AnalaR grade barium hydroxide octahydrate.

(b) Silica employed was a stable suspension of amorphous silica in water, supplied by Monsanto Chemicals Limited, under the trade name 'Syton-2X'. This had a silica content of 29.7% by weight, specific gravity 1.2, a pH $\sim$ 10 and contained a trace of chloride.

(c) Alumina The aluminium hydroxide was made by the method of Wislicenus.⁹⁹ Aluminium foil was divided into small pieces and amalgamated lightly by contact with a 2% solution of mercuric chloride for about 15 seconds. It was then well washed and allowed to stand overnight in a large volume of distilled water maintained at 0°C. The precipitated gel was separated from any unreacted foil by washing through a fine gauze. It was then filtered off, washed with water, alcohol and ether and dried.

It was then sieved through an 85-mesh sieve and allowed to stand overnight in an open vessel. The light grey powder was then analysed, by igniting a sample to

constant weight, and kept in a closed bottle. It was normally found to contain between 50 and 58% Al_2O_3 , and when freshly prepared was amorphous to X-rays. The gel was not used for more than about three weeks from its preparation because of its tendency to age and crystallize.

5.8.2 Preparation of Gels

From the chosen formula of the gel the quantities of the above reagents required to give a dry weight of 0.5 g oxides in 7 ml of water were calculated. The barium or strontium hydroxide octahydrate was weighed out, transferred to a mortar and ground up with a little water added from a burette. The weighed amount of aluminium hydroxide gel was added and mixed to a smooth paste with a little more water, then the calculated amount of Syton 2X was added from a graduated pipette, and carefully mixed in. The resultant gel was transferred to a conical flask with the remainder of the water, and stirred vigorously for about two hours, taking precautions to exclude carbon dioxide from the air which otherwise would react with the hydroxides. Sufficient gel for 10 experiments was prepared in one batch and 7 ml of suspension was added to each autoclave, using a small measuring cylinder.

5.8.3 Reaction Vessels

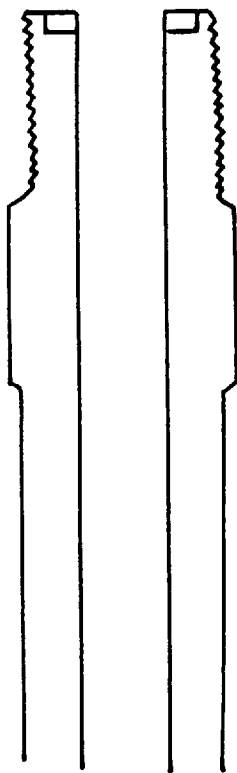
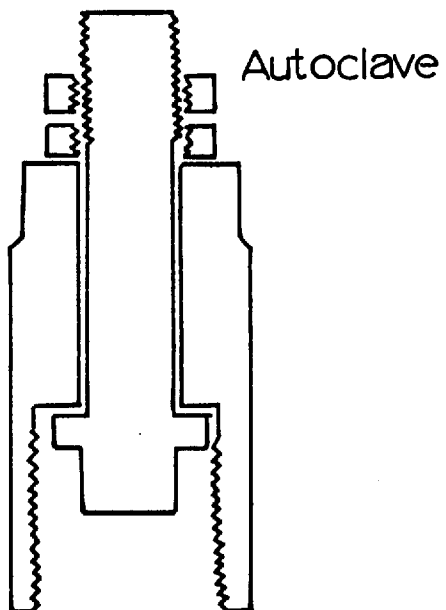
Stainless steel tube autoclaves supplied by Messrs. Baskerville and Lindsey were used. These had a capacity of 14 ml and were sealed with silver washers, which flowed slightly on closing the autoclave and also expanded more than steel on heating. (Fig. 15). Provided that the washers were renewed at six monthly intervals the seal was satisfactory. A molybdenum sulphide anti-scuffing paste was used on the autoclave screw threads to prevent seizure at high temperatures. The paste was supplied by Rocol Limited.

5.8.4 Ovens and Furnaces

Electrically heated air ovens, thermostatically controlled to $\pm 3^{\circ}\text{C}$, were used for experiments upto 300°C . For higher temperatures a specially constructed furnace was used. This consisted of a large copper block having nine cavities drilled in it to closely fit the autoclaves, and packed around with asbestos wool inside a Sindanyo case. The temperature was measured directly with a pyrometer, using chromel/alumel thermocouples also inserted into the copper block.

After the required period of crystallisation the autoclaves were removed from the oven or furnace and

FIG 15



quenched in cold water. The autoclaves were opened, the mother liquor decanted, and its pH measured to the nearest 0.5 unit with Universal indicator paper. The product was washed out of the autoclave, filtered, washed with cold water and dried at 100°C.

The products were examined under a Leitz IIIc polarizing microscope, the crystal habit of the products was studied, and the purity of the preparations estimated. X-ray diffraction patterns of the specimens were also obtained with a Guinier camera (used with a quartz monochromator).

5.9 Ion Exchange

Homionic forms of lithium, sodium, potassium and calcium ferricrite and calcium-J were prepared by treating strontium ferricrite and barium-J respectively with 3M brine solutions. The exchanger solution and zeolite, sealed in a glass tube, was rotated for 24 hours in an oven maintained at 80°C. The crystals were filtered, and the whole process repeated four times.

The ion exchange samples contained included salt. This was removed by washing the zeolite in a Buchner funnel with hot distilled water, until the washings showed no residual anion to be present. The extent of ion exchange after each treatment was determined by analysis of the Sr^{++} removed from the zeolite in the

case of the ferrierite samples, and analysis of the Ba^{++} removed from the synthetic J sample. An Ethylene-diamine Tetraacetic Acid titration of the Sr^{++} or Ba^{++} present in the exchanger solution proved satisfactory¹⁰⁰. Before determining the amount of cation in the parent zeolite removed during calcium exchanges, the Ca^{++} ions were removed from the ion exchange solution after exchange and converted to calcium nitrate which was then extracted with an absolute alcohol/ether mixture. This prevented calcium interference in the E.D.T.A. titrations¹⁰¹. Analysis of strontium in the presence of lithium was carried out by the method described by Belcher and Wilson¹⁰².

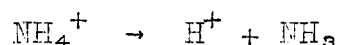
5.9.1 Acid Treatment of Strontium Ferrierite

Two hydrochloric acid solutions were used, 1N and .088N. The treatments were identical to those outlined for the brine exchanges. Analysis of the exchange mother liquors indicated that aluminium had not been removed from the ferrierite framework in either treatments.

5.9.2 Ammonium ion exchange

An identical ion-exchange procedure was used to effect ammonium ion exchange as with the monovalent and divalent metal cations, 2N ammonium chloride solution was used and four treatments were necessary to ensure complete

exchange. The crystals were then outgassed at 345°C for 52 hours under vacuum until the reaction

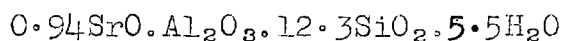


was complete¹⁰³.

All the zeolites subjected to ion exchange were X-rayed to show that no breakdown in structure had occurred and that no gross impurities were present.

5.9.3. Strontium Ferrierite Analysis

The ferrierite was decomposed by heating with 6N hydrochloric acid for 48 hours. The silica and aluminium contents were determined by standard gravimetric techniques^{104,105}, the strontium by an E.D.T.A. titration (the aluminium being masked with triethanolamine) and the water content by a separate dehydration on the Stanton balance of part of the same sample of strontium ferrierite. The analysis yielded the following oxide formula:-



5.9.4. Thermogravimetry

In order to find the water content of zeolites prepared in the synthetic work and the sorbents employed in the sorption experiments samples were dehydrated on a Stanton thermobalance. A fast heating rate, 1000°C in

90 minutes, was used and the temperature and weight loss was automatically recorded. A dummy run was carried out to determine the bouyancy correction.

CHAPTER 6.Experimental Results - Synthesis6.1. Index of Products6.1.1. Species obtained from strontium gels

<u>Reference Letter</u>	<u>Species</u>
C	Polymorph of strontium felspar.
D	Strontium ferrierite.
G	Sr-near-Chabazite.
H	α -Cristobalite.
K	Unidentified.
M	Sr-Mordenite.
P	Hexagonal polymorph of Sr-felspar.
Q	A strontium zeolite.

6.1.2. Species obtained from barium gels.

<u>Reference Letter</u>	<u>Species</u>
C	Celsian (barium feldspar).
H	α -Cristobalite.
J	Barium zeolite.
K	Barium zeolite.
M	Ba-Harmotome.
P	Hexagonal polymorph of feldspar.
Z	Unidentified, possibly a zeolite.

6.2. Synthesis Products

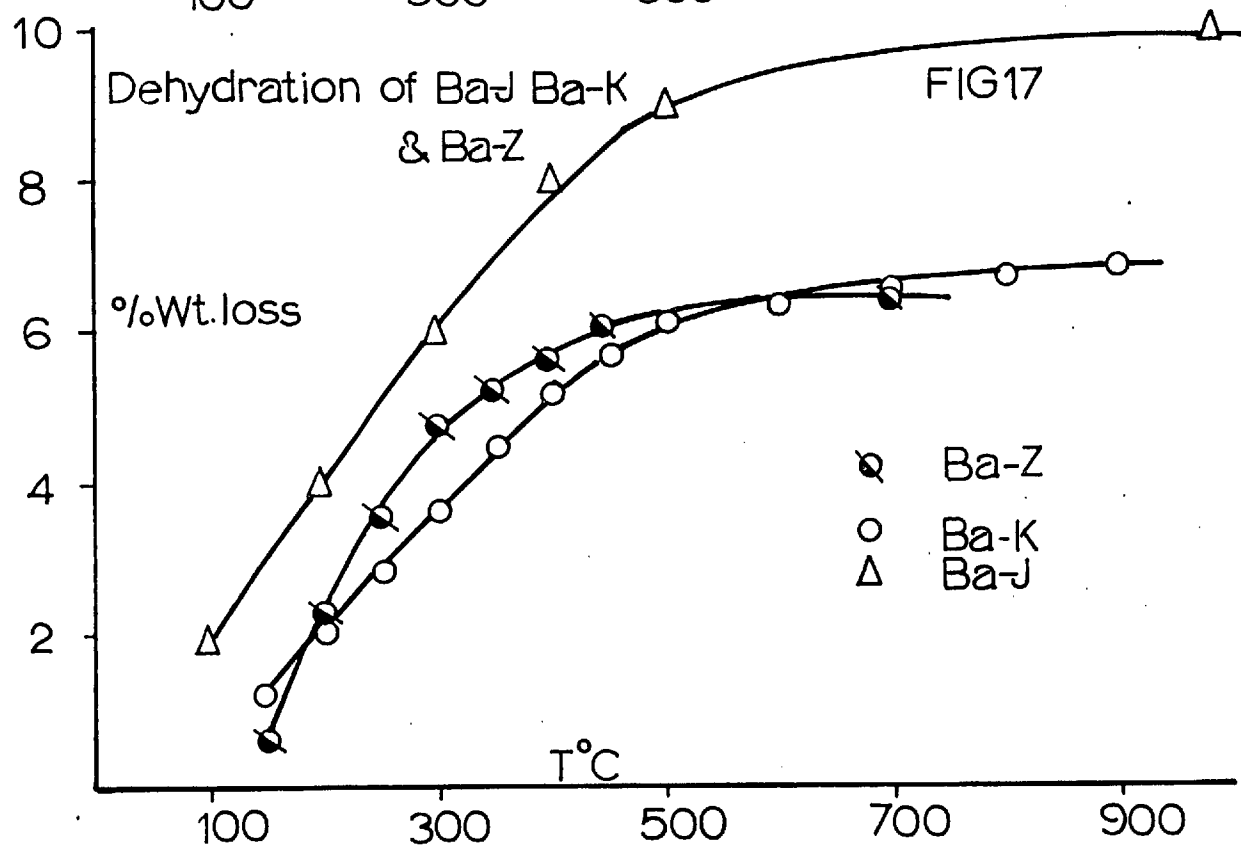
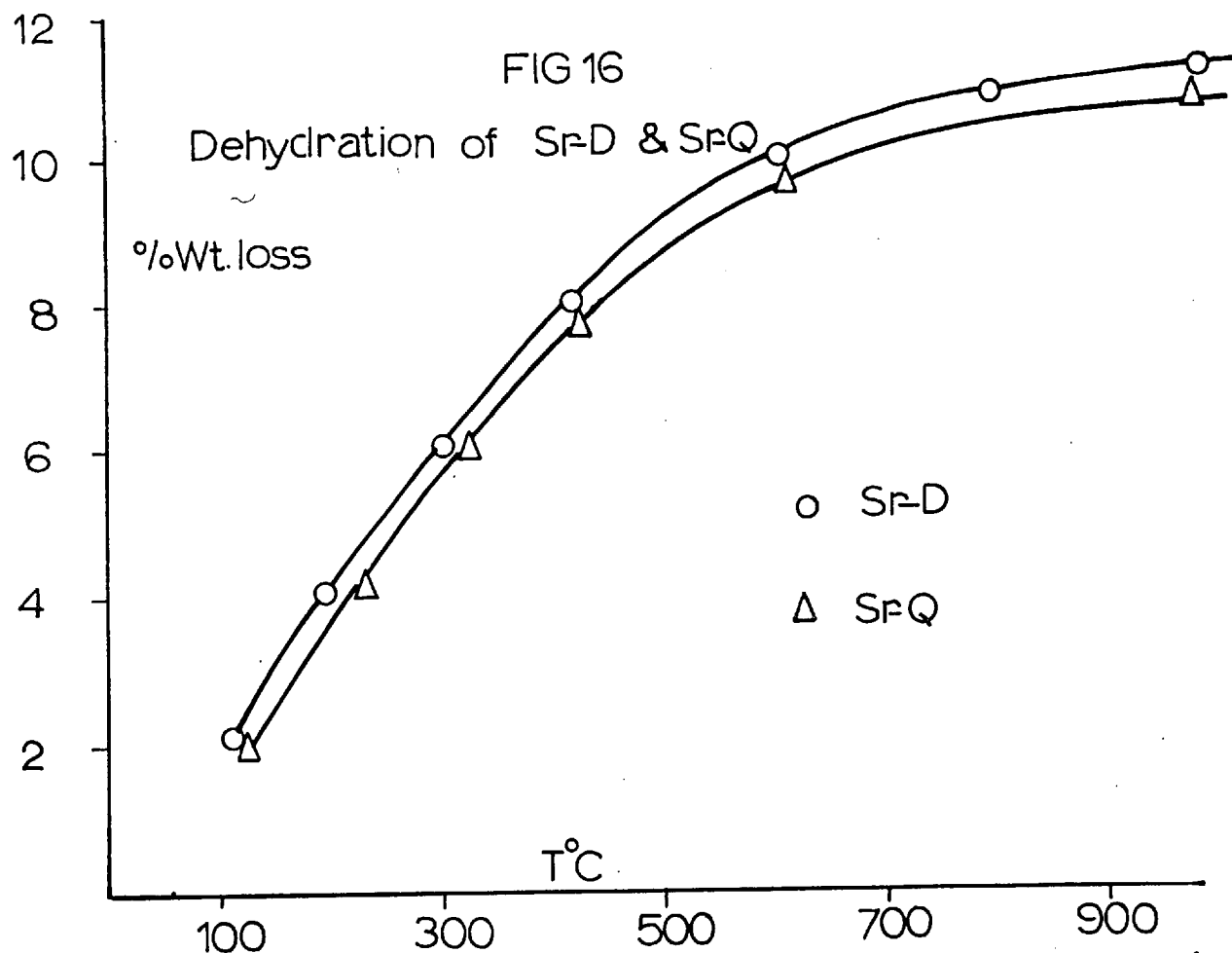
The present work was concerned with the reinvestigation of Sr-D, Sr-Q, Ba-K, Ba-J and Ba-Z crystallisation fields.

6.2.1. Sr-D, synthetic strontium ferrierite

Sr-D crystallised in a sharply defined region. The temperature range of formation was 340°-380°C and the initial gel composition $x\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2$, where x had values from 1 to 1.2 and n from 7 to 9. The optimum yields were obtained from gels of composition $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2$ maintained at 340°C. for 3-8 days. Sr-D showed a weight loss on ignition of 11.2%. Ignition to 1000°C. recrystallised Sr-D to an unidentified product, whose X-ray powder pattern is given in Table R1. Sr-D is orthorhombic, body-centred with $a = 18.5\text{\AA}$, $b = 21.0\text{\AA}$, $c = 7.12\text{\AA}$. These dimensions are close to those of mordenite but mordenite is c-centred.

6.2.2. Sr-Q, near-yugawaralite

Sr-Q crystallised between 300° and 350°C from gels with a high silica: alumina ratio, with eight as the optimum value for this ratio. The crystals displayed a fibrous or spherulitic habit. Sr-Q loses 10.7% by weight on heating and is completely destroyed by continued heating to 1000°C. 90% of the weight loss occurs below 450°C



suggesting the species may be a zeolite. It is reported to have no sorption properties⁴⁷.

6.2.3. Ba-J

Ba-J crystallised from gels $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2$, where n varied from 8 to 8.5. The temperature range was 300°-350°C. It was very often mixed with other species, particularly Ba-K. Thermogravimetric analysis showed a weight loss of 8.9% up to 450°C. and a further loss of 1% between 450 and 1000°C. The sample became amorphous on ignition. The X-ray pattern of the species (Table R3) could not be matched with that of any known zeolite. The crystals had an irregular fibrous habit.

6.2.4. Ba-K

Ba-K crystallised at 300-350°C in a distinctive variation of the spherulitic habit from aqueous gels having silica: alumina ratios between 7.5:1 and 9.5:1. It was often mixed with Ba-J or Ba-P. A weight loss of 6.9% indicated by thermogravimetric analysis, most of which had occurred by 500°C, is low for a zeolite. The samples prepared may have contained some amorphous silica. The X-ray powder pattern of Ba-K is given in Table R3, but it was not possible to identify this species with any known zeolite.

6.2.5. Ba-Z

Ba-Z crystallised from aqueous gels of oxide composition $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$ and $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 8.5\text{SiO}_2$ at 300°C . The crystals appeared as large spherules. Thermogravimetric analysis indicated a 6.4% weight loss, most of which occurred below 500°C . The water content is low if Ba-Z is a zeolite, although amorphous silica also may be present. The X-ray pattern given in Table R4 is unlike any known species.

The sorption properties of Sr-D, Ba-J, Ba-K and Ba-Z will be discussed later.

6.3. Other products obtained in the syntheses

(i) Sr-C, polymorph of strontium-felspar

This species formed from gels with silica: alumina ratios 7, 8 and 9 at temperatures 300° and 350°C , 380°C and 450°C . respectively. In nearly all cases the Sr-C was mixed with other species. The other component of the mixture from gels with the oxide formula $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 8$ or 9SiO_2 was Sr-H (α -cristobalite). With the silica: alumina ratio 7 Sr-M (Sr-mordenite) was obtained with Sr-C, but in one case, after nine days at 300°C . the gel $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2$ crystallized to give only C. The X-ray powder pattern, given in Table R5, was similar to that of paracelsian (a near orthorhombic polymorph of the barium felspar celsian).

Sr-C appeared to be quite unaffected by heating up to at least 1000°C, as it suffered no appreciable weight loss or loss of crystallinity during prolonged ignition.

(ii) Sr-G, near-chabazite

Sr-G, appeared together with Sr-P from the gel of composition $1.2\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2$ at 300°C. Marshall⁴⁷ reports a high yield of this product but from gels of lower silica: alumina ratios below 200°C. A similar species has been obtained in the corresponding region of the crystallisation field of the potassium aluminosilicates. An X-ray powder pattern of the mixture showed that Sr-G corresponded closely to natural chabazite. Sr-G recrystallised to Sr-P during a thermogravimetric analysis in the Stanton balance.

(iii) Sr-H α -cristobalite

α -cristobalite formed from gels of the following compositions.

(a) $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2$ at 340°C.

(b) $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$ at 380°C.

(c) $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 9\text{SiO}_2$ at 450°C.

and often with Sr-C when the parent gel contains a higher ratio of silica than the crystalline products which are formed, then the excess silica may crystallise out as α -cristobalite. At these temperatures of formation (i.e. >340°C) α -cristobalite is metastable

with respect to α -quartz. However, in this work no α -quartz was prepared and so the excess silica either remained amorphous or crystallised as α -cristobalite. Marshall¹⁰⁶ subjected a silica sol to hydrothermal treatment at 380°C and found a predominance of quartz. Perhaps the Sr^{++} ions and/or the pH of the media (7-8) catalyse the formation of α -cristobalite.

(iv) Sr-K

This species occurred from gels of composition $0.9\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2$ at 300° and 340°C. It was stable up to 1000°C and its X-ray powder pattern although similar to that of strontium-anorthite was not identified with that of any other previously known mineral.

(v) Sr-M-nordenite

This species was observed on one occasion, mixed with Sr-C from a gel of composition $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2$ at 300°C. The "wheatsheaf" habit of nordenite was observed and the X-ray powder pattern showed good agreement with that of the natural mineral (Table R8).

(vi) Sr-P-hexagonal polymorph of Sr-felspar

Sr-P appeared on two occasions; once from a gel of composition $1.2\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2$ at 300°C together with Sr-G, and also from a gel of composition $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$ at 380°C mixed with Sr-D and Sr-H.

Marshall⁴⁷ reported crystallisation of Sr-P often mixed with Sr-C and suggested that Sr-P changed to Sr-C as the time of hydrothermal treatment increased. Although Marshall's Sr-P formed from gels of lower silica: alumina ratios experimental evidence supports Marshall's view. After 4 days at 380°C. the gel $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$ crystallised to give a mixture of Sr-D, Sr-P and Sr-H. After 15 days the same gel formed Sr-H and Sr-C only, no Sr-D or Sr-P appeared. The X-ray powder pattern was similar to the barium hexagonal feldspar Ba-P. Sr-P showed no weight loss on ignition.

(vii) Ba-C-celsian (barium feldspar)

A trace of Ba-C was formed at 350°C from aqueous gels of oxide formula $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 7.5\text{SiO}_2$. The X-ray powder pattern was extremely close to that of natural celsian.

(viii) Ba-H- α -cristobalite

Trace amounts of Ba-H occurred from aqueous gels of oxide formula $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 7.5\text{SiO}_2$, $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 9\text{SiO}_2$ and $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 9.5\text{SiO}_2$ at 340° or 350°C. However, when the silica: alumina ratio was 8.5 moderate (after 24 days) to good (after 67 days) yields were obtained. Ba-H seems to take several days to crystallise. The X-ray powder pattern (Table R7) is similar to Sr-H and naturally occurring α -cristobalite.

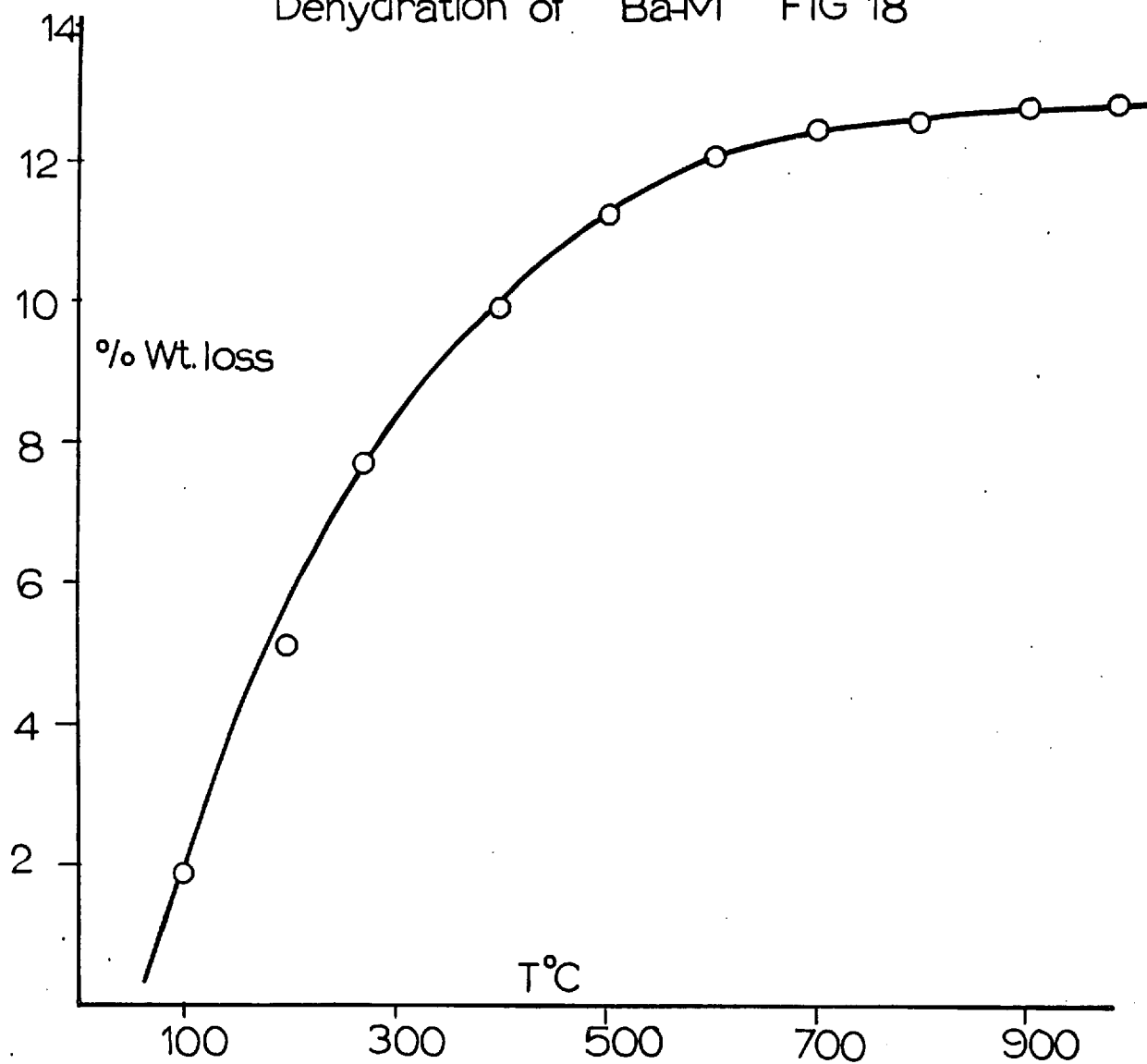
(ix) Ba-M, harmotome

This zeolite was formed at 150°C. from aqueous gels in which the silica: alumina ratio was 3, and with crystallisation times from 2 to 10 weeks. The crystallinity of the product improved as the period of hydrothermal treatment increased. On heating, the water loss was 12.8%, most of the dehydration occurring before 450°C. This compares with that of 13.9-15.0% recorded for natural samples. The X-ray powder pattern is extremely close to that of natural monoclinic barium harmotome. Previous workers in these laboratories have reported the synthesis of various members of the phillipsite-harmotome family,^{48,50} with sodium, potassium, calcium or dimethylammonium as the cation, but these have been cubic, tetragonal, or orthorhombic forms not identical with the natural monoclinic phase. Sadanaga⁷ et al suggested that the space occupied by the barium cation in harmotome is too large to be satisfactorily filled by a calcium ion, and that no simple adjustment of the co-ordination polyhedron is possible.

(x) Ba-P-hexagonal polymorph of barium feldspar

Ba-P appeared mainly in trace quantities from gels of oxide composition $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$ and $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 9\text{SiO}_2$ at 300° or 340°C. A moderate yield was obtained from the gel $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 7.5\text{SiO}_2$ at 350°C. Ba-P has been prepared pyrolytically and is known by various names ,

Dehydration of Ba-M FIG 18



in the literature. The X-ray powder pattern is given in Table R4.

6.4. Discussion

In the temperature range 295°C-450°C gels of oxide formulae $x\text{MO}_y\text{Al}_2\text{O}_3\text{nSiO}_2$ [$x = 0.9$ or 1 , $y = 0.9$ or 1 , $n = 7.0 - 9.5$, and $M = \text{Sr}$ or Ba] produced fourteen different species. Seven of these were zeolites, Sr-D, Sr-Q, Sr-G, Sr-M, Ba-J, Ba-K and Ba-Z; four were feldspars, Sr-C, Sr-P, Ba-C and Ba-P, two were α -cristobalite, Sr-H and Ba-H, and Sr-K was a phase unidentified with any known species. From gels of oxide formula $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ at 150°C the only product obtained was Ba-M, harmotome.

High temperatures are needed to effect crystallization when the silica: alumina ratios of the parent gels are large. At 200°C. gels of composition $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2$ did not produce crystalline materials. However, at temperatures of 300°C. and above gels of this composition yielded a variety of products. It is difficult to trace any systematic effects resulting from increasing the duration of heat treatment. Sometimes prolonged treatment improved yields, for example, of ferrierite from gels $\text{SrO} \cdot 0.9\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ and harmotome from gels $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ - (Table 11 and 12). On other occasions longer periods produced

different species from those obtained from shorter hydrothermal treatments. (Tables 10 and 16). In some cases the type and yield were unaffected by variation of the time of crystallisation.

Mordenite was synthesised from the gel with composition $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2$ at 300°C . Numerous attempts to repeat this synthesis, using an identical gel under the same conditions for both longer and shorter times resulted in other products or in uncrystallised gel. Attempts to seed this gel with the desired product were unsuccessful. Marshall¹⁰⁶ also reports the irreproducible appearance of this and some other zeolites from strontium aluminosilicate gels. Barium aluminosilicates gels did not show irreproducible crystallisation although the overlap in crystallisation fields of the zeolites was considerable. Ba-K and Ba-J often formed under identical hydrothermal conditions and it was difficult to predict which would be formed.

Table 7

Products from gels of composition
 $0.9\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2$

<u>300°C.</u>	<u>5 days</u>
	Poor K
	Trace P.
	p H. mother liquor 7.5.
<u>340°C.</u>	<u>5 days</u>
	Good K.
	p H. mother liquor 7.0.

Table 8

Products from gels of composition
 $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2$

<u>200°C.</u>	<u>2 days</u>	<u>20 days</u>	
	Non crystall- ine product	Non crystall- ine product.	
<u>300°C.</u>	<u>3 days</u>	<u>5 days</u>	<u>9 days</u>
	Non crystall- ine product	Moderate C Good M	Poor C
	p H. mother liquor 7.0.	p H. mother liquor 7.0.	p H. mother liquor 7.0.
<u>340°C.</u>	<u>2 days</u>	<u>2 days</u>	<u>3 days</u>
	Non crystall- ine product	Very good D Good D	Very good D Moderate D
	p H. mother liquor 7.5.	p H. mother liquor 7.5.	p H. mother liquor 7.5.

Table 8 (contd.)

Products from gels of composition
 $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2$

<u>340°C.</u>	<u>4 days</u>	<u>5 days</u>	<u>6 days</u>
	Very good D	Very good D	Poor D
		Good D	Poor H
			Good D
			Good Q
	p H. mother liquor 7.5.	p H. mother liquor 7.5.	p H. mother liquor 7.5.
	<u>7 days</u>	<u>8 days</u>	
	Good D	Very good D	
	p H. mother liquor 7.5.	p H. mother liquor 7.5.	
<u>350°C.</u>	<u>2 days</u>	<u>3 days</u>	<u>5 days</u>
	Good D	Very good D	Good D
	Good Q		Good Q
	p H. mother liquor 8.0.	p H. mother liquor 7.0.	p H. mother liquor 8.0.
	<u>6 days</u>	<u>13 days</u>	<u>17 days</u>
	Moderate Q	Very good Q	Very good Q
	Trace D	Trace D	Very good D
	p H. mother liquor 7.0.	p H. mother liquor 7.5.	p H. mother liquor 7.5.

Table 9Products from gels of composition $1.2\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2$ 300°C.5 daysNon crystalline
product

Poor G

Trace P

p H. mother
liquor 7.5.350°C.2 days

Very good D

Good Q

Poor C

p H. mother
liquor 7.5.3 days

Very good D

Very good Q

p.H. mother
liquor 7.0.4 days

Good Q

Trace D

p.H. mother
liquor 7.5.5 days

Moderate Q

Moderate D

p.H. mother
liquor 7.5.7 days

Poor C

p H. mother
liquor 7.5.82 days

Fair Q

Poor D

p H. mother
liquor 7.0.

Table 10

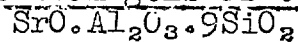
Products from gels of composition
 $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$

<u>340°C.</u>	<u>2 days</u>	<u>4 days</u>	<u>7 days</u>
	Non crystall- ine product	Good Q	Good Q
	p.H. mother liquor 7.0.	p H. mother liquor 7.0.	p.H. mother liquor 7.0.
<u>380°C.</u>	<u>2 days</u>	<u>4 days</u>	<u>15 days</u>
	Good D	Moderate D	Very good H
		Moderate P	Good C
		Some H	
	p.H. mother liquor 7.0.	p.H. mother liquor 7.0.	p H. mother liquor 7.0.

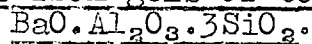
Table 11

Products from gels of composition
 $\text{SrO} \cdot 0.9\text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$

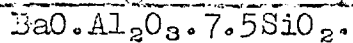
<u>340°C</u>	<u>2 days</u>	<u>6 days</u>	<u>12 days</u>
	Non crystall- ine product	Some D	Good D
	p H. mother liquor 8.0.	p H. mother liquor 7.5.	p H. mother liquor 8.5.

Table 12Products from gels of composition

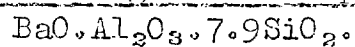
<u>450°C.</u>	<u>3 days</u>	<u>5 days</u>
	Very good H	Very good H
	Trace C	Trace C
	p. H. mother liquor 6.0.	p. H. mother liquor 5.5.
<u>350°C.</u>	<u>13 days</u>	
	Good D	
	Trace Q	
	p. H. mother liquor 7.0.	
<u>300°C.</u>	<u>2 days</u>	<u>20 days</u>
	Non crystalline product	Good Q
	p. H. mother liquor 8.0.	p. H. mother liquor 8.0.

Table 13Products from gels of composition

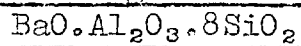
<u>150°C.</u>	<u>17 days</u>	<u>23 days</u>	<u>31 days</u>
	Moderate M	Good M	Very good M
	p. H. mother liquor 9	p. H. mother liquor 9	p. H. mother liquor 9
	<u>74 days</u>		
	Very good M		
	p. H. mother liquor 9		

Table 14Products from gels of composition

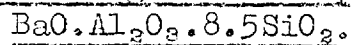
<u>350°C.</u>	<u>6 days</u>	<u>8 days</u>	<u>14 days</u>
	Good K	Moderate P	Good K
	Trace H	Trace H	Trace H
	Trace C		Trace P
	p H. mother liquor 7.0.	p H. mother liquor 7.5.	p H. mother liquor 7.5.

Table 15Products from gels of composition

<u>295°C.</u>	<u>7 days</u>	<u>8 days</u>
	Non crystall- line product	Moderate Z
	p H. mother liquor 8.0.	p H. mother liquor 8.0.

Table 16Products from gels of composition

<u>300°C.</u>	<u>7 days</u>	<u>8 days</u>	<u>9 days</u>
	Poor K	Moderate K	Good J
	Poor J	Moderate Z	Moderate Z
	Trace Z		Trace P
	p H. mother liquor 8.0.	p.H. mother liquor 8.5.	p H. mother liquor 8.0.
	<u>10 days</u>	<u>15 days</u>	
	Moderate K	Good J	
	Trace P		
	Trace J		
	p H. mother liquor 8.0.	p.H. mother liquor 9.0.	

Table 17Products from gels of composition

<u>300°C.</u>	<u>5 days</u>	<u>25 days</u>		
	Good Z	Good Z		
	p.H. mother liquor 8.0.	p.H. mother liquor 8.5.		
<u>340°C.</u>	<u>2 days</u>	<u>4 days</u>	<u>24 days</u>	<u>67 days</u>
	Non crystalline product	Moderate K	Moderate K	Good K
		Trace J	Moderate H	Good H
			Trace J	
	p.H. mother liquor 8.0.	p.H. mother liquor 8.5.	p.H. mother liquor 8.0.	p.H. mother liquor 8.5.

Table 18

Products from gels of composition
 $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 9\text{SiO}_2$.

<u>340°C.</u>	<u>7 days</u>	
	Moderate K	
	Trace P	
	p. H. mother liquor 7.0.	
<u>350°C.</u>	<u>6 days</u>	<u>9 days</u>
	Good K	Good K
	Trace H	Trace H
	Trace Z	Trace Z
	p. H. mother liquor 8.0.	p. H. mother liquor 8.0.

Table 19

Products from gels of composition
 $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 9.5\text{SiO}_2$.

<u>340°C.</u>	<u>7 days</u>
	Good K
	Trace H
	p. H. mother liquor 8.5.

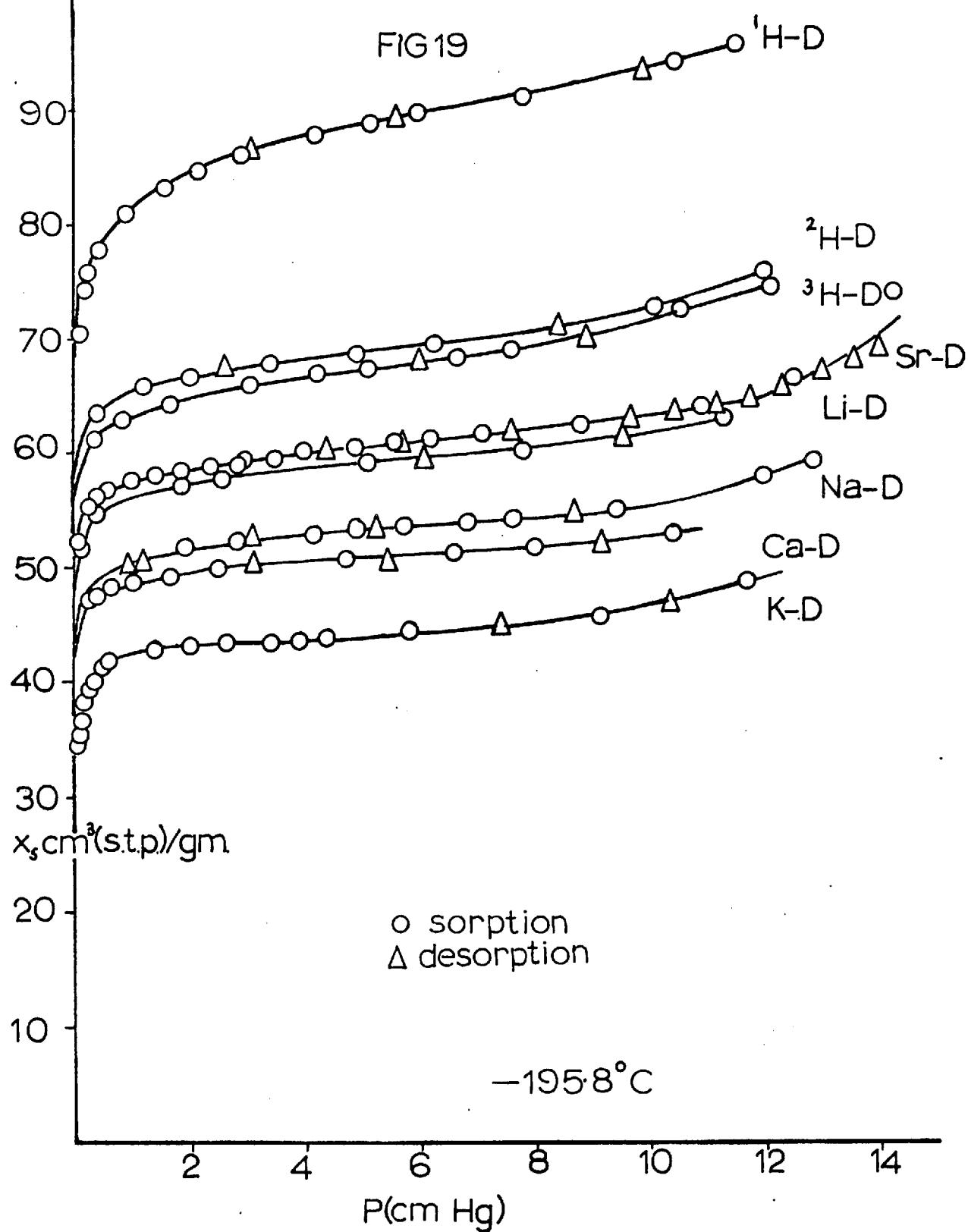
CHAPTER 7

Experimental Results - Sorption Characteristics

7.1 Sorptive Properties of some Ion-exchanged Ferrierites

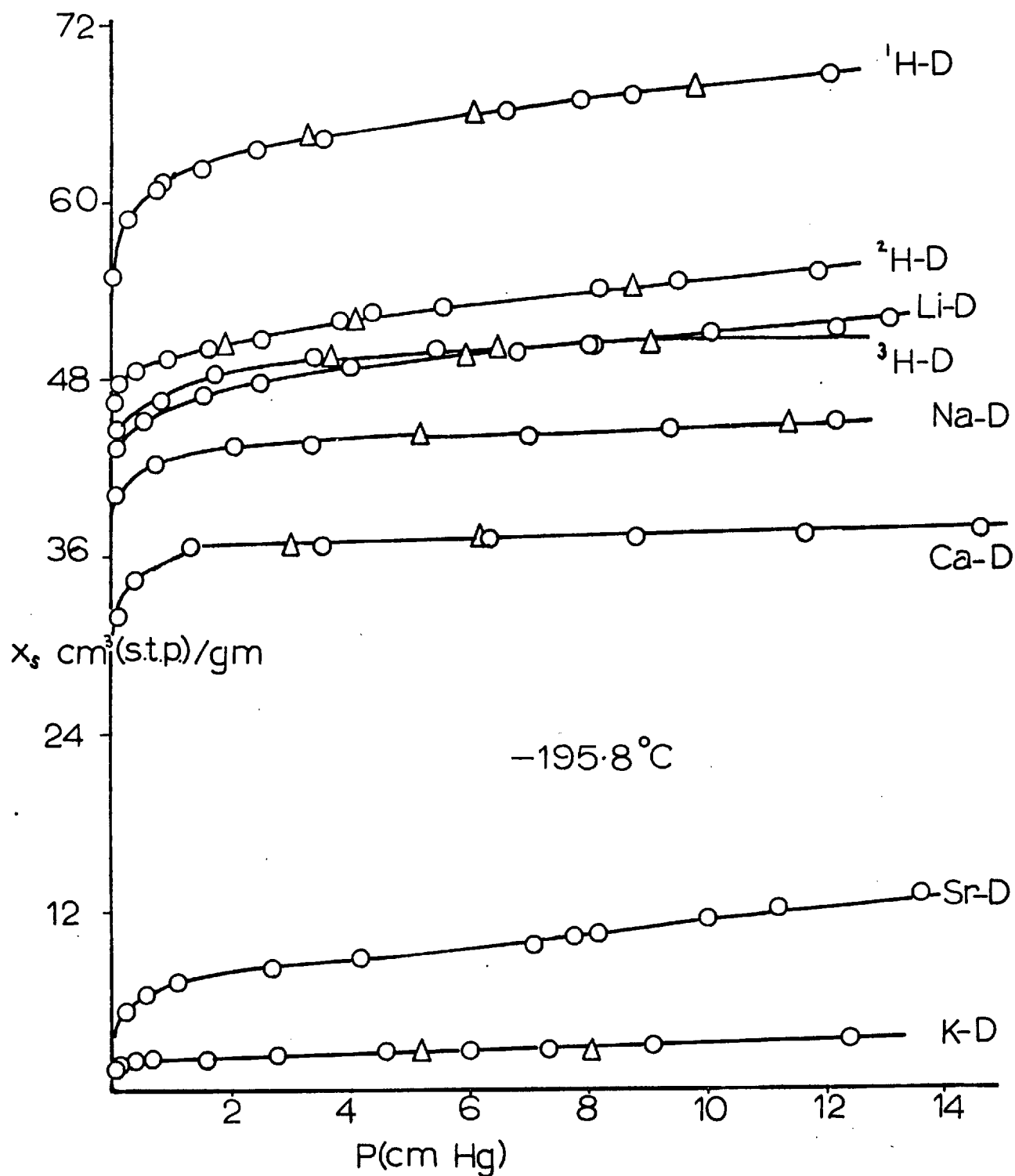
Lithium, sodium, potassium, calcium, strontium and three hydrogen forms of synthetic ferrierite were investigated. The hydrogen forms designated $^1\text{H-D}$, $^2\text{H-D}$, $^3\text{H-D}$ were prepared from strontium ferrierite by treatment with, respectively 0.088N hydrochloric acid, 2N ammonium chloride solution, followed by removal of ammonia by outgassing, and 1N hydrochloric acid. The various cationic forms were prepared from the same parent synthetic strontium ferrierite. However, the sorptive characteristics of strontium ferrierite were investigated with a sample synthesised identically but from a different batch to the strontium ferrierite employed in the preparation of the ion-exchanged forms. The various isotherms for the eight sorbates oxygen, nitrogen, argon, krypton, xenon, neon, carbon dioxide and methane are shown in Figures (19) - (26).

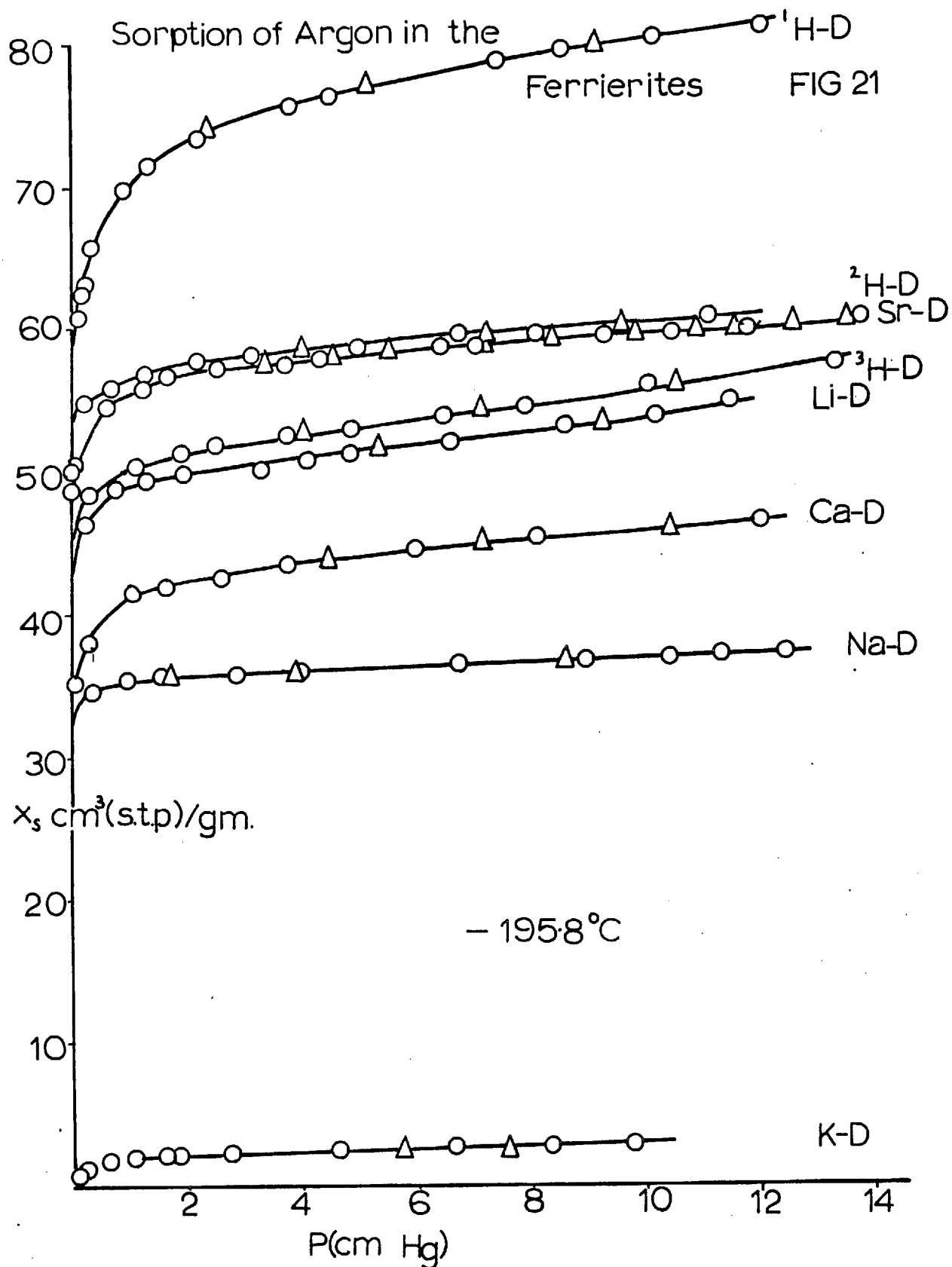
Isotherms for the zeolites were measured at -195.8°C for the sorbates oxygen, nitrogen, neon and argon, at -183.1°C for krypton and methane; at -77.5°C for xenon and room temperature for carbon dioxide. Almost all isotherms measured were reversible and reproducible. Equilibrium was established quickly, the exceptions

Sorption of O_2 in the Ferrierites

Sorption of N_2 in the Ferrierites

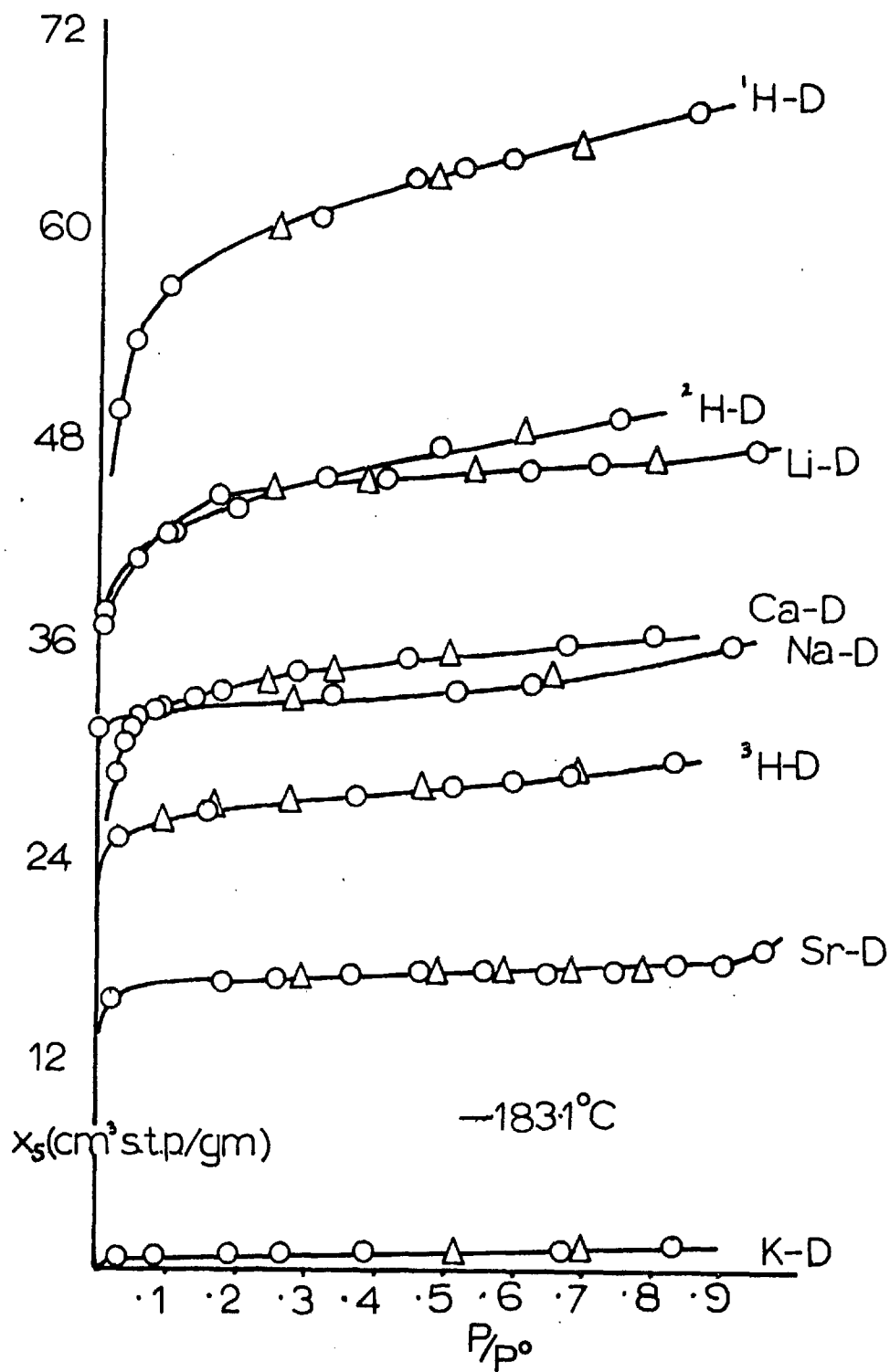
FIG 20





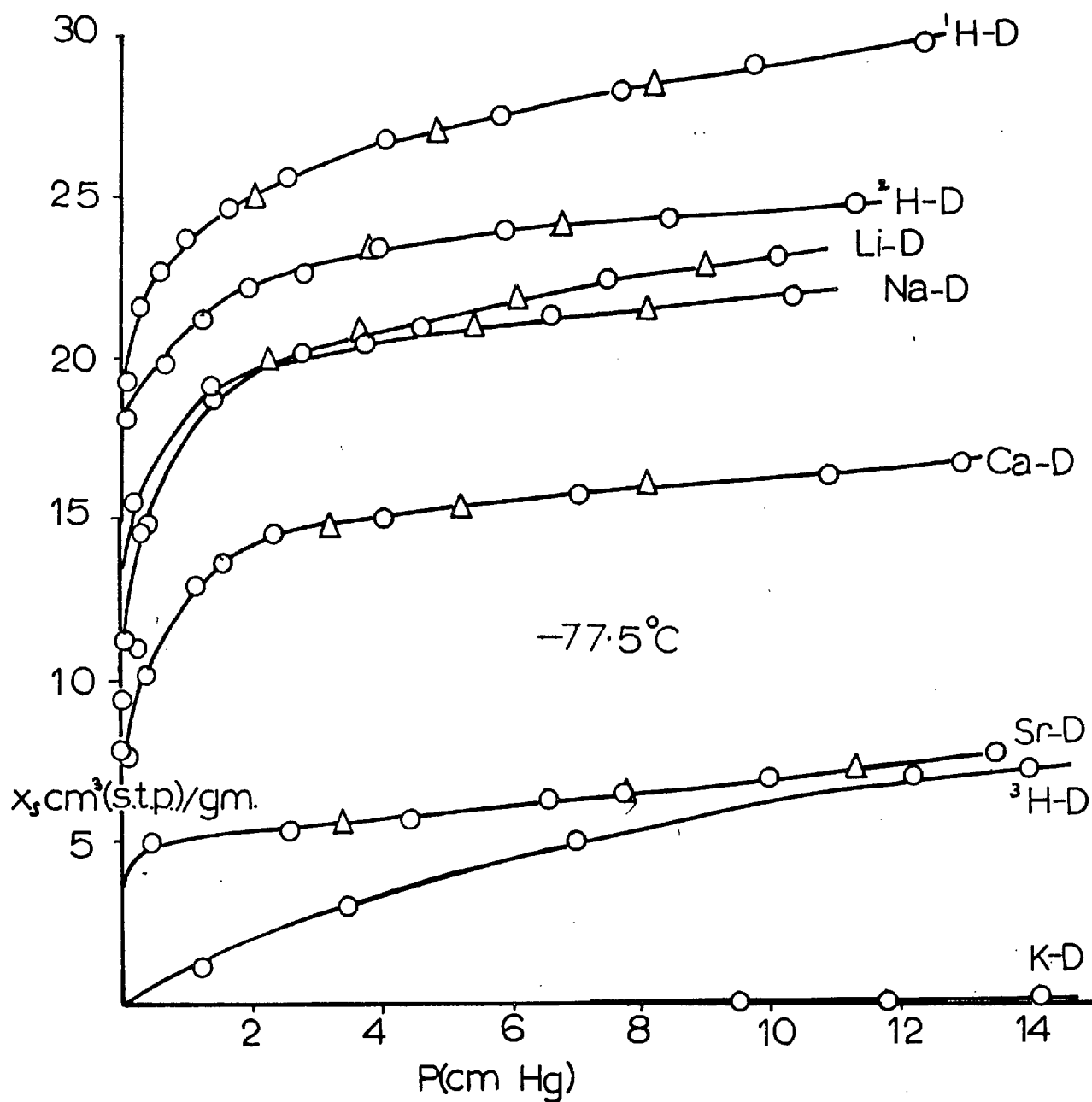
Sorption of Kr in the Ferrierites

FIG 22



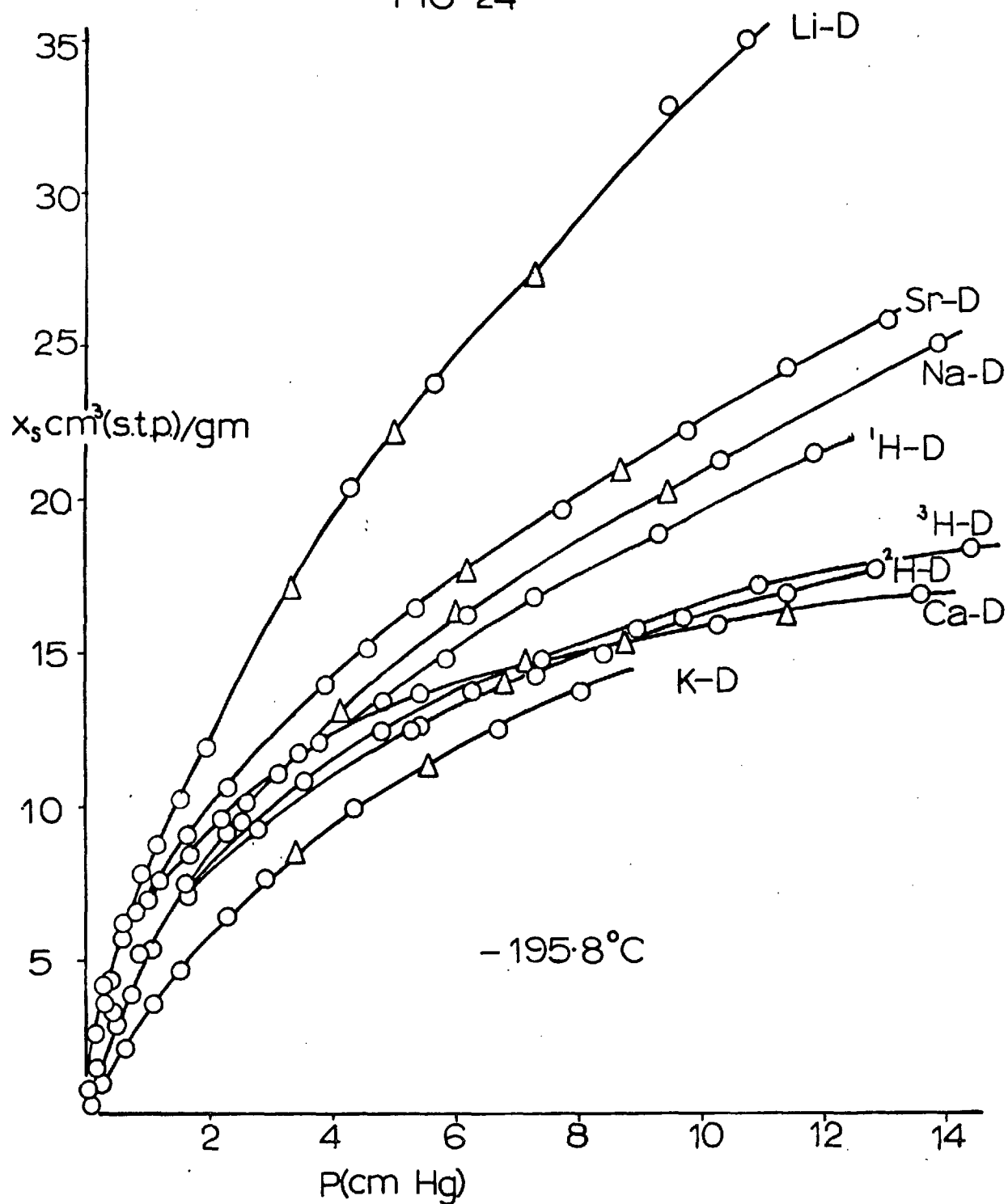
Sorption of Xenon in the Ferrierites

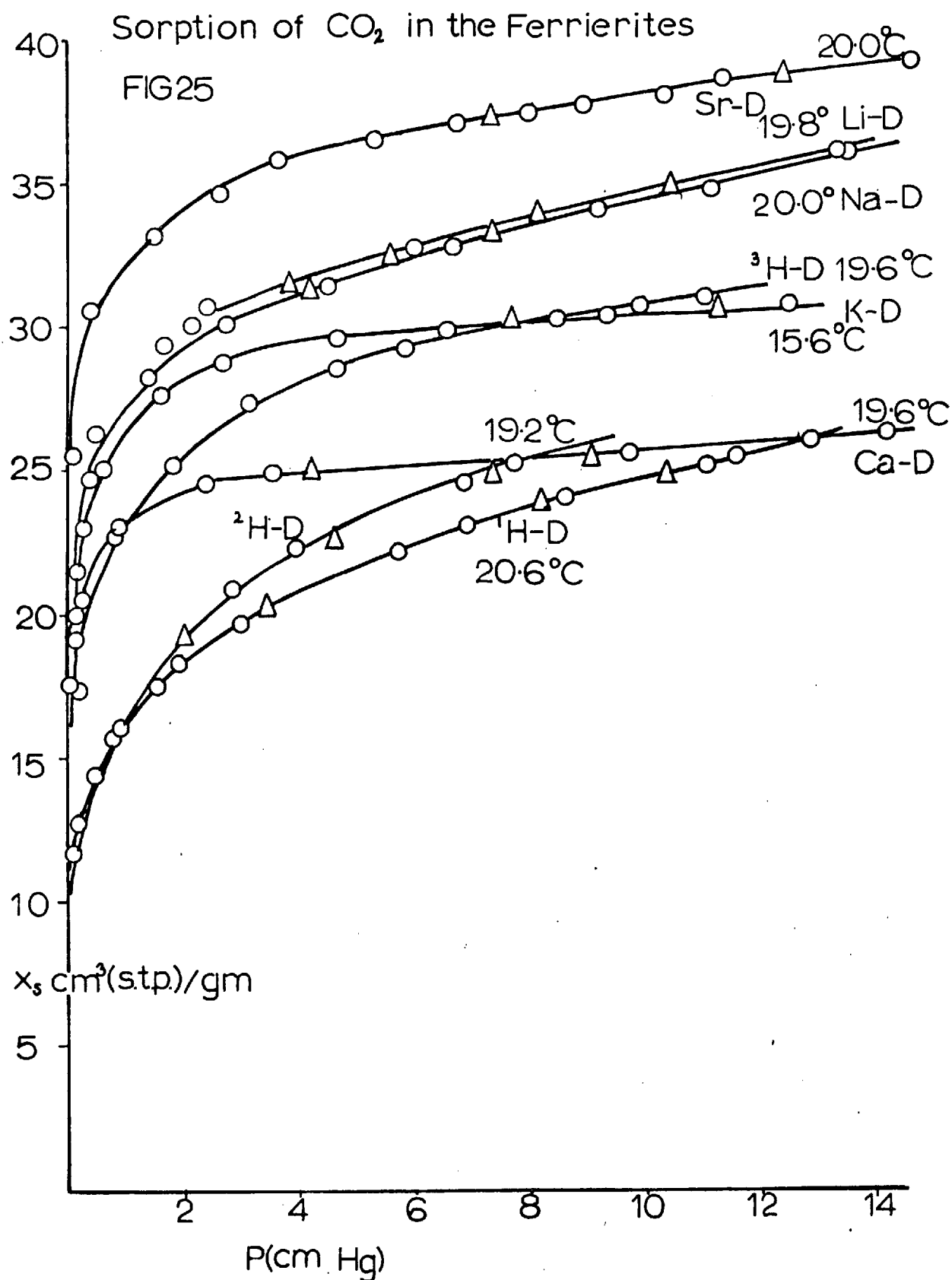
FIG 23



Sorption of Neon in the Ferrierites

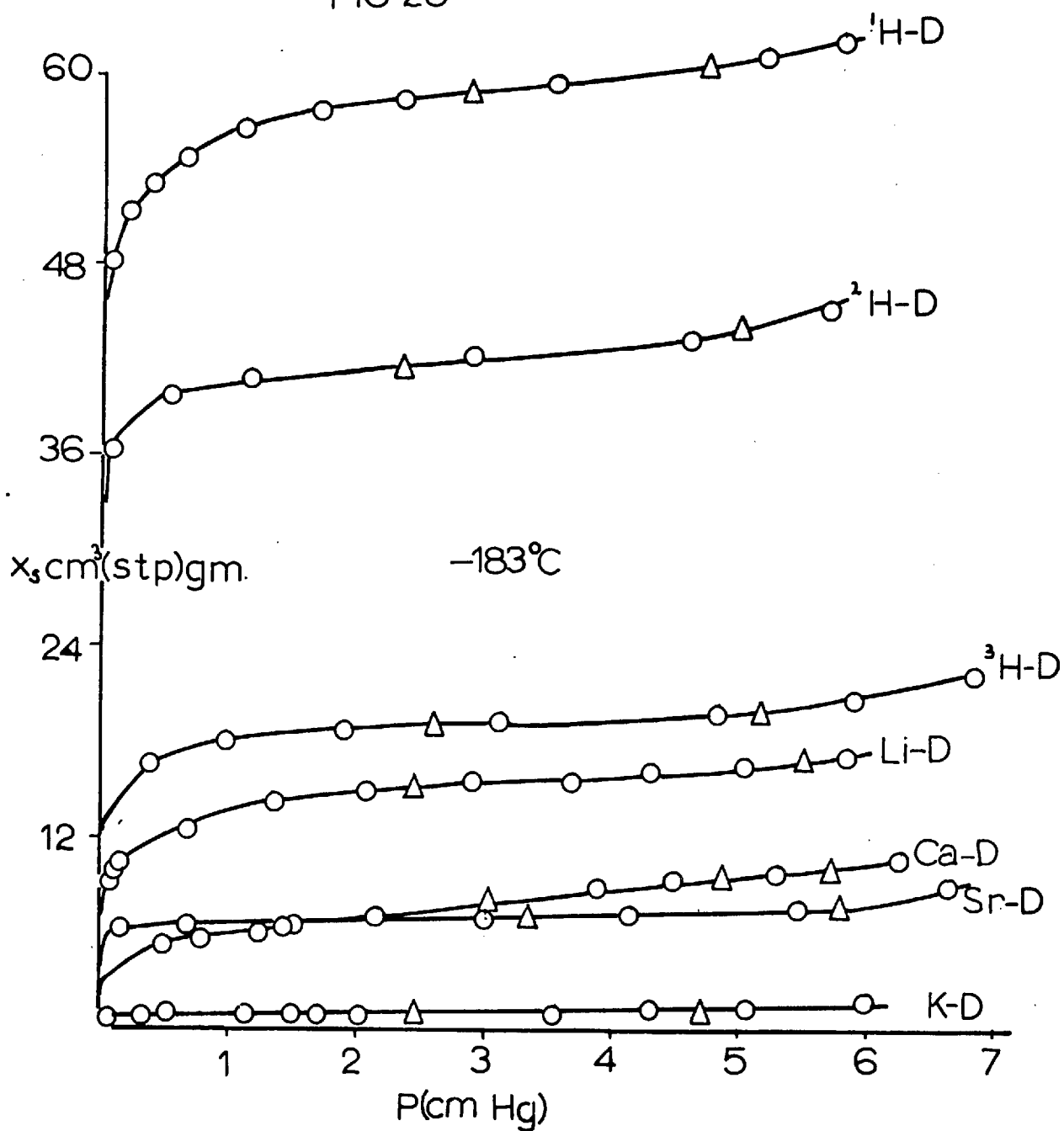
FIG 24





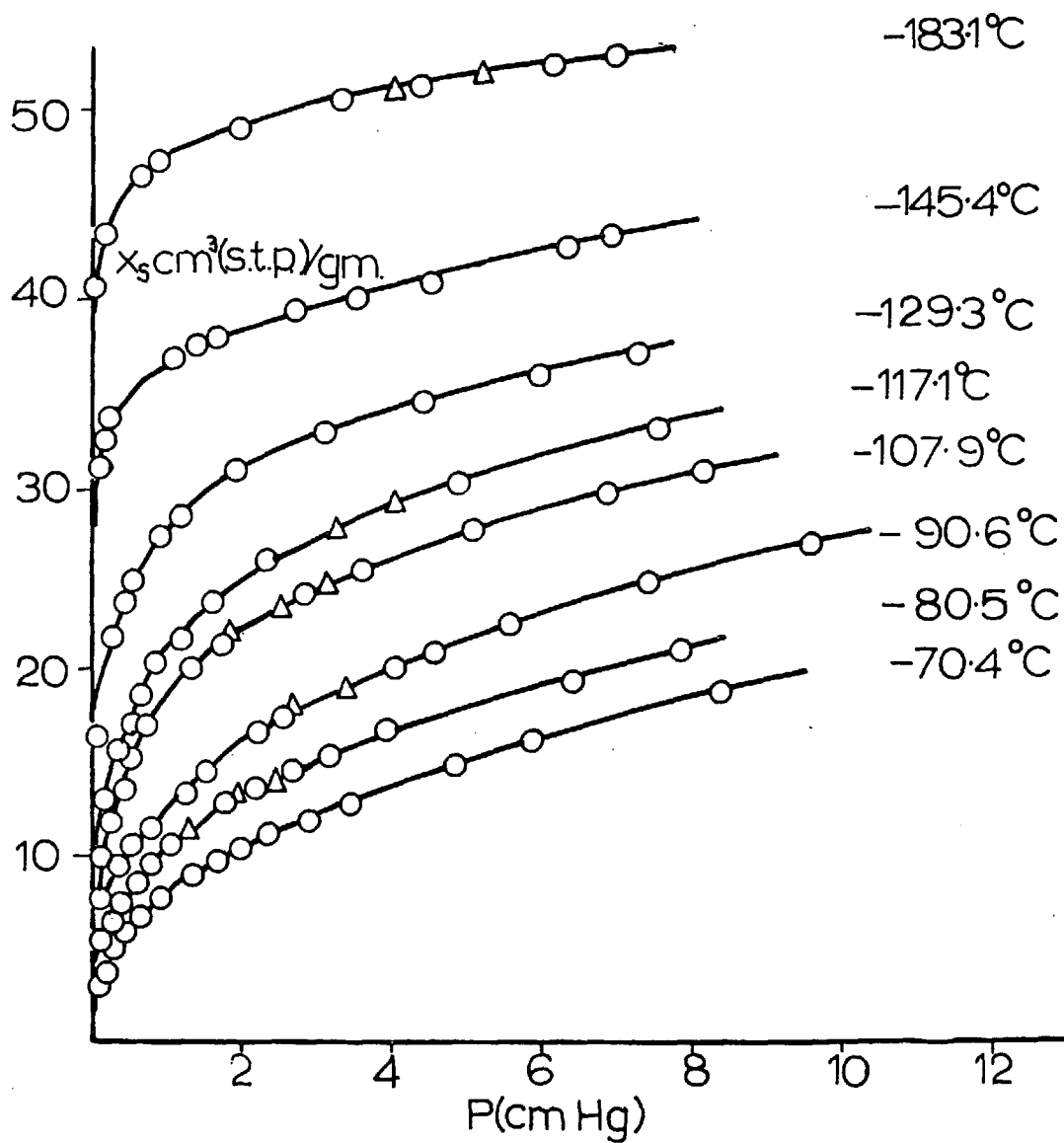
Sorption of Methane in the Ferrierites

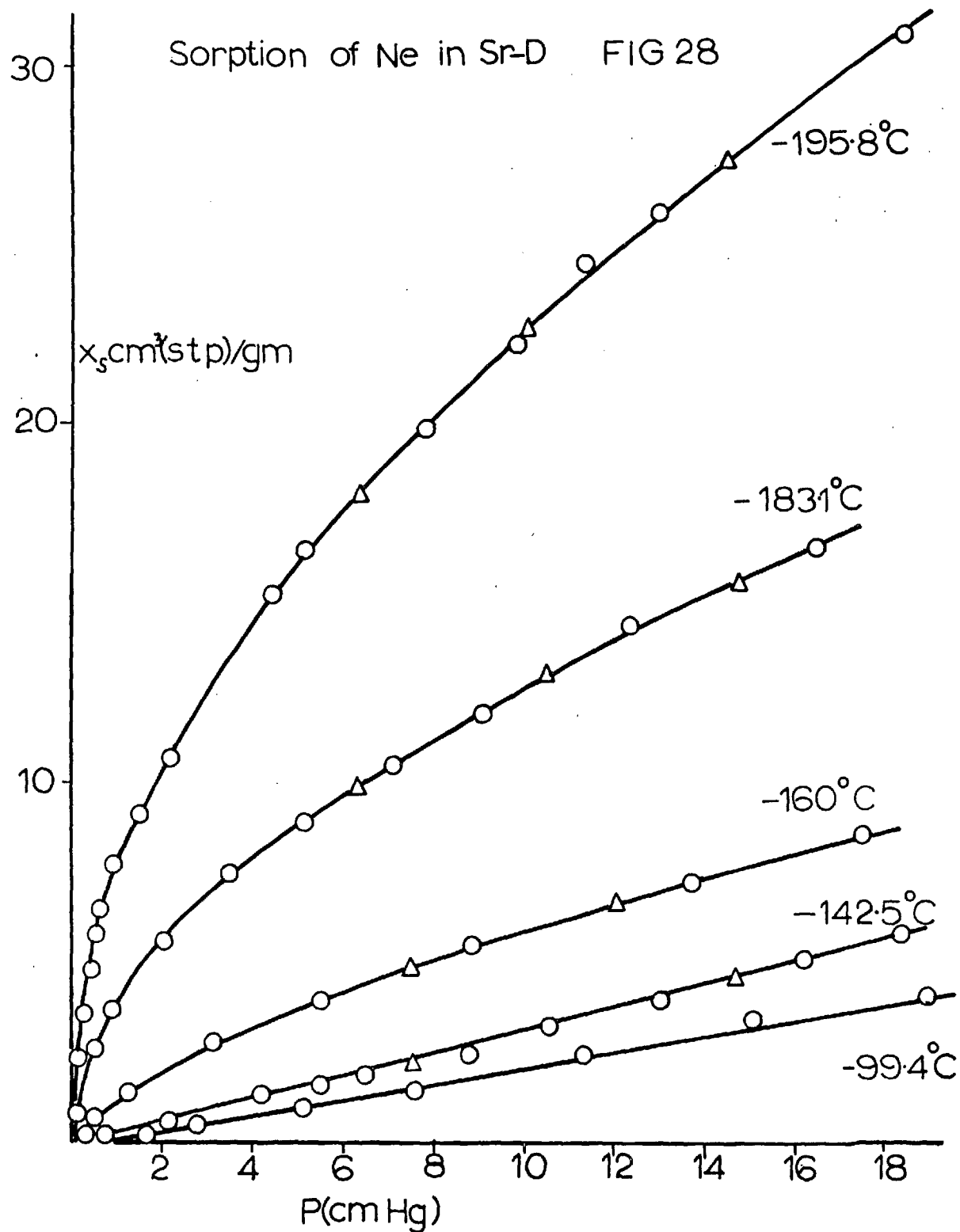
FIG 26



Sorption of O₂ in Sr-D

FIG 27





being the occlusion of methane in sodium ferrierite, nitrogen in strontium ferrierite and xenon in IN acid treated ferrierite. In these cases it was impossible to obtain equilibrium.

It is seen from the plots that all the isotherms are of type 1 (Brunauer's classification). The amounts sorbed, x_s , are recorded as cm^3 (s.t.p.)/outgassed gram. In order to compare sorption capacities of the various cationic forms values of x_s are given on a common basis (Sr - D) so that the amounts sorbed for all the ferrierites are expressed for the number of unit cells contained in one gram of strontium ferrierite.

Saturation Capacities of the Ferrierites (ccs s.t.p./

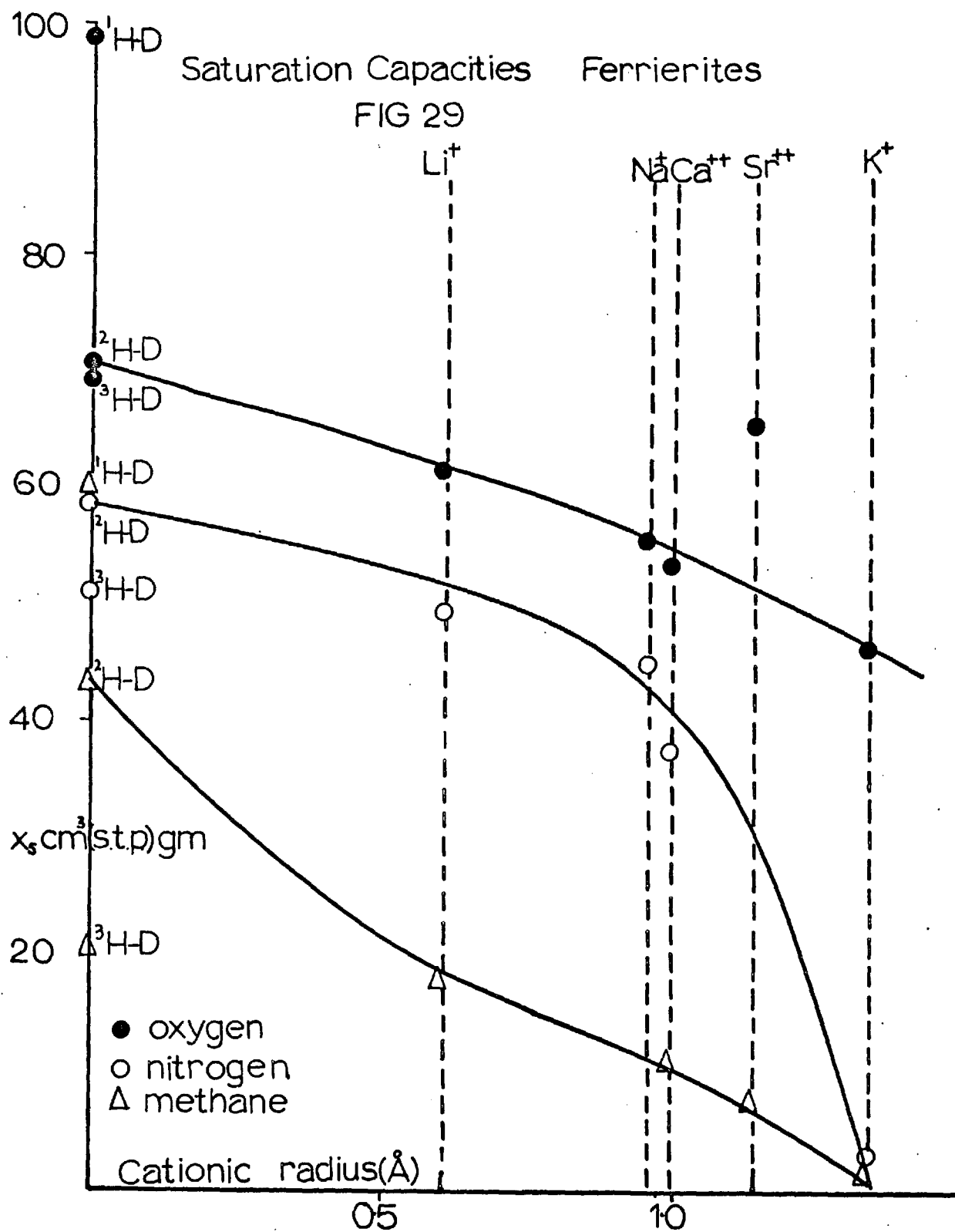
No. of unit cells in 1 g of Sr -D)

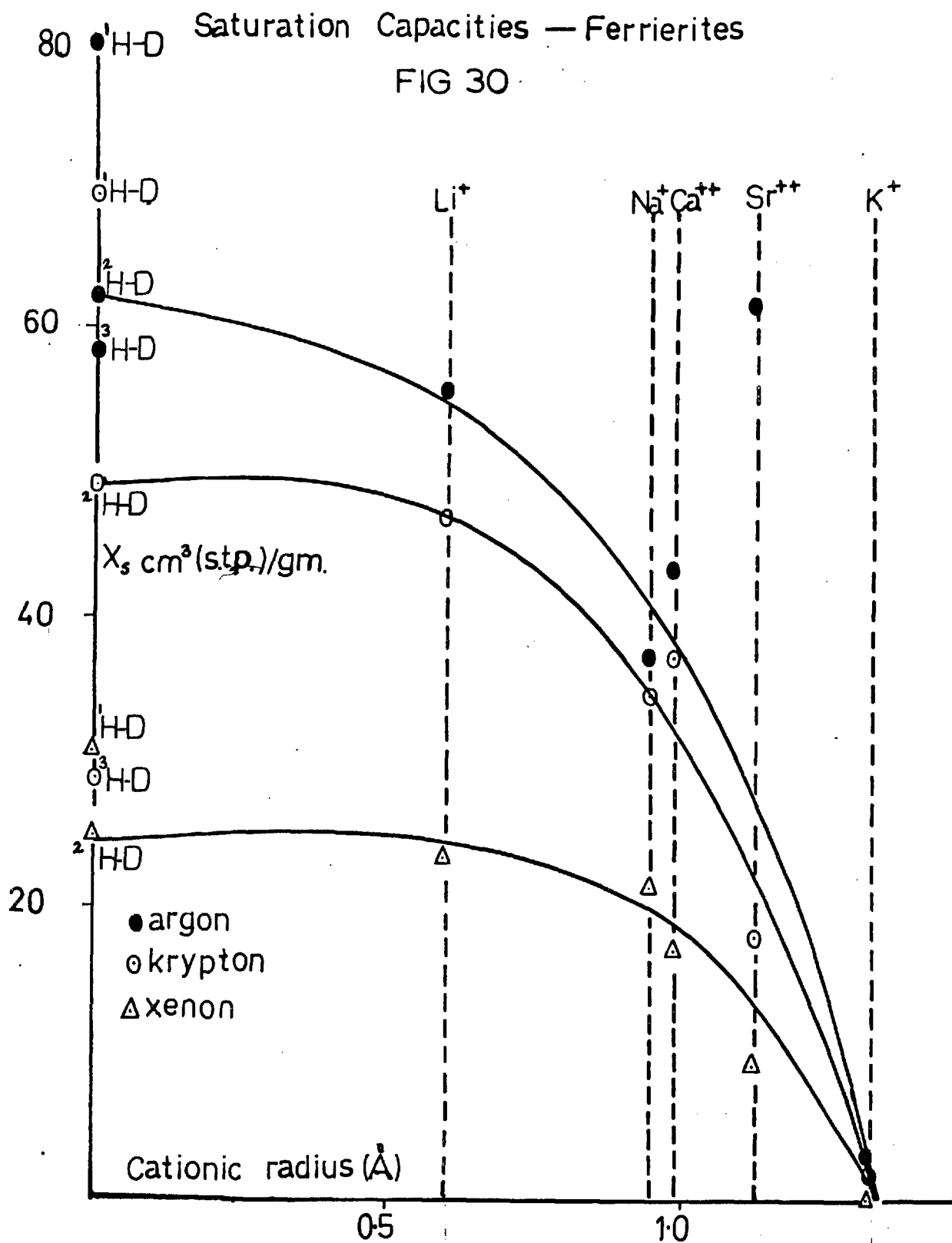
Table 20

Sorbent	O ₂	N ₂	Ar	KR	Xe	CO ₂	CH ₄
¹ HD	99.1	69.4	79.7	69.1	30.9	-	60.6
² HD	70.8	58.8	62.2	49.0	24.6	29.6	43.5
³ HD	69.3	51.1	58.1	28.9	-	33.3	20.9
LiD	61.4	49.7	55.8	47.0	23.7	35.9	18.0
NaD	55.9	45.1	37.2	34.8	21.7	41.3	-
KD	46.3	2.7	3.0	1.9	No uptake	31.1	1.7
CaD	53.4	37.5	46.3	37.2	17.2	25.4	11.3
SrD	65.8	-	61.9	18.0	9.3	42.6	7.8
Temperature °C	-195.8	-195.8	-195.8	-183.1	-77.5	~20°C	-183.1

The saturation capacities were estimated from Langmuir plots of p/x against p . These plots give reasonably straight lines, from the slope of which x_{sat} values follow. Near saturation, when the volume sorbed changes little with p , such linear plots are inevitable and are not a test of Langmuir's isotherm. The saturation capacities are plotted as functions of cationic radii in Figs. (29) and (30). For the monovalent cation forms of ferrierite it is seen that as the size of the cation increases the saturation capacities decrease. This is to be expected, if the cation positions within the zeolite remain the same for each type of ion, as the available free interstitial volume to the sorbate becomes smaller as the cations become larger. However, the cations may have different positions within the zeolite and in some ferrierites the cations may block the entry of guest molecules into one or other of the main channels and so reduce the available volume for the guest molecules. The divalent ferrierites, which have only half the number of cations may be expected to have larger saturation capacities than monovalent types of similar cationic radii provided that the positions of the ions in the zeolite are the same. This is not always the case; x_{sat} for O_2 , N_2 , Xe in Ca - D, and x_{sat} for Kr and Xe in Sr - D are examples.

The ferrierite treated with 0.088 N HCl has considerably higher saturation capacities than the IN treated





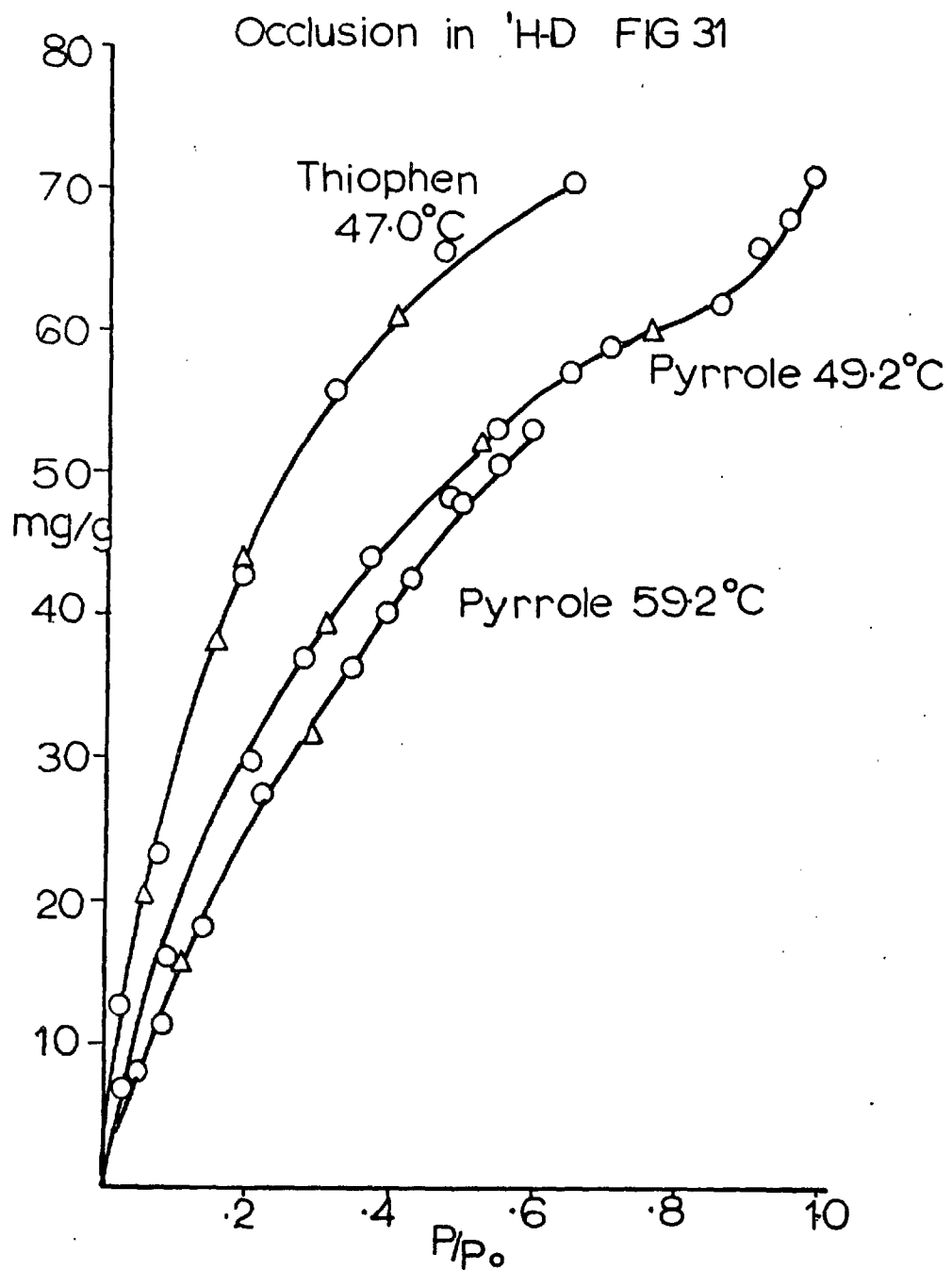
product for all the sorbates studied. Barrer and Makki¹⁰⁷ treated clinoptilolite with HCl of normalities ranging from .08 to 1.0N; they found that the sorbents showing the largest sorptive capacities were those produced by treatment with HCl of normality .16N - .67N. Coughlan⁹⁵ found that clinoptilolite treated with .25N HCl showed the largest sorptive capacity for carbon dioxide. These results could be due to the replacement of the cations by protons thus making a larger interstitial volume available to the sorbate molecules. However, the ferrierite treated with 1N HCl unlike 1N acid treated clinoptilolite was not dealuminated and so the lower sorptive capacity is not explained by a partial removal of aluminium from the framework. The hydrogen ferrierite (²H - D) formed from ammonium ferrierite shows very similar sorptive capacities to those of the 1N HCl treated ferrierite (³H - D) for oxygen, nitrogen and argon occlusion, but for the larger molecules krypton and methane the sorptive capacity is 40 - 50% higher. It seems that part of the interstitial volume of ³H - D is not available to krypton and methane.

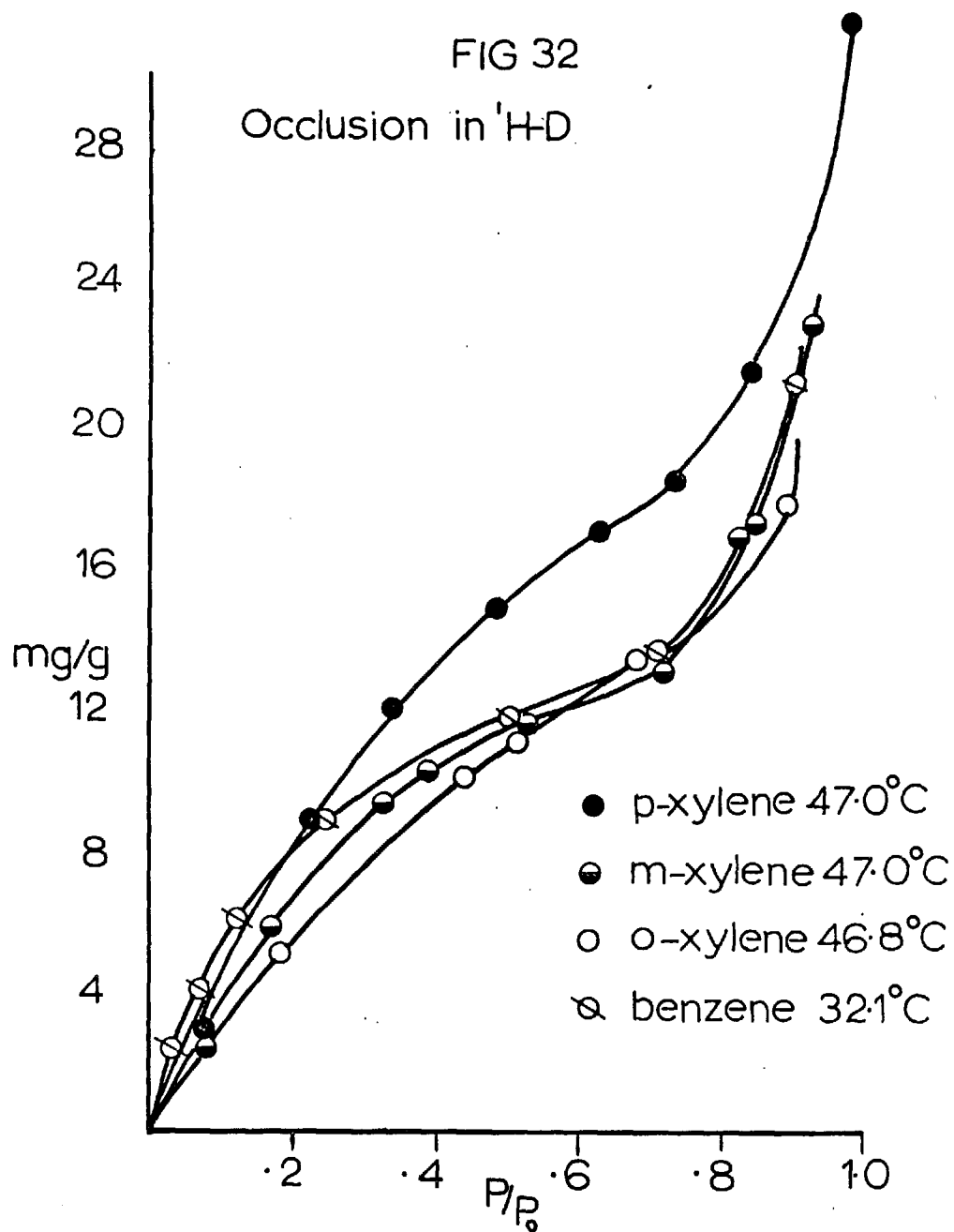
Potassium ferrierite sorbs oxygen rapidly, but argon, nitrogen, krypton, xenon and methane are excluded. Because the energy barrier to the entry of guest molecules into the cavity of a zeolite depends upon the close range repulsive forces called into play when the electron clouds of the guest molecule and cation begin to interpenetrate,

the barrier can render the crystals selective to pairs of molecules whose critical dimensions differ only slightly. Levynite sorbs oxygen at -183°C but shows negligible uptake of argon¹⁰⁸, at the same temperature Linde Sieve 4A sorbs oxygen rapidly but shows a very slow sorption rate for nitrogen¹⁰⁹. It appears that the potassium ions in ferrierite may also partially block the ten and eight numbered rings leading into two sets of channels in the crystal.

7.1.1 Sorption of Some Organic Molecules in .088 N Acid Treated Ferrierite

The approximately elliptical cross-section of the main channel in ferrierite has major and minor diameters of $5.4 \text{ \AA}$ and $4.2 \text{ \AA}$. An attempt was made to find out if molecules with cross-sectional diameters near $5.4 \text{ \AA}$ were occluded. The isotherms for pyrrole (critical cross-sectional diameter for penetration $\sim 4.9 \text{ \AA}$) and thiophen (critical cross-sectional diameter for penetration $\sim 5.2 \text{ \AA}$) are shown in Fig. (31). Equilibrium was rapid, 30 minutes for each dose of sorbate and the sorption reversible. The isotherms for o-, m- and p-xylene (critical cross-sectional diameters for penetration $\sim 5 \text{ \AA} - 5.6 \text{ \AA}$) and benzene (critical cross-sectional diameter for penetration $\sim 5 \text{ \AA}$) are shown in Fig. 32. The uptakes in these cases are nearly the same but are much lower than the polar





molecules pyrrole and thiophen. Each equilibrium point was reached in 20 minutes for the sorption of the xylenes but 24 hours was the equilibration time for the benzene sorption.

7.2 Sorptive Properties of Some Other Zeolites

7.2.1 Ba-J and Ca-J

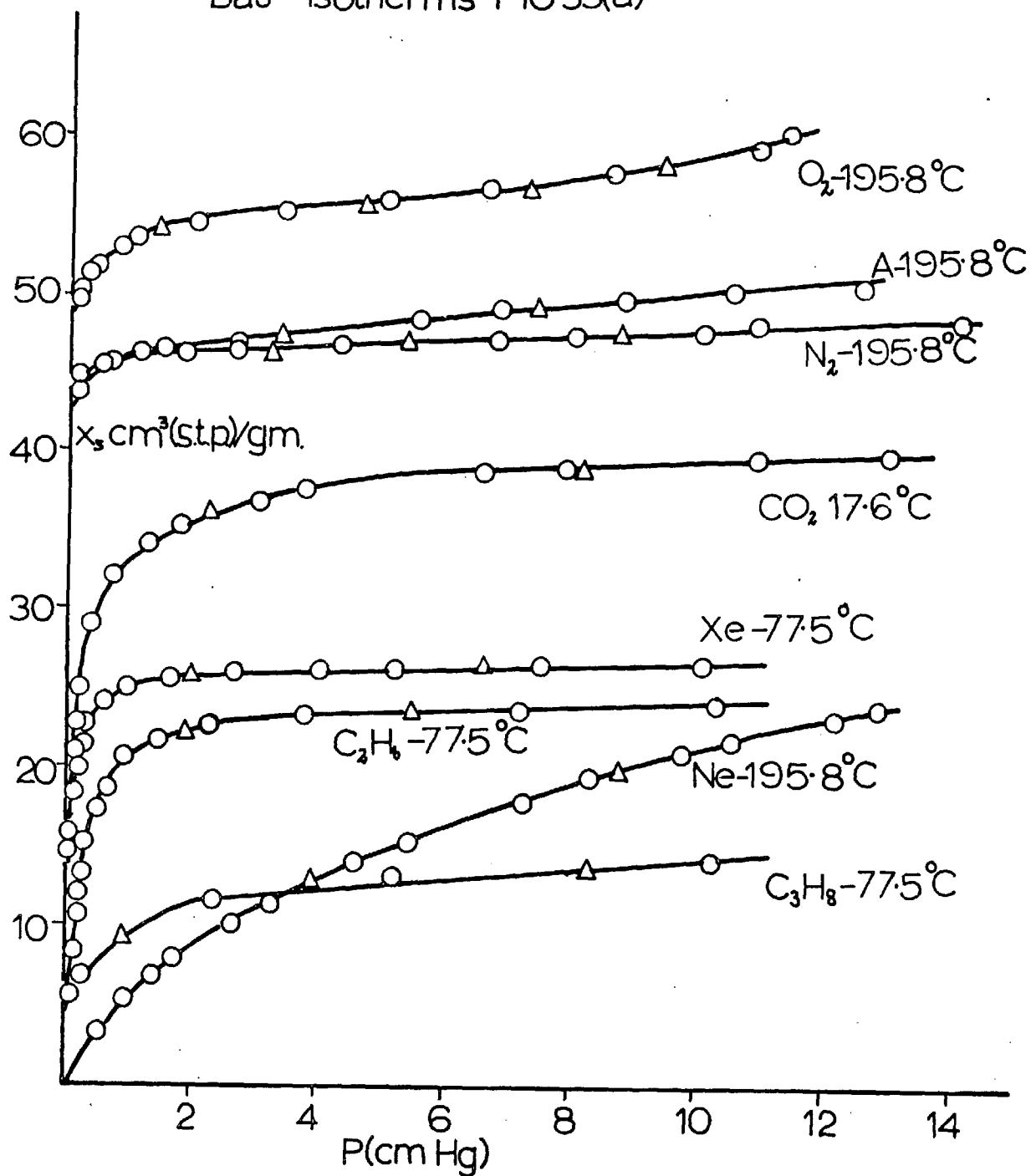
The various isotherms for the ten sorbates oxygen, nitrogen, argon, krypton, xenon, neon, carbon dioxide, methane, ethane and propane are shown in Figures 33 (a) and (b). The isotherms were measured at -195.8°C for oxygen, nitrogen, neon and argon; at -183.1°C for methane and krypton; at -77.5°C for xenon and propane and room temperature for carbon dioxide. Equilibration was rapid and the isotherms (type 1 Brunauer's classification) were reversible. A list of the saturation capacities (cm^3 (s.t.p.)/outgassed gm) is given in the table below.

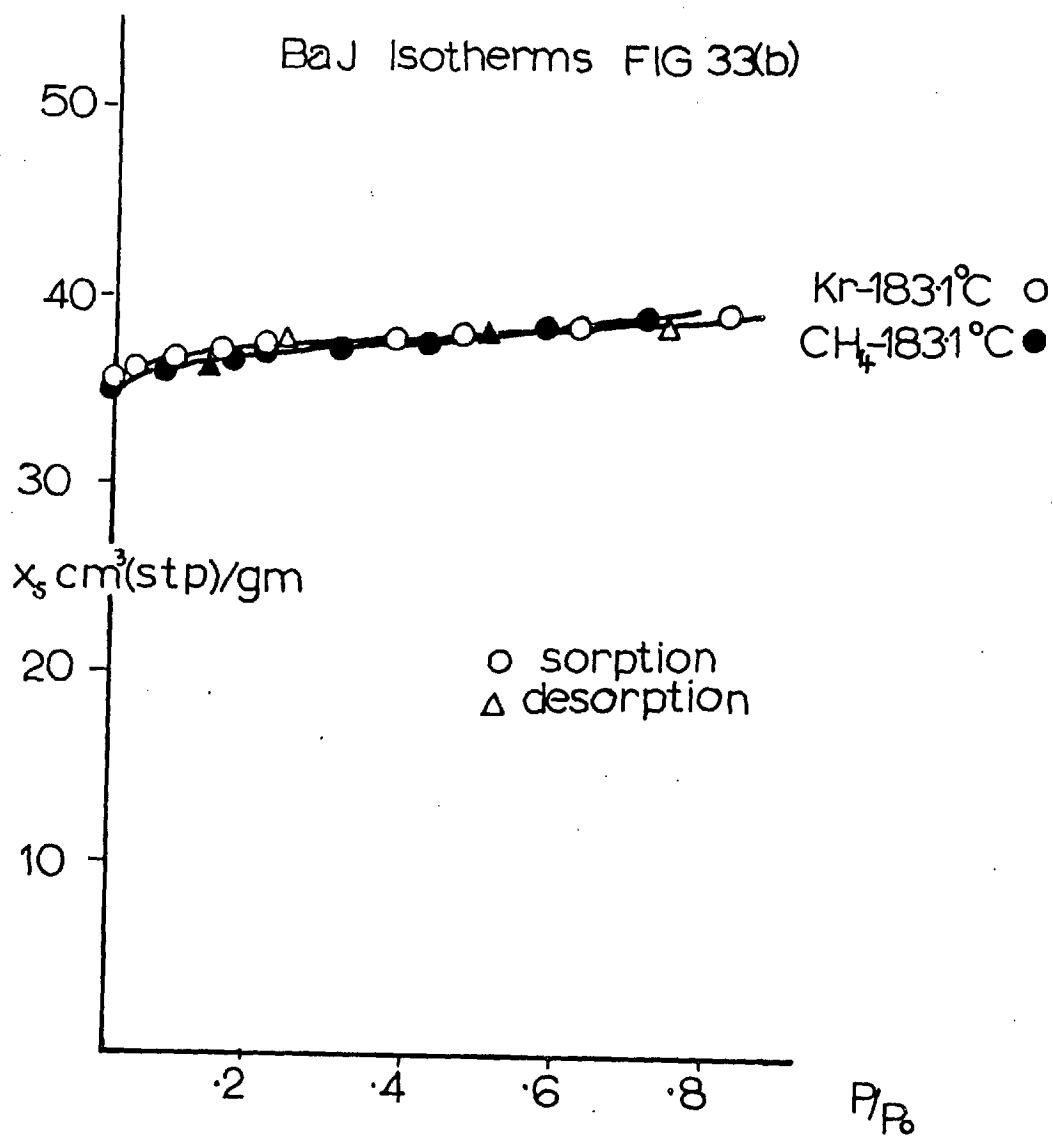
Table 21

Saturation Capacities of Ba-J and Ca-J (ccs s.t.p./
dehydrated g)

	O ₂	N ₂	Ar	Kr	Xe	CO ₂	CH ₄	C ₂ H ₆	C ₃ H ₈
Ba-J	59.5	49.2	51.7	38.8	27.0	40.7	39.4	25.2	14.7
Ca-J	55.6	-	-	-	-	-	-	-	-
Temperature $^{\circ}\text{C}$	-195.8	-195.8	-195.8	-183.1	-77.5	+17.6	-183.1	-77.5	-77.5

BaJ Isotherms FIG 33(a)





It can be seen that saturation values, x^{sat} , for oxygen and argon in Ba-J are a little lower than the corresponding x^{sat} values for strontium ferrierite. BaJ, however, has a higher sorptive capacity for krypton, xenon and methane.

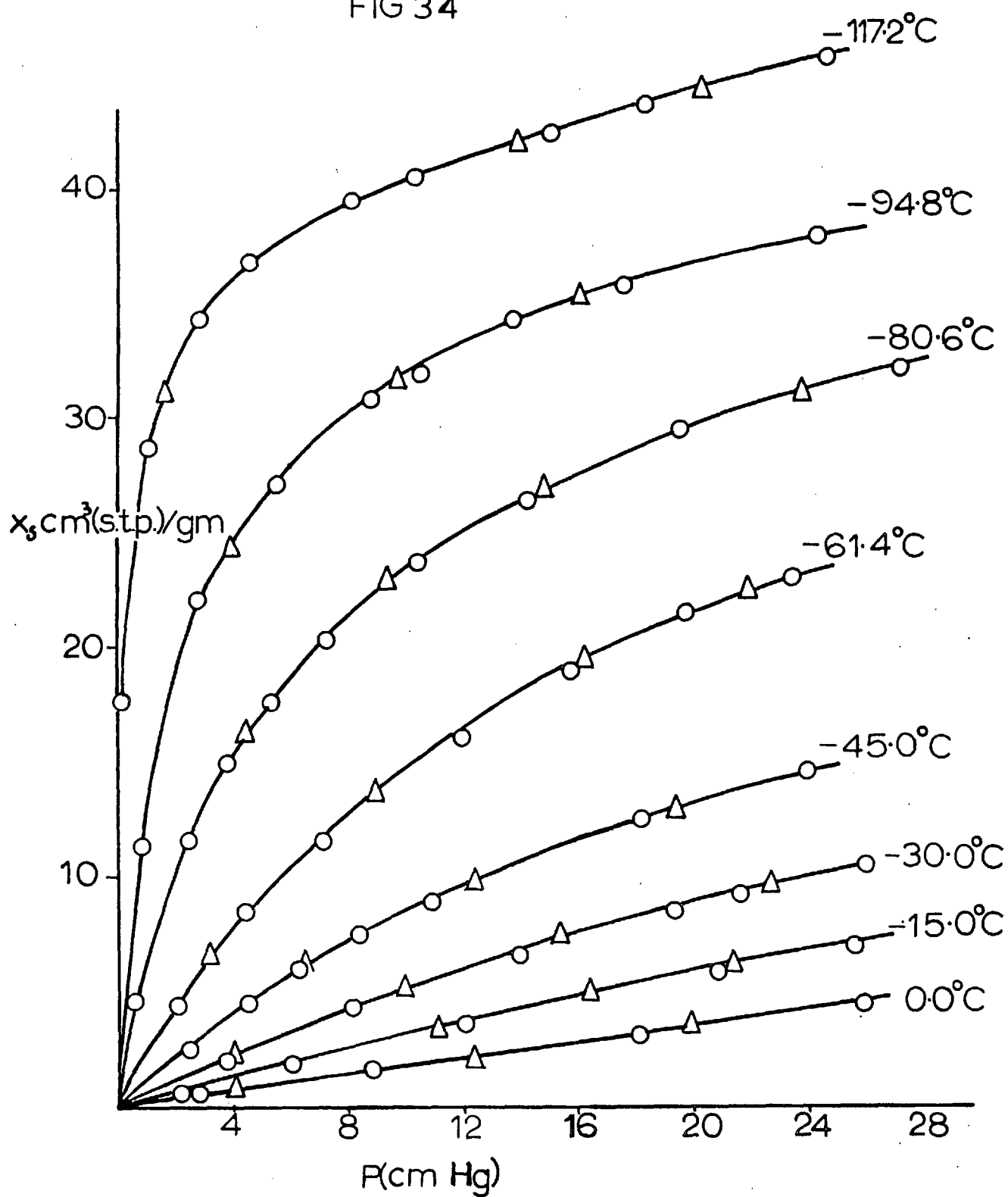
An estimate of 80% for the purity of the Sr-D sample was made from a comparison of the water contents of the naturally occurring ferrierite and the synthetic sample. Since Ba-J has no natural counterpart a similar estimate of purity for this zeolite cannot be made. However, it is probable that the purity of Ba-J is not higher than 80% and so the recorded saturation capacities for BaJ and Sr-D are minimum capacities.

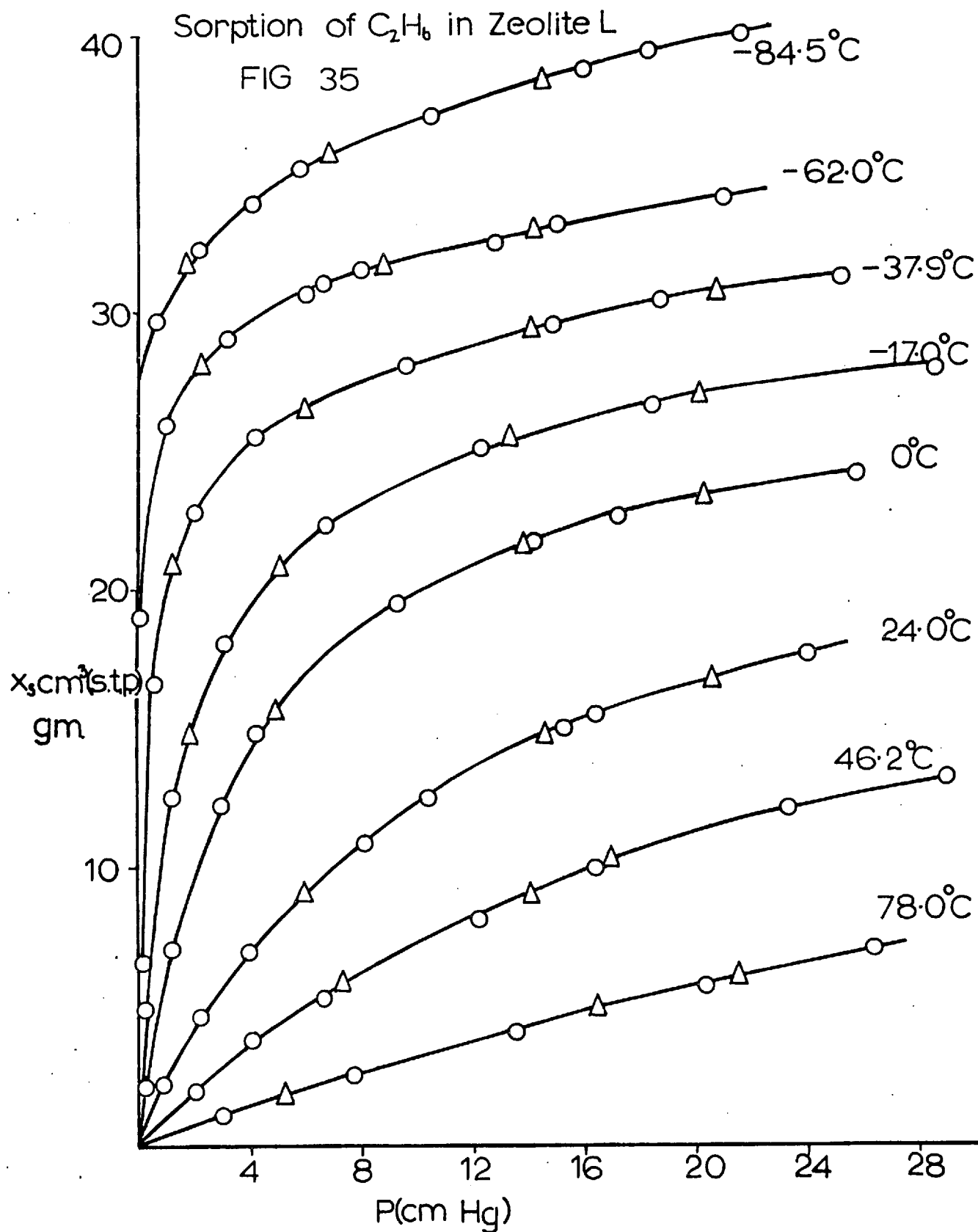
7.2.2 Zeolite L - A Mixed Sodium and Potassium Form.

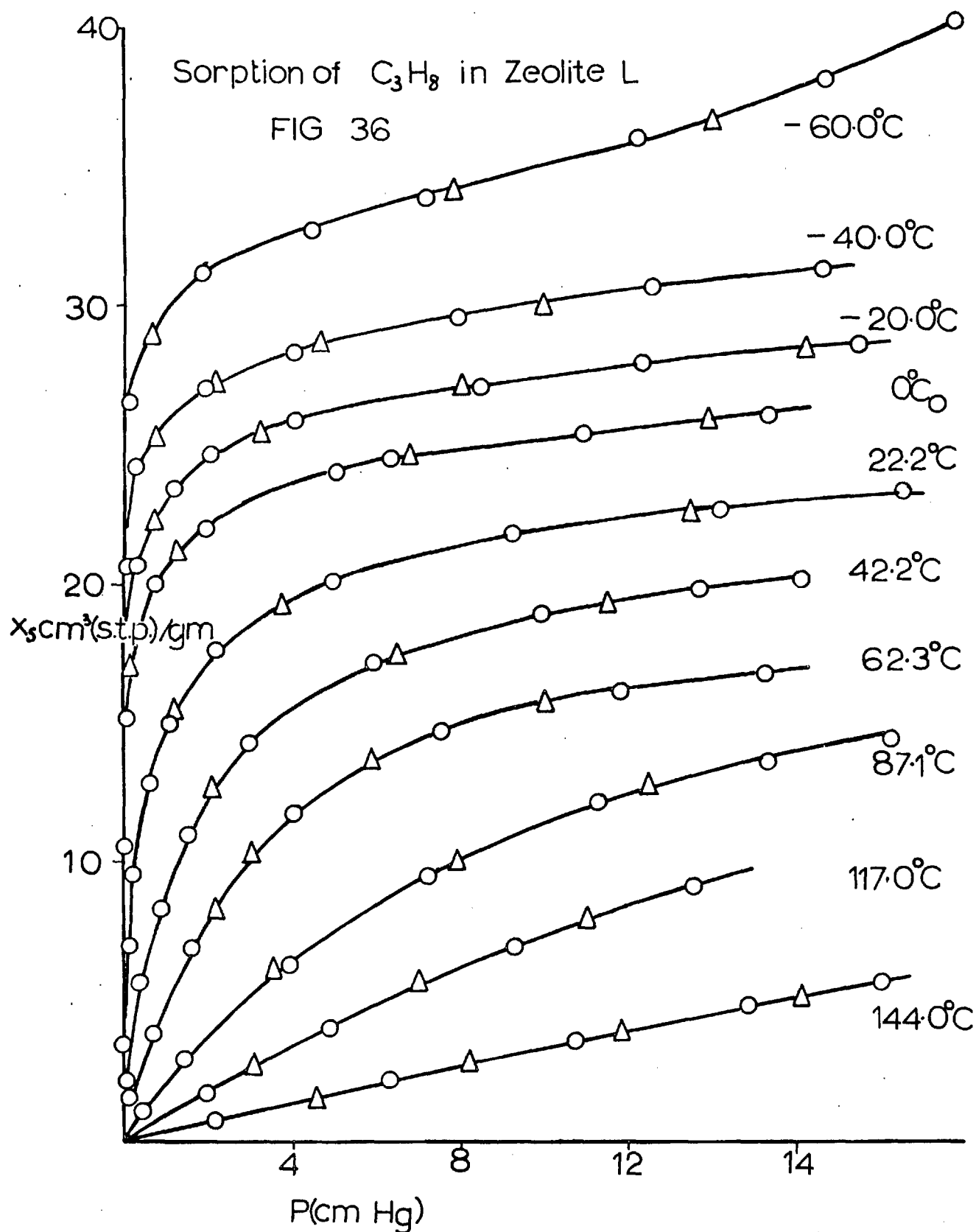
Families of isotherms for methane, ethane, propane, n-butane, iso-butane and neo-pentane are plotted in Figures 34 - 39. Equilibrium was reached quickly and all the isotherms were reversible and reproducible. Estimate of the apparent saturation capacity, x^{sat} were made for methane in the temperature range -183.0°C to -95°C , ethane in the range -85°C to 0°C , propane in the range -60.0°C to $+42.2^{\circ}\text{C}$, n-butane in the range 0°C to $+90^{\circ}\text{C}$, iso-butane in the range -25.0°C to $+81.0^{\circ}\text{C}$ and neo-pentane in the range $+10^{\circ}\text{C}$ to $+169.0^{\circ}\text{C}$. The saturation capacities are plotted against temperature for the

Sorption of CH_4 in Zeolite L

FIG 34

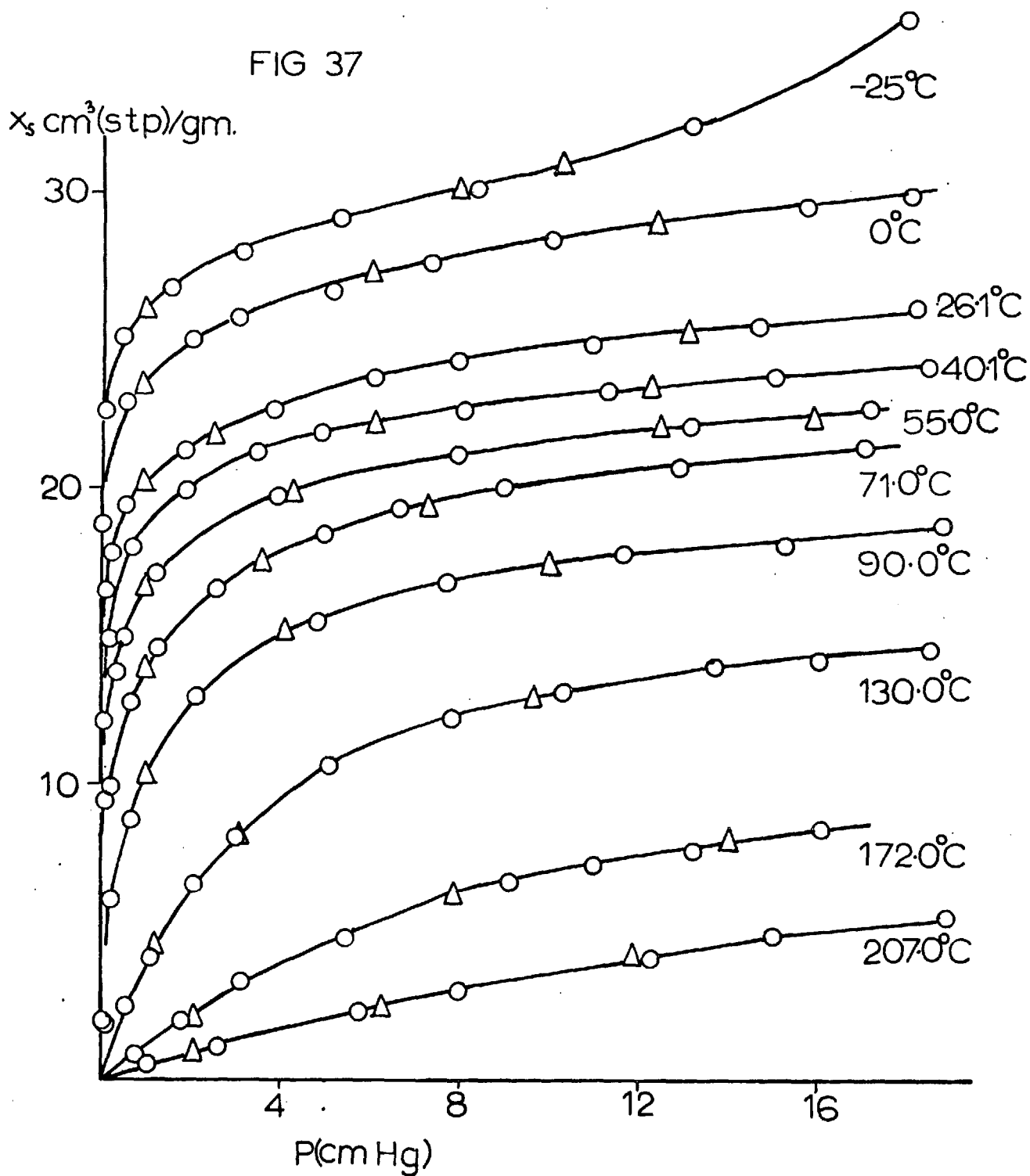


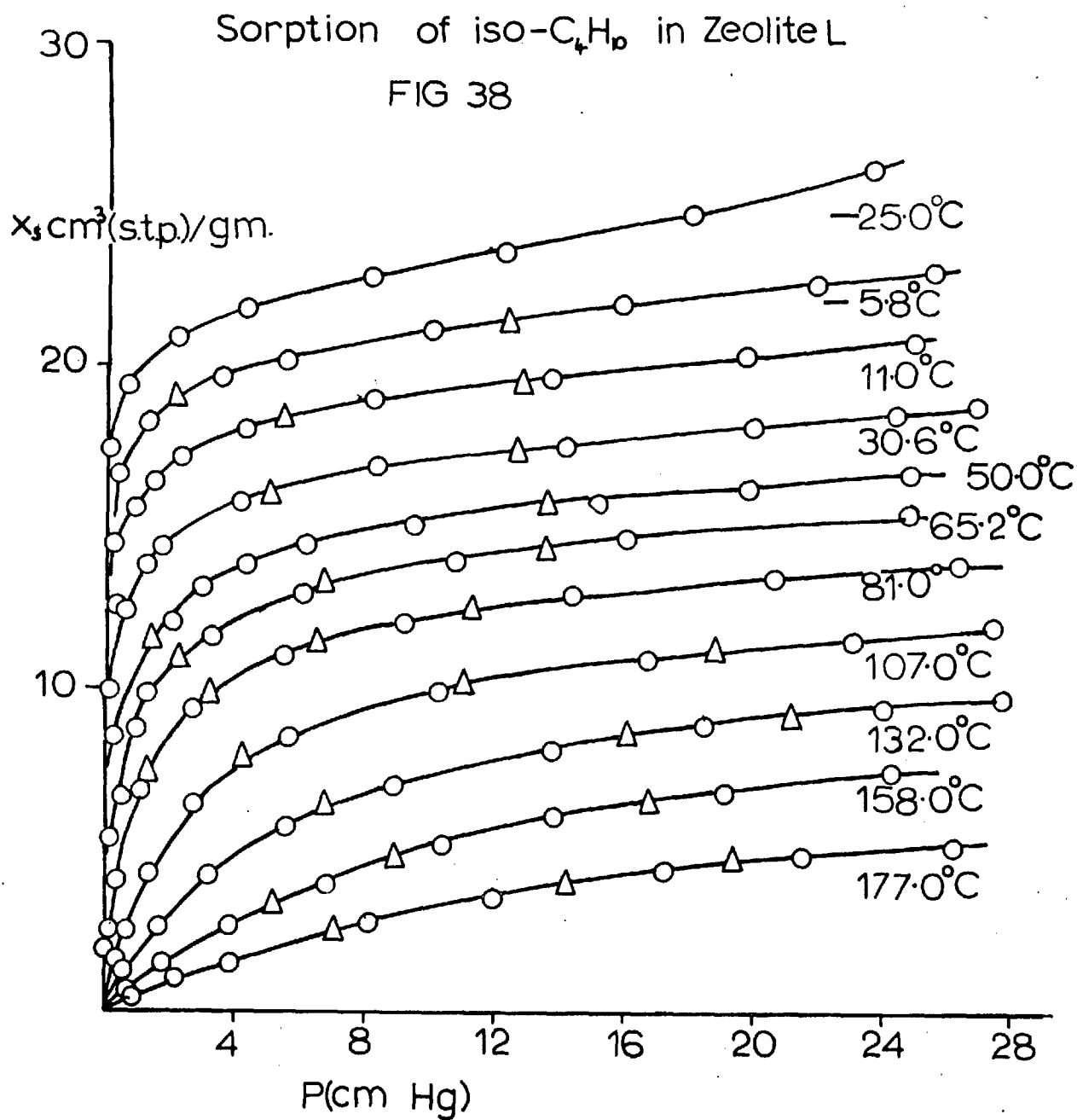




Sorption of $n\text{-C}_4\text{H}_{10}$ in Zeolite L

FIG 37





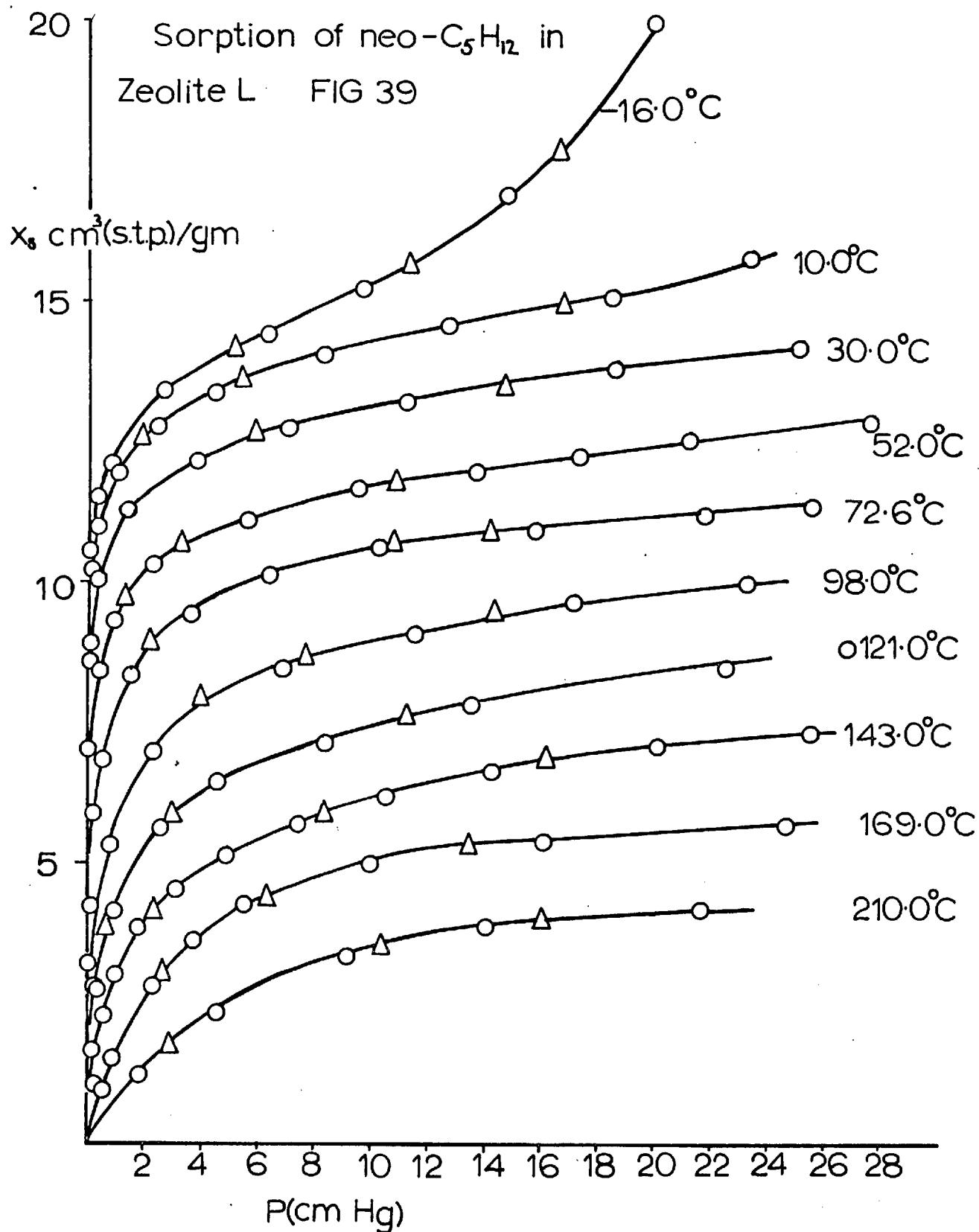


Table 22

Saturation Capacities (ccs N.T.P./g) in Zeolite LMethane/Na, K.L.

Saturation Capacity	69.3	49.7	42.9
Temperature °C	-183.1	-117.2	-94.8

Ethane/Na, K.L.

Saturation Capacity	41.6	36.9	32.3	29.7	26.0
Temperature °C	-84.5	-62.0	-37.9	-17.0	0.0

Propane/Na, K.L.

Saturation Capacity	36.4	32.5	29.6	27.3	24.6	22.4
Temperature °C	-60.0	-40.0	-20.0	0.0	22.2	42.2

Butane/Na, K.L.

Saturation Capacity	30.3	27.7	25.6	23.9	22.6	20.4
Temperature °C	0.0	26.0	40.1	55.0	71.0	90.0

Iso-butane/Na, K.L.

Saturation Capacity	25.0	22.9	21.4	19.7	17.8	16.7	15.0
Temperature °C	-25.0	-5.8	11.0	30.6	50.0	65.2	81.0

Neo Pentane/Na, K.L.

Saturation Capacity	15.7	14.8	13.6	11.8	10.9	9.3	8.3	6.4
Temperature °C	10.0	30.0	52.6	72.6	98.0	121.0	143.0	169.0

six hydrocarbons in Fig. 40.

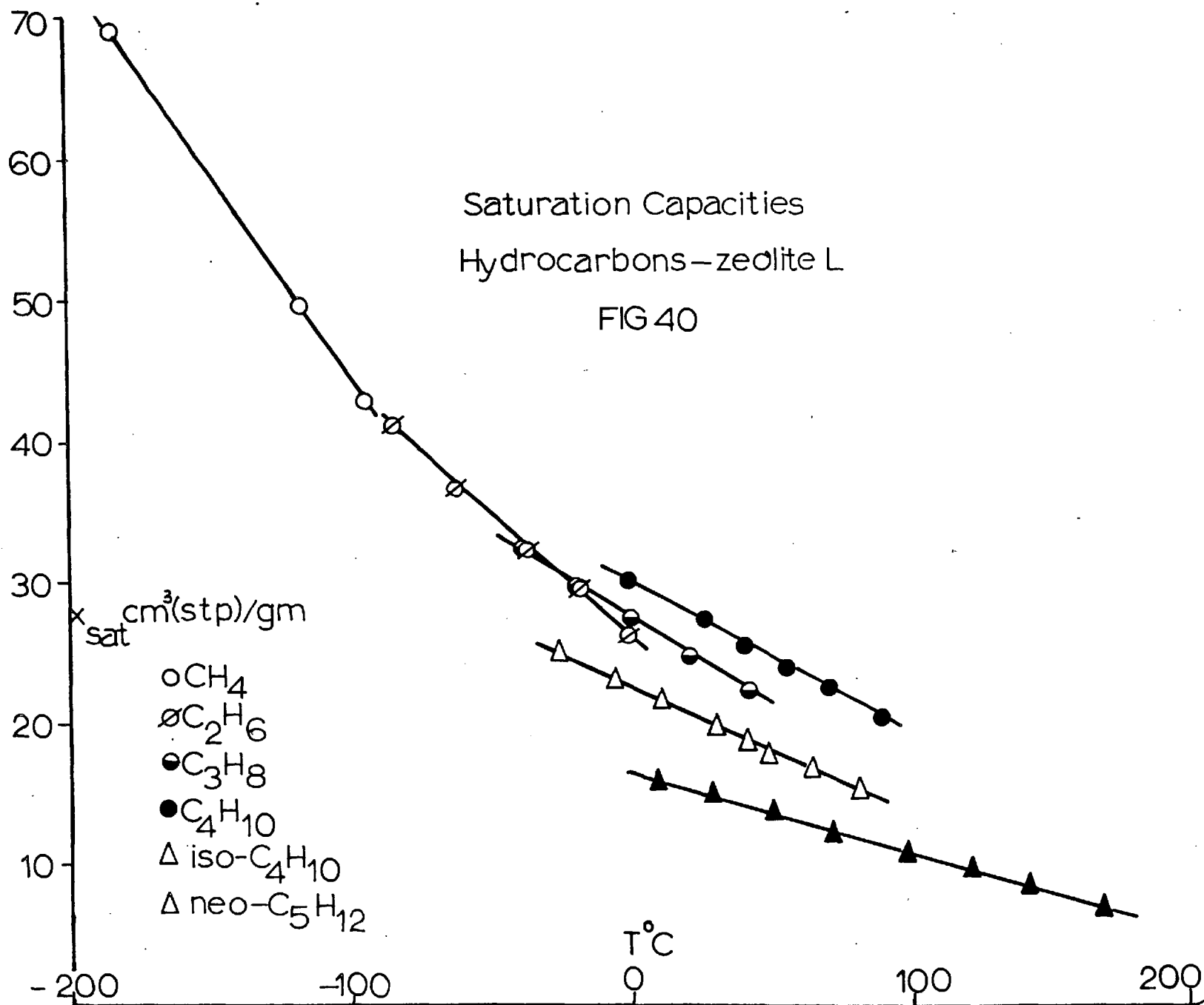
If the expansion of the sorbent is neglected over the temperature ranges studied, an approximate coefficient of cubical expansion of the sorbate can be calculated from the slopes of the plots in Fig. 40. The mean coefficients of cubical expansion obtained in this manner are given in Table 23.

Table 23

Sorbate	Temperature Range °C	Mean Coefficient of expansion $\times 10^3$
Methane	-183.1 - -94.8	5.62
Ethane	-84.5 - 0.0	5.80
Propane	-60.0 - +42.2	4.83
n-Butane	0.0 - +90.0	4.51
Iso-Butane	-25.0 - +81.0	5.01
Neo-Pentane	+10 - +169.0	6.37

7.2.3 Zeolites Ba-K and Ba-Z

Oxygen isotherms were measured on these two sorbents at -195.8°C. Equilibrium was reached very slowly in both cases and the isotherms were reversible. It seems that the sorption is diffusion controlled and probably at



Sorption Isotherms FIG 41

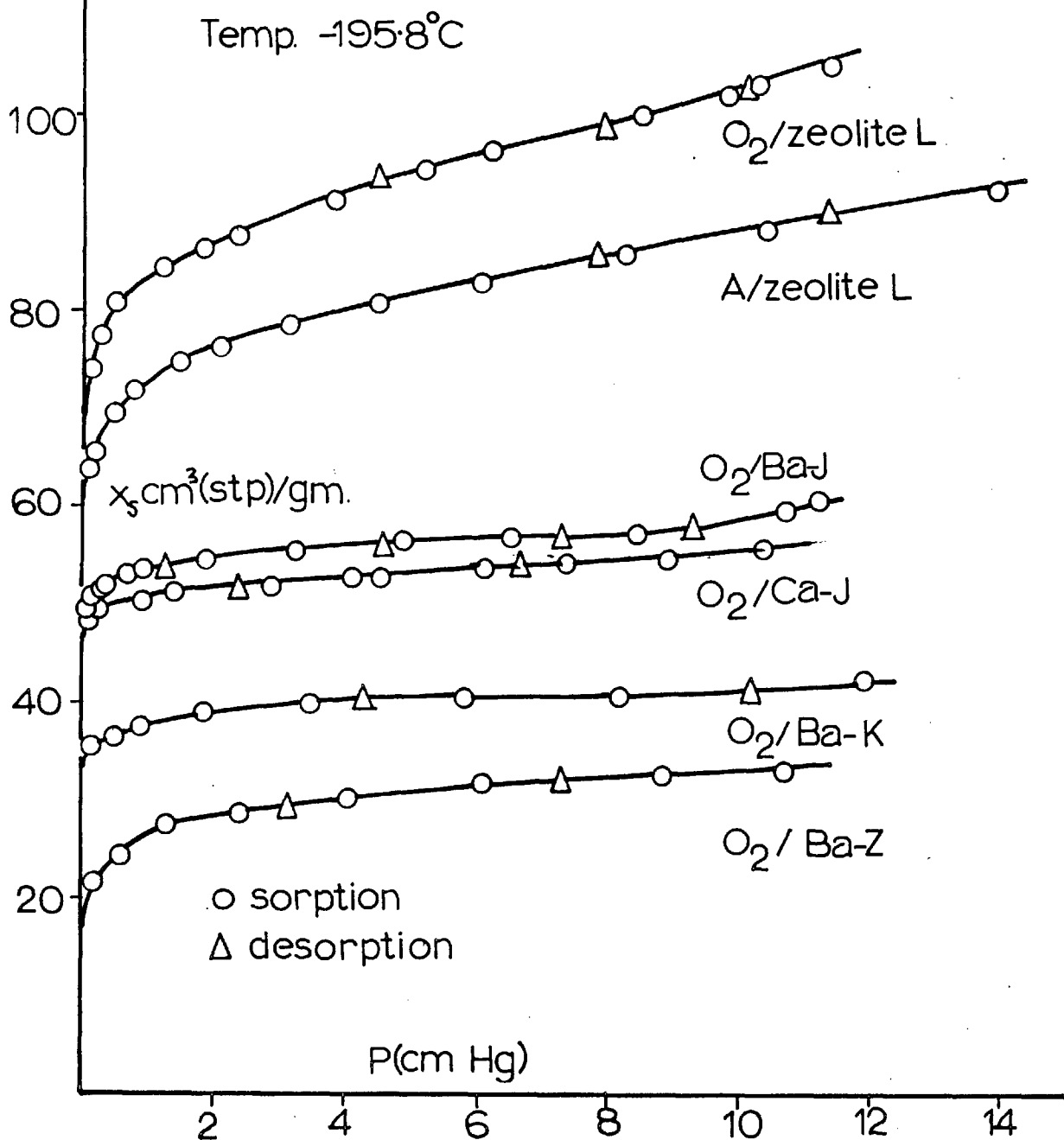
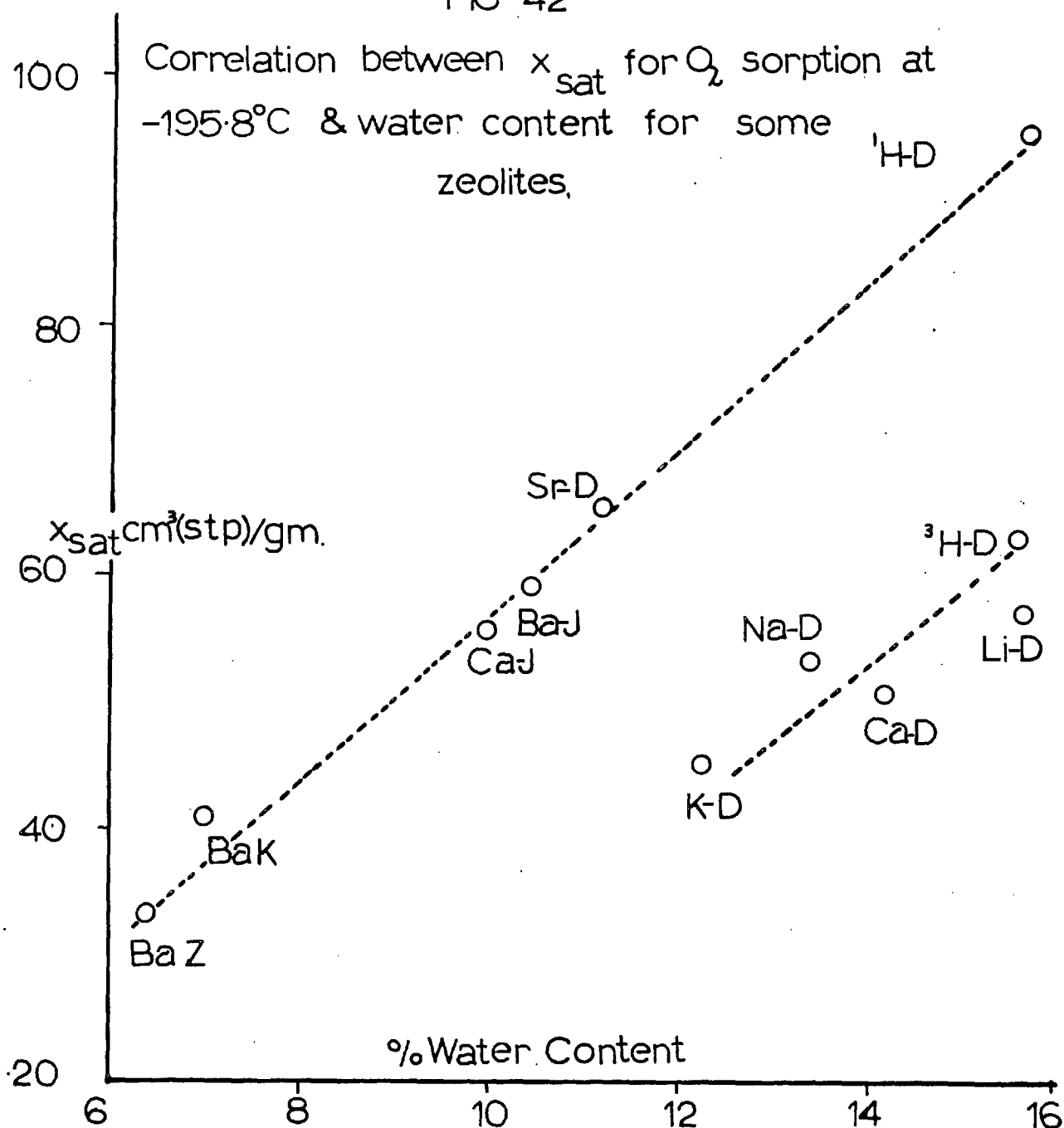


FIG 42



higher temperatures the occlusion of oxygen would be rapid. A comparison of oxygen isotherms for the barium zeolites and zeolite L is made in Fig. 41. It is seen that Ba-K and Z have the lowest sorptive capacities. It is not possible to estimate accurately the purity of these samples and the saturation capacities recorded are minimum values. Correlation between saturation capacity for oxygen and water content for some zeolites is shown in Fig. 42. BaK and BaZ have very low water contents, this may be due to sample impurities as the sorbents were hydrothermally synthesised and a little amorphous silica could be present. The water content is obviously related to the available free volume for sorption and the oxygen sorptive capacities for Ba-Z, BaK, Ca-J, Ba-J, Sr-D and 'H-D show an expected linear dependence on water contents of the original zeolites. However, some of the zeolites, namely lithium, sodium, potassium, calcium and IN acid treated ferrierite have different affinities for oxygen and their sorptive capacities have a different linear dependence on water content.

7.2.4 Gurvitsch's Rule¹¹⁰

If this rule is applicable to the present sorption results then the product of the sorbate molar volume and the saturation capacity for the particular sorbent

should be the same for all sorbates. Tables 24 and 25 give the values of this product for many of the systems investigated.

Table 24

Product of Molar Volume and Saturation Capacity ($\text{cm}^6 \text{g}^{-1}$)

Ferrierites

	O ₂	N ₂	A	Kr	Xe	CO ₂
¹ H-D	2636	2415	1944	1983	1418	-
² H-D	1883	2046	1511	1406	1129	1690
³ H-D	1843	1778	1418	829	-	1898
Li-D	1633	1729	1362	1349	1088	2049
Na-D	1487	1569	908	999	996	2358
K-D	1232	94	73	55	No uptake	1776
Ca-D	1420	1305	1130	1068	789	1450
SrD	1750	-	1510	517	427	2432

Table 25

Other Zeolites

	O ₂	N ₂	A	Kr	Xe	CO ₂
BaJ	1583	1712	1261	1114	1239	2324
CaJ	1479	-	-	-	-	-
BaK	-	-	-	-	-	-
BaZ	888	-	-	-	-	-
Na-K,L	2801	-	2206	-	-	-

Since the zeolites studied show various selectivities towards the sorbate molecules a close adherence to the rule is not expected. However, it can be seen from Tables 24 and 25 that some of the rare gases in the ferrierites and BaJ obey the rule. The low value for potassium ferrierite reflect the small uptakes and the higher values for oxygen and carbon dioxide indicate its selectivity for these sorbates.

7.2.5 Monolayer Equivalent Nitrogen Areas¹²¹

Table 26 shows equivalent areas of some porous crystals, the ferrierites and Ba-J.

Table 26

Monolayer equivalent N ₂ area (m ² /g)	Zeolite
1030	Near-faujasite ⁶³ Na-form
440	Mordenite ¹¹¹
276	¹ H-D
234	² H-D
203	³ H-D
200	Li-D
188	Na-D
155	Ca-D
11	K-D
214	Ba-J

¹H-D, the ferrierite with the highest uptake for nitrogen has a modest equivalent area, approximately one-quarter of the faujasite value and two-thirds that of mordenite. Ba-J has an equivalent of one half that of mordenite. The equivalent areas of the ferrierites and Ba-J are minimum values as the sorbents were not 100% pure.

7.3 Thermodynamic Properties of the Sorbed Phase

7.3.1 Isosteric Heat of Sorption

Isosteric heats were evaluated from series of isotherms by plotting $\log_{10} p$ vs $1/T$ for fixed amounts adsorbed.

$$\left(\frac{\partial \ln p}{\partial 1/T} \right)_n = \frac{\Delta \bar{H}_1}{R} \quad \dots \quad \dots \quad (1)$$

The isosteric heats of sorption of oxygen and neon in strontium ferrierite are shown in Fig. 43 plotted against amount sorbed ($\text{cm}^3(\text{s.t.p.})/\text{gm}$). In Fig. 44 qst for oxygen is plotted against ϕ where $\phi = \frac{x_s}{x_{\text{sat}}}$, x_{sat}

the saturation sorption, is that measured at -195.8°C and x_s is the amount adsorbed at the experimental temperature and pressure. The values of the isosteric heats for methane, ethane, propane, n-butane, iso-butane and neo-pentane in zeolite L are shown in Fig. 45 for

FIG 43

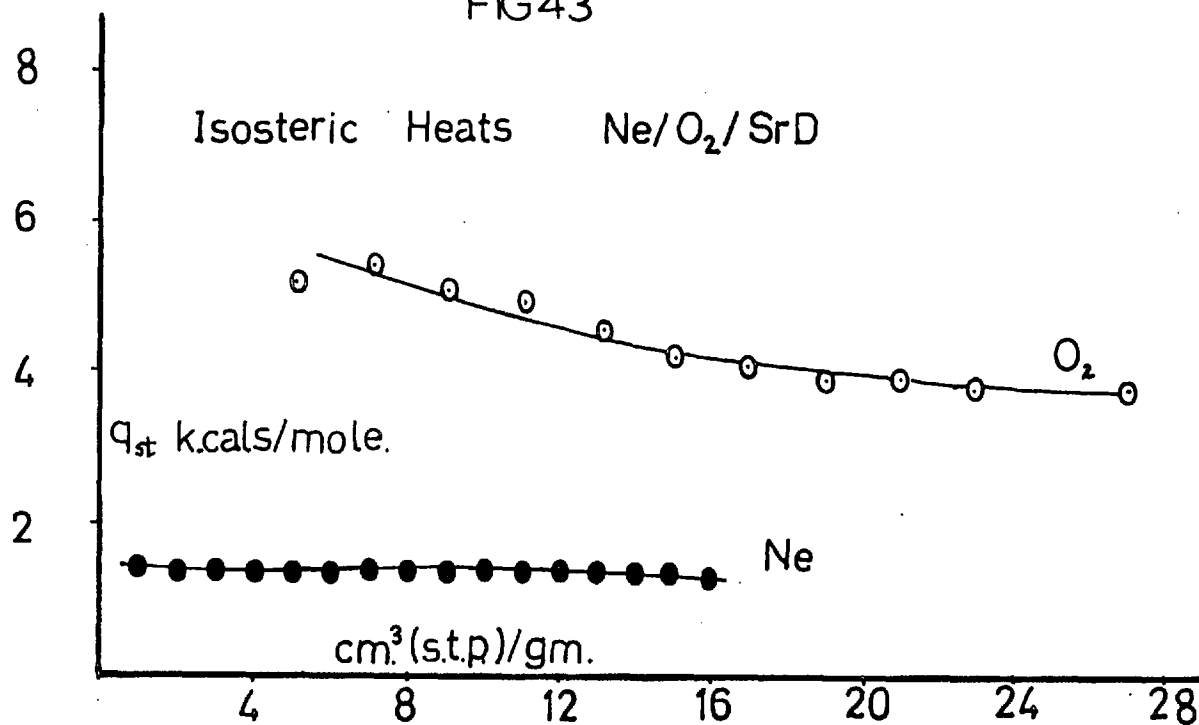


FIG 44

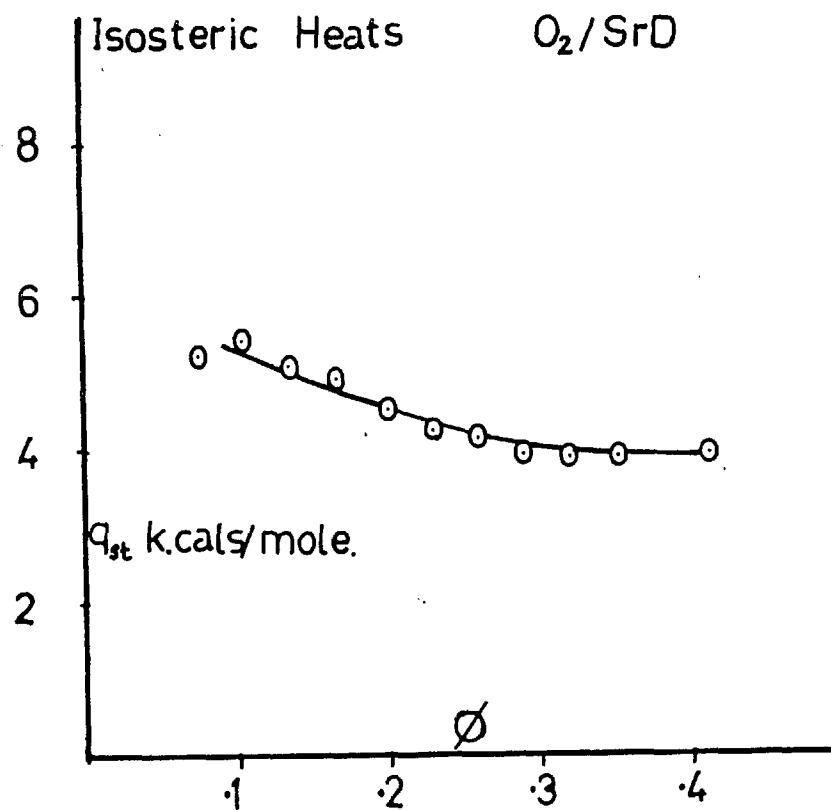
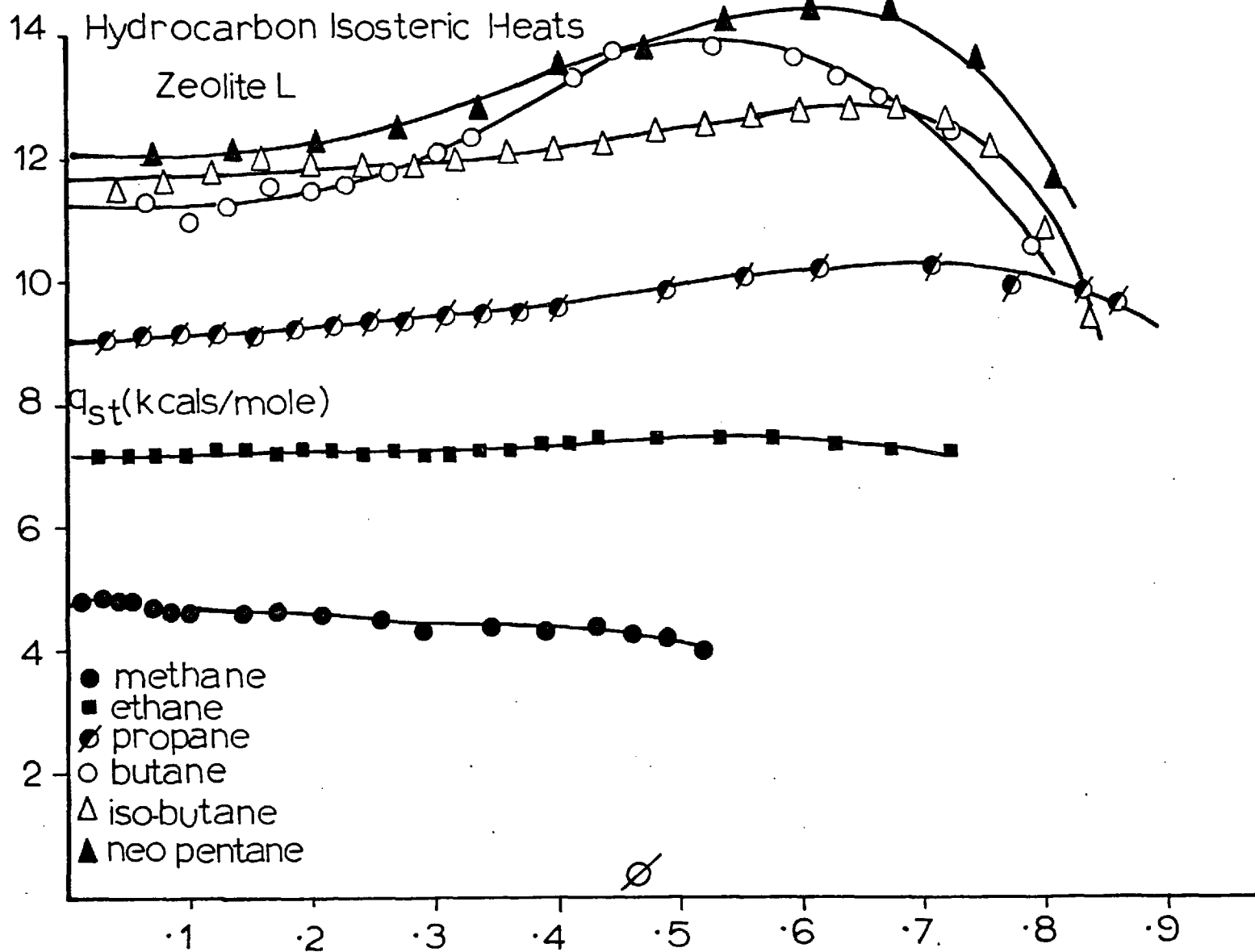


FIG 45



different values of θ . Again $\theta = \frac{x_s}{x_{\text{sat}}}$ where x_{sat} , the

saturation sorption, is that measured at -183.1°C for methane, -84.5°C for ethane, -40.0°C for propane, 0.0°C for butane, -5.8°C for iso-butane, and 30.0°C for neopentane. Since x_{sat} can be temperature dependent, the value of θ is not to be regarded as a true measure of the degree of saturation of the sorbents at experimental temperatures, but it does provide a convenient horizontal scale.

It is seen that the isosteric heat of occlusion of neon in strontium ferrierite falls off slightly with coverage and the initial value of 1.4 k cal/mole is comparable with the value obtained by Barrer-Peterson¹¹² for sodium mordenite which has a similar aluminosilicate framework to that of ferrierite. Kiselev¹¹³ reports a value of 1.0 k cal/mole for sodium A, a more open framework structure. The isosteric heat for oxygen occlusion in strontium ferrierite varies with amount sorbed, although further results are required for assessment of q_{st} at extremely low coverage. The value of q_{st} at $x/x_{\text{sat}} = .1$ is approximately $.4\text{ k cal/mole} > q_{\text{st}}$ for sodium mordenite at a comparable coverage. This seems reasonable since the strontium ion is divalent.

Zeolite L is a homogeneous sorbent with respect to all the hydrocarbons investigated. The isosteric heat

for occlusion of methane, initially 4.8 k cal/mole, decreases as ϕ increases. Barrer and Sutherland⁶³ report a similar value for occlusion in a synthetic faujasite. The isosteric heat of ethane remains constant with coverage, whereas for propane, n-butane, iso-butane and neo-pentane adsorbate-adsorbate interactions manifest themselves and the corresponding heats increase to a maximum as saturation is approached.

Table 27.

qst.(max)-qst.(int)	Hydrocarbon
1.2	Propane
2.9	n-butane
1.4	iso-butane
2.4	neo-pentane

Schirmer et al¹¹⁴ report similar isosteric heat curves for propane and n-butane in zeolite 5A with an 'energy hump' of 2 k cal/mole for propane. Dzहित¹¹⁵, Kiselev and Muttich studied the occlusion of propane, n-hexane and methyleyclohexane in zeolite X and found a similar dependence of the corresponding isosteric heats upon the degree of pore filling. The adsorbate -

adsorbate interaction increases with chain length but in the branched molecules, iso-butane and neo-pentane the 'energy hump' is less than that expected for a straight-chain counterpart as one or more carbon atoms are hidden by surrounding groups, and cannot so closely approach other interacting centres.

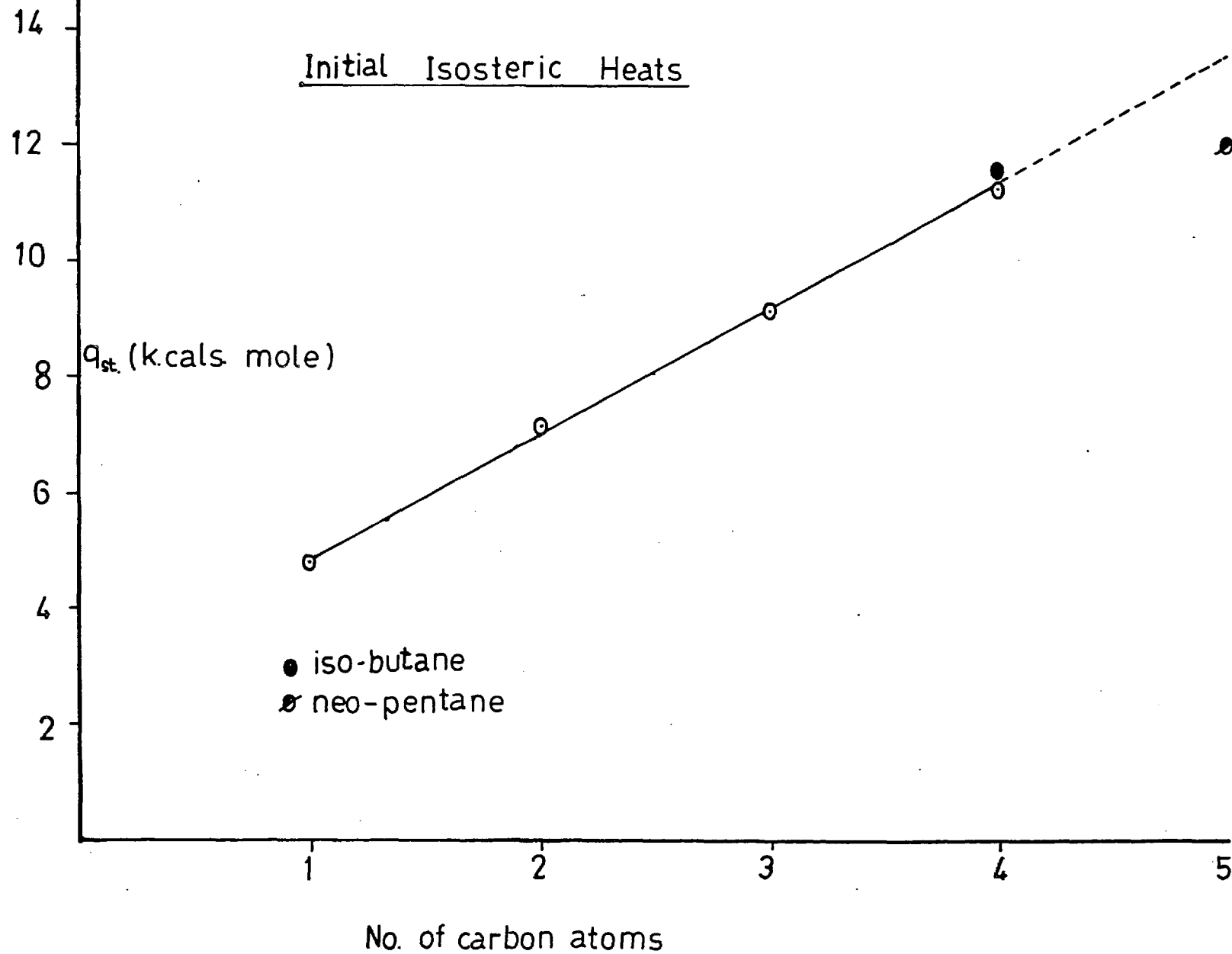
The initial isosteric heats of adsorption obtained for the n-paraffins were plotted against the number of carbon atoms in the chain, Fig. 46. The values fall along a straight line given by

$$q_{st} = 4.8 + 2.2(n - 1) \quad \dots \quad \dots \quad (2)$$

where n is the number of carbon atoms. This equation is in agreement with one proposed by Kiselev¹¹³ for n-alkane sorption in NaX, and similar to one reported by Schirmer¹¹⁴ for n-alkane sorption in 5A zeolite.

When the heats of condensation of liquid sorbate and $q_{st}(\text{initial})$ for occlusion of these same sorbates are plotted as a function of the number of carbon atoms in the molecule a similar course is shown Fig. 47. The heats are in each case functions of molecular weight, modified by molecular configuration. The ratios of the two heats are given below:

FIG 46



Initial Isosteric Heats vs Heats of Condensation

FIG 47

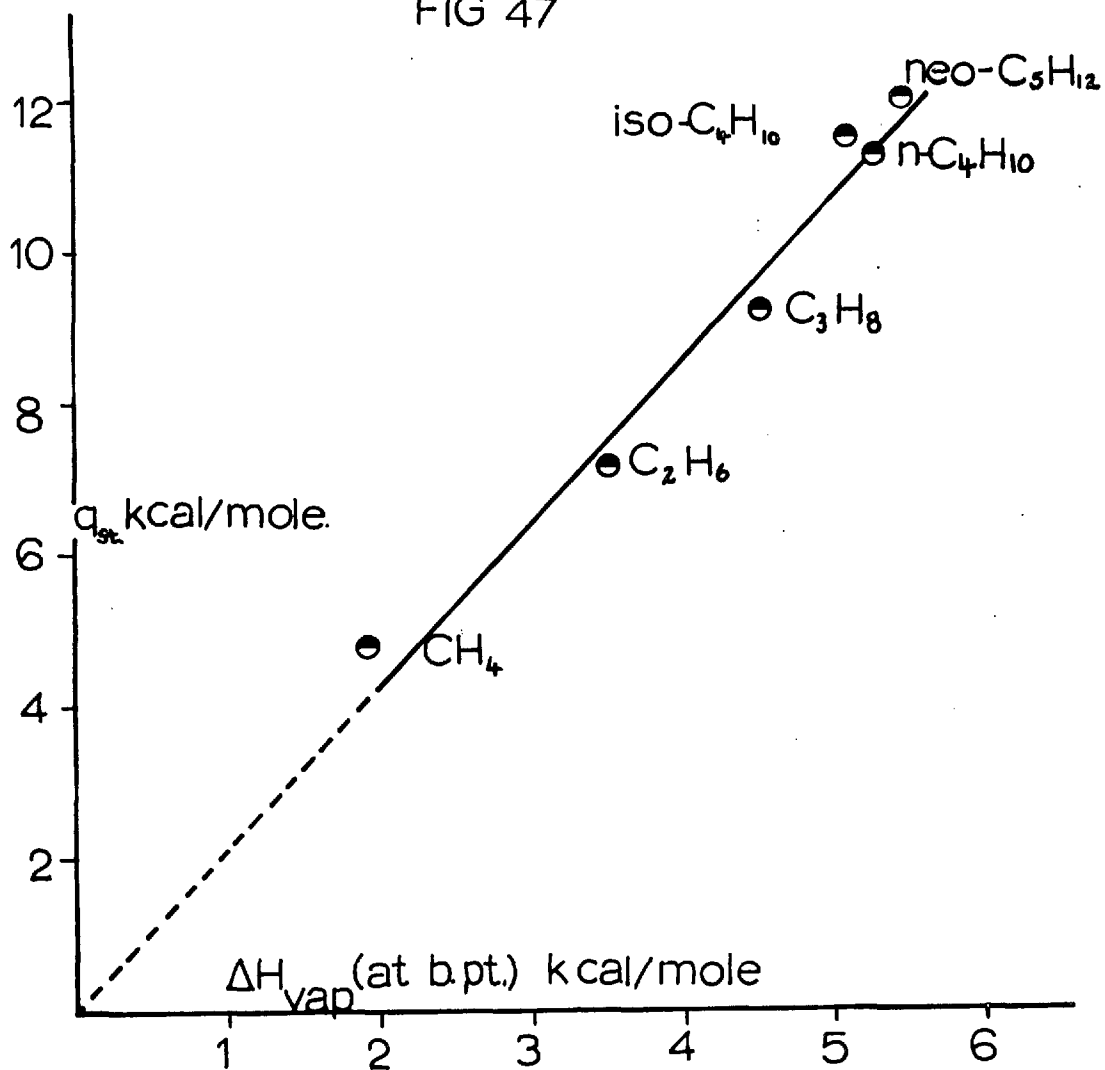


Table 28

Hydrocarbon	CH ₄	C ₂ H ₆	C ₃ H ₈	nC ₄ H ₁₀	iso-C ₄ H ₁₀	neo-C ₅ H ₁₂
$\frac{q_{st}(\text{initial})}{\Delta H(\text{liquefaction})}$	2.47	2.01	2.05	2.10	2.25	2.19

This ratio seems constant for the hydrocarbons studied in the present work. Barrer and Sutherland⁶³ evaluated $\frac{\Delta H(\text{sorption})}{\Delta H(\text{liquefaction})}$ where $\Delta H(\text{sorption})$ was a mean value of the isosteric heats over the coverage measured, and found the ratio increased with increasing molecular weight of the paraffin for sorption in synthetic faujasite. The ratios of Barrer and Sutherland were measured for increasing amounts sorbed and as the molecular weight of the sorbate increased there was a larger contribution to $\Delta H(\text{sorption})$ from sorbate-sorbate interactions.

7.3.2 Integral Heats of Sorption

The integral heats of sorption were calculated by graphical integration of curves of the isosteric heat against amount adsorbed according to the equation

$$\Delta \tilde{H}_1 = \frac{1}{n} \int_0^{n_1} \bar{\Delta H}_1 dn \quad (3)$$

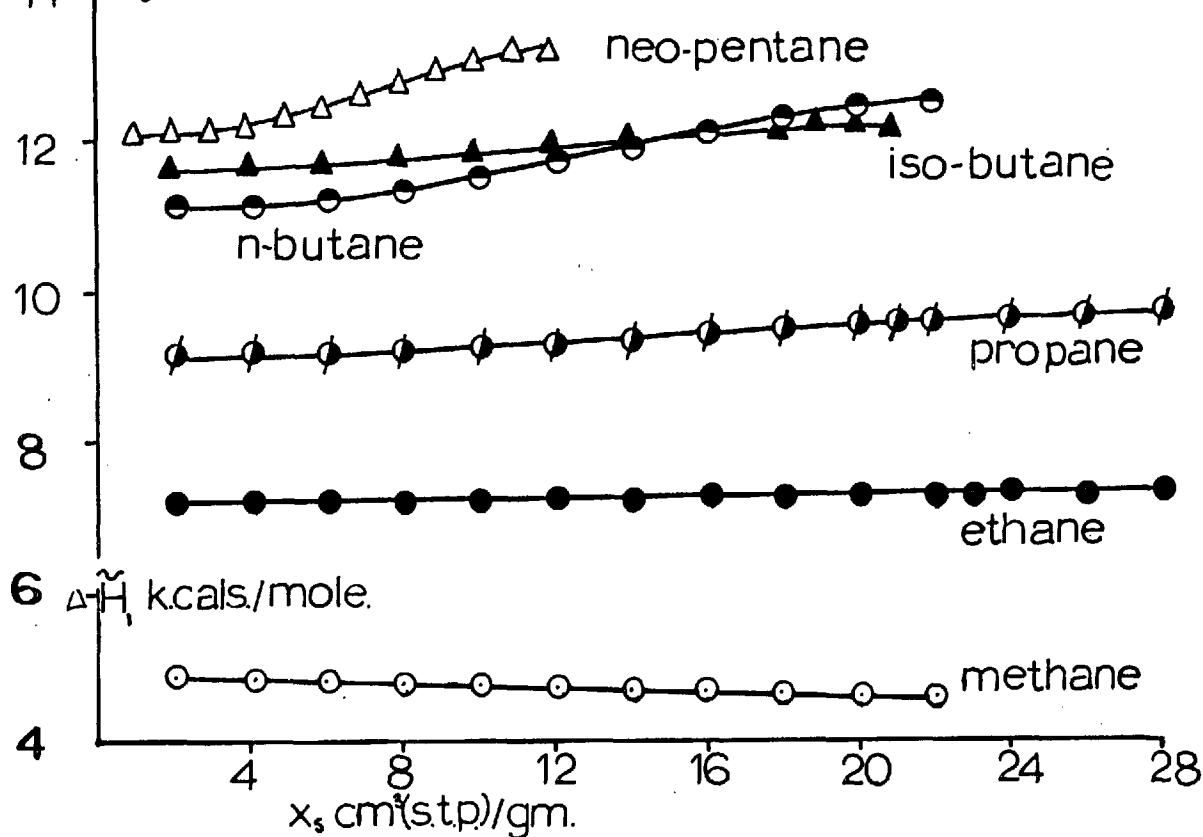
An extrapolation to zero coverage is necessary for the

integration of (3) to be carried out. The integral heat of sorption of oxygen in strontium ferrierite was obtained using the equation -

$$\Delta\tilde{H}_1 = \frac{1}{n_1 - n_2} \int_{n_2}^{n_1} \Delta\bar{H}_1 dn \quad (4)$$

The lower limit of integration, n_2 , was not zero because it would have been too inaccurate to extrapolate to zero coverage. Integral heats of sorption are shown in Figs. 48 and 49. The integral heat may be compared with the latent heat of evaporation. The integral heat should be between one and two times the latent heat of vaporisation, because of a difference in mechanism. When a molecule is removed from the interior of a liquid into the gas phase the hole left behind collapses and the liquid regains about half the heat required to remove the molecule. When the molecule is removed from a cavity in a zeolite, however, the cavity remains intact. The molecule-molecule and molecule-sorbent atom interaction energies responsible for sorption and liquefaction would of course have to be similar for the above ratio to approach two. Also the integral heat of sorption corresponds to taking not single molecules but clusters of molecules from the sorbent into the gas phase and dispersing them therein. This reduces the ratio towards unity. A comparison of values is made in the table below. It is seen that the integral heats are approximately twice

Hydrocarbons/zeolite L Integral Heats FIG48



Integral heats Strontium Ferrierite FIG49

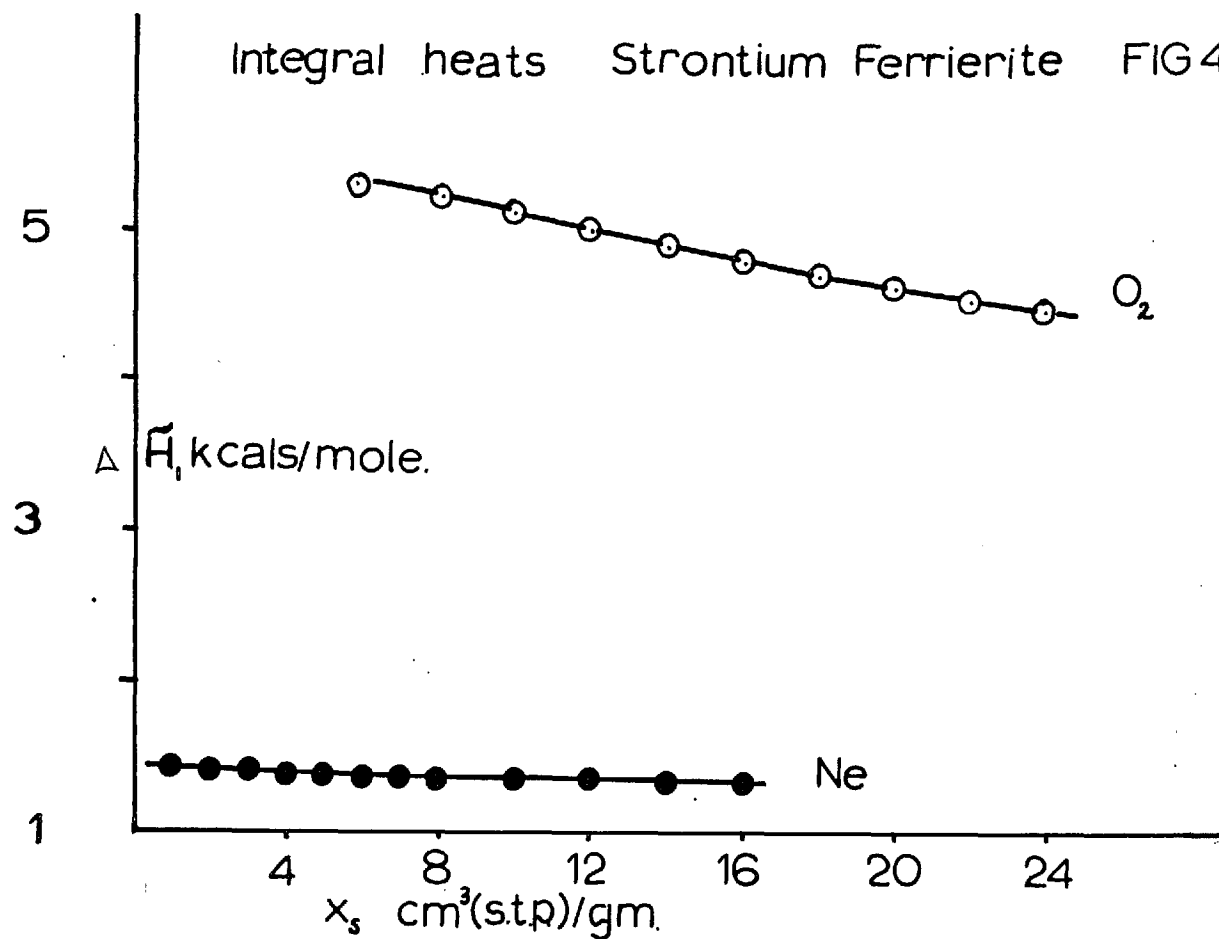


Table 29

System	C ₂ H ₆ /L	C ₃ H ₈ /L	C ₄ H ₁₀ /L	iso-C ₄ H ₁₀ /L	O ₂ /SrD
$\Delta \tilde{H}_1$ (k cal/mole)	7.1	9.5	11.5	11.9	4.8
Latent heat of evaporation of sorbate k cal/mole	2.7(0°C)	4.3(20°C)	5.9(20°C)	5.4(20°C)	1.8(-196°C)

the latent heats.

7.3.3 Differential Entropy of the Sorbates.

The differential molar entropies were obtained from the isosteric heats of sorption using the equation,

$$\bar{S}_1 = \tilde{S}_g^0 + R \ln p_0/p + \Delta \bar{H}_1/T \quad (5)$$

where p is in cm. Hg and $\Delta \bar{H}$, is in calories per mole. The standard entropy, ($\tilde{S}_g^0$) for oxygen, neon and the hydrocarbons were obtained from standard tables of entropy data.

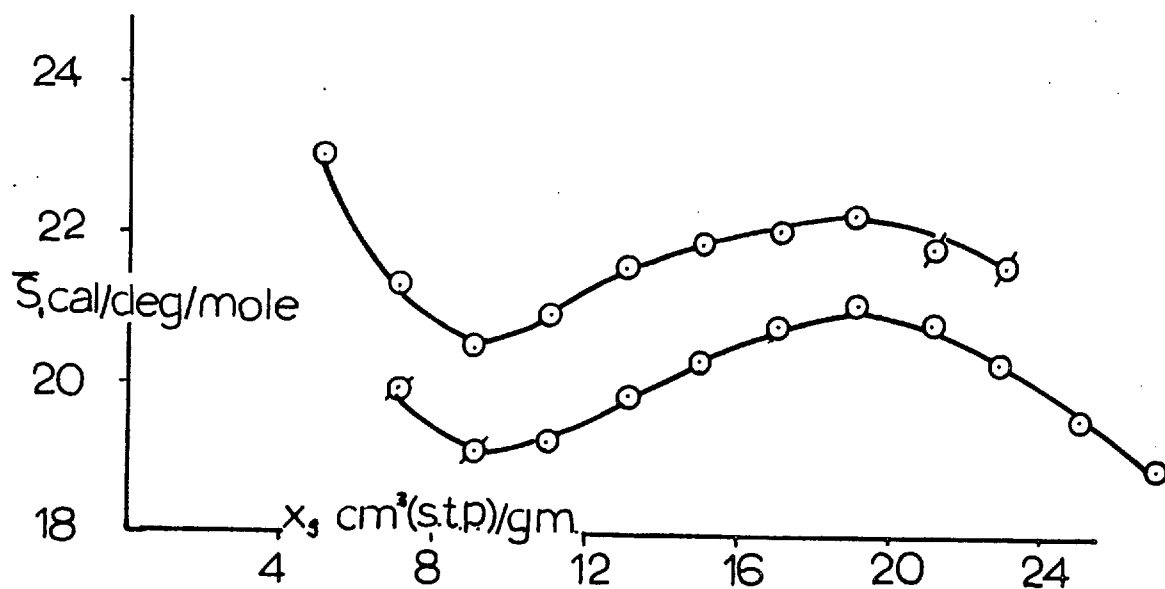
The differential molar entropies are plotted in Figs. 50 to 56. Certain portions of the curves were calculated using the temperature independence of the half standard differential entropy of sorption, according to the method of Barrer and Sutherland⁶³, (Chapter 3).

The differential entropy data for the hydrocarbons occluded in zeolite L indicate that at constant loading

Differential Entropies

 $O_2/Sr-D$

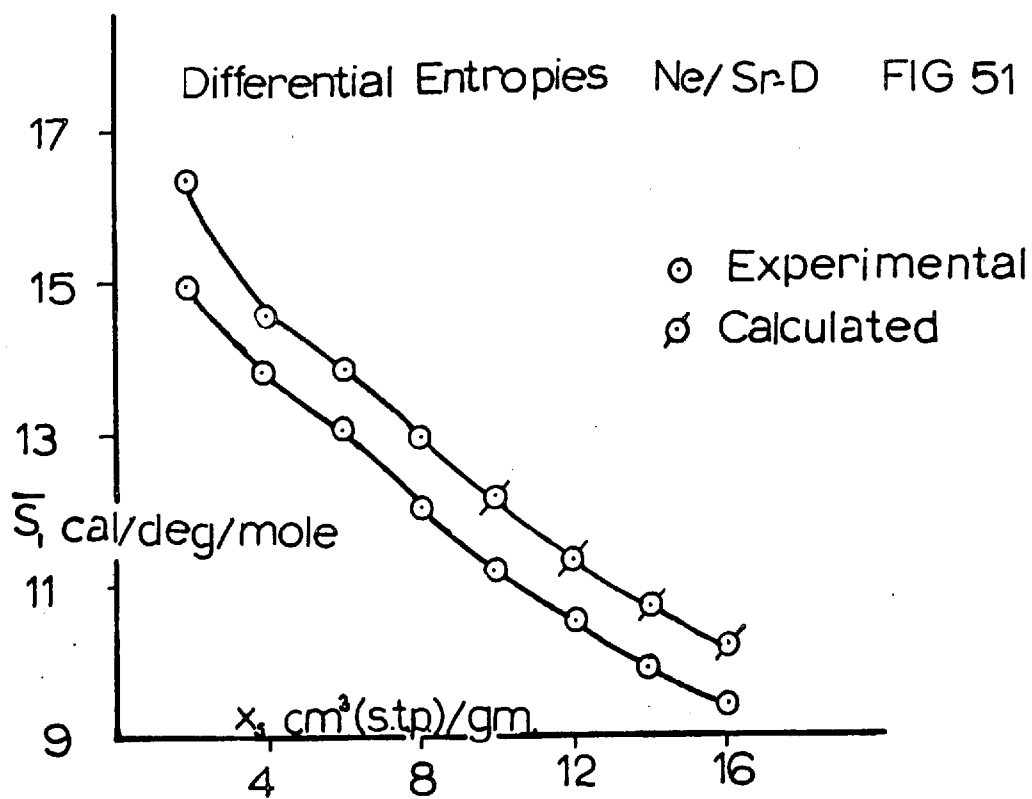
FIG 50

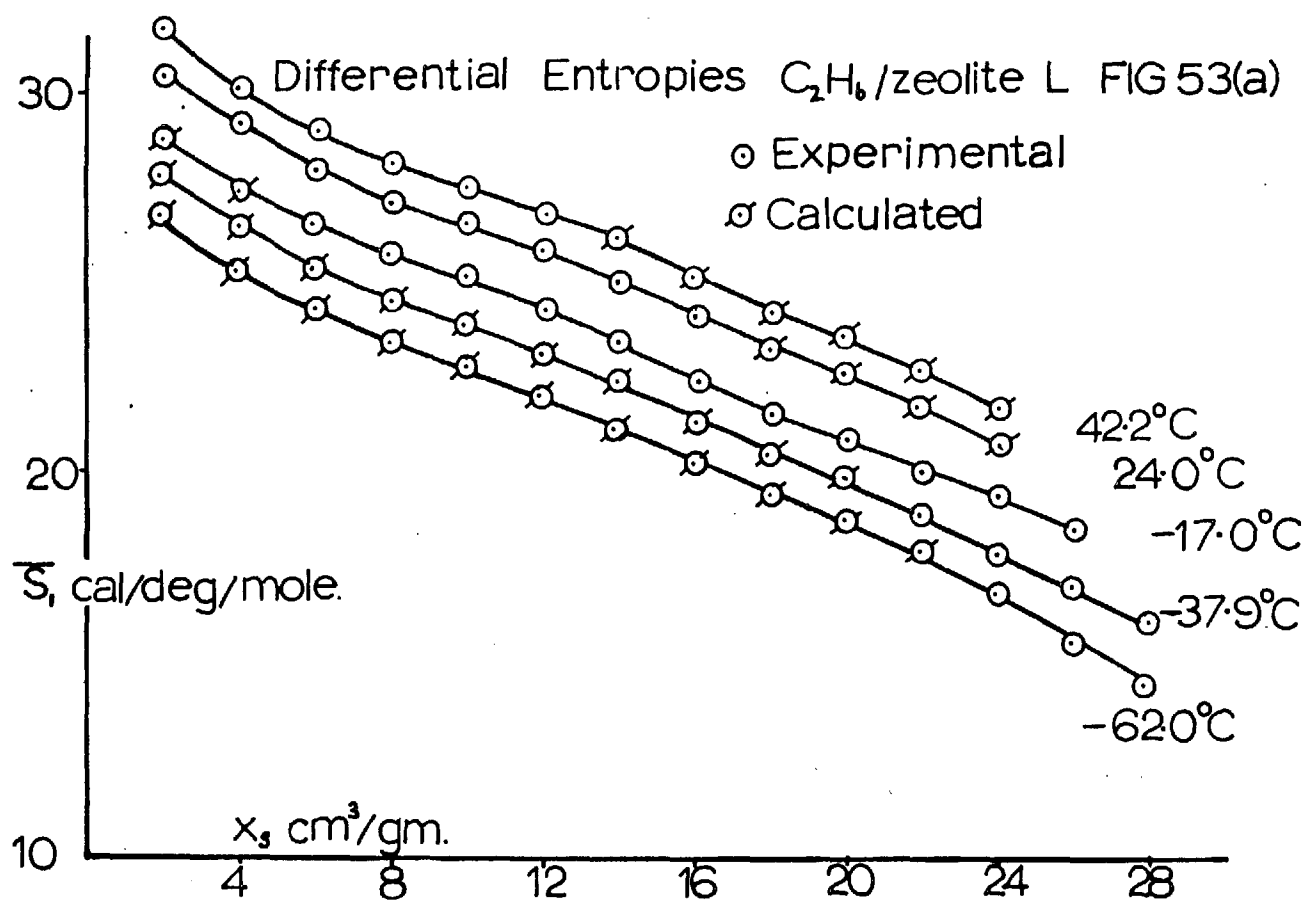
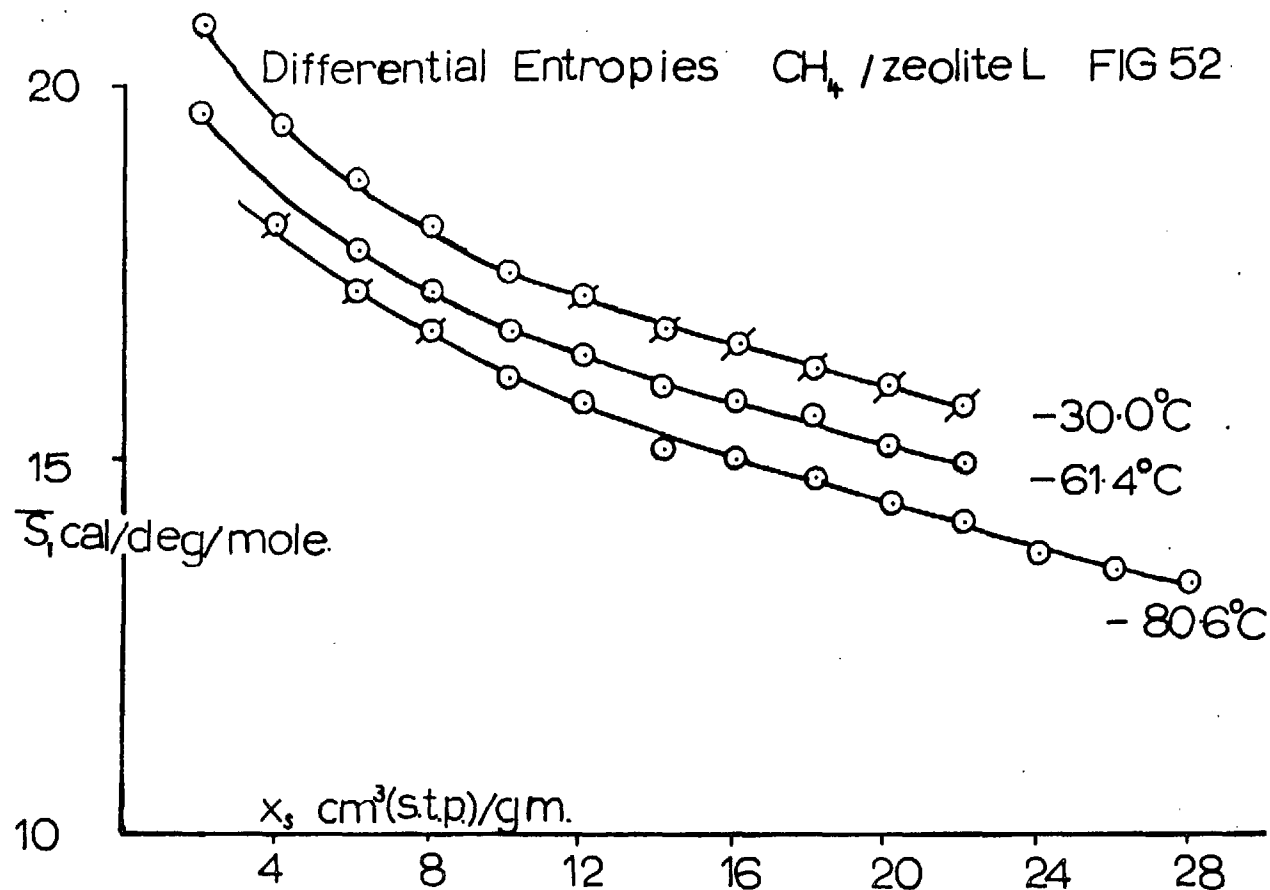


Differential Entropies

 $Ne/Sr-D$

FIG 51





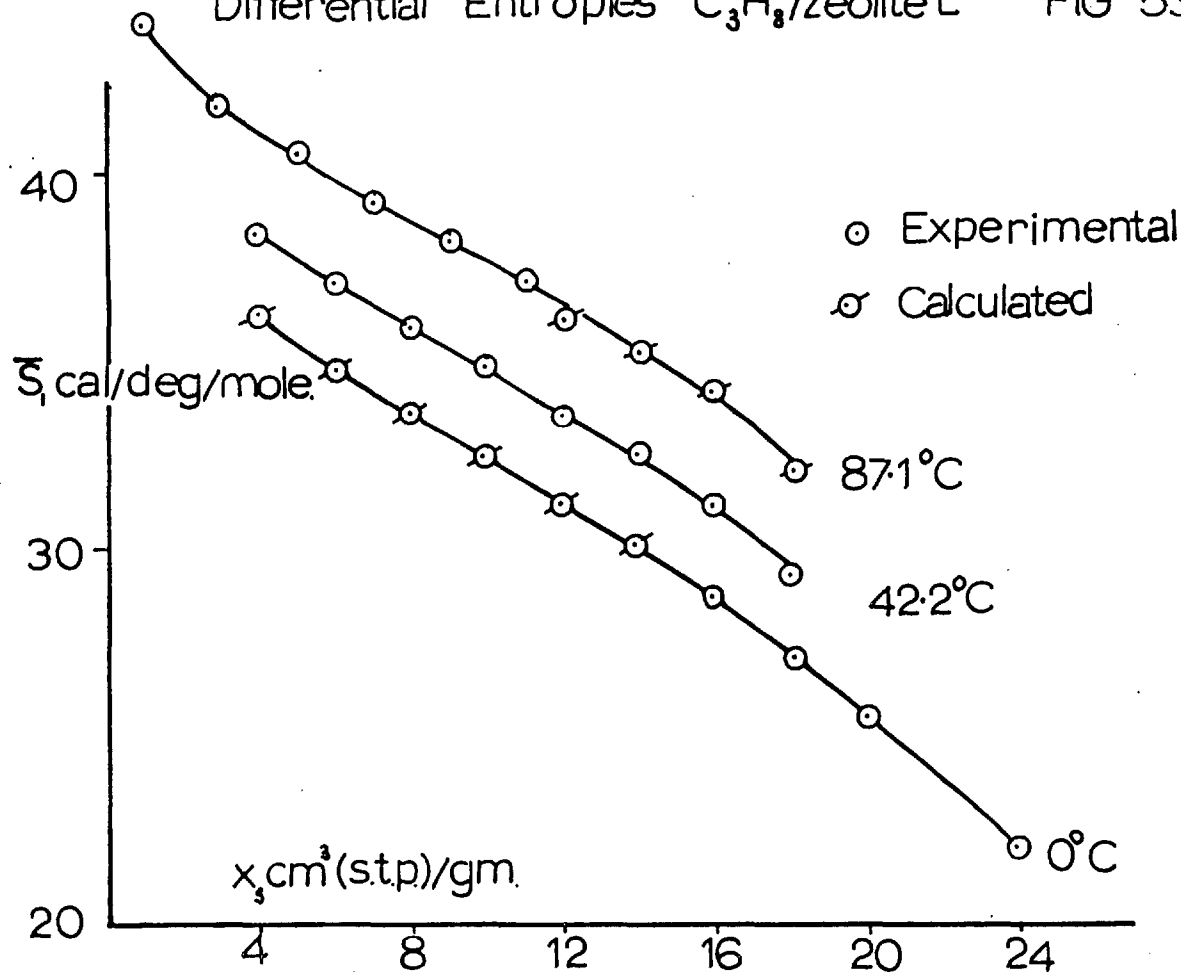
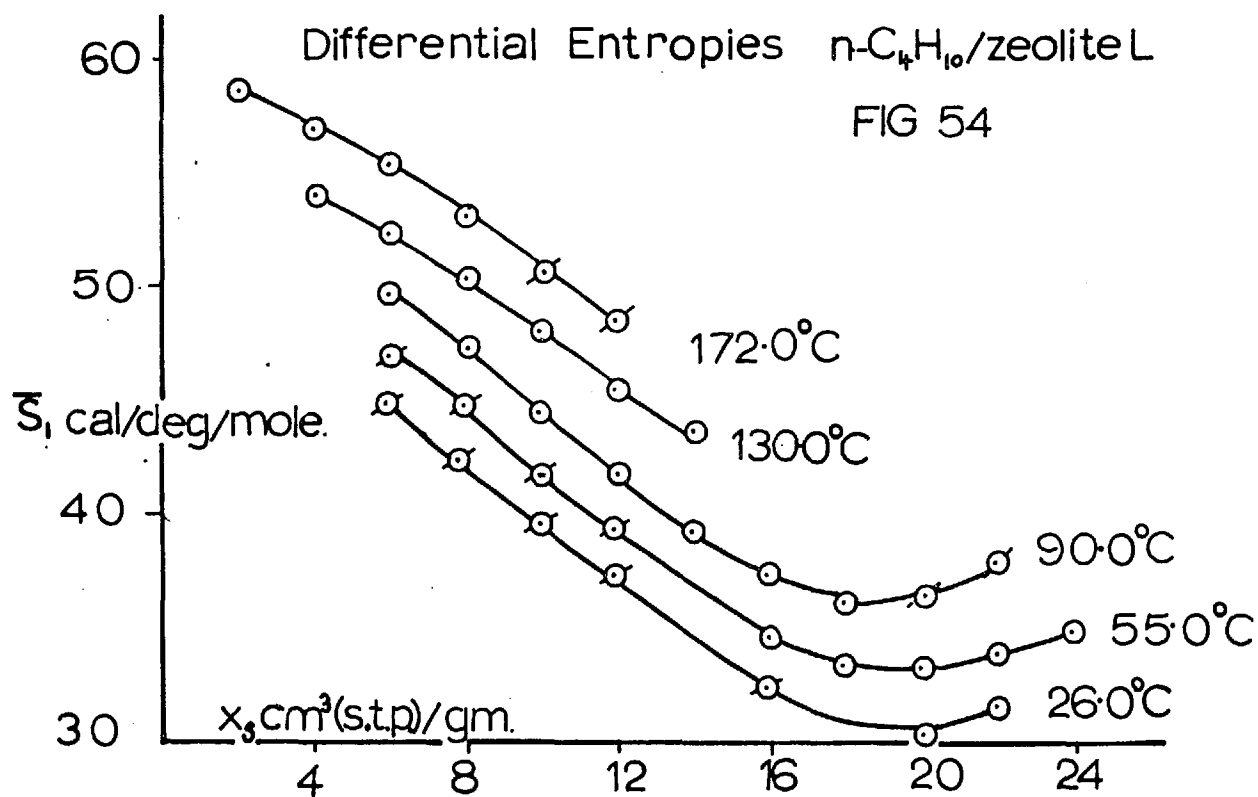
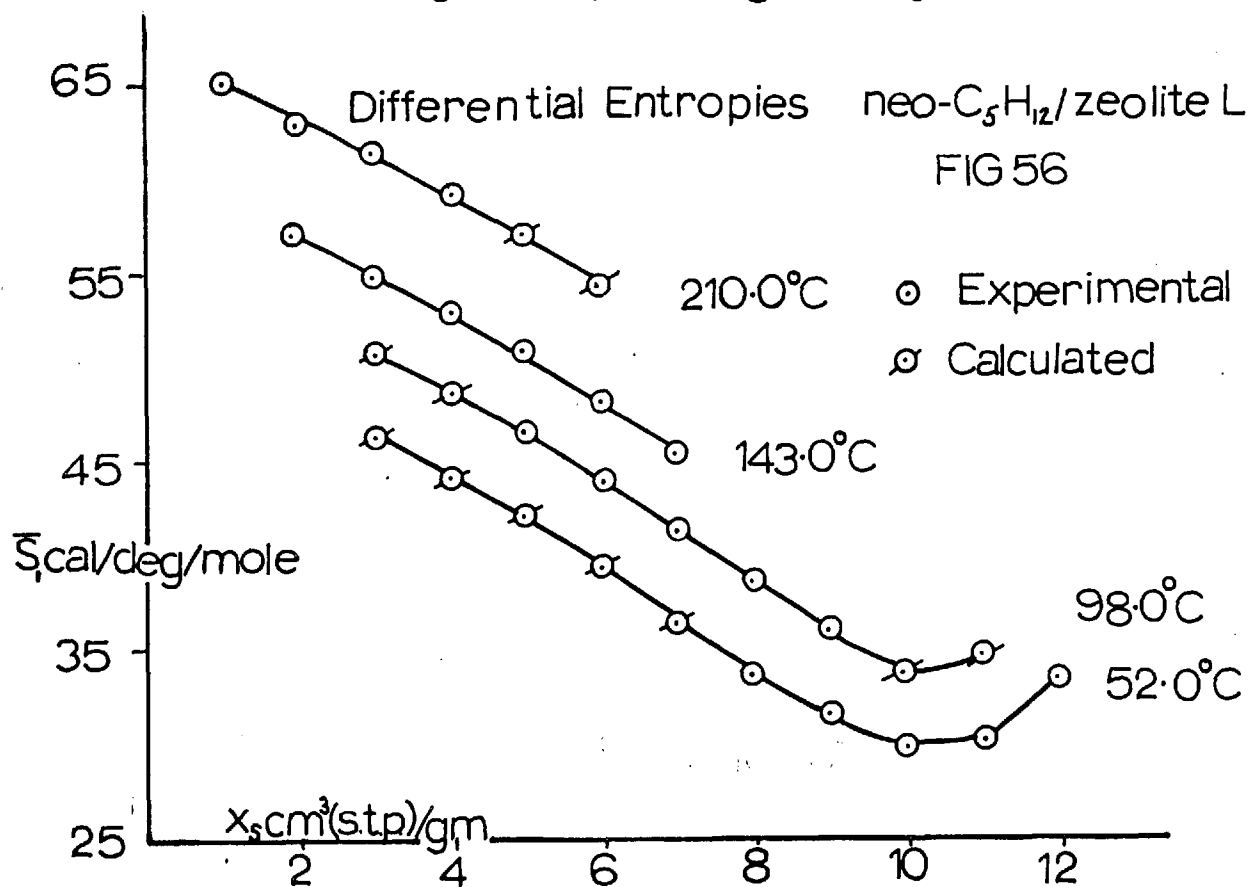
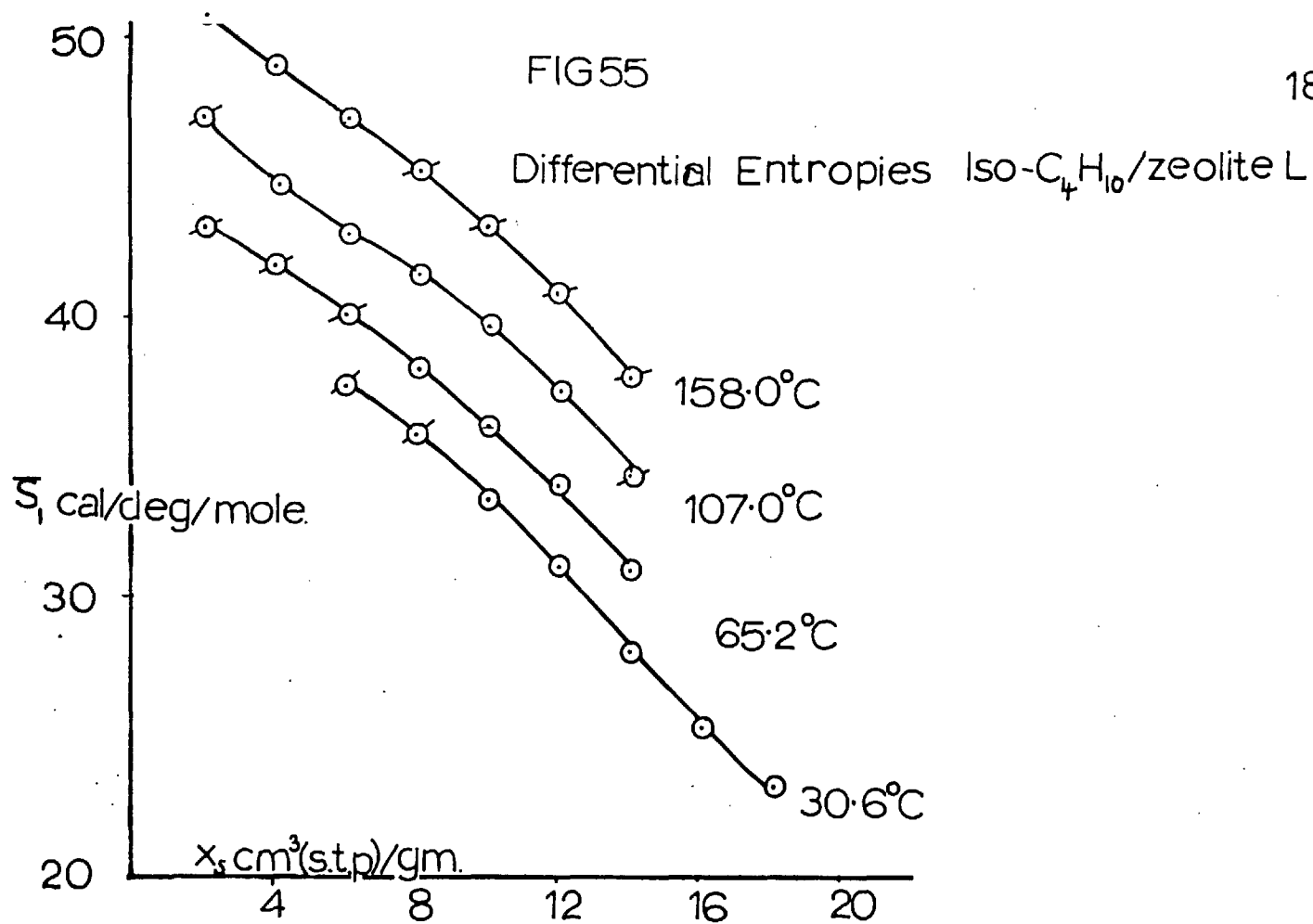
Differential Entropies C_3H_8 /zeolite L FIG 53(b)Differential Entropies $n-C_4H_{10}$ /zeolite L

FIG 54





$\bar{S}_1$ increases with the temperature as expected and at constant temperature $\bar{S}_1$ decreases with increasing loading of the adsorbent. $\bar{S}_1$ for n-butane and neo-pentane show minima at larger coverages associated with multilayer sorption and with capillary condensation involving the external surfaces of the crystallites. The differential entropy of oxygen occluded in strontium ferrierite shows a maximum at a low coverage which is characteristic of energetically heterogeneous systems¹¹⁶.

7.3.3.1 Half Standard Entropy of Adsorption

It was shown on theoretical grounds in a previous section that the half standard differential entropy of adsorption was given by -

$$\Delta\bar{S}_1 = \bar{S}_g^\circ - \bar{S}_1 \quad (6)$$

$\Delta\bar{S}_1$ should be independent of temperature for a fixed amount adsorbed, provided $\Delta\bar{H}_1$ is independent of temperature. The expected behaviour is well established by the data in Tables 36 to 42. $\Delta\bar{S}_1$ is seen to be independent of temperature for any given amount sorbed, but increases both with amount sorbed and with molecular weight of sorbate. The hydrocarbon data ~~are~~ in agreement with the observations of Barrer and Sutherland⁶³ and of Schirmer¹¹⁴ and co-workers for zeolites X and 5A.

7.3.4 Integral Entropy of Adsorption

Integral entropies of adsorption were obtained by graphical integration of plots of $\bar{S}_1$ against amount adsorbed and use was made of the equation -

$$\tilde{S}_1 = \frac{1}{n_1} \int_0^{n_1} \bar{S}_1 dn_1 \quad (7)$$

Integral entropies of adsorption calculated in this manner are shown in Figs. 57 to 59. It is of interest to compare these values with the entropies of the liquid sorbate at the same temperatures. $\tilde{S}_L = 40.0$ and 53.4 e.u. for ethane and propane respectively at temperatures 0°C and 87.1°C . These values are larger than $\tilde{S}_1$ for sorption and so it seems that the sorbate molecules within the zeolite framework have less freedom than in the liquid state.

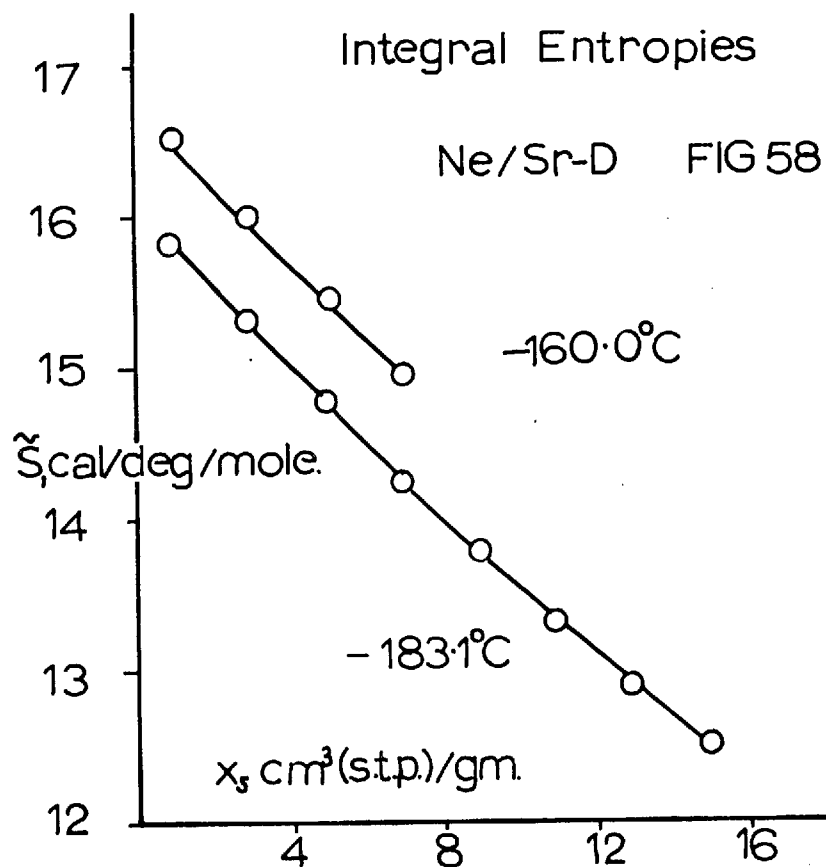
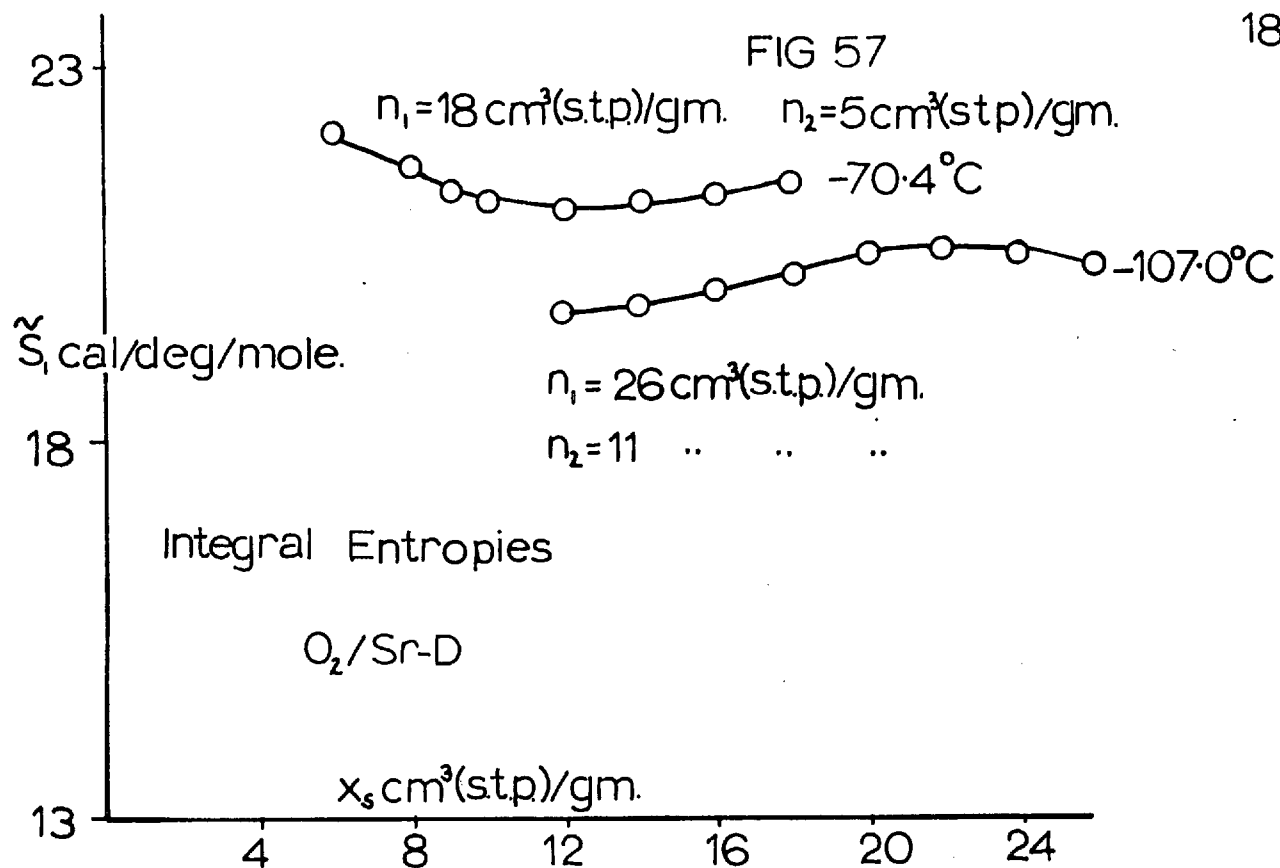
The half-standard integral entropy of sorption defined as -

$$\Delta\tilde{S}_1 = \tilde{S}_g^\circ - \tilde{S}_1 \quad (8)$$

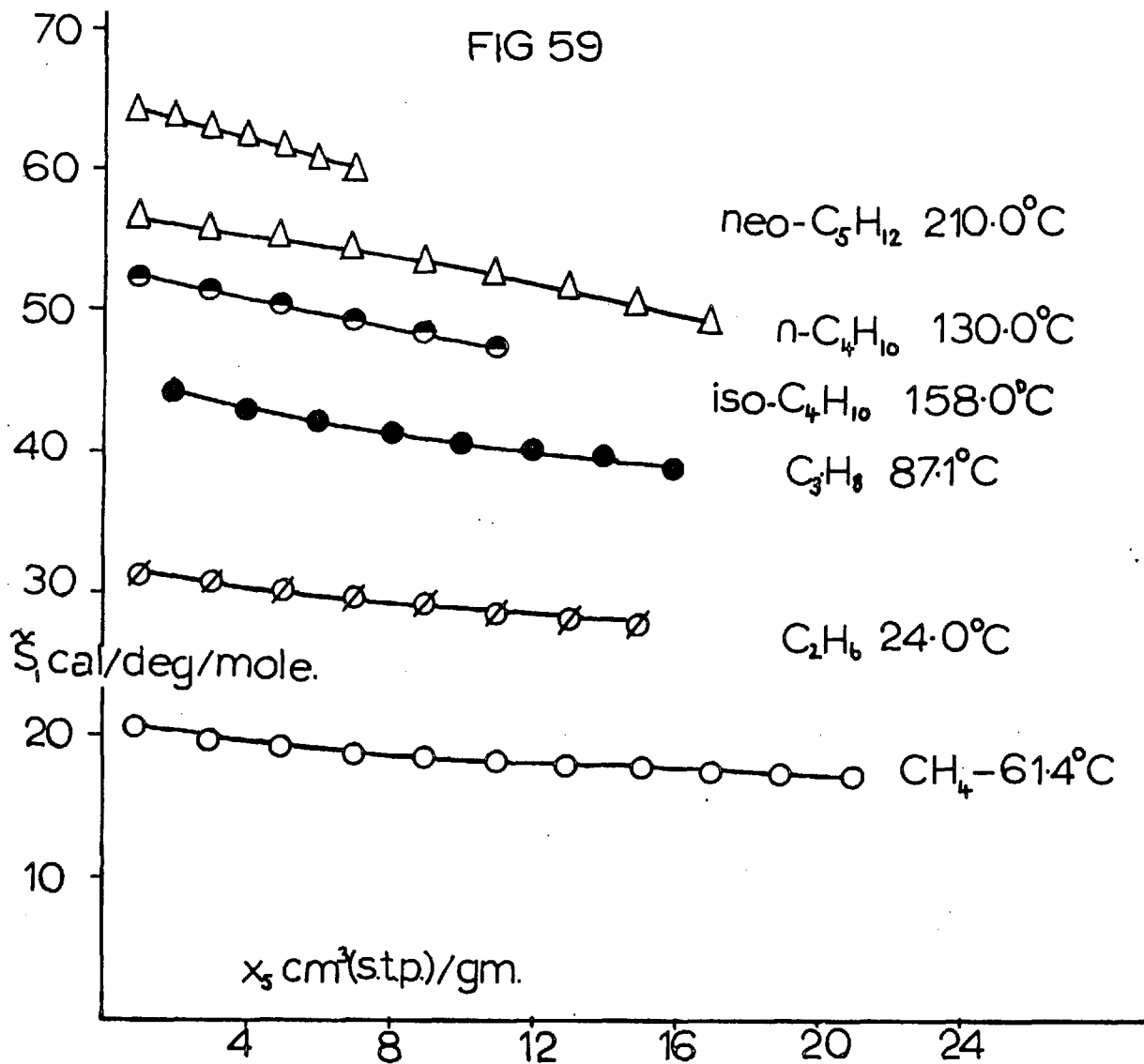
should be independent of temperature for a fixed amount sorbed, provided $\Delta\bar{H}_1$ is independent of temperature⁶³.

The expected behaviour is well established by the data in Tables 43 and 48.

FIG 57



Integral Entropies Zeolite L



Isosteric Heat TablesAll qst. values are expressed in k.cals/mole.Table 30Methane-Na,K.L. Isosteric Heats

θ (Coverage)	qst.
•014	4•8
•029	4•9
•043	4•8
•058	4•8
•072	4•7
•087	4•6
•101	4•6
•144	4•6
•173	4•7
•216	4•6
•259	4•5
•289	4•3
•346	4•4
•390	4•3
•433	4•4
•462	4•3
•491	4•2
•519	4•0

x_{sat} for methane = 69•3 ccs
 N.T.P./g. at -183•1°C.

Table 31Ethane-Na,K.L. Isosteric Heats

θ (Coverage)	qst.
•024	7•2
•048	7•2
•072	7•2
•096	7•2
•120	7•3
•144	7•3
•168	7•2
•192	7•3
•216	7•3
•240	7•2
•264	7•3
•288	7•2
•313	7•2
•337	7•3
•361	7•3
•385	7•4
•409	7•4
•433	7•5
•481	7•5
•529	7•5
•577	7•5
•625	7•4
•673	7•3
•721	7•3

x_{sat} for ethane = 41•6ccs
 N.T.P./g. at -84•5°C

Table 32Propane-Na,K.L. Isosteric Heats

θ (Coverage)	qst.
•031	9•1
•062	9•2
•092	9•2
•123	9•2
•154	9•1
•185	9•3
•215	9•3
•246	9•4
•277	9•4
•308	9•5
•338	9•5
•369	9•6
•400	9•6
•492	9•9
•554	10•2
•615	10•3
•708	10•3
•769	10•0
•831	9•9
•862	9•8
•923	9•5

x_{sat} for propane = 32•5 ccs
 N.T.P./g.at -40•0°C

Table 33n-Butane-Na,K.L. Isosteric Heats

θ (Coverage)	qst.
•066	11•4
•099	11•0
•132	11•3
•165	11•7
•198	11•5
•231	11•6
•264	11•8
•297	12•2
•330	12•4
•429	13•4
•495	13•8
•528	13•8
•595	13•7
•627	13•4
•660	13•1
•726	12•5
•792	10•5

x_{sat} for n Butane = 30•3 ccs
 N.T.P./g.at 0•0°C

Table 34Iso-Butane-Na,K.L. Isosteric Heats

θ (Coverage)	qst.
•040	11•5
•080	11•7
•120	11•8
•160	12•1
•200	12•0
•240	11•9
•280	11•9
•320	12•0
•360	12•2
•400	12•2
•440	12•3
•480	12•5
•520	12•6
•560	12•8
•600	12•8
•640	12•9
•680	12•9
•720	12•7
•760	12•3
•800	10•9
•840	9•4

Table 35Neo-pentane-Na,K.L. Isosteric Heats

θ (Coverage)	qst.
•068	12•1
•135	12•2
•203	12•3
•270	12•5
•338	12•7
•405	13•6
•473	13•8
•541	14•3
•608	14•5
•676	14•5
•743	13•7
•810	11•7

 x_{sat} for neo-pentane = 14•8 ccs

N.T.P./g. at 30•0°C

 x_{sat} for iso butane = 22•9 ccs

N.T.P./g. at 5•8°C

Table 36

Oxygen/Sr-DNeon/Sr-D

x_s cm ³ (s.t.p.)/gm	-70.4°C	-107.9°C	x_s cm ³ (s.t.p.)/gm	-160°C	-183.1°C
11	25.40	25.57	2	13.87	14.18
13	24.87	25.01	4	15.47	15.52
15	24.45	24.68	6	16.14	16.18
17	24.28	24.26	8	17.05	17.24
19	24.02	23.98			

$$\Delta \bar{S}_1 = \bar{S}_{g^0} - \bar{S}_1$$

Table 37

Methane/zeolite L

x_s cm ³ (s.t.p.)/gm	-30.0°C	-61.4°C	-80.6°C
2	22.21	22.55	-
4	23.56	23.87	-
6	24.25	24.33	-
8	24.79	24.82	-
10	25.46	25.41	25.49
12	-	25.68	25.80
14	-	26.25	26.47
16	-	26.34	26.39
18	-	26.52	26.80
20	-	27.02	27.03
22	-	27.18	27.28

$$\Delta \bar{S}_1 = \bar{S}_{g^0} - \bar{S}_1$$

Table 38Ethane/zeolite L

x_s cm ³ (s.t.p.)/gm	-62.0°C	-37.9°C	-17.0°C	24.0°C	46.2°C
2	-	-	-	24.21	24.02
4	-	-	-	25.58	25.55
6	-	-	26.40	26.69	26.74
8	-	-	27.40	27.58	27.56
10	-	-	27.89	28.11	28.12
12	-	-	38.65	28.88	28.94
14	-	-	29.50	29.64	-
16	-	-	30.57	30.66	-
18	-	-	31.59	-	-
20	-	-	32.05	-	-
22	-	32.96	32.98	-	-
24	34.01	34.05	-	-	-

Table 39Propane/zeolite L

x_s cm ³ (s.t.p.)/gm	0°C	42.2°C	87.1°C
4		26.91	26.80
6		28.35	28.35
8		29.47	29.39
10		30.54	30.51
16	34.33	34.29	-
18	36.10	36.20	-

Table 40n Butane/zeolite L

x_s cm ³ (s.t.p.)/gm	26.0°C	55.0°C	90.0°C	130.0°C	172.0°C
2				25.40	26.38
4				27.92	28.10
6			29.35	29.52	29.58
8			31.41	31.50	31.63
10			34.36	34.16	-
12			36.76	36.60	-
14			39.02	38.90	-
16		41.74	41.41	-	-
18		42.99	42.93	-	-
20	44.12	44.19	-	-	-
22	42.74	42.54	-	-	-

Table 41Iso-butane/zeolite L

x_s cm ³ (s.t.p.)/gm	30.6°C	65.2°C	107.0°C	158.0°C
4			31.50	31.92
6			33.62	33.61
8		35.09	35.00	
10		37.01	36.90	
12	39.56	39.52	39.56	
14	42.53	42.56		

Table 42

Neo-pentane/zeolite L

x_s cm ³ (s.t.p.)/gm	52.0°C	98.0°C	143.0°C	210°C
2			27.38	27.23
3			29.66	29.55
4			31.52	31.53
5		33.60	33.53	
6		36.21	36.33	
7		38.92	38.92	
8	41.57	41.55		

Table 43

Methane/zeolite L $\Delta \tilde{S}_1 = \tilde{S}_{g^0} - \tilde{S}_1$

Volume occluded cm ³ (s.t.p.)/gm	-61.4°C	-30.0°C
1	21.53	21.53
3	22.43	22.33
5	22.84	22.70
7	23.32	23.40
9	23.65	23.67

Table 44Ethane/zeolite L $\Delta \tilde{S}_1 = \tilde{S}_g^0 - \tilde{S}_1$

Volume occluded cm ³ (s.t.p.)/gm	46.2°C	24.0°C
1	23.55	23.58
3	23.98	23.92
5	24.60	24.59
7	25.25	25.19
9	25.68	25.71
11	26.08	26.16

Table 45Propane/zeolite L $\Delta \tilde{S}_1 = \tilde{S}_g^0 - \tilde{S}_1$

Volume occluded cm ³ (s.t.p.)/gm	87.1°C	42.2°C
2	23.80	23.78
4	24.88	24.87
6	25.71	25.62
8	26.42	26.46
10	27.07	27.03

Table 46n-Butane/zeolite L $\Delta\tilde{S}_1 = \tilde{S}_g^0 - \tilde{S}_1$

Volume occluded cm ³ (s.t.p.)/gm	130.0°C	90.0°C
7	27.61	27.60
9	28.48	28.56
11	29.46	29.45
13	30.66	30.61

Table 47Iso-Butane/zeolite L $\Delta\tilde{S}_1 = \tilde{S}_g^0 - \tilde{S}_1$

Volume occluded cm ³ (s.t.p.)/gm	158°C	107°C
1	27.58	27.59
3	28.65	28.60
5	29.89	29.87

Table 48Neo-pentane/zeolite L $\Delta\tilde{S}_1 = \tilde{S}_g^0 - \tilde{S}_1$

Volume occluded cm ³ (s.t.p.)/gm	210°C	143°C
1	26.52	26.44
2	27.20	27.08
3	27.87	27.57
4	28.56	28.44

CHAPTER 8.Ideal Models and Empirical Isotherm Equations

In this chapter attempts will be made to interpret isotherm data in terms of limiting isotherm models. These models are summarized below:

1. Localized sorption without interaction:

$$K_L = p \left(\frac{1-\theta}{\theta} \right)$$

2. Localized sorption with interaction (Bragg-Williams equation):

$$K_{B.W.} = p \left(\frac{1-\theta}{\theta} \right) \exp.(b\theta)$$

3. Sorbate mobile, obeys Volmer equation of state:

$$K_V = p \left(\frac{1-\theta}{\theta} \right) \exp. \left(\frac{-\theta}{1-\theta} \right)$$

4. Sorbate mobile, obeys van der Waals equation of state:

$$K_{VW} = p \left(\frac{1-\theta}{\theta} \right) \exp. \left(\frac{\theta}{1-\theta} - a\theta \right)$$

8.1. Sorption in the Ferrierites and Ba-J

The equations predicted by the statistical models 1 to 4 were tested by plotting $\log_{10} K_L$ and $\log_{10} K_V$ against θ . Owing to the high rectangularity of most of the isotherms the spread of θ values obtained was small and near to one and so restricted some model tests to a narrow θ range. Some of these plots are shown in Figs. 60) and 61 Tables 49 and 50

list systems which showed some agreement with models.

Other systems did not obey the models (1 to 4).

Table 49

Xenon

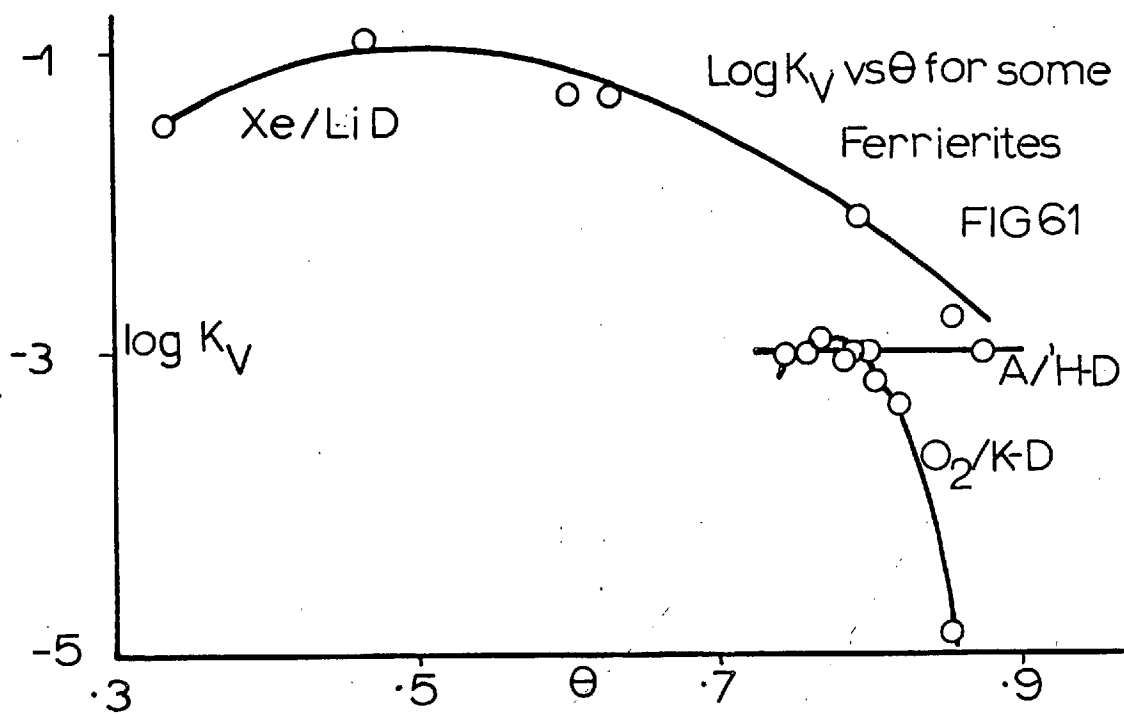
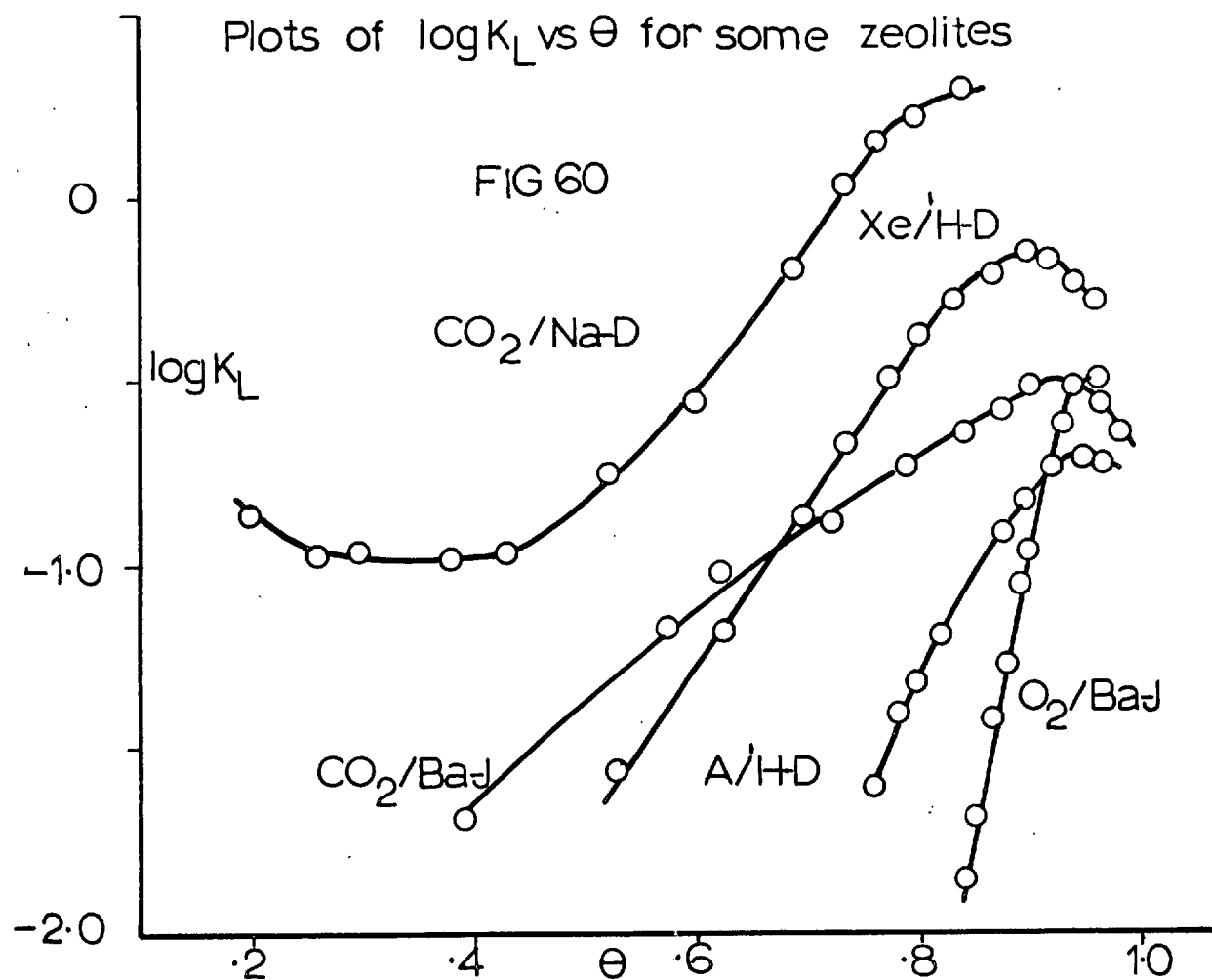
Sorbate/Sorbent	Model Test	θ Range
Xe/ ¹ H-D	$\log_{10}K_L$ vs. θ linear.	0.55-0.85
Xe/ ² H-D	K_L vs. θ constant.	0.85-0.95
Xe/Ba-J	" " " "	0.65-0.85

Table 50

Carbon Dioxide

Sorbate/Sorbent	Model Test	θ Range
CO ₂ / ³ H-D	$\log_{10}K_L$ vs. θ linear.	0.50-0.85
CO ₂ /Na-D	K_L vs. θ constant.	0.25-0.45
CO ₂ /Ca-D	$\log_{10}K_L$ vs. θ linear.	0.75-0.95
CO ₂ /K-D	" " " " "	0.70-0.90
CO ₂ /Sr-D	" " " " "	0.60-0.90
CO ₂ /Ba-J	" " " " "	0.40-0.90

Although the experimentally measurable range in θ was often small even in these ranges no isotherm obeyed any model isotherm equation for all values of θ . Plots of $\log_{10}K_L$ against θ were straight lines in many cases but at higher coverage they became curves.



The slopes of the lines were positive and the equation which reproduces this plot is of the form:-

$$p = K \left(\frac{e}{1-e} \right) \exp.(b\theta) \quad (1)$$

It was not possible to measure intercepts of the lines at $\theta = 0$ and hence find K but from the slopes b values were obtained. A number of b values are given in Table 51.

Table 51

Sorbate/Sorbent	Temperature	b
Xe/ ¹ H-D	-77.5°C.	4.50
CO ₂ /Na-D	+20.0°C.	0
CO ₂ /Ba-J	+17.6°C.	2.24
O ₂ /Ba-J	-195.8°C.	13.20

Equation (1) has the same form as the Bragg-Williams equation but the sign of b in the latter is negative. When b = 0 equation (1) reduces to the Langmuir model isotherm equation.

None of the systems, except possibly the sorption of argon on ¹H-D, gave any agreement with the tests for mobile sorption. It seems that the model isotherm equations are unsatisfactory in describing sorption in the ferrierites and Ba-J.

8.2. Sorption in Zeolite L

Plots of $\log_{10}K_L$ against θ are shown in Figs. (62) to (68) for the hydrocarbons methane, ethane, propane, n-butane, iso-butane and neo-pentane sorbed in zeolite L. These are straight lines in all cases except for n-butane but at higher coverages the plots develop into curves. The equation which best reproduces the plots is equation (1) of the previous section:

$$p = K \left(\frac{\theta}{1-\theta} \right) \exp.(b\theta) \quad (1)$$

The slopes of the lines were positive at lower temperatures, but as the temperatures increased the slopes decreased and in the cases of ethane, propane and isobutane sorption the slopes became small and negative. Some values of b , the slope of the plots $\log_{10}K_L$ vs. θ , are given in Table 55 at different temperatures.

The sign of b is determined by the change in thermal entropy of the sorbate with coverage.

Agreement with Langmuir's isotherm was obtained for methane at -80.6°C . and at -30.0°C . in the θ ranges $0.4 < \theta < 0.75$ and $0.3 < \theta < 0.5$, for ethane at 0°C . in the θ range $0.15 < \theta < 0.70$ and possibly for propane at 42.2°C . in the θ range $0.5 < \theta < 0.8$. Values of K_L , the isotherm constant are given for these three sorbates in Tables 52, 53 and 54.

The models for non-localised sorbate failed to fit any of the zeolite L isotherm data and plots of $\log_{10}K_V$ vs. θ are shown in Fig. (66) for n-butane sorption.

8.2.1. Examination of Differential Thermal Entropy

As seen from the previous section the ideal localised sorption model of Langmuir is applicable. The differential entropy of sorption predicted by the Langmuir model may be factorized as below:-

$$\bar{S}_1 = \bar{S}_c + \bar{S}_{th} \quad (2)$$

where $\bar{S}_c$ and $\bar{S}_{th}$ are the partial molar configurational and thermal entropies. For polyatomic hydrocarbon molecules $\bar{S}_{th}$ may in turn be expressed as

$$\bar{S}_{th} = {}_3\bar{S}_v + \bar{S}_I + \bar{S}_R \quad (3)$$

${}_3\bar{S}_v$ denotes the partial molar vibrational entropy of a molecule as a whole for its vibrational degrees of freedom within its intra-crystalline environment; $\bar{S}_I$ is the partial molar entropy associated with internal vibrational and rotational degrees of freedom of the molecule, and $\bar{S}_R$ is the partial molar entropy associated with the principal rotations of the whole molecule, or with the restricted rotations, or the vibrations, which may have replaced them.

Table 52

Isotherm Constants K_L for CH_4 sorbed in zeolite L

$t = -80.6^\circ\text{C.}$		$t = -30.0^\circ\text{C.}$	
θ	K_L	θ	K_L
.16	5.21	.05	36.46
.27	5.54	.09	38.56
.34	5.94	.14	37.50
.39	6.12	.18	37.20
.44	6.30	.22	36.10
.48	6.42	.27	33.24
.56	6.24	.29	34.58
.61	6.47	.32	34.08
.65	6.57	.35	33.84
.68	6.62	.38	33.40
.71	6.51	.40	33.44
.74	6.36	.42	33.60
.77	6.14	.44	33.28
.82	5.50		

Table 53Isotherm Constants K_L for C_2H_6 sorbed in zeolite L

$t = 0^\circ\text{C.}$	
θ	K_L
.15	3.18
.31	3.15
.38	3.24
.47	3.33
.55	3.27
.61	3.22
.65	3.17
.69	3.12
.72	3.06
.77	3.07
.84	2.77
.88	2.43
.92	1.99

Table 54Isotherm Constants K_L for C_3H_8 in zeolite L

$t = 42.2^\circ\text{C}$	
θ	K_L
.18	1.09
.27	1.29
.36	1.44
.45	1.61
.54	1.70
.64	1.69
.70	1.69
.74	1.75
.78	1.74
.80	1.78
.82	1.78
.85	1.75
.90	1.62

Table 55b values from Plots of $\log_{10} K_T$ vs. θ

Sorbate	Temperature°C.	b
CH_4	-117.2	2.1
C_2H_6	-62.0	3.6
C_2H_6	-46.2	-0.2
C_3H_8	-20.0	3.2
C_3H_8	87.1	-0.3
iso C_4H_{10}	81.0	0.7
iso C_4H_{10}	132.0	-0.2
neo C_5H_{12}	30.0	4.2
neo C_5H_{12}	98.0	1.3
neo C_5H_{12}	143.0	0.8

The configurational entropy term can be defined as follows if the localised model holds:

$$\bar{S}_c = R \ln \frac{1-\theta}{\theta} \quad (4)$$

Using equations (2) and (4) values for the partial molar thermal entropies can be estimated and are shown in Tables (56), (57) and (58) for methane, ethane and propane in zeolite L, and plots of $\bar{S}_{th}$ against

Table 56

θ	$\bar{S}_1$	$\bar{S}_{th}$
.39	15.08	14.23
.44	14.82	14.36
.48	14.60	14.47
.56	14.14	14.63
.61	13.82	14.69
.65	13.60	14.80
.68	13.49	14.98
.71	13.37	15.17

Methane -80.6°C

Mean $\bar{S}_{th} = 14.73$ e.u.

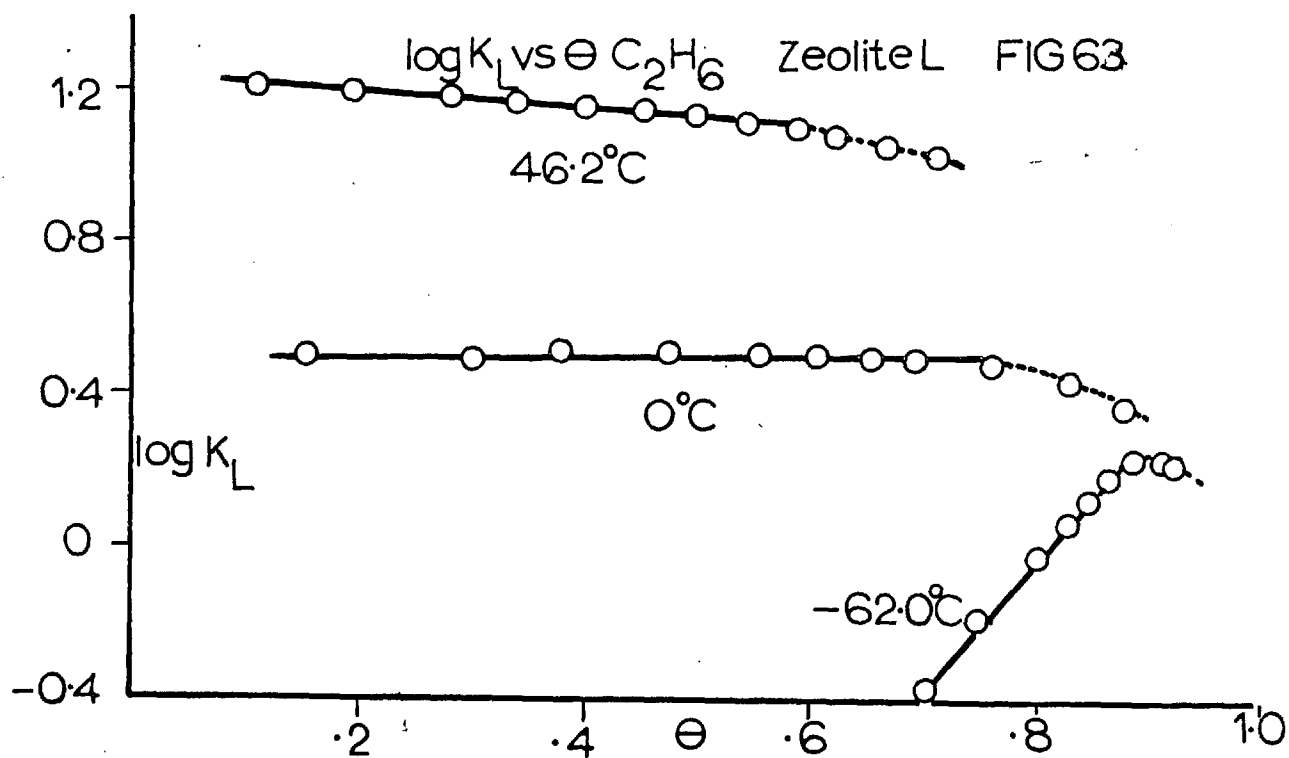
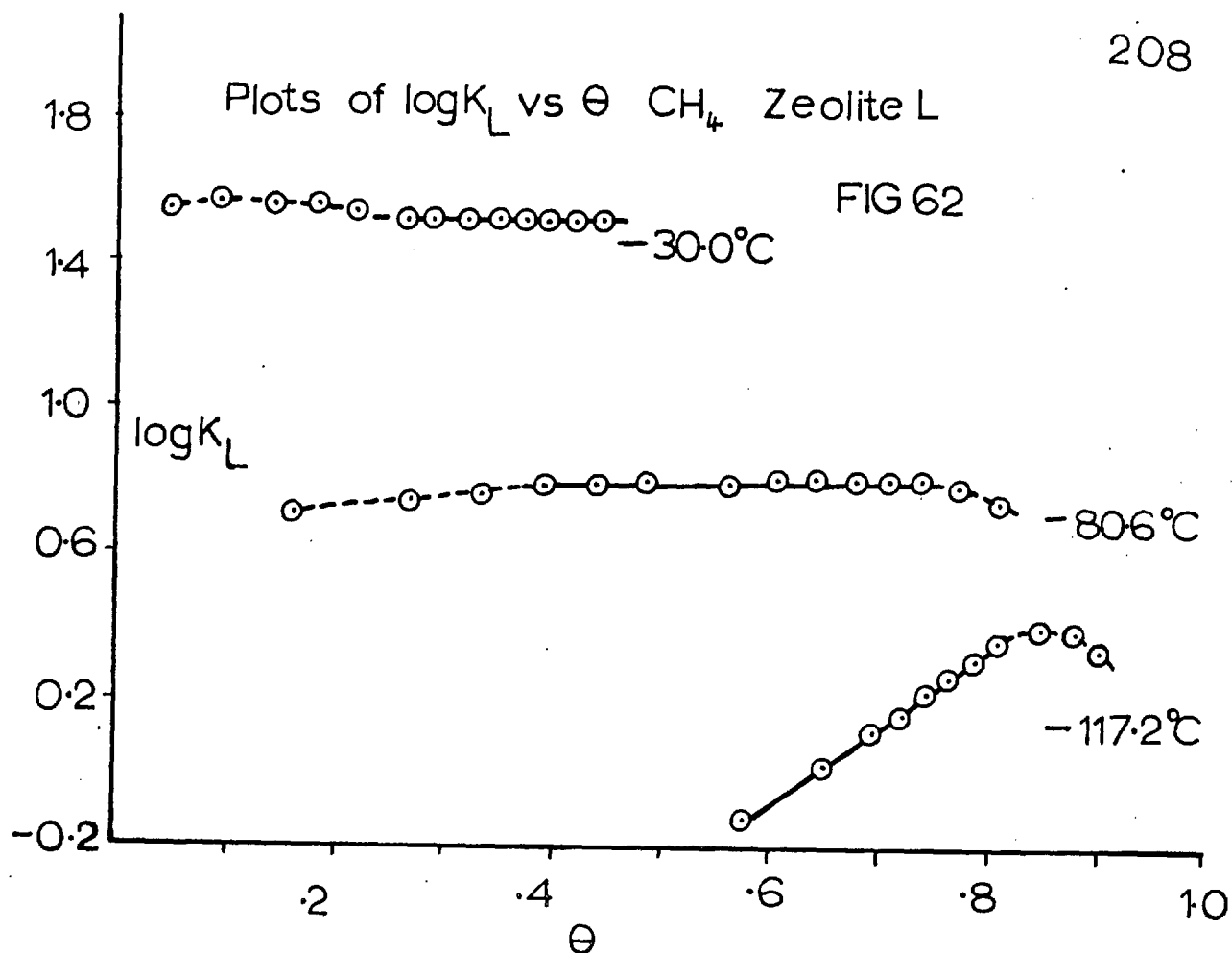
Table 57

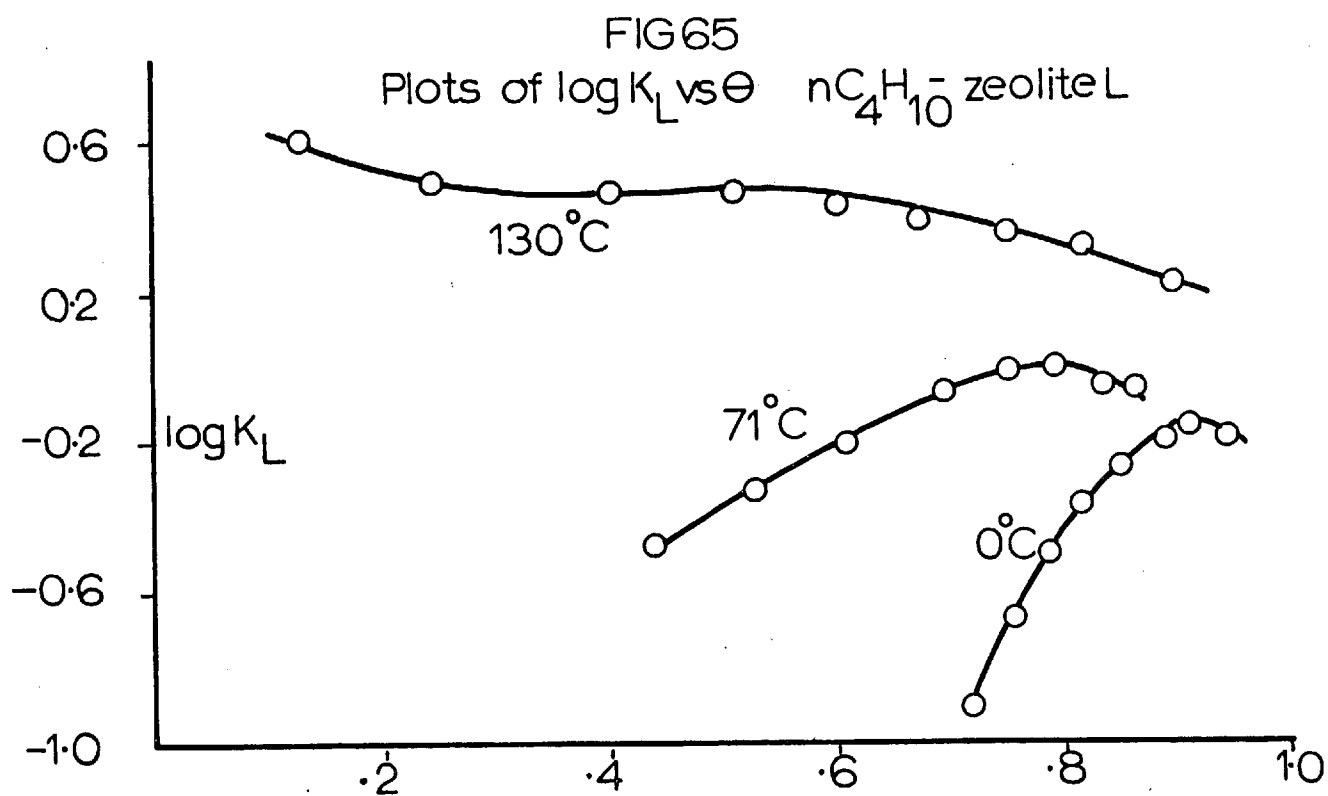
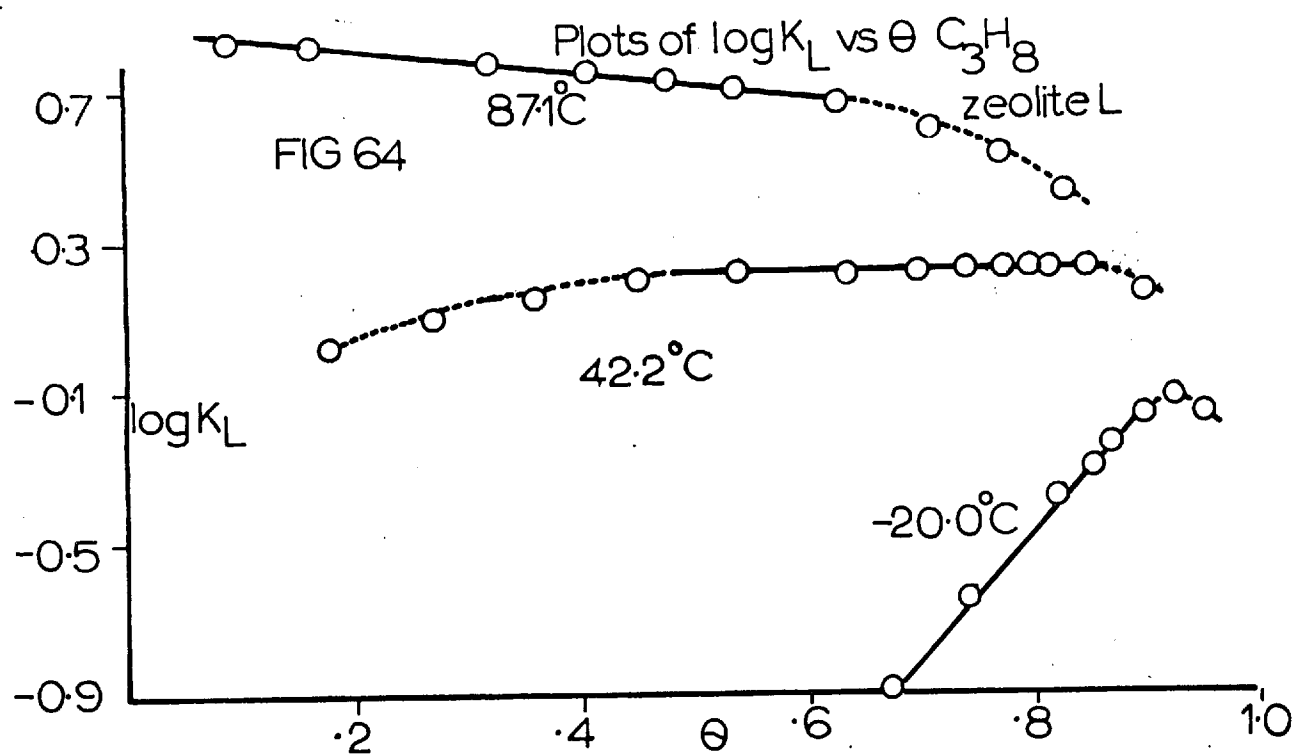
θ	$\bar{S}_1$	$\bar{S}_{th}$
.15	28.41	25.01
.31	26.29	24.67
.38	25.95	24.99
.47	25.14	24.93
.55	24.20	24.60
.61	23.39	24.28
.65	23.03	24.30
.69	22.36	23.98
.72	22.07	23.99

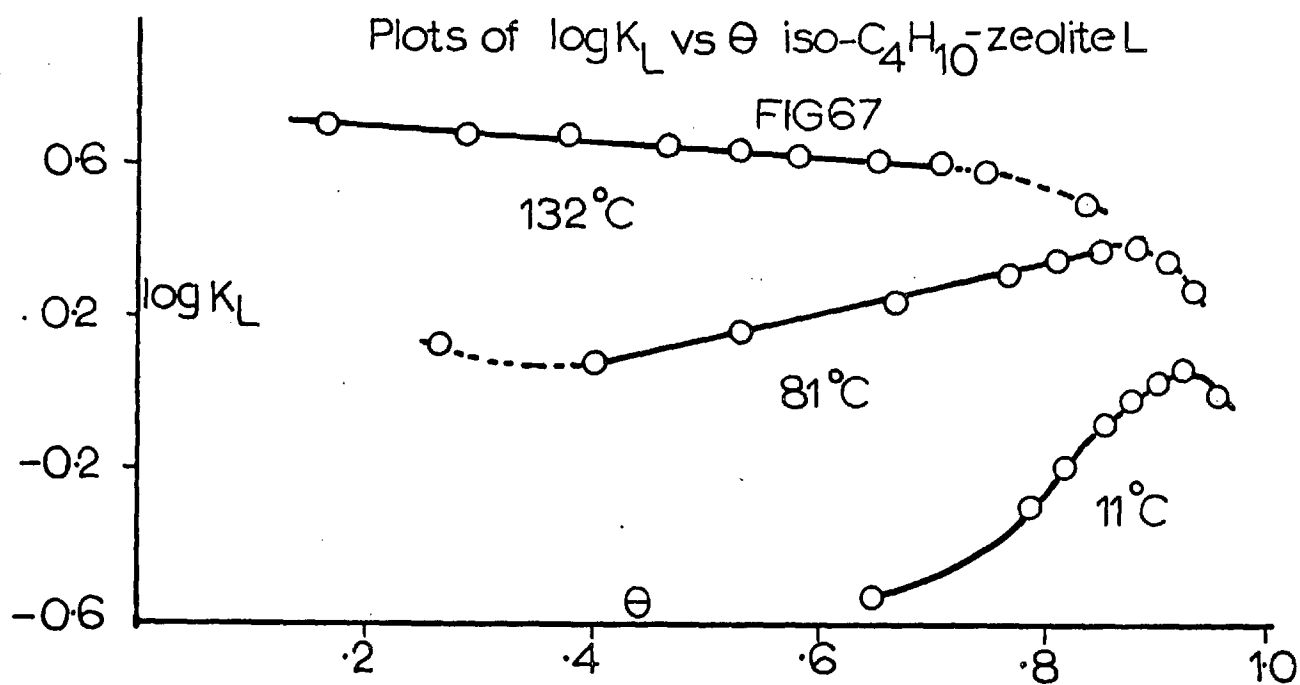
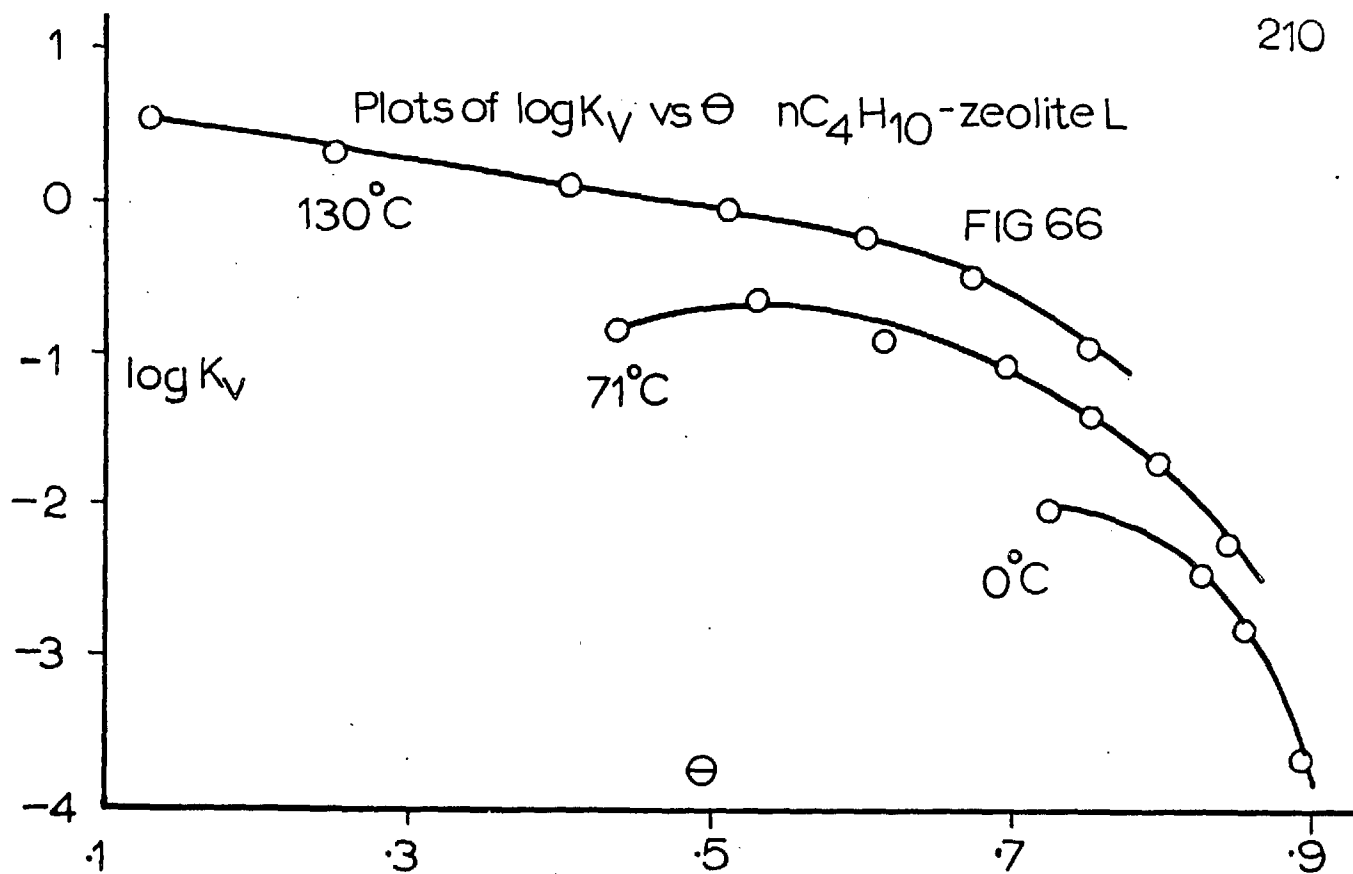
Ethane 0°C.Mean $\bar{S}_{th} = 24.53$ e.u.Table 58

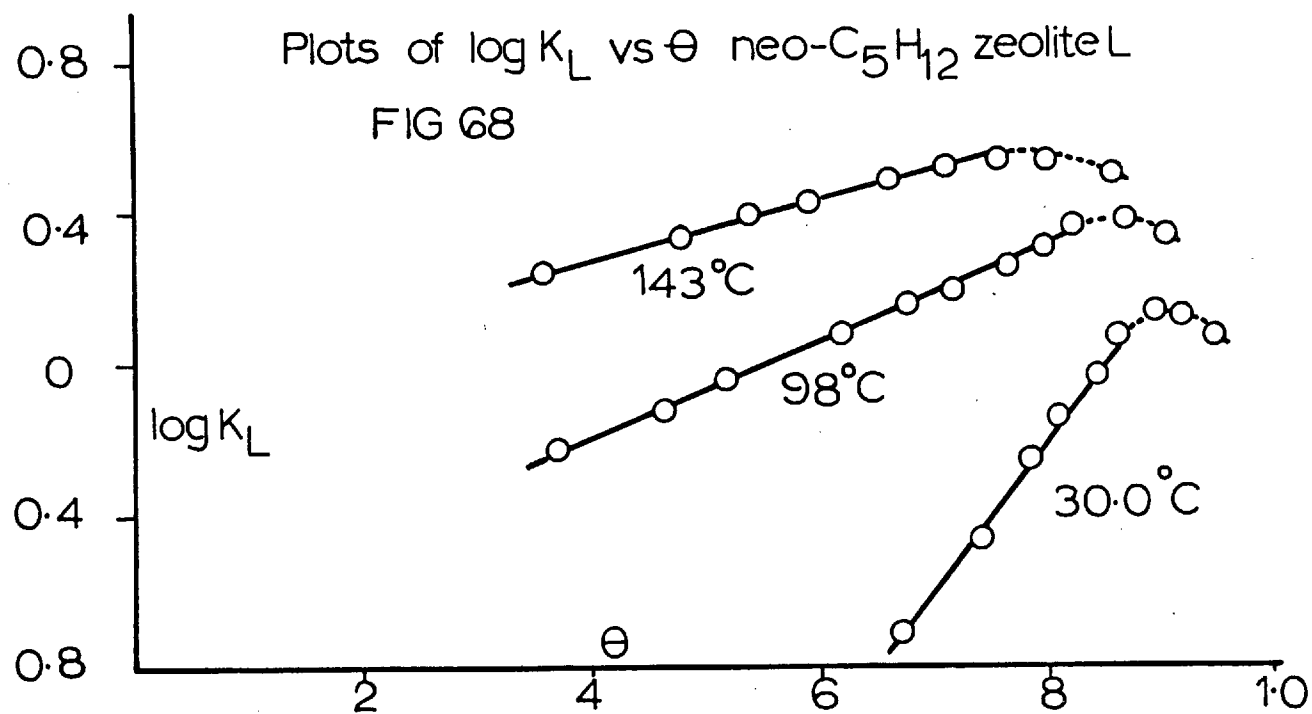
θ	$\bar{S}_1$	$\bar{S}_{th}$
.54	33.55	33.88
.64	32.36	33.50
.70	31.61	33.33
.74	31.00	33.09
.78	30.38	32.84
.80	29.85	32.57
.82	29.25	32.24
.85	29.17	32.64
.90	28.90	33.19

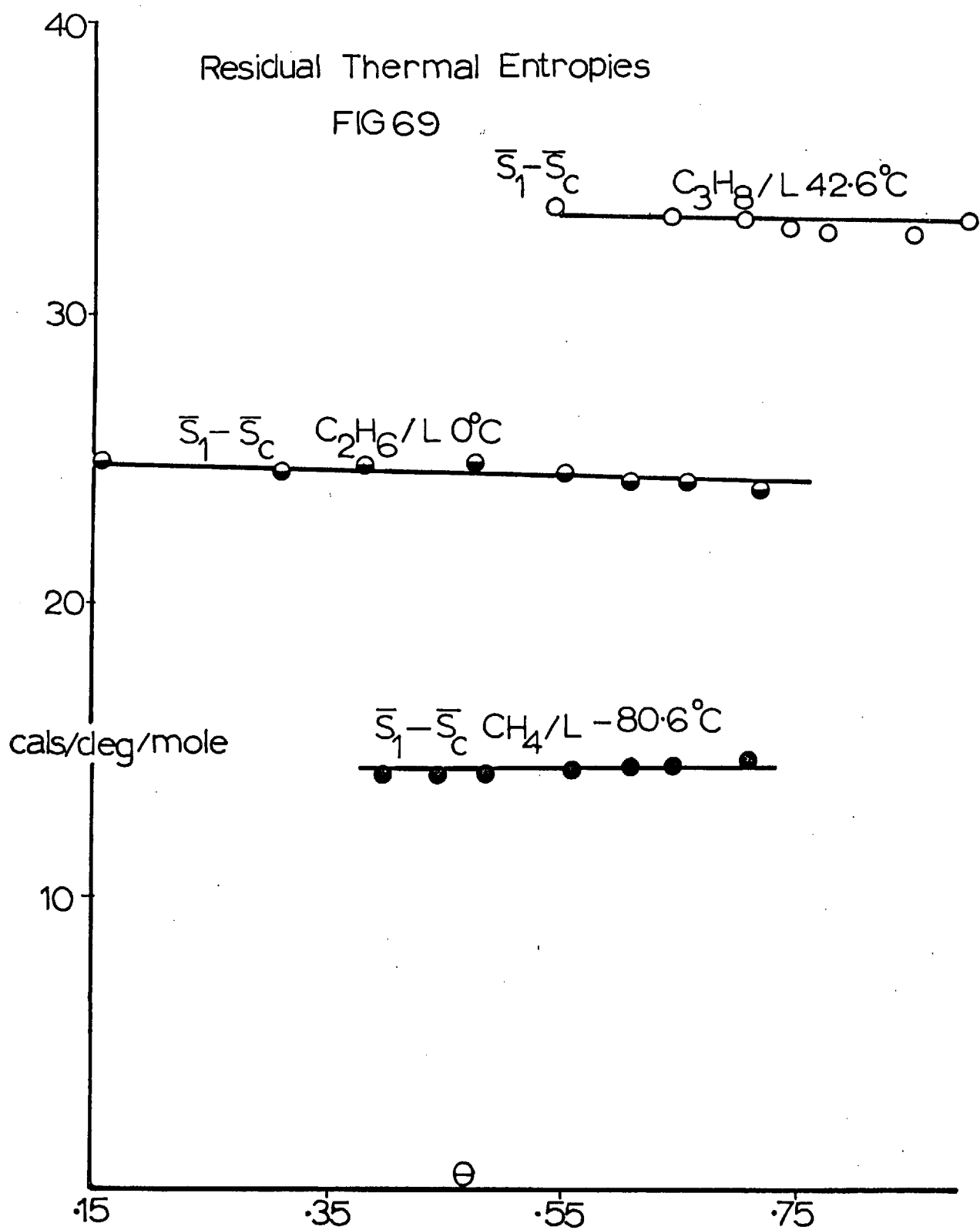
Propane 42.2°C.Mean $\bar{S}_{th} = 33.03$ e.u.All entropy values expressed
in cal./deg./mole.











θ in Fig. 69. As can be seen the $\bar{S}_{th}$ values are positive and reasonably constant with coverage; the maximum deviation from the average value for the methane-zeolite L system at -80.6°C . is ca. $0.5 \text{ cal deg}^{-1} \text{ mole}^{-1}$ in the interval of θ , $0.4 < \theta < 0.75$, ca. $0.6 \text{ cal deg}^{-1} \text{ mole}^{-1}$ for the ethane-zeolite L system at 0°C . in the interval of θ , $0.15 < \theta < 0.7$, and ca. $0.8 \text{ cal deg}^{-1} \text{ mole}^{-1}$ in the interval of θ , $0.5 < \theta < 0.9$ for the propane-zeolite L system at 42.2°C . These fluctuations in $\bar{S}_{th}$ are well within the range of experimental error. If the small drift in $\bar{S}_{th}$ is neglected, then the differential entropies may be equated with the corresponding molar entropies, $\tilde{S}_{th}$, over the ranges of validity of the localised sorption model.

$$\bar{S}_{th} \approx \tilde{S}_{th} = {}_s\tilde{S}_v + \tilde{S}_I + \tilde{S}_R \quad (5)$$

The molar entropies of the vapours $\tilde{S}_g^0$, at 1 atmosphere pressure and specified temperatures, are related to the internal and rotational entropies as follows:

$$\tilde{S}_g^0 = {}_g\tilde{S}_I + {}_g\tilde{S}_R + {}_g\tilde{S}_T^0 \quad (6)$$

where ${}_g\tilde{S}_T^0$ is the molar translational entropy in the gaseous state. (the subscript 'g' denotes the gaseous state). For a freely rotating vibrator in the sorbed state,

$${}_g\tilde{S}_I + {}_g\tilde{S}_R = \tilde{S}_I + \tilde{S}_R$$

therefore

$$\tilde{S}_{th} - {}_s\tilde{S}_V = \tilde{S}_g^o - \tilde{S}_T^o \quad (7)$$

where

$${}_g\tilde{S}_T^o = 6.864 \log_{10} M - 2.314 + 11.439 \log_{10} T^{1.18} \quad (8)$$

(M = molecular weight of the hydrocarbon).

Estimates of the molar vibrational entropies, ${}_s\tilde{S}_V$, may be made using equations (7) and (8) and are shown in Table 59 for methane, ethane and propane.

Table 59

Sorbate	Temperature	$\tilde{S}_{th}$	${}_g\tilde{S}_I + {}_g\tilde{S}_R$	${}_s\tilde{S}_V$
CH ₄	-80.6°C.	14.73	9.53	5.20
C ₂ H ₆	0°C.	24.53	18.20	6.33
C ₃ H ₈	422°C.	33.03	27.87	5.16

The vibrational frequencies, ν , corresponding to the $\tilde{S}_V$ values were determined assuming the vibrations to be simple harmonic and using equation (9)

$${}_s\tilde{S}_V = R \left[u(\exp^u - 1)^{-1} - \ln(1 - \exp^{-u}) \right] \quad (9)$$

where $u = \frac{h\nu}{kT}$.

It is also possible to derive approximate frequencies for the hydrocarbon vibrations using the standard vibrational frequency for argon localised in chabazite according to the relation^{71,119}

$$\frac{\nu_{\text{Ar}}}{\nu} = \left(\frac{\Delta E_{\text{Ar}}}{\Delta E} \frac{m}{m_{\text{Ar}}} \right)^{\frac{1}{2}} \quad (10)$$

where $\Delta E = \bar{E}_1 - \tilde{E}_g = \bar{H}_1 - RT = -3.6 \text{ kcal/mole}$ for argon,

m = the mass of the molecule, and

$$\nu_{\text{Ar}} = 2 \times 10^{12} \text{ sec}^{-1}$$

Table 60

	$\nu(\text{From eqn. 10}) \text{ sec}^{-1}$	$\nu(\text{From } {}_1\tilde{S}_V) \text{ sec}^{-1}$
CH_4	3.3×10^{12}	4.7×10^{12}
C_2H_6	3.1×10^{12}	5.5×10^{12}
C_3H_8	3.0×10^{12}	7.9×10^{12}

Since it is assumed that the sorbates within the crystal environment are freely rotating and equation (10) is approximate, the agreement between the frequencies derived from ${}_1\tilde{S}_V$ and equation (10) is reasonable and consistent with localised sites of sorption.

8.2.2. Entropy of Liquid Methane, Ethane and Propane

The entropy of the liquid hydrocarbons is the sum of two terms:

$$\tilde{S}_L = {}_L\tilde{S}_c + {}_L\tilde{S}_{th} \quad (11)$$

where ${}_L\tilde{S}_c$ and ${}_L\tilde{S}_{th}$ are the molar configurational and thermal entropies of the liquid. ${}_L\tilde{S}_c$ is small (~ 0.33 cal $\cdot$ deg $^{-1}$ mole $^{-1}$ in one estimate)¹²⁰ and can be neglected. The thermal entropy of the liquids are compared with the sorbed species in Table 61.

Table 61

	$\tilde{S}_L$ e.u.	$\tilde{S}_{th}$ e.u.
CH ₄ (-80.6°C.)	29.1	14.7
C ₂ H ₆ (0°C.)	38.0	24.5
C ₃ H ₈ (42.2°C)	48.5	33.0

There is a large difference between $\tilde{S}_L$ and $\tilde{S}_{th}$, which is well outside any possible value for ${}_L\tilde{S}_c$. It seems the molecules occluded interstitially with zeolite L possess much less freedom than they do in the liquid state. This is consistent with localised sorption.

8.3. Osmotic Pressures and Empirical Isotherm Equations

In the previous section, it was observed that

Langmuir's isotherm and the isotherm of equation (1) had useful but limited application to the experimental data, and therefore a general method of expressing isotherm equations is used, based on the osmotic ratio π / CRT .

The following equation for the osmotic pressure was previously derived:¹¹⁷

$$\pi / CRT = \frac{\rho}{mC} \int_0^p \frac{y}{p} dp \quad (12)$$

where ρ is the density of the outgassed zeolite, and C the concentration of the sorbent in the sorbate-zeolite solution; y is the weight in grams of the sorbate of molecular weight in per gram of zeolite. Similarly equation (13) relating the change in chemical potential, $\Delta\mu_2$, of the sorbent to the osmotic pressure was discussed

$$-\Delta\mu_2 = \pi V = \frac{MRT}{m} \int_0^p \frac{y}{p} dp \quad (13)$$

where V is the molecular volume of the lattice-forming units of molecular weight M . It is of interest that for $-\Delta\mu_2$, the lattice-forming unit chosen is definitive, but that for π no particular unit is involved.

Plots of y/p against p for many of the systems were integrated graphically and osmotic pressures calculated using equation (13). If C , ($= \rho \frac{V}{m}$) is in moles/cm.³, and R is taken as 82.06 cm³.atm.deg⁻¹ mole⁻¹, then the values of π obtained from equation (13) will

be in atmospheres. Tables (62) to (66) summarize values for osmotic pressure for some of the systems studied. They are large and increase with temperature. Plots of π/CRT against volume of sorbate sorbed (in $\text{cm}^3\text{s.t.p./gm.}$) are shown in Figures 70 to 72.

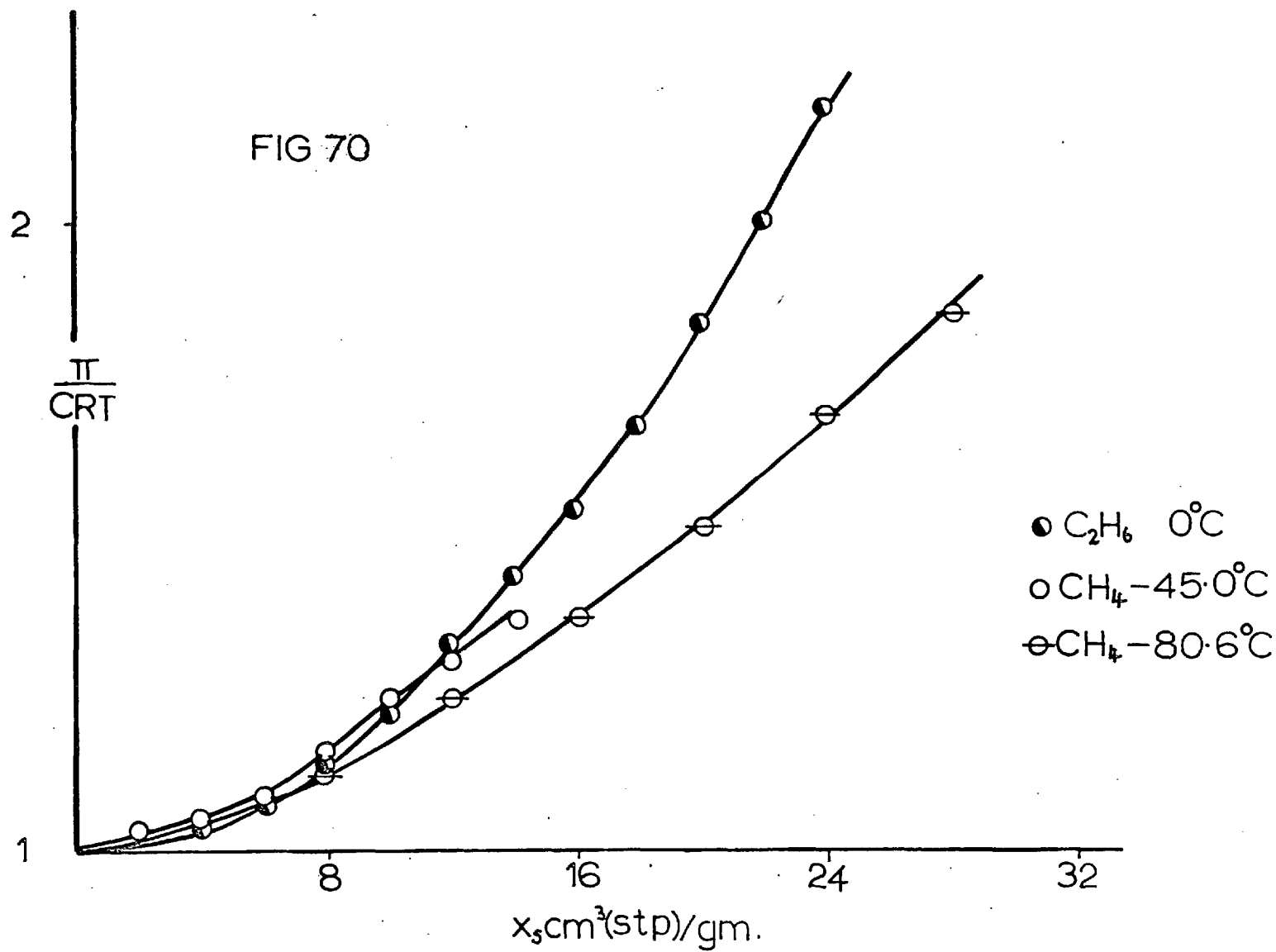
Table 62

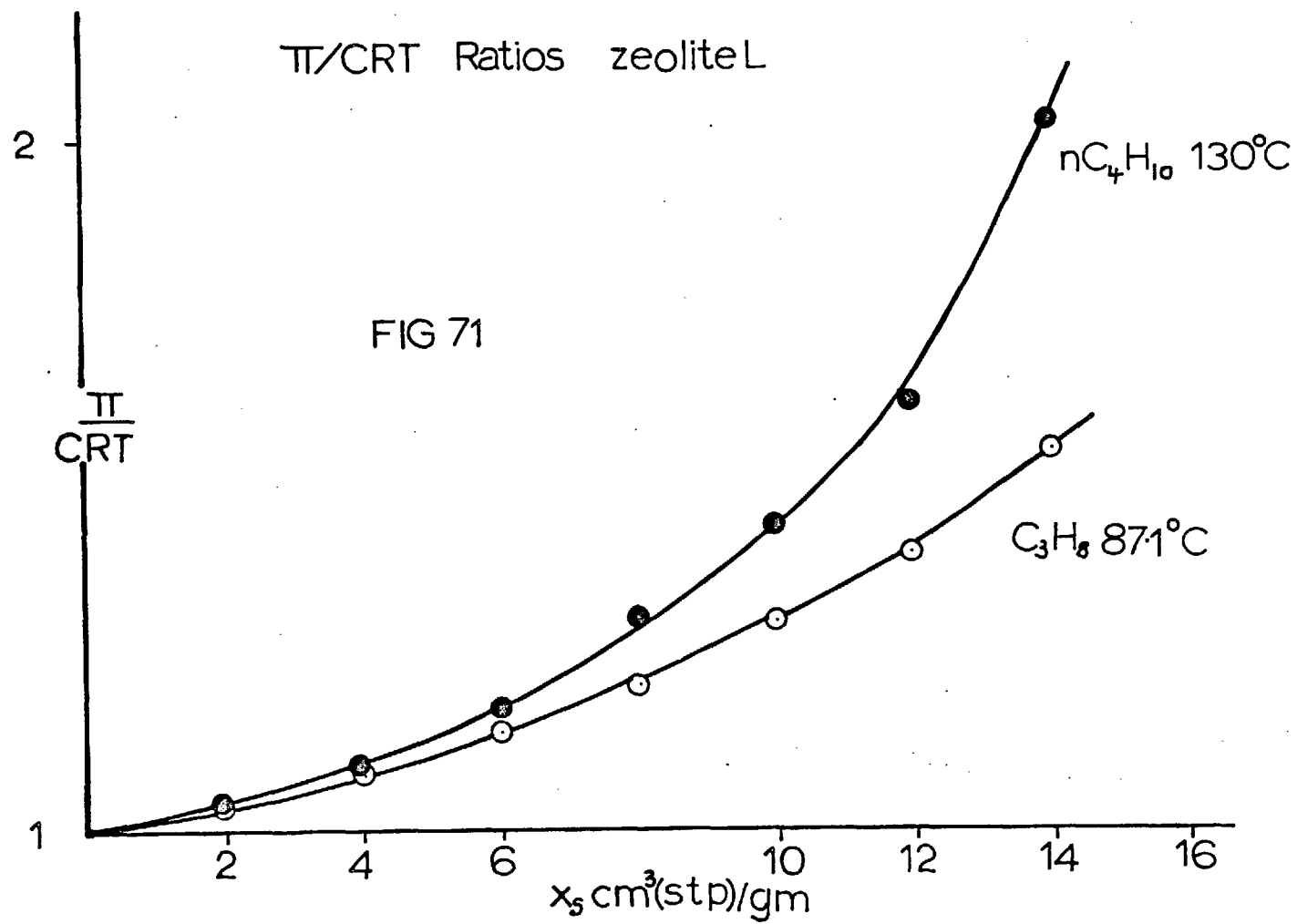
Osmotic Pressures in Atmospheres

$\text{CH}_4/\text{zeolite L}$			$\text{C}_2\text{H}_6/\text{zeolite L}$	
$x_s \text{ cm}^3\text{s.t.p./gm.}$	-80.6°C.	-45.0°C.	-62.0°C.	0°C.
2	-	3.20	-	-
4	5.47	6.45	-	7.73
6	-	10.06	-	11.78
8	11.85	14.34	-	17.30
10	-	19.25	-	23.18
12	19.25	24.07	-	30.18
14	-	29.66	-	37.35
16	28.64	-	-	45.26
20	39.48	-	-	68.45
24	52.09	-	65.63	103.92
28	67.56	-	117.16	-
32	86.81	-	183.73	-

π/CRT Ratios zeolite L

FIG 70





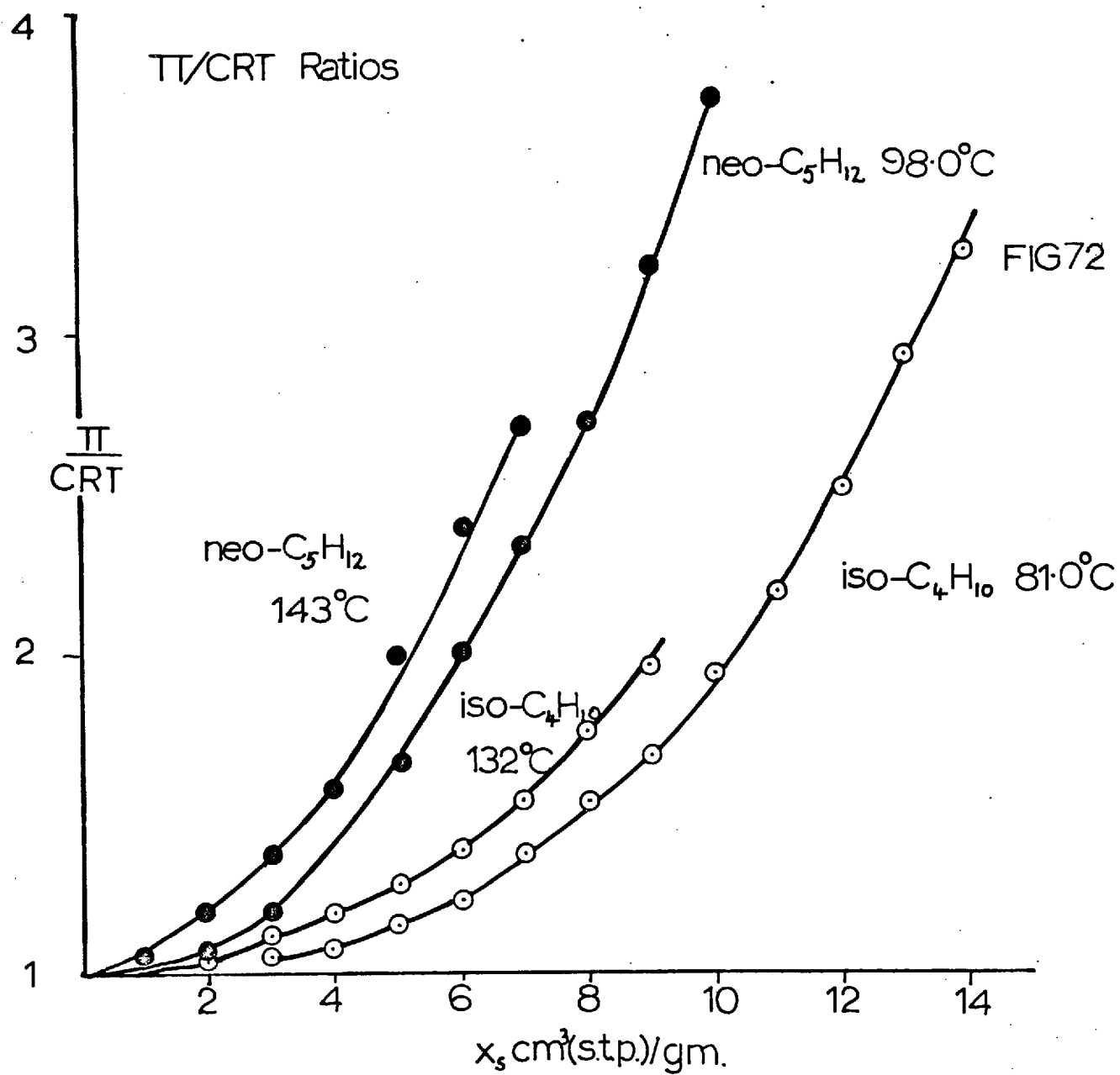


Table 63

x_s cm ³ s.t.p./gm.	C ₃ H ₈ /zeolite L		nC ₄ H ₁₀ /zeolite L
	42.2°C.	87.1°C.	130°C.
2	—	5.02	5.65
4	8.90	10.56	11.90
6	18.19	16.74	19.17
8	26.08	23.57	28.30
10	34.85	31.77	39.11
12	44.31	40.99	53.12
14	54.91	52.76	77.81
16	69.09	—	—
18	90.18	—	—
20	117.43	—	—

Table 64Osmotic Pressures in Atmospheres

x_s cm ³ s.t.p./gm.	iso-C ₄ H ₁₀ /zeolite L.		neo-C ₅ H ₁₂ /zeolite L.	
	81°C.	132.0°C.	98°C.	143°C.
1	-	2.84	-	2.94
2	4.92	5.98	5.38	6.79
3	7.61	9.23	9.15	11.64
4	10.40	13.13	12.66	17.78
5	14.05	17.66	20.88	28.26
6	17.73	22.79	30.76	40.74
7	23.22	29.76	41.24	53.50
8	29.61	38.79	54.80	-
9	36.39	46.95	72.58	-
10	46.36	-	93.89	-
11	57.72	-	-	-
12	72.55	-	-	-
13	91.26	-	-	-
14	109.11	-	-	-

Table 65

x_s cm ³ s.t.p./gm.	A/'H-D-195.8°C.	O ₂ /'H-D-195.8°C.
60	54.34	-
62	85.76	-
64	106.33	-
66	121.17	-
68	139.28	-
70	157.71	-
72	178.17	56.40
74	197.78	109.09
76	215.48	157.49
78	230.39	208.93
80	248.02	263.81
82		311.97
84		366.28
86		420.99
88		475.31

Table 66

Osmotic Pressures in Atmospheres

x_s cm ³ s. t. p. / gm.	C ₂ H ₆ / Ba-J-77.5°C.	Xe / ³ H-D-77.5°C.
6	12.44	-
8	22.39	-
10	29.38	-
12	32.95	-
14	37.59	-
16	43.97	-
18	53.55	26.95
20	65.27	56.34
22	85.16	86.17
24	139.74	125.73
26	-	156.91
28	-	187.71
30	-	214.17

Table 67

Sorbate Coeff.	CH ₄		C ₂ H ₆		C ₃ H ₈
	-80.6°C.	-45.0°C.	0°C.	46.2°C.	87.1°C.
A ₁	127.60	69.30	-17.85	52.04	194.92
A ₁ ¹	0.41	0.17	- 0.12	0.07	0.27
A ₂	11.96x10 ⁴	24.79x10 ⁴	34.91x10 ⁴	37.13x10 ⁴	22.10x10 ⁴
A ₂ ¹	1.22	1.33	1.90	0.80	0.40

Table 68

Sorbate Coeff.	nC ₄ H ₁₀	iso-C ₄ H ₁₀		neo-C ₅ H ₁₂	
	130°C.	81.0°C.	132.0°C.	98°C.	143°C.
A ₁	134.92	-289.85	507.73	-247.42	487.0
A ₁ ¹	0.17	-0.35	0.32	-0.23	0.33
A ₂	49.30x10 ⁴	162.8x10 ⁴	-2.48x10 ³	43.22x10 ⁵	43.51x10 ⁴
A ₂ ¹	0.83	2.46	0.39	3.55	2.03

8.3.1. Empirical Isotherm Equations

The plots of π/CRT against C (or θ) can be represented by a virial equation:

$$\pi/CRT = 1 + A_1C + A_2C^2 + \dots + A_nC^n + \dots \quad (14)$$

Since $C = k_1\theta$, where $k_1 = \left(\frac{p}{m}\right)_{\text{sat.}}$ equation (14) may also be written:-

$$\pi/CRT = 1 + A_1^1\theta + A_2^1\theta^2 + \dots + A_n^1\theta^n + \dots \quad (15)$$

If all the terms on the righthand side of equations (14) and (15) except the first three are neglected, then the coefficients may then be substituted in the empirical isotherm equations (17) and (18).

$$p = KC \exp(2A_1C + 3/2A_2C^2 + \dots) \quad (16)$$

$$p = K^1\theta \exp(2A_1^1\theta + 3/2A_2^1\theta^2 + \dots) \quad (17)$$

The coefficients of the empirical equations and the equilibrium constants K and K^1 for many of the systems are given in the following tables.

Table 69

Sorbate Coeff.	O ₂	Xe	CO ₂
	'H-D	'H-D	Ba-J
	-195.8°C.	-77.5°C.	+17.6°C.
A ₁	-5.83x10 ³	2.541x10 ³	165.53
A ₁ ¹	-44.49	-8.73	0.46
A ₂	107.0x10 ⁴	-171.99x10 ⁴	34.89x10 ⁴
A ₁ ¹	63.10	16.53	3.55

Table 70

Sorbate Coeff.	A	N ₂	CH ₄
	'H-D	Na-D	'H-D
	-195.8°C.	-195.8°C.	-183.1°C.
A ₁	-1770	665.7	4470
A ₁ ⁻¹	-11.59	-	-22.40
A ₂	44.97x10 ⁴	-22.28x10 ⁴	123.8x10 ⁴
A ₂ ⁻¹	17.88	-	28.91

K and K⁻¹ ValuesTable 71

	CH ₄		C ₂ H ₆		C ₃ H ₈
	-80.6°C.	-45.0°C.	0°C.	46.2°C.	87.1°C.
K	1707	1.066x10 ⁴	1759	1.253x10 ⁴	5636
K ⁻¹	5.48	25.03	7.19	18.33	7.64

Table 72

	nC ₄ H ₁₀	isoC ₄ H ₁₀		neoC ₅ H ₁₂	
	130°C.	81.0°C.	132°C.	98.0°C.	143°C.
K	2675	1232	6224	606.4	3221
K ⁻¹	3.48	1.52	4.88	0.52	1.55

Table 73

Ne/Na-D	O ₂ / ¹ H-D	CO ₂ /Ba-J	Xe/ ¹ H-D	A/ ¹ H-D	CH ₄ / ¹ H-D
-195.8°C.	-195.8°C.	+17.6°C.	-77.5°C.	-195.8°C.	-183.1°C.
K 1524	-	4.69	-	-	-
K ¹ -	1304	0.02	0.20	0.79	

Since the equilibrium constants K_z can be written as $K = a_g/a_z = p/\theta \cdot \gamma$; or $K^1 = p/\theta \cdot \gamma$ where a_g and a_z are the equilibrium activities of the sorbate in the gas phase and in the zeolite respectively, the exponential terms in equations (16) and (17) represent the activity coefficient γ . Tables of activity coefficients calculated from equation (17) for the hydrocarbons in zeolite L are shown below

Table 74

Methane -80.6°C.		Ethane 0°C.		Propane 87.1°C.	
θ	γ	θ	γ	θ	γ
.10	1.11	.23	1.09	.12	1.07
.41	1.92	.54	2.08	.49	1.49
.82	6.55	.92	9.03	.85	2.41

Table 75

n-butane 130°C		iso-butane 81.0°C.		neo-pentane 143°C.	
θ	γ	θ	γ	θ	γ
.25	1.16	.27	1.09	.12	1.13
.63	2.03	.53	1.99	.48	2.39
.89	3.78	.80	6.49	.84	14.58

As was noted in an earlier section, for the Langmuir and Volmer isotherms the following relationships hold: (Chapter 3)

$$\pi/CRT = \frac{1}{\theta} \ln (1-\theta) \quad (\text{Langmuir}) \quad (18)$$

$$\pi/CRT = \frac{1}{1-\theta} \quad (\text{Volmer}) \quad (19)$$

Similarly, equation (1) corresponds to:-

$$\pi/CRT = -\frac{1}{\theta} \ln (1-\theta) + \frac{b\theta}{2} \quad (20)$$

In equations (18) and (19) π/CRT is a universal function of θ ; in equation (20) b introduces in addition a possible temperature dependence. In the previous section, it was observed that Langmuir's isotherm and the isotherm of equation (1) had useful but limited application to the experimental data. Some osmotic ratios for the sorption of hydrocarbons in zeolite L were calculated using equations (17) to (20) and compared with experimental values (Tables 76, 77 and 78). It is seen that agreement with the

experimental π/CRT ratios, and with those obtained from the empirical isotherm equations is excellent. π/CRT ratios for C_2H_6 sorption in zeolite L at 0°C . show very little scatter from the characteristic ~~Langmuir curve in~~ π/CRT Ratios

Table 76

C_2H_6 0°C zeolite L

θ	Experimental	Langmuir	Empirical
.15	1.04	1.08	1.03
.23	1.08	1.14	1.07
.31	1.18	1.19	1.15
.39	1.26	1.26	1.24
.46	1.35	1.34	1.35
.54	1.45	1.44	1.48
.62	1.55	1.55	1.55
.69	1.67	1.70	1.63
.77	1.86	1.91	1.86
.85	2.04	2.22	2.04
.92	2.35	2.79	2.35

π /CRT RatiosTable 77C₃H₈ 87.1°C. zeolite L

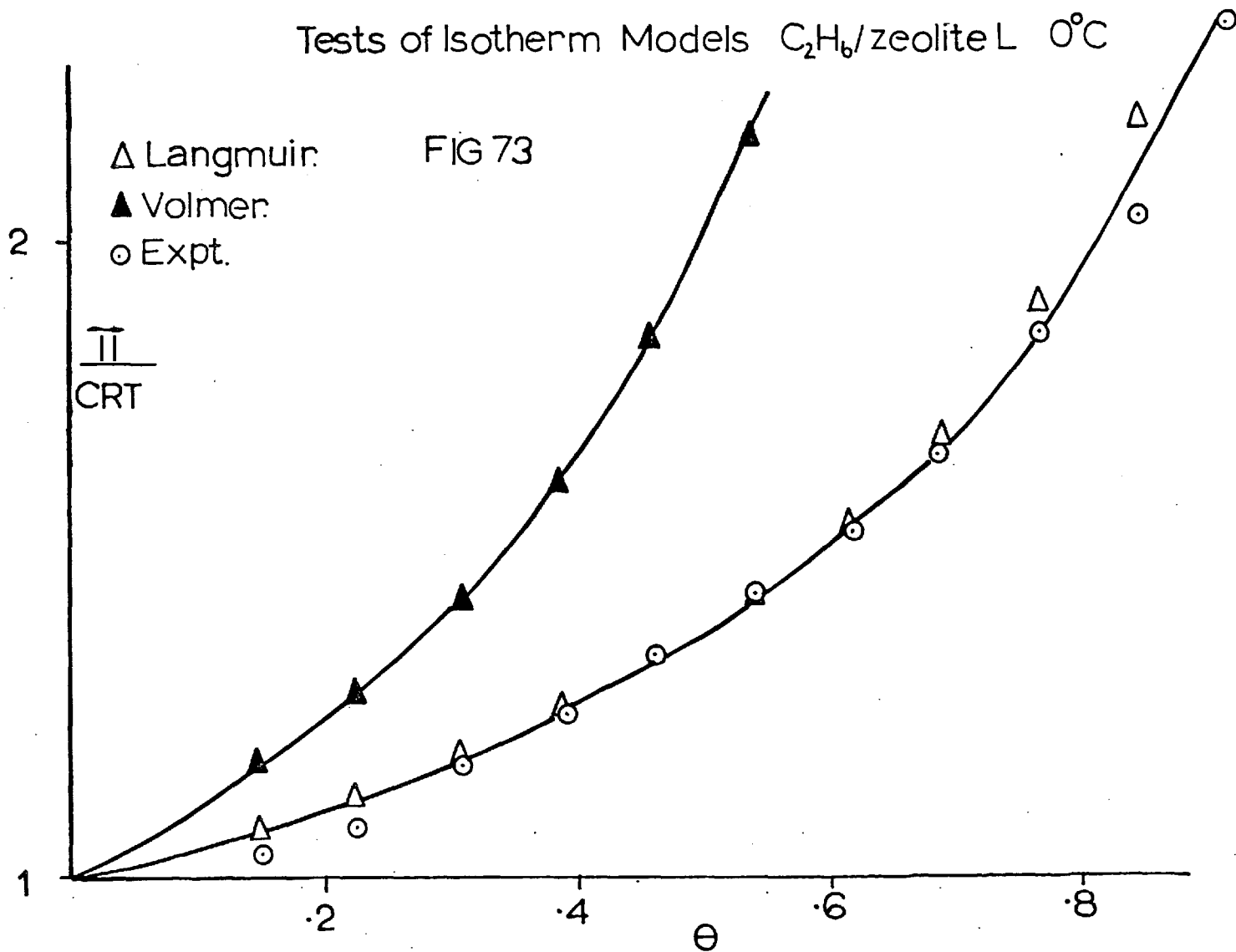
θ	Experimental	Eqn. 1.	Empirical
.12	1.03	1.04	1.04
.24	1.09	1.10	1.09
.36	1.15	1.17	1.15
.49	1.22	1.26	1.22
.61	1.31	1.43	1.31
.73	1.41	1.65	1.41
.85	1.51	2.07	1.55

Table 78.neo-C₅H₁₂ 143°C zeolite L

θ	Experimental	Eqn. 1	Empirical
.12	1.05	1.11	1.06
.24	1.21	1.23	1.20
.36	1.38	1.38	1.38
.48	1.59	1.55	1.62
.60	2.01	1.76	1.99
.72	2.42	2.06	2.40
.84	2.72	2.52	2.72

~~scatter from the characteristic~~ Langmuir curve in the θ range $0.15 < \theta < 0.70$. π/CRT ratios for C_3H_8 sorption at 87.1°C . and neo- C_5H_{12} at 143°C . show very little scatter from the characteristic curves obtained from equation (20) in the θ ranges $0.1 < \theta < 0.5$. None of the experimental osmotic ratios show similarity to those based on equation (19), the Volmer isotherm. (see Fig. 73-75).

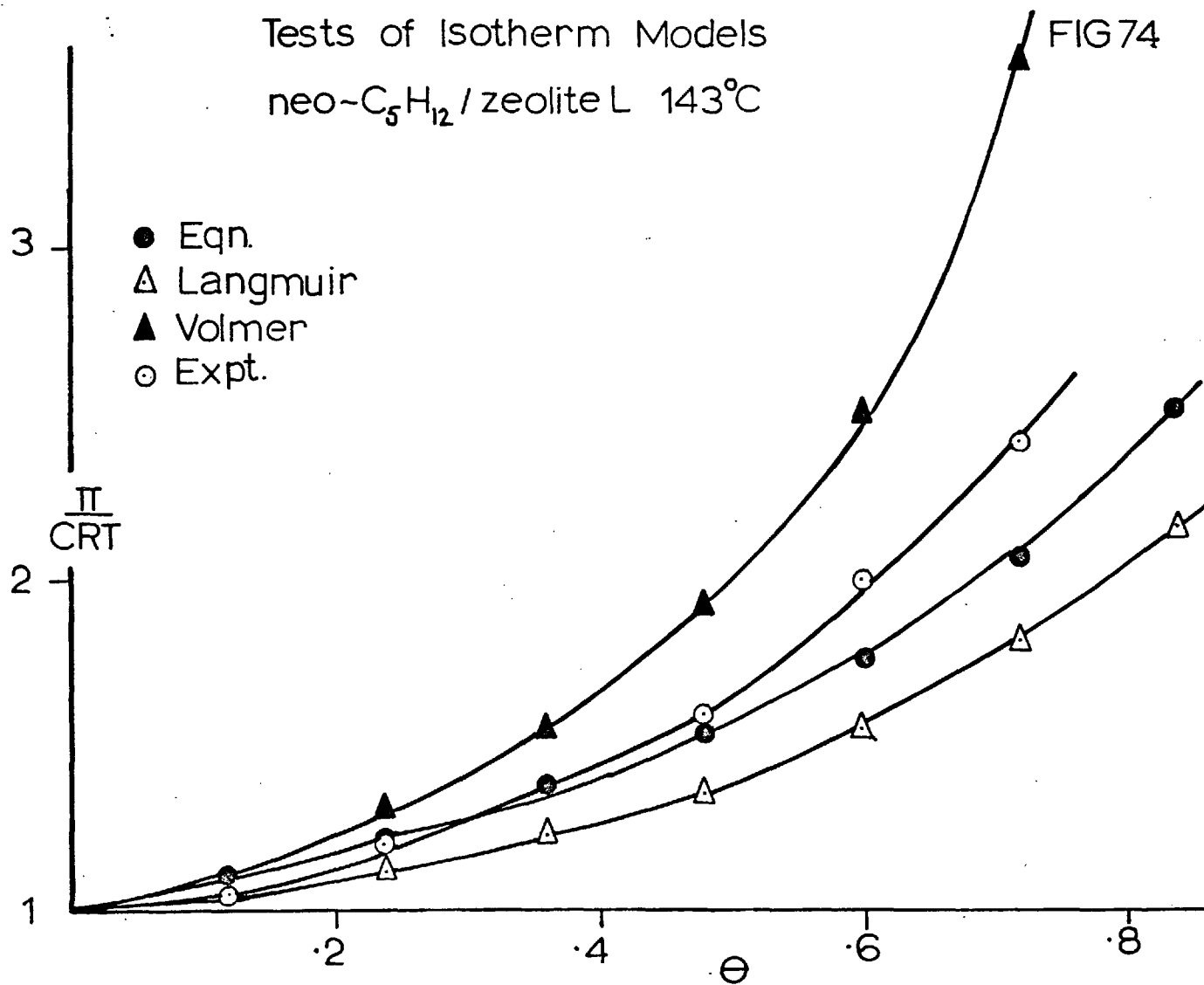
Tests of Isotherm Models $C_2H_6/zeolite\ L\ 0^\circ C$



Tests of Isotherm Models
neo-C₅H₁₂ / zeolite L 143°C

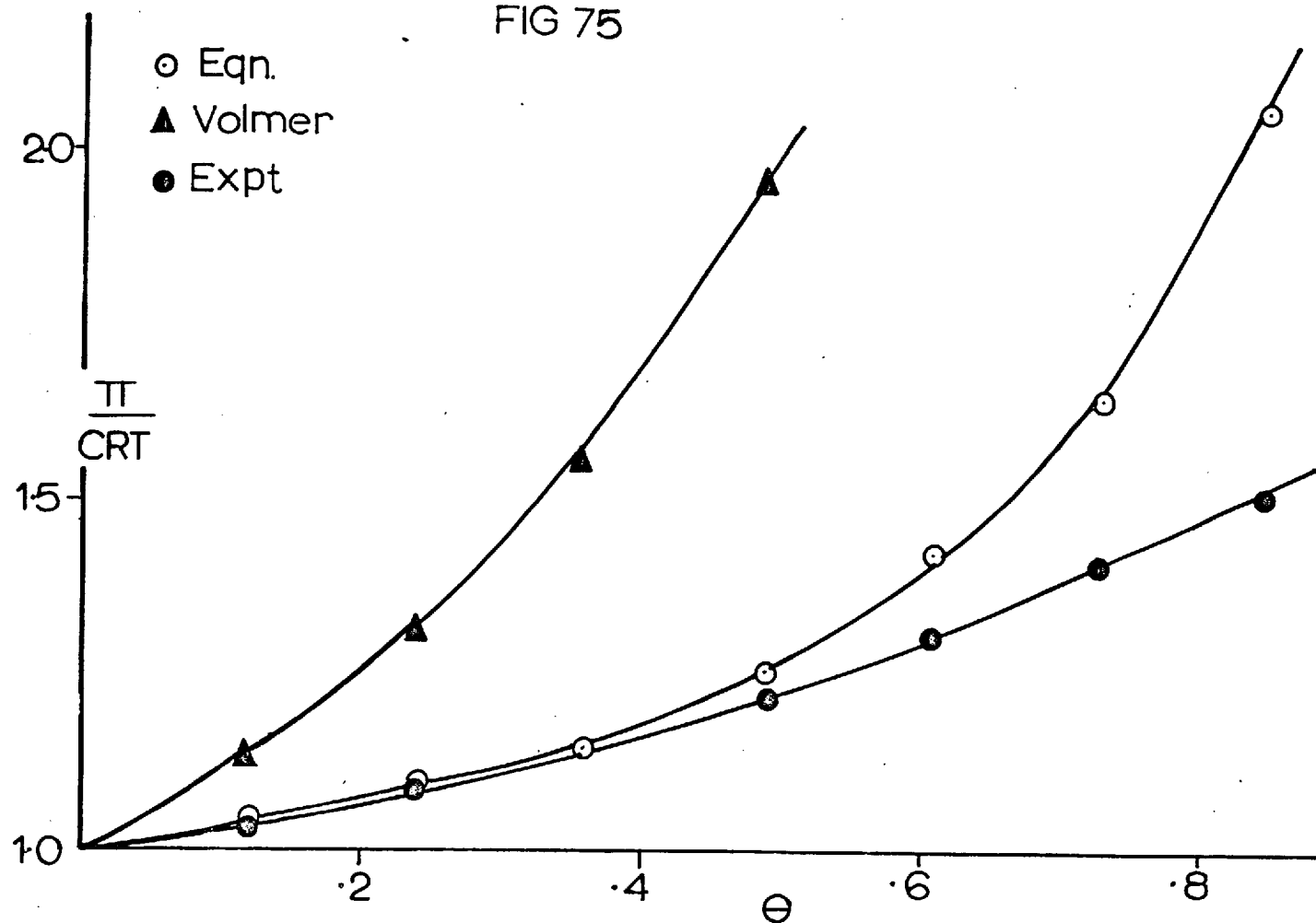
FIG 74

- Eqn.
- △ Langmuir
- ▲ Volmer
- Expt.



Tests of Isotherm Models $\text{C}_3\text{H}_8/\text{zeolite L}$ 87.1°C

FIG 75



CHAPTER 9

Summary of Results and Discussion

Crystallization fields of strontium and barium aluminosilicates were investigated using a hydrothermal technique. Sorption isotherms of the prepared zeolites and of zeolite L, supplied by M. Damm, were measured. In many cases equilibration was rapid and the isotherms reversible and reproducible.

Evaluation of the thermodynamic properties associated with the sorption processes were made for strontium ferrierite and zeolite L. Oxygen sorbed on the ferrierite possibly showed energetic heterogeneity at low coverages. Zeolite L behaved as an energetically homogeneous sorbent towards hydrocarbons. The isosteric heats of sorption in zeolite L showed maxima which were attributed to molecule-molecule interaction in the sorbate.

Integral heats were obtained from the isosteric heats and were found to be considerably larger than corresponding heats of evaporation. This was attributed to the nature of the environment of the sorbed molecules in the intracrystalline channels and cavities.

Differential and integral entropies were deduced and integral entropies were found to be less than the corresponding integral entropies of the liquid

sorbates. The temperature invariance of the half-standard integral and differential entropies of a fixed amount adsorbed was demonstrated and was used for extrapolation and interpolation of entropies of the sorbate.

An attempt was made to interpret the isotherm data in terms of limiting isotherm models. Empirical isotherm equations based on a virial equation of state for the sorbed phase were more successful and isotherm equilibrium constants were derived from these.

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TABLES R1 - R10

X-RAY POWDER DIFFRACTION PATTERNS

Table R1

<u>Sr-D</u>				<u>Ignition Product of Sr-D</u>			
d(Å)	Int.	d(Å)	Int.	d(Å)	Int.	d(Å)	Int.
9.55	ms	3.22	w	11.13	s	2.88	m
7.13	vw	3.14	vvw	8.61	w	2.83	m
6.96	vvw	3.06	w	6.91	s	2.688	w
6.63	ms	3.03	ms	6.66	w	2.656	w
5.88	mw	2.96	ms	5.57	m	2.626	w
4.97	vw	2.93	vw	5.49	s	2.494	w
4.75	w	2.89	w	5.29	vw	2.450	vw
4.65	vw	2.712	w	4.97	w	2.318	w
4.31	vw	2.644	m	4.65	m	2.302	mw
3.99	m	2.580	mw	4.31	m	2.267	w
3.94	mw	2.479	mw	4.05	s	2.159	vw(b)
3.86	w	2.411	m	3.88	w	2.041	w(b)
3.78	m	2.352	w	3.72	w	1.943	ww
3.73	vw	2.307	w	3.68	m	1.878	ms
3.68	w	1.923	w	3.65	w	1.726	m
3.54	s	1.867	m	3.56	vs	1.665	vw
3.48	s	1.483	w	3.34	m	1.623	vw
3.44	vvw	1.422	w	3.19	w	1.592	vw
3.39	vvw	1.308	vvw	3.13	w	1.434	w
3.31	w	1.268	vw	3.07	s	1.413	vw
3.26	vvw	1.233	vw	2.92	s	1.358	vw

Table R2Sr-Q

d(Å)	Int.	d(Å)	Int.	d(Å)	Int.	d(Å)	Int.
9.66	w	3.48	w	2.374	vw	1.701	mw
7.89	vvw	3.30	w	2.328	w	1.651	mw
6.96	mw	3.27	s	2.196	w	1.609	mw
6.61	vw	3.14	w	2.146	w	1.586	mw
6.30	w	3.10	ms	2.129	vw	1.568	vw
5.88	vw	3.03	vs	2.095	w	1.527	w
4.76	vs	2.95	w	2.076	vw	1.497	vvw
4.65	s	2.93	ms	2.032	vw	1.475	vw
4.31	s	2.89	vvw	2.000	m	1.465	vw
4.16	ms	2.768	mw	1.976	vw	1.455	vw
4.06	w	2.738	mw	1.954	vw	1.427	w
3.94	ms	2.657	m	1.924	vw	1.396	w
3.76	mw	2.542	vvw	1.894	ms	1.346	vw
3.67	vw	2.454	w	1.828	vw	1.333	vw
3.54	w	2.416	m	1.730	m	1.306	vw

Table R3

<u>Ba-J</u>				<u>Ba-K</u>			
d(Å)	Int.	d(Å)	Int.	d(Å)	Int.	d(Å)	Int.
11.39	s	3.70	w	10.59	ms	3.025	ms
10.53	vw	3.56	ms	7.39	mw	2.94	m
10.22	w	3.51	s	6.87	w	2.88	vw
7.39	m	3.45	s	6.07	ms	2.791	mw
7.04	w	3.28	w	5.58	ms	2.719	m
6.23	m	3.20	w	5.29	w	2.648	w
6.08	vw	3.16	w	5.08	w	2.613	mw
5.84	m	3.12	vs	4.72	m	2.554	w
5.73	mw	2.98	m	4.59	ms	2.493	m
5.63	vw	2.92	w	4.30	ms	2.469	w
4.79	m	2.88	m	4.205	ms	2.433	w
4.58	s	2.82	w	3.885	w	2.336	w
4.52	s	2.797	w	3.67	vw	2.301	m
4.295	vw	2.709	m	3.525	ms	2.234	vw
4.19	w	2.664	m	3.49	m	2.206	w
4.08	w	2.636	vw	3.445	w	2.117	w
4.02	ms	2.605	w	3.34	vw	1.965	w
3.97	m	2.455	ms	3.29	mw	1.919	m
3.91	ms	2.419	ms	3.16	s	1.846	w
3.81	m	2.370	ms	3.06	w	1.801	w

Table R3 (contd.)

<u>Ba-J</u>		<u>Ba-K</u>	
d($\overset{\circ}{\text{\AA}}$)	Int.	d($\overset{\circ}{\text{\AA}}$)	Int.
2.332	w	1.700	w
2.307	vw	1.730	vw
2.287	vw	1.694	vw
2.262	m	1.650	vw
2.213	vw	1.559	w
2.189	vw	1.539	w
2.169	vw	1.625	vw
2.125	vvw	1.509	vw
2.107	vvw	1.286	w
2.028	vw	1.271	vw
1.987	vw		
1.953	vw		
1.847	ms		
1.819	w		
1.794	w		
1.775	vw		
1.708	m		
1.670	mw		
1.632	w		
1.596	w		

Table R4

<u>Ba-P</u>		<u>Ba-Z</u>	
d(Å)	Int.	d(Å)	Int.
7.74	m	10.56	w
3.96	s	8.90	m
2.97	s	6.90	mw
2.67	ms	5.07	w
2.31	mw	4.60	s
2.250	m	3.45	vs
2.215	m	3.29	w
1.982	vw	3.17	m
1.933	w	2.91	m
1.854	m	2.84	w
1.702	m	2.421	ms
1.592	m	2.373	w
1.561	mw	1.988	vw
1.540	w	1.785	vw
1.464	w	1.765	vw
1.445	vw(b)	1.592	mw
1.331	w		
1.319	vw		
1.282	w		
1.262	vw		

Table R5

<u>Sr-C</u>		<u>paracelsian</u>		<u>Sr-C</u>		<u>paracelsian</u>	
d($\text{\AA}$)	Int.	d($\text{\AA}$)	Int.	d($\text{\AA}$)	Int.	d($\text{\AA}$)	Int.
6.46	mw	6.582	20	2.308	ms	2.194	45
6.22	m	6.379	20	2.291	vw	2.154	5
5.12	vw	5.217	7	2.227	vw	2.144	15
4.17	m	4.004	100	2.180	ms	2.054	7
3.92	vs	3.797	70	2.151	ms	2.034	7
3.71	s	3.696	4	2.109	mw	2.030	7
3.62	w	3.593	45	2.101	mw	1.874	20
3.50	s	3.290	35	2.088	m	1.849	10
3.22	ms	3.194	15	2.022	vw	1.831	5
3.11	mw	3.115	7	2.007	w	1.807	5
3.045	w	3.074	7	1.986	mw	1.798	7
2.940	m	3.010	35	1.903	w	1.782	7
2.920	ms	2.990	50	1.862	m	1.744	7
2.900	mw	2.961	30	1.833	m	1.718	13
2.890	mw	2.880	5	1.812	mw	1.664	13
2.830	w	2.731	50	1.794	w	1.590	20
2.681	m	2.621	20	1.771	vw	1.551	15
2.666	vw	2.609	35	1.752	m		
2.553	s	2.555	50	1.713	w		
2.506	m	2.393	20	1.703	w		
2.349	vw	2.370	45	1.694	vvw		
2.349	vw	2.281	3	1.630	mw		
2.338	m	2.229	20	1.615	vvw		

Table R5 (contd.)

<u>Sr-C</u>	
d($\text{\AA}$)	Int.
1.599	vw
1.557	m(b)
1.533	vw
1.520	vw
1.516	mw
1.483	w
1.470	n
1.438	vw
1.434	vw
1.417	w
1.395	w
1.388	mw
1.340	w(b)

Table R6

<u>Sr-G</u>		<u>Natural Chabazite</u>				<u>Sr-K</u>	
d(Å)	Int.	d(Å)	Int.	d(Å)	Int.	d(Å)	Int.
9.43	m	9.47	s	6.46	vw	1.61	vw(b)
6.80	m	6.93	mw	4.05	s	1.56	vw(b)
5.54	m	5.55	m	3.95	vw	1.48	mw(b)
5.12	m	5.02	m	3.88	mw	1.37	w(b)
4.48	vvw	4.32	s	3.74	ms		
4.37	vw	3.89	ms	3.54	vw		
4.30	ms	3.57	ms	3.45	ms		
3.95	m	3.34	ms	3.22	vs(b)		
3.68	w	3.16	mw	3.14	vw		
3.21	w	2.91	vs	2.95	vw		
3.12	m	2.59	m	2.91	mw		
2.95	vw	2.30	m	2.845	w		
2.91	s	2.08	m	2.761	w		
2.82	vvw	1.87	m	2.602	w		
2.78	vw	1.80	s	2.53	mw(b)		
2.74	vvw	1.72	ms	2.487	m		
2.54	m	1.65	m	2.310	w		
2.28	mw	1.56	m	2.160	m		
2.09	mw			2.116	mw		
1.81	mw			1.94	mw(b)		
1.71	mw			1.788	m		
				1.755	vw		
				1.715	w		

Table R7

<u>Sr-H</u>		<u>Ba-H</u>		<u>α-cristobalite</u>	
d($\text{\AA}$)	Int.	d($\text{\AA}$)	Int.	d($\text{\AA}$)	Int.
6.50	w	4.04	vs	4.04	100
4.03	vs	3.74	w	3.138	12
3.93	vW	3.54	w	2.845	14
3.75	m	3.48	w	2.489	18
3.45	m	3.245	s	2.468	6
3.23	s	3.171	mW	2.121	4
3.09	w	2.868	m	2.024	3
2.975	vW	2.507	m	1.932	4
2.90	vW	2.328	vW	1.874	4
2.848	w			1.613	5
2.758	w				
2.543	mW				
2.489	ms				
2.160	w				
2.12	vW				
2.06	vW				
1.96	vW				
1.93	vW				
1.87	vW				
1.79	w				
1.61	w				
1.59	vW				
1.49	vW				

Table R8

<u>Sr-M</u>		<u>Mordenite</u>		<u>Sr-P</u>	
d(Å)	Int.	d(Å)	Int.	d(Å)	Int.
13.56	mw	13.56	m	7.65	m
9.10	m	9.04	ms	4.49	vvw
6.63	m	6.60	m	3.875	vvs
6.43	w	6.41	mw	3.80	vw
6.07	vw	6.08	w	2.905	vs
5.86	m	5.80	mw	2.601	s
4.76	mw	5.11	vw	2.252	w
4.55	m	4.66	vw	2.210	m
4.32	vw	4.53	m	2.159	ms
4.18	m	4.26	vvw	1.937	mw
4.00	ms	4.14	vw	1.901	m
3.84	vw	4.00	s	1.814	ms
3.76	w	3.84	vw	1.659	m
3.64	w	3.77	w	1.551	m
3.48	s	3.63	vw	1.531	m
3.40	ms	3.49	vs	1.498	m
3.23	s(b)	3.41	s	1.438	w
3.04	mw	3.22	s(b)	1.409	vw
2.92	s(b)	2.98	vw	1.296	w
2.69	mw	2.90	ms	1.257	mw
2.563	ms	2.75	w	1.229	ww
2.523	ms	2.703	w	1.183	mw
2.182	w	2.642	w		

Table R8 (contd.)

<u>Sr-M</u>		<u>Mordenite</u>	
d(Å)	Int.	d(Å)	Int.
2.090	w	2.569	mw
1.886	w	2.529	m
1.821	w	2.464	w(b)
1.798	vw	2.442	w(b)
1.705	vw	2.174	vw
1.638	vw	2.102	w
		1.887	m
		1.818	w
		1.796	w
		1.710	vw
		1.626	vw

Table R9

<u>Ba-C</u>		<u>Natural celsian*</u>		<u>Ba-C</u>	
d(Å)	Int.	d(Å)	Int.	d(Å)	Int.
6.51	s	6.53	s	1.995	vw
5.85	w	5.88	m	1.950	mw
4.62	mw	4.63	ms	1.910	w
3.90	w	3.90	mw	1.797	mw
3.80	m	3.81	ms	1.672	w
3.63	w	3.63	w	1.649	w
3.56	mw	3.56	ms	1.627	w
3.47	s	3.50	s	1.577	w
3.35	s	3.35	s	1.533	w
3.28	mw	3.29	w	1.522	w
3.25	mw	3.27	w	1.502	mw
3.02	m	3.25	w	1.450	vw
2.91	mw	3.03	m		
2.77	m	2.92	mw		
2.608	w	2.778	m		
2.583	ms	2.613	w		
2.425	w	2.590	m		
2.326	mw	2.430	vw		
2.260	w	2.337	vw		
2.218	w	2.275	vw		
2.173	m	2.258	vw		
2.110	w	2.221	vw		
2.093	w	2.178	w		
2.061	w				
2.014	vw				

* From Jakobsberg,
Sweden.

Table R10Ba-M

d	Int.	d	Int.	d	Int.
8.24	vs	3.07	m	2.084	vw
7.56	vw	2.91	ms	2.062	m
7.18	s	2.838	w	2.052	m
7.03	w	2.745	w	2.021	mw
6.39	vs	2.724	s	2.008	vw
6.11	vw	2.674	s	1.996	vw
5.02	ms	2.668	s	1.964	w
4.24	ms	2.624	w	1.947	m
4.10	s	2.557	w	1.921	w
4.06	s	2.525	w	1.894	mw
4.03	s	2.058	w	1.840	vw
3.89	m	2.464	m	1.818	mw
3.66	w	2.368	m	1.802	w
3.57	vvw	2.315	ms	1.73	m(b)
3.52	w	2.295	m	1.71	ms(b)
3.46	mw	2.256	w	1.670	m
3.23	s	2.236	m	1.634	w
3.19	mw	2.213	w	1.530	m
3.16	ms	2.147	m	1.473	w
3.12	vs	2.119	w		

TABLES R11 - R30ISOTHERM DATA

Table R11

<u>'H-D/Oxygen-195.8°C.</u>		<u>'H-D/Nitrogen-195.8°C.</u>	
<u>P</u>	<u>X_S</u>	<u>P</u>	<u>X_S</u>
.064	70.64	.047	54.71
.176	74.27	.355	58.94
.250	75.81	.798	60.77
.404	77.80	.907	61.19
.893	81.12	1.530	62.24
1.516	83.41	2.481	63.69
2.180	84.72	3.561	64.32
2.876	85.98	5.190	65.34
4.143	87.80	6.682	66.18
5.140	88.81	7.967	66.72
5.914	89.83	8.763	67.23
7.762	91.35	12.298	68.32
10.461	94.25	9.946	67.63
11.455	95.63	6.101	65.72
9.951	93.28	3.344	64.09
5.602	89.49		
3.034	86.32		

Table R11 (contd.)'H-D/Argon-195-8°C.'H-D/Krypton-183,1°C.

<u>P</u>	<u>x_s</u>	<u>P/P₀</u>	<u>x_s</u>
.025	57.55	.029	49.65
.078	60.69	.100	56.85
.141	62.51	.319	60.87
.195	63.55	.456	63.28
.300	65.80	.521	63.92
.864	69.90	.597	64.32
1.307	71.38	.862	67.06
2.191	73.47	.695	65.01
3.778	75.76	.491	63.52
4.469	76.51	.261	60.16
7.449	79.05		
8.577	79.76		
10.113	80.58		
12.044	81.55		
9.222	80.16		
5.160	77.36		
2.431	74.19		

Table R11 (contd.)

<u>$^1\text{H-D/Xenon-775}^\circ\text{C.}$</u>		<u>$^1\text{H-D/Neon-195.8}^\circ\text{C.}$</u>	
<u>P</u>	<u>X_S</u>	<u>P</u>	<u>X_S</u>
.019	16.24	.382	4.46
.108	19.25	.654	5.84
.308	21.61	1.106	7.17
.597	22.71	1.733	
1.064	23.77	2.601	10.16
1.699	24.73	3.092	11.09
2.577	25.72	3.815	12.15
4.057	26.81	4.804	13.48
5.833	27.56	5.853	14.72
7.749	28.38	7.280	16.84
9.878	29.16	9.280	18.97
12.343	29.63	11.801	21.55
8.321	28.52		
4.890	27.09		
2.107	25.18		

Table R11 (contd.)

¹H-D/Carbon Dioxide 20.6°C. ¹H-D/Methane-183.1°C.

<u>P</u>	<u>α_s</u>	<u>P</u>	<u>α_g</u>
.187	11.73	.063	48.28
.561	14.56	.208	51.48
.944	15.97	.395	52.98
1.588	17.51	.627	54.39
1.993	18.31	1.109	56.77
3.012	19.75	1.690	57.72
5.711	22.25	2.350	58.53
6.944	23.11	3.555	59.64
8.675	24.07	5.211	61.27
11.112	25.21	5.811	62.11
12.967	26.34	4.741	60.62
10.414	24.82	2.894	58.53
8.211	23.76		
3.401	20.26		

Table R12

<u>$^2\text{H-D/Oxygen-195.8}^\circ\text{C.}$</u>		<u>$^2\text{H-D/Neon-195.8}^\circ\text{C.}$</u>	
<u>P</u>	<u>$\bar{x}_s$</u>	<u>P</u>	<u>$\bar{x}_s$</u>
.453	63.47	.471	3.42
1.231	65.79	.898	5.37
2.016	66.76	1.640	7.24
3.400	67.70	2.836	9.39
4.982	68.84	5.264	12.51
6.260	69.68	7.303	14.34
10.187	72.61	9.772	16.19
12.002	75.60	11.429	17.08
8.433	70.78	8.838	15.43
2.641	67.65	6.842	13.92
<u>$^2\text{H-D/Argon-195.8}^\circ\text{C.}$</u>		<u>$^2\text{H-D/Nitrogen-195.8}^\circ\text{C.}$</u>	
<u>P</u>	<u>$\bar{x}_s$</u>	<u>P</u>	<u>$\bar{x}_s$</u>
.026	49.26	.015	46.33
.280	54.43	.125	47.82
.681	55.78	.445	48.68
1.307	56.82	.988	49.39
2.195	57.52	1.699	50.00
3.146	58.10	2.546	50.70
5.001	58.63	3.882	52.01
6.749	59.34	4.464	52.41
11.291	60.75	5.637	52.95
9.742	60.13	8.277	53.93
7.301	59.49	9.577	54.43
4.133	58.28	11.913	55.07
		8.766	53.93
		4.130	52.16
		1.932	50.46

Table R12 (contd.) $^2\text{H-D/Xenon-77.5}^\circ\text{C.}$

$\underline{P}$	$\underline{x}_s$
.114	18.11
.700	19.76
1.297	21.17
1.969	22.24
2.840	22.95
4.006	23.39
5.953	23.87
8.410	24.37
11.341	24.68
6.860	24.01
3.912	23.26

 $^2\text{H-D/Krypton-183.1}^\circ\text{C.}$

$\underline{P/P_0}$	$\underline{x}_s$
.009	37.96
.104	42.51
.204	44.05
.332	45.94
.492	47.37
.749	49.30
.610	48.60
.251	45.03

 $^2\text{H-D/Methane } 183.1^\circ\text{C.}$

$\underline{P}$	$\underline{x}_s$
.119	36.25
.539	39.48
1.148	40.86
2.958	42.17
4.631	43.30
5.712	45.44
5.044	44.00
2.363	41.27

 $^2\text{H-D/Carbon dioxide } 19.2^\circ\text{C.}$

$\underline{P}$	$\underline{x}_s$
.238	12.80
.788	15.73
2.842	20.90
3.984	22.34
6.850	23.62
9.738	24.77
14.239	26.31
7.421	23.76
4.611	22.38
2.107	19.15

Table R13 $^3\text{H-D/Oxygen-195.8}^\circ\text{C.}$

<u>P</u>	<u>$\bar{x}_S$</u>
.380	61.10
.874	62.87
1.693	64.34
3.037	65.86
4.289	67.05
5.071	67.45
6.672	68.48
7.610	69.24
9.129	72.46
10.573	72.96
12.045	74.77
8.943	70.69
6.039	68.25

 $^3\text{H-D/Nitrogen-195.8}^\circ\text{C.}$

<u>P</u>	<u>$\bar{x}_S$</u>
.049	43.26
.165	44.68
.904	46.58
1.757	48.54
3.475	49.25
5.531	49.98
8.057	50.03
12.213	51.10
6.580	49.96
3.726	48.74

 $^3\text{H-D/Argon-195.8}^\circ\text{C.}$

<u>P</u>	<u>$\bar{x}_S$</u>
.345	48.22
1.115	50.37
1.885	51.25
2.534	51.88
3.788	52.33
4.922	52.71
6.500	54.15
7.898	54.48
10.074	56.55
13.403	57.51
10.581	56.73
7.151	54.94
4.039	53.69

 $^3\text{H-D/Krypton-183.1}^\circ\text{C.}$

<u>P/P₀</u>	<u>$\bar{x}_S$</u>
.030	25.16
.169	26.58
.363	27.63
.511	28.02
.595	28.29
.689	28.60
.833	29.31
.698	28.74
.470	28.05
.283	27.10
.165	26.46
.102	26.04

Table R13 (contd.) $^3\text{H}^3\text{-D/Xenon-77.5}^\circ\text{C.}$

<u>P</u>	<u>x_s</u>
1.353	1.34
3.506	3.18
7.010	5.11
9.982	5.83
12.154	7.10
14.330	7.12

 $^3\text{H}^3\text{-D/Neon-195.8}^\circ\text{C.}$

<u>P</u>	<u>x_s</u>
1.632	7.60
2.312	9.13
3.579	10.86
4.889	12.59
6.265	13.75
7.488	14.82
8.990	15.88
10.928	17.39
12.865	17.81
14.411	18.53
15.780	19.41
12.401	17.99
9.322	16.28
6.053	13.67

 $^3\text{H-D/Carbon dioxide-20.0}^\circ\text{C.}$

<u>P</u>	<u>x_s</u>
.221	17.29
.849	22.70
1.898	25.11
3.192	27.47
4.704	28.51
5.912	29.19
8.508	30.30
9.975	30.70
11.074	31.06
15.576	31.83
9.713	30.65
7.246	29.72
5.211	28.79

 $^3\text{H-D/Methane-183.1}^\circ\text{C.}$

<u>P</u>	<u>x_s</u>
.073	9.82
.403	16.77
1.008	18.29
1.939	18.71
3.133	19.39
3.907	19.46
4.842	19.89
5.904	20.74
6.852	22.21
5.188	19.95
2.604	19.04

Table RL4Li-D/Oxygen-195.8°C.

$\underline{P}$	$\underline{x}_S$
.087	52.37
.407	54.66
1.850	57.02
2.606	57.73
5.136	59.20
7.824	60.14
11.241	63.17
9.564	61.19
6.133	59.45

Li-D/Nitrogen-195.8°C.

$\underline{P}$	$\underline{x}_S$
.128	43.41
.587	45.27
1.582	46.84
2.533	47.79
4.028	48.48
6.862	49.65
8.086	50.29
10.112	51.04
13.125	51.80
11.343	50.88
9.101	49.99
6.040	49.04

Li-D/Argon-195.8°C.

$\underline{P}$	$\underline{x}_S$
.203	46.41
.748	49.10
1.332	49.17
1.925	49.18
3.323	49.99
4.116	50.83
4.883	51.62
6.621	52.14
8.648	53.21
10.116	54.03
11.565	54.95
9.234	53.56
5.401	51.52

Li-D/Krypton-183.1°C.

$\underline{P/P_0}$	$\underline{x}_S$
.004	37.40
.064	40.84
.11	42.87
.17	44.34
.41	45.73
.62	46.14
.72	46.50
.95	47.18
.81	46.97
.54	46.22
.39	45.63

Table R14 (contd.)

<u>Li-D/Xenon-77.5°C.</u>		<u>Li-D/Neon-195.8°C.</u>	
<u>P</u>	<u>x_s</u>	<u>P</u>	<u>x_s</u>
.031	7.96	.141	2.63
.250	11.01	.306	4.25
.335	14.74	.624	6.35
.450	14.95	.930	7.90
1.451	18.87	1.160	8.88
2.854	20.24	1.527	10.32
4.656	21.07	1.989	11.99
7.501	22.51	2.546	13.61
10.093	23.08	3.158	15.81
9.133	22.79	3.620	17.75
6.150	21.76	4.290	20.53
3.743	20.63	5.660	23.84
		9.400	33.32
		10.758	35.26
		7.397	27.42
		5.018	22.21
		3.403	17.08

Table R14 (contd.)

<u>Li-D/Carbon dioxide+19.8°C.</u>		<u>Li-D/Methane-183.1°C.</u>	
<u>P</u>	<u>x_S</u>	<u>P</u>	<u>x_S</u>
.569	26.35	.113	9.72
1.662	29.36	.163	10.07
2.161	30.03	.706	12.34
2.418	30.76	1.381	14.55
6.029	32.68	2.131	15.03
9.172	34.18	2.945	15.45
13.973	36.13	3.754	15.79
10.471	34.84	4.353	16.25
8.220	33.89	5.085	16.47
5.634	32.58	5.849	17.03
8.861	31.58	5.500	16.60
		2.401	15.09

Table R15Na-D/Oxygen-195.8°C.

<u>P</u>	<u>x_s</u>
.736	47.25
1.965	51.78
2.915	52.32
4.173	52.85
4.926	53.18
5.765	53.51
6.827	53.83
7.691	54.13
9.488	54.90
12.001	58.01
12.887	59.04
8.782	54.34
5.324	52.87
3.099	52.21
1.208	50.61
1.038	50.03

Na-D/Nitrogen-195.8°C.

<u>P</u>	<u>x_s</u>
.061	40.12
.771	42.10
2.112	43.16
3.419	43.30
7.026	44.05
9.415	44.24
12.186	44.82
15.314	45.28
11.401	44.29
5.251	43.83

Na-D/Argon-195.8°C.

<u>P</u>	<u>x_s</u>
.337	34.72
.959	35.32
1.672	35.45
2.893	35.67
4.095	35.78
6.771	36.48
8.992	36.63
10.418	36.93
11.333	37.08
12.533	37.34
8.721	36.42
3.972	35.91
1.737	35.59

Na-D/Krypton-183.1°C.

<u>P/P₀</u>	<u>x_s</u>
.052	31.44
.104	32.47
.342	33.06
.519	33.40
.632	34.21
.919	36.00
.654	34.53
.284	32.95

Na-D/Xenon-77.5°C.

<u>P</u>	<u>x_s</u>
.029	7.34
.052	9.41
.094	11.38
.230	15.58
1.455	19.02
3.815	20.48
6.610	21.34
10.385	21.94
17.176	23.37
8.133	21.58
5.464	21.03
2.308	19.92

Na-D/Neon-195.8°C.

<u>P</u>	<u>x_s</u>
.151	1.49
.505	2.87
.749	3.91
1.111	5.39
1.651	7.09
2.539	9.55
3.455	11.73
6.161	16.26
10.307	21.42
13.913	25.10
9.478	20.33
5.964	16.24
4.223	13.17
3.078	11.14

Table R15 (contd.)

<u>Na-D/Carbon dioxide 20.0°C.</u>		<u>Na-D/Methane-183.1°C.</u>	
<u>P</u>	<u>x_s</u>	<u>P</u>	<u>x_s</u>
.033	8.17		
.037	10.68		
.046	12.25	Sorpton was extremely slow, it was not possible to obtain an isotherm.	
.061	15.59		
.083	17.67		
.198	21.51		
.414	24.76		
1.417	28.34		
2.725	30.11		
4.530	31.45		
6.733	32.86		
11.165	34.72		
13.610	36.12		
7.367	33.15		
4.235	31.15		
2.618	30.13		

Table R16K-D/Oxygen-195.8°C.K-D/Nitrogen-195.8°C

<u>P</u>	<u>x_s</u>	<u>P</u>	<u>x_s</u>
.052	34.53	.039	1.34
.115	35.55	.152	1.50
.130	36.39	.462	1.54
.164	37.22	.633	1.61
.198	38.55	1.549	1.87
.291	39.36	2.747	2.19
.379	39.89	4.613	2.31
.513	41.11	6.041	2.39
.632	41.97	7.349	2.49
1.433	42.75	9.165	3.00
1.996	42.95	12.377	3.26
2.628	43.26	8.133	2.38
3.435	43.50	5.261	2.22
3.879	43.63		
4.414	43.81		
5.858	44.60		
9.173	45.95		
11.706	48.75		
10.429	46.88		
7.451	44.87		

Table R16 (contd.)K-D/Argon-195.8°C.

$\underline{P}$	$\underline{x}_S$
.086	.84
.280	1.12
.659	1.86
1.071	1.92
1.650	2.03
1.840	2.17
2.766	2.24
4.647	2.31
6.704	2.49
8.377	2.61
9.837	2.62
7.649	2.52
5.836	2.40

K-D/Xenon-77.5°C.

$\underline{P}$	$\underline{x}_S$
9.514	.04
11.874	.21
14.201	.23

K-D/Krypton-183.1°C.

$\underline{P/P_0}$	$\underline{x}_S$
.037	.64
.087	.78
.198	.95
.266	1.06
.385	1.07
.671	1.24
.832	1.33
.706	1.23
.524	1.05

K-D/Neon-195.8°C.

$\underline{P}$	$\underline{x}_S$
.086	.34
.272	.83
.623	2.12
1.113	3.66
1.511	4.70
2.337	6.39
2.916	7.60
4.393	9.97
6.719	12.56
8.063	13.80
7.240	13.03
5.633	11.46
3.464	8.44

Table R16 (contd.)

<u>K-D/Carbon dioxide +15.6°C.</u>		<u>K-D/Methane-183.1°C.</u>	
<u>P</u>	<u>x_s</u>	<u>P</u>	<u>x_s</u>
.045	11.88	.074	.57
.052	13.91	.320	.78
.065	15.52	.522	.80
.151	19.95	1.141	.87
.288	23.10	1.524	.89
.617	25.07	2.054	.95
1.632	27.69	3.566	.97
2.666	28.83	4.339	1.23
4.649	29.62	5.062	1.28
6.593	29.90	6.016	1.73
9.339	30.41	4.724	1.23
12.533	30.84	2.560	1.03
11.246	30.63		
7.739	30.30		

Table R.17.Ca-D/oxygen-195° 8° C

<u>P</u>	<u>x_s</u>
.241	47.07
.674	48.28
1.088	48.68
1.686	49.07
2.587	49.80
4.764	50.59
6.597	51.26
8.033	51.84
10.418	52.93
9.211	51.73
5.505	50.61
3.107	50.06

Ca-D/nitrogen-195° 8° C

<u>P</u>	<u>x_s</u>
.026	31.91
.433	34.33
1.351	36.53
3.558	36.89
6.303	36.98
8.842	37.03
11.660	37.30
14.721	37.62
6.333	36.99
3.150	36.71

Ca-D/Argon-195° 8° C

<u>P</u>	<u>x_s</u>
.040	35.33
.319	38.16
1.031	41.41
1.633	41.79
2.670	42.83
3.793	43.75
6.049	44.79
8.144	45.41
12.069	46.47
10.471	46.06
7.144	45.15
4.544	44.19

Ca-D/Krypton-183° 1° C

<u>P/P₀</u>	<u>x_s</u>
.03	28.52
.04	30.72
.05	31.14
.06	31.59
.09	32.03
.14	33.07
.17	33.43
.29	34.61
.45	35.73
.68	36.11
.80	36.50
.51	35.45
.34	34.59
.25	33.48

Table R.17C₂-D/Xenon-77.5°C

<u>P</u>	<u>x_s</u>
.046	4.62
.091	7.95
.426	10.29
1.196	12.84
1.554	13.62
2.423	14.62
4.102	15.01
7.080	15.69
10.976	16.44
12.972	16.69
8.133	16.03
5.261	15.48
3.214	14.96

C₂-D/Neon-195.8°C

<u>P</u>	<u>x_s</u>
.051	2.06
.143	3.13
.368	4.74
.634	5.50
1.017	7.04
2.203	9.64
3.013	11.09
5.417	13.67
8.472	15.08
10.324	15.99
13.691	16.92
11.404	16.38
7.211	14.63

Ca-D/Carbon Dioxide

<u>P</u>	<u>x_s</u>
.151	19.24
.257	20.47
.920	23.07
2.436	24.70
3.626	24.94
7.753	25.31
11.611	25.36
9.131	25.33
4.266	25.16

Ca-D/Methane-183.1°C

<u>P</u>	<u>x_s</u>
.483	5.64
.805	5.73
1.249	5.80
1.455	6.76
2.175	8.13
3.909	9.11
4.508	9.49
5.327	9.62
6.270	10.80
5.741	10.03
4.904	9.76
3.113	8.03

Table R.18SrD/oxygen-195.8°CSrD/nitrogen-195.8°C

<u>P</u>	<u>x_s</u>	<u>P</u>	<u>x_s</u>	<u>P</u>	<u>x_s</u>
.316	55.23	7.671	62.20	.286	5.39
.387	55.66	5.729	61.12	.539	6.35
.489	56.13	4.444	60.79	1.128	7.37
.681	56.73			2.724	8.14
.837	56.90			4.155	8.96
1.056	57.36			7.114	9.68
1.267	57.62			7.882	10.56
1.442	57.81			8.299	10.61
1.915	58.27			10.031	11.76
2.439	58.66			11.275	12.27
2.856	58.99			13.698	13.23
3.006	59.51				
3.509	59.69				
3.984	60.02				
4.402	60.32				
4.906	60.48				
5.647	60.65				
6.235	61.36				
7.105	61.58				
8.833	62.51				
10.975	64.14				
12.541	66.47				
14.246	74.05				
14.012	69.04				
13.625	67.69				
13.079	67.05				
12.413	65.55				
11.792	64.84				
11.167	64.30				
10.530	63.77				
9.732	63.56				
8.873	62.89				

Table R.18SrD/Argon-195.8°C

<u>P</u>	<u>x_S</u>
.025	48.42
.096	50.63
.600	54.80
1.244	55.88
1.688	56.63
2.543	57.18
2.627	57.21
3.784	57.48
4.444	57.97
6.460	58.74
7.051	58.96
8.127	59.40
9.307	59.62
10.536	59.72
11.772	59.95
13.833	60.54
15.400	61.07
14.478	60.81
13.652	60.57
12.650	60.17
11.691	59.92
10.944	59.90
9.857	59.55
8.403	59.21
7.265	58.95
6.442	58.78
5.583	58.45
4.623	58.10
3.479	57.65

SrD/Neon-195.8°C

<u>P</u>	<u>x_S</u>
.069	.84
.149	2.24
.305	3.53
.448	4.87
.691	5.83
.829	6.51
1.202	7.79
1.663	9.05
2.324	10.72
3.870	14.01
4.589	15.27
5.364	16.54
7.773	19.86
9.770	22.39
11.393	24.46
13.055	25.99
16.162	28.91
18.508	31.17
11.421	24.09
8.746	21.14
6.191	17.74

Table R.18.

<u>SrD/Krypton-183.1°C</u>		<u>SrD/Xenon-77.0°C</u>	
<u>P/Po</u>	<u>x_s</u>	<u>P</u>	<u>x_s</u>
.027	15.83	.495	5.03
.187	16.46	2.616	5.48
.261	16.65	4.492	5.87
.369	16.91	6.616	6.39
.470	17.23	7.826	6.56
.564	17.25	10.023	7.11
.651	17.31	13.577	7.71
.753	17.47	11.346	7.30
.841	17.56	7.935	6.57
.913	17.71	3.416	5.58
.971	18.12		
.761	17.33		
.685	17.26		
.582	17.23		
.485	16.93		
.379	16.70		
.307	16.54		
.119			

Table R.18.SrD/Methane-183.1°C

<u>P</u>	<u>x_s</u>
.189	6.03
.702	6.32
1.551	6.60
2.388	6.89
3.023	6.97
3.669	7.15
4.322	7.26
5.481	7.67
6.650	9.13
5.834	7.72
3.361	6.93

SrD/Carbon Dioxide-15.0°C

<u>P</u>	<u>x_s</u>
.089	25.51
.370	30.69
1.513	33.28
2.668	34.66
3.668	35.92
5.366	36.61
6.838	37.13
8.053	37.59
8.943	37.69
10.353	38.15
11.359	38.63
14.676	39.29
17.403	40.12
12.521	38.74
7.464	37.32

Table R.19.O₂/SrD-70.4°C

<u>P</u>	<u>x_S</u>
.111	2.51
.195	3.52
.342	4.79
.544	5.80
.684	6.77
.971	7.76
1.360	8.76
1.708	9.63
2.066	10.46
2.398	11.01
2.939	11.85
3.506	12.86
4.923	15.00
5.887	16.19
8.428	18.84
11.581	20.55

O₂/SrD-80.5°C

<u>P</u>	<u>x_S</u>
.196	5.39
.304	6.25
.421	7.69
.600	8.88
.811	9.62
1.100	10.56
1.586	12.19
1.796	12.69
2.204	13.59
2.729	14.36
3.223	15.43
3.977	16.50
6.432	19.17
7.881	20.79
2.647	14.93
2.041	13.45
1.690	12.12
1.371	11.18

Table R.19.O₂/SrD-90.6°C

<u>P</u>	<u>x_S</u>
.123	5.79
.165	6.59
.213	7.61
.404	9.79
.557	10.57
.837	11.67
1.303	13.65
1.599	14.17
2.343	16.22
2.571	17.40
4.108	19.86
4.620	20.44
5.596	22.14
7.487	24.67
3.453	19.00
2.700	17.89

Table R.19.O₂/SrD-145.4°C

<u>P</u>	<u>x_S</u>
.038	21.84
.042	25.06
.086	26.50
.114	30.80
.199	32.67
.264	33.42
1.103	36.39
1.371	37.62
1.662	37.92
2.697	39.25
3.522	39.85
4.501	40.24
5.671	41.24
6.322	42.17
6.879	43.32

O₂/SrD-183.1°C

<u>P</u>	<u>x_S</u>
.030	40.13
.145	43.35
.638	46.71
.854	47.65
1.987	49.19
3.388	50.51
4.378	51.29
6.183	52.31
6.983	52.89
5.299	52.22
4.051	51.64

Table R.19.O₂/SrD-107.9°C

<u>P</u>	<u>x_s</u>
.099	7.42
.133	9.81
.206	11.52
.342	11.97
.491	13.77
.607	15.64
.757	17.04
1.384	20.04
1.751	21.14
2.852	24.07
3.646	25.54
5.100	27.44
6.841	29.42
8.149	30.64
3.125	24.36
2.593	23.65
1.881	22.06
1.652	20.93

O₂/SrD-129.3°C

<u>P</u>	<u>x_s</u>
.073	10.26
.075	12.56
.098	14.54
.119	16.39
.332	21.60
.446	23.82
.538	24.64
.930	27.24
1.136	28.14
1.899	30.62
3.052	32.46
4.458	33.79
5.971	35.53
7.285	36.36
5.056	35.15
3.765	33.52
3.002	32.51
2.400	31.61
1.835	31.45
1.495	29.43

Table R.19.O₂/SrD-117.1°C

<u>P</u>	<u>x_s</u>	<u>P</u>	<u>x_s</u>
.067	9.15	4.144	29.31
.146	12.10	3.381	27.48
.230	13.30		
.483	15.53		
.548	16.59		
.653	18.52		
.657	20.10		
1.200	21.75		
1.695	23.52		
2.327	25.06		
3.625	25.96		
4.968	29.29		
7.526	32.82		
5.478	30.93		

Table R.20.

<u>SrD/Neon-195.8°C</u>		<u>SrD/Neon-183.1°C</u>	
<u>P</u>	<u>x_s</u>	<u>P</u>	<u>x_s</u>
.069	.84	.119	.44
.149	2.24	.272	.97
.305	3.53	.427	1.57
.448	4.87	.694	2.64
.691	5.83	1.181	3.82
.829	6.51	2.110	5.62
1.202	7.79	3.554	7.22
1.663	9.05	5.223	8.84
2.324	10.72	7.264	10.64
3.870	14.01	9.294	11.97
4.589	15.27	12.396	14.20
5.364	16.54	16.631	16.64
7.773	19.86	14.692	15.45
9.770	22.39	10.724	13.05
11.393	24.46	6.342	9.78
13.055	25.99		
16.162	28.91		
18.508	31.17		
14.491	27.53		
10.620	23.38		
6.434	17.99		

Table R.20.SrD/Neon-160.0°C

<u>P</u>	<u>x_s</u>
.639	.82
1.482	1.60
3.120	2.67
5.594	3.92
8.582	5.33
10.314	5.99
13.844	7.199
17.499	8.41
12.132	6.59
8.094	5.08

SrD/Neon-142.5°C

<u>P</u>	<u>x_s</u>
.396	.18
.788	.35
2.247	.63
4.212	1.29
5.500	1.68
6.445	2.00
8.876	2.58
10.511	3.32
13.030	4.10
16.266	5.13
18.327	5.80
14.424	4.53
7.682	2.43

SrD/Neon-99.4°C

<u>P</u>	<u>x_s</u>
.452	.15
1.054	.30
1.291	.33
1.842	.40
2.500	.49
3.131	.57
5.250	1.10
7.678	1.70
11.259	2.57
14.921	3.50
18.841	4.31

Table R.21.'H-D/pyrrole 49.2°C

<u>P</u>	<u>x_s(mg/g)</u>
.222	8.52
.444	16.23
.568	19.41
.892	29.98
1.179	37.03
1.555	44.17
2.021	48.33
2.314	53.14
2.730	57.42
2.975	59.22
3.366	61.70
3.749	66.48
3.991	67.98
4.176	71.41
3.061	60.06
2.316	53.15
1.303	39.17

'H-D/pyrrole 59.2°C

<u>P</u>	<u>x_s(mg/g)</u>
.184	6.94
.521	11.10
.875	16.22
1.369	27.64
2.117	36.39
2.386	40.34
2.613	42.59
3.031	48.12
3.373	50.69
3.697	52.73
2.471	41.21
1.733	31.69
.811	15.89

'H-D/o-xylene 46.8°C

<u>P</u>	<u>P/Po</u>	<u>x_s(mg/g)</u>
.392	.178	5.04
.974	.443	10.02
1.134	.515	11.05
1.520	.691	13.44
1.878	.854	15.03
1.959	.890	17.86
1.887	.858	15.30
1.681	.764	14.32
1.425	.648	12.73

'H-D/m-xylene 47°C

<u>P</u>	<u>P/Po</u>	<u>x_s(mg/g)</u>
.225	.090	2.15
.434	.174	5.75
.846	.338	9.31
.971	.388	10.43
1.349	.539	11.58
1.804	.722	12.99
2.067	.827	16.88
2.102	.841	17.33
2.350	.940	22.90

Table R.21.¹H-D/p-xylene 47.0°C

<u>P</u>	<u>P/Po</u>	<u>x_s(mg/g)</u>
.215	.078	2.98
.626	.228	8.44
.953	.347	11.90
1.332	.485	14.85
1.733	.630	17.09
2.075	.754	18.15
2.300	.836	21.57
2.721	.989	31.61

¹H-D/Benzene 32.1°C

<u>P</u>	<u>P/Po</u>	<u>x_s</u>
.450	.036	2.30
.912	.073	3.89
1.605	.129	6.01
3.195	.256	8.98
6.275	.503	11.76
8.901	.714	13.74
11.301	.906	21.29
10.291	.825	15.30
9.034	.724	13.88
8.438	.677	13.17
7.210	.578	12.47
4.957	.398	11.32
2.713	.241	8.58

¹H-D/Thiophen 47.0°C

<u>P</u>	<u>x_s(mg/g)</u>
.548	12.89
1.504	23.14
3.543	43.09
5.927	55.98
8.655	66.73
7.312	61.29
3.749	43.22
2.991	38.11
1.190	20.07

Table R.22.Ba-J/O₂-195.8°C

<u>P</u>	<u>x_s</u>
.070	49.76
.113	50.42
.252	51.48
.373	51.98
.739	53.00
.981	53.38
1.873	54.26
3.295	55.37
4.897	56.03
6.513	57.12
8.457	57.94
10.796	59.34
11.232	60.56
9.331	58.21
7.296	56.83
4.613	55.81
1.303	54.16

Ba-J/N₂-195.8°C

<u>P</u>	<u>x_s</u>
.135	44.76
.597	45.76
1.797	46.31
2.589	46.59
4.216	46.86
6.667	47.39
7.928	47.64
9.946	48.05
10.879	48.36
13.904	49.20
8.471	47.81
5.301	47.01
3.124	46.18

Table R.22.Ba-J/A-195.8°C

<u>P</u>	<u>x_s</u>
.096	44.05
.456	45.48
1.031	46.21
1.371	46.49
2.544	47.05
5.495	48.78
6.718	49.55
8.721	49.90
10.390	50.20
12.548	50.65
7.309	49.12
3.260	47.20

Ba-J/Neon-195.8°C

<u>P</u>	<u>x_s</u>
.529	3.36
.970	5.37
1.380	6.73
1.695	7.85
2.591	10.11
3.207	11.44
4.493	14.03
5.371	15.42
7.163	18.06
8.222	19.30
9.664	20.87
10.454	21.64
12.051	23.13
12.828	23.83
8.613	20.07
3.920	13.00

Table R.22.Ba-J/Xenon-77.5°C

<u>P</u>	<u>x_s</u>
.031	14.81
.053	15.65
.074	16.46
.097	18.42
.167	20.10
.218	21.55
.284	22.73
.566	24.22
.896	25.14
1.588	25.80
2.632	26.12
3.919	26.32
5.151	26.44
7.399	26.60
10.003	26.70
6.491	26.51
1.909	25.81

Ba-J/Krypton-183.1°C

<u>P/Po</u>	<u>x_s</u>
.039	36.05
.088	36.68
.152	37.09
.211	37.76
.382	37.87
.466	38.26
.622	38.67
.810	39.41
.741	38.13
.234	37.80

Ba-J/Propane-77.5°C

<u>P</u>	<u>x_s</u>
.045	5.94
.141	6.91
1.604	9.65
2.223	11.71
5.077	13.25
10.118	14.29
8.196	13.82
.930	9.41

Ba-J/Methane-183.1°C

<u>P/Po</u>	<u>x_s</u>
.015	35.10
.079	36.20
.160	36.90
.209	37.18
.312	37.60
.572	38.42
.716	39.07
.504	38.01
.139	36.25

Table R.22.Ba-J/Ethane-77.5°C

<u>P</u>	<u>x_s</u>
.039	5.76
.095	8.34
.123	10.47
.180	12.08
.205	13.44
.211	14.57
.257	15.42
.441	17.39
.615	18.82
.883	20.90
1.415	21.76
2.234	22.68
3.641	23.58
7.044	23.89
10.210	24.14
5.397	23.71
1.841	22.18

Ba-J/Carbon Dioxide-17.6°C

<u>P</u>	<u>x_s</u>
.021	15.90
.047	17.98
.076	21.14
.090	22.98
.156	25.30
.330	29.32
.679	32.25
1.191	34.16
1.681	35.36
2.961	36.83
3.673	37.73
6.473	38.79
7.776	39.13
10.813	39.60
12.894	39.82
8.041	39.02
2.163	36.01

Table R.23.CaJ/O₂-195.8°C

<u>P</u>	<u>x_S</u>
.067	48.56
.138	49.08
.976	50.09
1.441	50.81
2.875	51.74
4.096	52.71
4.580	52.90
6.124	53.62
7.339	54.12
8.969	54.63
10.352	55.96
6.641	53.99
2.333	51.86

BaK/O₂-195.8°C

<u>P</u>	<u>x_S</u>
.177	35.41
.499	36.19
.905	38.01
1.817	39.21
3.472	40.04
5.771	40.73
8.171	41.32
11.919	42.71
10.177	42.17
4.310	40.47

BaZ/O₂-195.8°C

<u>P</u>	<u>x_S</u>
.297	21.86
.604	24.79
1.294	27.35
2.464	28.66
4.087	30.25
6.052	31.89
8.845	32.57
10.727	32.81
7.343	31.94
3.171	29.53

Table R.24.Na-K L/Argon-195.8°C

<u>P</u>	<u>x_s</u>
.094	63.96
.206	65.71
.263	66.77
.518	69.84
.760	71.48
1.538	74.77
2.105	76.24
3.131	78.72
4.485	80.64
6.027	82.80
8.262	85.35
10.431	87.92
13.899	92.45
18.118	101.45
15.883	95.43
11.303	90.03
7.824	84.97

Na-K L/Oxygen-195.8°C

<u>P</u>	<u>x_s</u>
.041	71.91
.100	74.05
.303	77.75
.604	80.75
1.231	84.18
1.807	86.28
2.382	87.87
3.819	91.54
5.228	94.27
6.222	95.99
8.482	99.99
9.829	102.17
12.100	109.01
11.432	105.53
10.211	103.30
7.922	97.92
4.536	93.06

Table R.25.

Na-K L/Methane-117.2°C

<u>P</u>	<u>x_s</u>
.286	17.68
1.166	28.71
2.820	34.37
4.554	36.85
8.076	39.52
10.344	40.67
14.977	42.47
18.287	43.73
24.621	45.78
20.364	44.49
13.830	42.06
7.932	39.45
1.665	31.13

Na-K L/Methane-94.8°C

<u>P</u>	<u>x_s</u>
.888	11.31
2.762	22.07
5.500	27.16
8.732	30.79
10.549	31.90
13.619	34.46
17.611	35.67
24.252	37.85
16.002	35.23
9.707	31.84
3.902	24.32

Na-K L/Methane-80.6°C

<u>P</u>	<u>x_s</u>
.751	4.65
2.445	11.58
3.790	15.02
5.332	17.70
7.262	20.37
10.437	23.71
14.18	26.59
19.437	29.59
27.144	32.10
23.790	31.36
14.777	27.12
9.303	22.81
4.397	16.46

Na-K L/Methane-61.4°C

<u>P</u>	<u>x_s</u>
2.070	4.48
4.421	8.53
7.073	11.61
11.939	16.21
15.863	18.97
19.702	21.76
23.450	23.13
21.939	22.58
16.242	19.20
9.900	13.63
3.317	6.70

Table R.25.Na-K L/Methane-45.0°C

<u>P</u>	<u>x_s</u>
2.418	2.56
4.417	4.63
6.286	6.13
8.333	7.59
10.968	8.89
18.103	12.42
23.816	14.56
19.354	12.97
12.346	9.79
6.432	6.32

Na-K L/Methane-30.0°C

<u>P</u>	<u>x_s</u>
3.759	2.18
8.166	4.43
13.915	6.75
19.327	8.73
21.517	9.42
25.901	10.54
22.811	9.78
15.399	7.56
9.913	5.17
4.014	2.41

Na-K L/Methane-15.0°C

<u>P</u>	<u>x_s</u>
2.030	.69
6.028	1.98
12.186	3.63
20.699	6.01
25.487	7.23
21.392	6.29
16.301	5.04
11.132	3.30

Na-K L/Methane-0°C

<u>P</u>	<u>x_s</u>
2.743	.66
8.867	1.74
18.155	3.21
26.071	4.63
19.931	3.61
12.416	2.24
4.177	0.76

Table R.26.Na-K L/Ethane-84.5°C

<u>P</u>	<u>x_s</u>
.703	29.76
2.117	32.32
4.079	33.91
5.986	35.11
10.464	37.03
15.947	38.68
18.393	39.47
21.848	40.07
14.701	38.50
6.917	35.95
1.813	31.91

Na-K L/Ethane-62.0°C

<u>P</u>	<u>x_s</u>
.169	18.94
1.026	26.03
3.253	29.16
6.013	30.64
6.647	31.06
8.097	31.52
12.860	32.52
15.071	33.18
21.007	34.15
14.307	33.89
8.736	31.76
2.316	28.17

Na-K L/Ethane-37.9°C

<u>P</u>	<u>x_s</u>
.129	6.51
.722	16.73
2.047	22.83
4.235	25.47
9.613	28.09
14.802	29.62
18.699	30.32
25.380	31.26
20.666	30.76
14.011	29.42
5.986	26.60
1.307	20.91

Na-K L/Ethane-17.0°C

<u>P</u>	<u>x_s</u>
.343	4.86
1.334	12.52
3.161	18.17
6.876	22.42
12.396	25.11
18.512	26.61
28.663	28.02
20.172	27.06
15.310	25.42
5.017	20.83
1.799	14.73

Table R.26.Na-K L/Ethane 0°C

<u>P</u>	<u>x_s</u>
.278	2.18
1.253	7.06
3.039	12.23
4.295	14.77
9.335	19.49
14.271	21.96
17.272	22.74
25.798	24.32
20.315	23.42
13.966	21.77
4.979	15.72

Na-K L/Ethane-24.0°C

<u>P</u>	<u>x_s</u>
.928	2.32
2.393	4.77
3.897	7.06
8.127	10.98
10.397	12.62
15.216	14.88
16.390	15.60
24.604	17.65
20.642	16.82
14.821	14.76
5.899	8.91

Na-K L/Ethane-46.2°C

<u>P</u>	<u>x_s</u>
2.101	2.06
4.165	3.82
6.712	5.42
12.161	8.19
16.350	10.01
23.268	12.22
29.084	13.34
16.990	10.35
14.061	9.19
7.313	6.01

Na-K L/Ethane-78.0°C

<u>P</u>	<u>x_s</u>
3.078	1.22
7.757	2.64
13.493	4.19
20.321	5.74
26.379	7.17
31.203	7.88
21.631	6.21
16.392	5.05
5.302	1.92

Table R.27.Na-K L/Propane-60.0°C

<u>P</u>	<u>x_s</u>
.021	21.34
.148	26.57
1.897	31.03
4.540	32.88
7.124	34.07
12.368	36.04
16.720	38.21
20.011	40.41
13.979	36.71
7.891	34.26
2.113	31.27
.761	29.04

Na-K L/Propane-40.0°C

<u>P</u>	<u>x_s</u>
.053	20.680
.392	24.33
2.039	27.14
4.065	28.39
7.814	29.66
12.553	30.72
16.720	31.40
10.046	30.09
4.617	28.64
2.176	27.29
.835	25.42

Table R.27.Na-K L/Propane-20.0°C

<u>P</u>	<u>x_s</u>
.037	15.95
.320	20.79
1.200	23.54
2.159	24.65
4.181	25.87
8.504	27.19
12.436	27.88
17.513	28.51
16.301	28.36
8.031	27.06
3.179	25.50
.809	22.23

Na-K L/Propane 0°C

<u>P</u>	<u>x_s</u>
.037	7.16
.074	10.59
.210	15.19
.891	20.04
1.900	21.98
4.910	24.01
6.431	24.52
10.956	25.54
15.373	26.13
19.530	26.54
13.909	25.96
6.841	24.71
1.321	21.20
.361	15.98

Table R.27.

Na-K L/Propane-22.2°C

<u>P</u>	<u>x_s</u>
.094	3.56
.253	7.06
.406	9.67
.746	12.85
1.173	15.04
2.253	17.89
5.056	20.29
9.263	21.86
14.269	22.76
18.621	23.36
13.604	22.69
3.766	19.14
1.203	15.46

Na-K L/Propane-42.2°C

<u>P</u>	<u>x_s</u>
.178	2.34
.536	5.82
.911	8.34
1.537	11.10
2.980	14.26
6.007	17.20
9.812	18.83
13.759	19.76
16.249	20.04
11.639	19.38
6.479	17.42
2.198	12.50

Na-K L/Propane-62.3°C

<u>P</u>	<u>x_s</u>
.313	1.69
.825	3.96
1.678	6.99
4.141	11.86
7.532	14.79
11.876	16.05
15.245	16.78
10.103	15.76
5.966	13.63
3.016	10.46
2.316	8.17

Na-K L/Propane-87.1°C

<u>P</u>	<u>x_s</u>
.569	1.16
1.601	3.07
3.958	6.41
7.214	9.45
11.449	12.29
15.415	13.63
18.304	14.21
12.501	12.89
8.009	10.01
3.716	6.23

Table R.27.Na-K L/Propane-117.0°C

<u>P</u>	<u>x_s</u>
1.999	1.79
5.044	4.14
9.438	7.01
13.601	9.13
11.182	8.06
7.039	5.59
3.241	2.63

Na-K L/Propane-144.0°C

<u>P</u>	<u>x_s</u>
2.195	0.77
6.483	2.34
10.799	3.72
14.899	4.89
18.049	5.68
16.302	5.13
11.816	3.93
8.267	2.84
4.619	1.42

Table R.28.Na-K L/n-Butane-25°C

<u>P</u>	<u>x_s</u>
.010	18.75
.069	22.63
.534	25.20
1.470	26.86
3.120	28.15
5.338	29.20
8.388	30.21
13.200	32.49
18.108	36.09
10.349	31.12
7.919	30.09
5.312	29.13
1.031	26.19

Na-K L/n-Butane-0°C

<u>P</u>	<u>x_s</u>
.052	9.09
.062	10.61
.072	13.60
.090	18.33
.579	23.20
1.996	26.10
2.986	25.78
4.940	26.71
7.328	27.82
9.924	28.51
15.797	29.53
18.192	29.87
12.390	29.01
6.007	27.24
1.101	23.62

Table R.28.Na-K L/n-Butane-26.0°C

<u>P</u>	<u>x_s</u>
.012	2.18
.020	8.38
.031	11.10
.108	15.44
.297	17.91
.655	19.54
1.818	21.39
3.817	22.69
6.124	23.80
8.030	20.39
10.918	24.89
14.680	25.54
78.381	26.03
13.052	25.39
2.501	21.91
.973	20.19

Na-K L/n-Butane-40.1°C

<u>P</u>	<u>x_s</u>
.026	3.71
.035	6.04
.042	7.66
.066	11.09
.199	14.85
.687	18.01
1.805	20.01
3.566	21.30
4.964	21.89
8.138	22.76
11.459	23.32
15.005	23.79
18.756	24.14
12.366	23.41
6.060	22.13
1.721	19.65

Table R.28.Na-K L/n-Butane-55.0°C

<u>P</u>	<u>x_s</u>
.024	1.86
.062	6.09
.124	9.52
.235	11.95
.563	15.02
1.203	17.15
3.909	19.82
7.918	21.20
13.204	22.17
17.294	22.79
20.295	23.07
16.003	22.46
12.508	22.02
4.309	19.91
1.292	16.73

Na-K L/n-Butane-71.0°C

<u>P</u>	<u>x_s</u>
.060	2.09
.266	7.30
.395	10.01
.767	12.75
1.325	14.63
2.601	16.65
5.054	18.43
6.765	19.47
9.068	20.03
12.968	20.72
17.010	21.28
20.905	21.58
7.395	19.47
3.667	17.61
1.007	13.80

Table R.28.Na-K L/n-Butane-90°C

<u>P</u>	<u>x_s</u>
.124	1.99
.269	4.10
.440	6.24
.787	8.87
2.235	13.09
4.822	15.58
7.774	16.90
11.703	17.97
15.436	18.14
18.875	18.93
10.032	17.40
4.144	15.16
1.039	10.39

Na-K L/n-Butane-130.0°C

<u>P</u>	<u>x_s</u>
.681	2.68
1.104	4.26
2.162	6.67
3.062	8.29
5.200	10.64
7.848	12.19
10.603	13.26
13.670	14.09
16.292	14.13
18.575	14.57
9.776	12.79
3.084	8.34
1.224	4.58

Na-K L/n-Butane-172°C

<u>P</u>	<u>x_s</u>
.726	.89
1.778	2.05
3.240	3.32
5.555	4.91
9.253	6.78
10.937	7.44
13.279	7.79
16.234	8.58
20.767	9.58
14.013	8.08
7.870	6.23
2.138	2.21

Na-K L/n-Butane-207°C

<u>P</u>	<u>x_s</u>
1.090	.59
2.676	1.29
5.776	2.39
8.088	3.15
12.349	4.24
15.117	4.84
19.059	5.61
20.020	5.81
11.967	4.17
6.390	2.60
2.201	1.01

Table R.29.

Na-K L/iso-butane-177.0°C Na-K L/iso-butane-158.0°C

<u>P</u>	<u>x_s</u>	<u>P</u>	<u>x_s</u>
.975	.48	.797	.66
2.330	1.03	1.919	1.53
3.251	1.37	3.946	2.73
3.990	1.59	6.790	3.95
8.063	2.81	10.434	5.20
11.955	3.59	13.815	6.03
17.344	4.38	19.253	6.74
21.644	4.87	24.292	7.41
26.260	5.17	16.793	6.47
19.371	4.61	8.901	4.71
14.342	3.93	5.110	3.31
7.034	2.50		

Na-K L/iso-butane-132.0°C Na-K L/iso-butane-107°C

<u>P</u>	<u>x_s</u>	<u>P</u>	<u>x_s</u>
.729	1.24	.394	1.61
1.620	2.58	.698	2.59
3.224	4.19	1.358	4.31
5.590	5.79	2.782	6.54
9.023	7.04	5.667	8.55
13.977	8.14	10.413	10.01
18.548	8.90	16.930	10.95
24.102	9.44	23.077	11.54
27.850	9.97	27.540	11.99
21.304	9.12	18.967	11.17
16.201	8.50	11.171	10.15
6.859	6.32	4.374	7.89

Table R.29.Na-K L/iso-butane 81.0°C

<u>P</u>	<u>x_s</u>
.251	2.42
.472	4.01
1.096	6.83
2.665	9.42
5.568	11.09
9.369	12.08
14.416	12.82
20.699	13.46
26.392	13.90
11.349	12.38
6.604	11.39
3.261	9.82
1.304	7.40

Na-K L/iso-butane 65.2°C

<u>P</u>	<u>x_s</u>
.094	2.14
.161	3.71
.314	5.50
.471	6.72
.912	8.75
1.389	9.83
3.304	11.74
6.097	12.97
10.887	13.99
16.098	14.73
24.966	15.59
13.597	14.33
6.776	13.39
2.320	10.99

Na-K L/iso-butane 50.0°C

<u>P</u>	<u>x_s</u>
.378	8.53
2.131	12.58
3.077	13.27
4.421	13.91
6.217	14.46
9.505	15.12
15.228	15.87
19.869	16.32
24.856	16.63
13.497	15.61
1.404	11.63

Na-K L/iso-butane 30.6°C

<u>P</u>	<u>x_s</u>
.090	8.08
.172	9.73
.607	12.46
1.275	13.85
1.751	14.49
4.046	15.83
8.356	16.94
14.101	17.66
20.017	18.25
24.541	18.61
26.968	18.83
12.738	17.49
5.593	16.17

Table R.29.Na-K L/iso-butane 11.0°C

<u>P</u>	<u>x_S</u>
.140	12.62
.879	15.69
1.502	16.53
2.347	17.26
4.303	18.11
8.227	19.03
13.770	19.76
19.691	20.59
24.998	20.88
12.899	19.72
5.507	18.46

Na-K L/iso-butane-5.8°C

<u>P</u>	<u>x_S</u>
.081	12.26
.157	14.46
.457	16.71
1.253	18.29
3.643	19.80
5.523	20.36
9.910	21.23
15.929	21.98
21.854	22.63
25.634	23.03
12.316	21.52
2.179	19.09

Na-K L/iso-butane-25.0°C

<u>P</u>	<u>x_S</u>
.055	14.77
.184	17.40
.664	19.37
2.215	20.94
4.308	21.87
8.052	22.86
12.323	23.74
18.030	24.92
23.638	26.20

Table R. 30.

Na-K L/neo-Pentane-169.0°C Na-K L/neo-Pentane 210.0°C

$\underline{P}$	$\underline{x}_s$	$\underline{P}$	$\underline{x}_s$
.553	1.07	1.820	1.22
.929	1.59	4.567	2.37
2.235	2.88	9.203	3.37
3.754	3.68	14.148	3.94
5.529	4.25	21.766	4.28
9.940	5.00	16.099	3.97
16.225	5.43	10.419	3.58
24.690	5.75	3.061	1.80
13.433	5.32		
6.319	4.41		
2.620	3.12		

Table R.30.

<u>Na-K L/neo-Pentane-72.6°C</u>		<u>Na-K L/neo-Pentane-98.0°C</u>	
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<u>P</u>	<u>x_S</u>	<u>P</u>	<u>x_S</u>
.046	3.27	.199	2.82
.096	4.25	.796	5.34
.272	5.91	2.330	6.98
.558	6.86	6.987	8.48
1.571	8.38	11.530	9.09
3.614	9.47	17.139	9.68
6.436	10.17	23.397	9.98
10.303	10.66	14.178	9.52
15.844	10.97	7.591	8.63
21.771	11.26	4.040	7.96
25.616	11.37		
14.272	10.90		
10.802	10.64		
2.177	8.94		

Table R.30.

Na-K L/neo-Pentane-121.0°C Na-K L/neo-Pentane-143.0°C

<u>P</u>	<u>x_s</u>	<u>P</u>	<u>x_s</u>
.216	1.72	.215	1.11
.421	2.84	.660	2.36
.931	4.17	1.007	3.02
2.548	5.69	1.766	3.90
4.529	6.47	3.160	4.59
8.453	7.29	4.888	5.17
13.580	7.87	7.538	5.70
22.550	8.50	10.576	6.16
26.861	8.76	14.313	6.65
11.204	7.60	20.225	7.11
3.061	5.87	25.592	7.29
.901	4.04	16.199	6.88
		8.372	5.89
		2.309	4.14

Table R.30.

Na-K L/neo-Pentane-16.0°C Na-K L/neo-Pentane+10.0°C

<u>P</u>	<u>x_s</u>	<u>P</u>	<u>x_s</u>
.114	10.60	.049	8.94
.361	11.53	.155	10.28
.737	12.14	.376	11.06
2.640	13.44	1.102	12.00
6.277	14.43	2.421	12.76
9.592	15.51	4.525	13.39
14.734	16.96	8.313	14.11
19.428	20.09	12.564	14.63
22.432	27.80	18.535	15.05
16.719	17.73	23.425	15.77
11.333	15.69	16.741	14.91
5.197	4.24	5.399	13.64
		1.937	12.70

Na-K L/neo-Pentane 30.0°C Na-K L/neo-Pentane 52.0°C

<u>P</u>	<u>x_s</u>	<u>P</u>	<u>x_s</u>
.031	7.07	.168	6.98
.140	8.62	.490	8.45
.395	10.05	.951	9.36
1.424	11.27	2.347	10.31
3.760	12.19	5.602	11.12
7.081	12.78	9.588	11.62
11.213	13.23	13.631	11.98
18.644	13.85	17.242	12.45
25.119	14.21	21.213	12.57
14.616	13.53	27.671	12.84
5.836	12.61	10.791	11.86
		3.174	10.72
		1.308	9.78