

"Sorption of Inorganic Vapours
by Porous Crystals"

by

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Abstract.

An apparatus has been developed for the study of sorption, at temperatures up to 350°C and pressures up to one atmosphere, of sorbates not readily volatile, and reactive and corrosive towards mercury and tap grease.

Using this apparatus perfectly reversible and reproducible families of isotherms, for occlusion of iodine in faujasite (NaX), Linde Sieve 5A (CaA), and chabazite, have been obtained over the temperature range 120-300°C. The sorption of aluminium chloride in faujasite was however found to be irreversible. The occlusion isotherms of iodine in the above three sorbents were used to evaluate the isosteric heats of occlusion, partial molar entropies, and free energy of occlusion of the iodine. The changes in the thermodynamic properties of the sorbents were also investigated.

It was found that at saturation the occluded iodine behaves as a condensed phase filling a limited container. This is reflected in the variation of saturation value with temperature, from which the coefficient of expansion of occluded iodine was found to be close to that of solid iodine.

It was found, over the range of coverage, $0.3 < \theta < 0.8$, that Langmuir's ideal localised model gives a reasonable description of the sorbed state. However, at $\theta < 0.3$ and at near saturation deviations arise due to the variation of the isosteric heat of occlusion and thermal entropy with amount sorbed. Overall, the Everett isotherm equation gives a better description of the sorbed state. The variation of thermal entropy with coverage arises from increasing

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restriction to rotation and increasing mean frequency of vibration of occluded molecules. Also it was found that the thermal entropy is linearly related to the isosteric heat of sorption.

The isosteric heat curves have shown an initially high value which drops to a minimum at $\theta \sim 0.3$ and then increases steadily till saturation. The main contribution to the isosteric heat comes from interaction between I_2 and lattice oxygens, an interaction which seems to remain reasonably constant over the whole range of coverage. The high values of $\Delta\bar{H} = -q_{st}$ at $\theta < 0.3$ are due to the contribution to $\Delta\bar{H}$ from the induced dipole-field interaction. The steady increase in $\Delta\bar{H}$ after $\theta \sim 0.3$ was shown to be compatible with increasing contribution from sorbate-sorbate interaction.

The energy of interaction of the iodine molecule with the framework oxygens was calculated, by summation of individual interactions, when the iodine molecule was placed in different positions in the cavity and in the plane of the 12-membered ring connecting the cavities in faujasite; and also as it approached the 8-membered ring in Linde Sieve A and chabazite. It has been concluded that:

- (i) all the iodine is located in the large cavities and the interconnecting windows;
- (ii) the iodine molecule preferentially takes up positions near the wall of the cavity with its longer diameter parallel to the plane of the wall;
- (iii) the iodine molecule must pass through the 8-membered ring (window), in Linde Sieve A and chabazite so oriented that its longer diameter is perpendicular to the plane of the window;

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(iv) thus oriented iodine diffuses easily into the cavities in Linde Sieve A, but a small activation energy may be required for iodine to diffuse into chabazite;

(v) in faujasite, the iodine molecule diffuses into the crystal by preferentially taking up positions near the frame of the 12-membered ring with its shorter diameter perpendicular to the frame, and then moves from one sorption site to a neighbouring one by jumping or rolling along the ribs of the framework.

X-ray diffraction photographs were obtained of the sorbents outgassed and then saturated with iodine and bromine. The analysis of the data showed that a small contraction of the unit cell after sorption had occurred. This was explained by strong sorbate-lattice and sorbate-sorbate interaction.

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General Introduction.

Much work has been done by Professor R. M. Barrer, F.R.S., and his co-workers on sorption and molecular sieve properties of robust, three-dimensional aluminosilicate crystals at temperatures up to 100°C. It became of an interest to study the sorption and thermodynamic properties of vapours of volatile solids at higher temperatures. Beside general information the study of a larger number of sorbates may lead to the development of vapour phase sorption chromatography.

During a study of sorption equilibria we have to make measurements under exacting conditions which led us to develop an apparatus suitable for this purpose. The upper limit of temperature is set by the thermal properties of the glass of the silica spring, used as microbalance, and of the spiral gauge used as pressure measuring device.

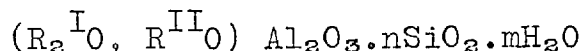
For the study of occlusion compounds formed by occlusion of vapours of volatile solids by zeolitic crystals three zeolites have been selected having different porosities and dimensions of cages. These are: synthetic faujasite (NaX), the calcium form of Linde sieve, and chabazite. Most of the study has been carried out on occlusion compounds formed by iodine and the three above mentioned forms of zeolitic crystals. The main object has been to measure occlusion isotherms over the temperature range 120 - 300°C, which allow the evaluation of relevant thermodynamic quantities over as large a degree of filling of the intracrystalline volume as possible. The data are then discussed in terms of models of the sorbed state, and the effect of the occlusion of the above mentioned molecules on the thermodynamic properties of the sorbents is investigated.

Also an attempt is made to interpret entropy and isosteric heat data in terms of the energy of sorbent-sorbate and sorbate-sorbate interactions which occur inside the crystals of these zeolites. Information obtained from X-ray diffraction is used to support the theory of the structure of occlusion compounds formed.

Chapter 1.

1.1 The Zeolites.

Zeolites are crystalline aluminosilicates. They may be considered as very open derivatives of SiO_2 in which aluminium replaces some silicon atoms, and they can be represented by the general formula:



where R^{I} and R^{II} represent monovalent and divalent cations respectively. n may vary between 2 and 10, and m between 0 and 10.

The structures of aluminosilicate frameworks are based on SiO_4 and AlO_4 tetrahedral units linked through common O atoms to form a lattice which may sometimes contain large interstitial volumes.

According to the manner in which these tetrahedral units are joined together zeolites can be divided into three classes:

1. fibrous - e.g. natrolite, scolecite;
2. lamellar - e.g. heulandite;
3. robust, three-dimensional network - e.g. analcite, chabazite, Linde sieve, faujasite.

Replacement of Si by Al requires the presence of cations to preserve the electrical neutrality. These cations are located in the intracrystalline channels.

In the natural state all zeolites are hydrated, but the water of hydration, which occupies the interstitial free volume, may be removed by subjecting the crystals to vacuum and heat.

In the case of fibrous and lamellar zeolites, dehydration tends to cause shrinkage and consequently the

collapse of the lattice. As a result of this dehydration curves show irreversibility and sometimes discontinuity⁽¹⁾.

The three-dimensional zeolites are generally robust and thermally stable up to at least 500°C. In these type of zeolites the pore space occupied normally by water, consists of cages linked into a system of inter-connecting channels which after dehydration may accommodate a variety of different molecules. In this way a variety of "zeolitic inclusion complexes" can be formed which are rather similar to the clathrate compounds of quinol and water, and the thio-urea adducts⁽²⁾. However, unlike the latter compounds, zeolitic inclusion complexes involve a host lattice which is stable in the absence of the occluded molecules.

Generally, the forces which hold the occluded molecules in the intracrystalline environment, are physical in nature and similar to the forces which bind a physically adsorbed molecule to the external surface of a solid. The terms 'occlusion', 'inclusion' and 'sorption' may therefore be used interchangeably when zeolitic inclusion complexes are considered. Sometimes the term 'persorption' is used to describe this phenomenon.

These features make the zeolitic inclusion complexes particularly amenable to interpretation using the thermodynamic and statistical mechanical methods which are used to investigate adsorption on external surfaces.

1.1.1 The structure of three-dimensional zeolites.

Aluminosilicate frameworks are based ultimately upon the tetrahedral (Al, Si)O₄ unit. However, structural considerations of nets of tetrahedra can be much simplified for some open frameworks by assembling the primary

building units to give secondary polyhedral building units⁽³⁾. These units can be then stacked in different ways in different co-ordinations.

A number of the robust three-dimensional zeolites have structures based on a cubo-octahedron usually referred to as a "sodalite cage". Fig. 1 illustrates such a cubo-octahedron.

The complete polyhedron comprises eight rings of six tetrahedra and six rings of four tetrahedra and is a truncated octahedron. These units can be assembled in three ways, and each has been realised in various syntheses by R. M. Barrer and co-workers. The resultant structures provide remarkable frameworks capable of forming non-stoichiometric phases in great numbers. In each framework every O-atom is joined to each of two Si-atoms or to one Si- and one Al-atom.

The three ways of assembling sodalite cages are:

1. In the first structural type the polyhedra are joined together in eight-fold co-ordination, by the sharing of the 8 x six-membered rings of a given central polyhedron with eight other polyhedra, one six-membered ring between two polyhedra. This type of structure is shown in fig. 2 and is found in the feldspathoid mineral sodalite and the ultramarines.

In the feldspathoids each polyhedron (or cage) contains amounts of salts (Na_2S_x , NaCl , Na_2SO_4 , Na_2CO_3 , NaOH , H_2O) in somewhat variable proportions. The frameworks are capable of some distortion, so that the crystal symmetries may vary. Until recently it was thought that the mineral zeolite, 'chabazite' came under this type⁽⁴⁾. The chabazite structure is now thought to be built up of eight-double six-membered rings forming one

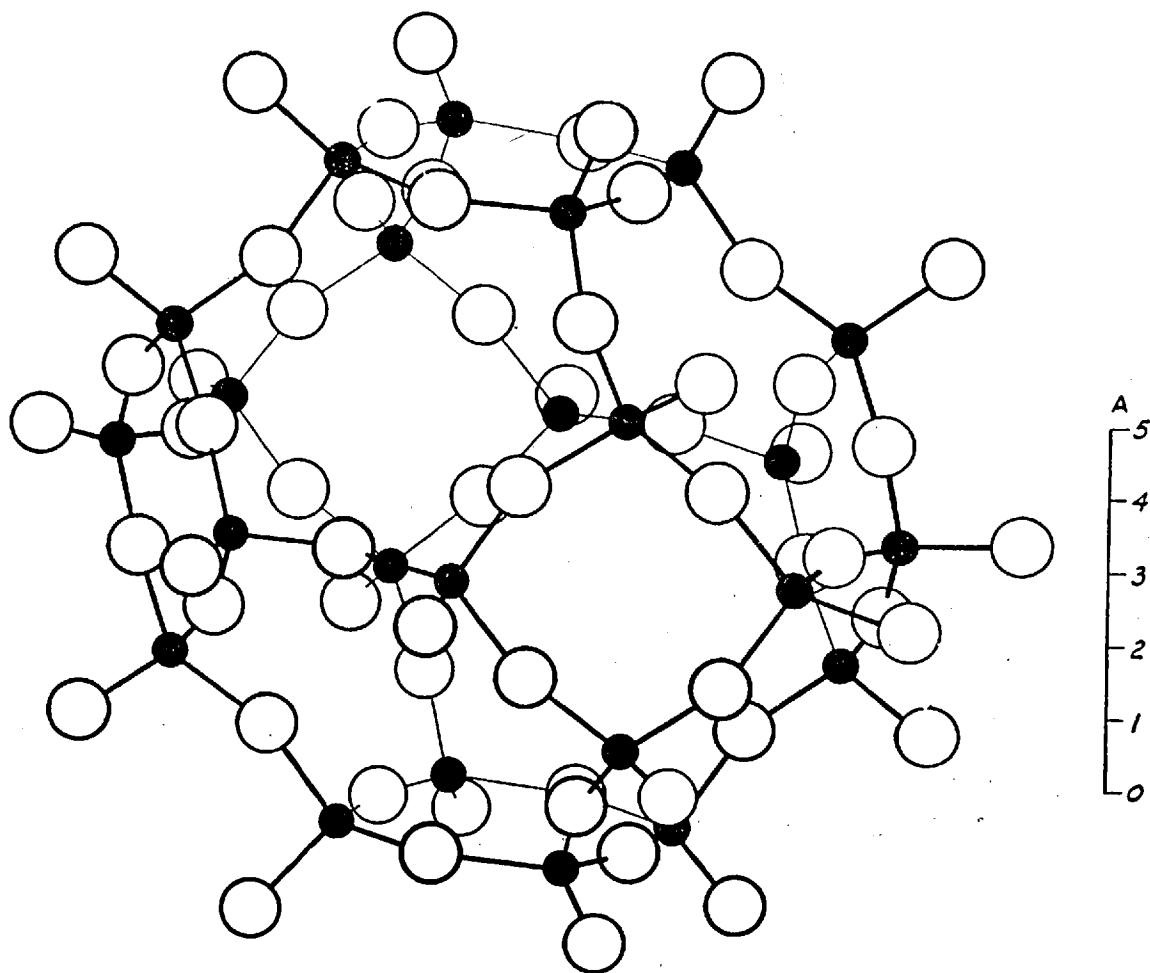


Fig. 1
Cubo-octahedron

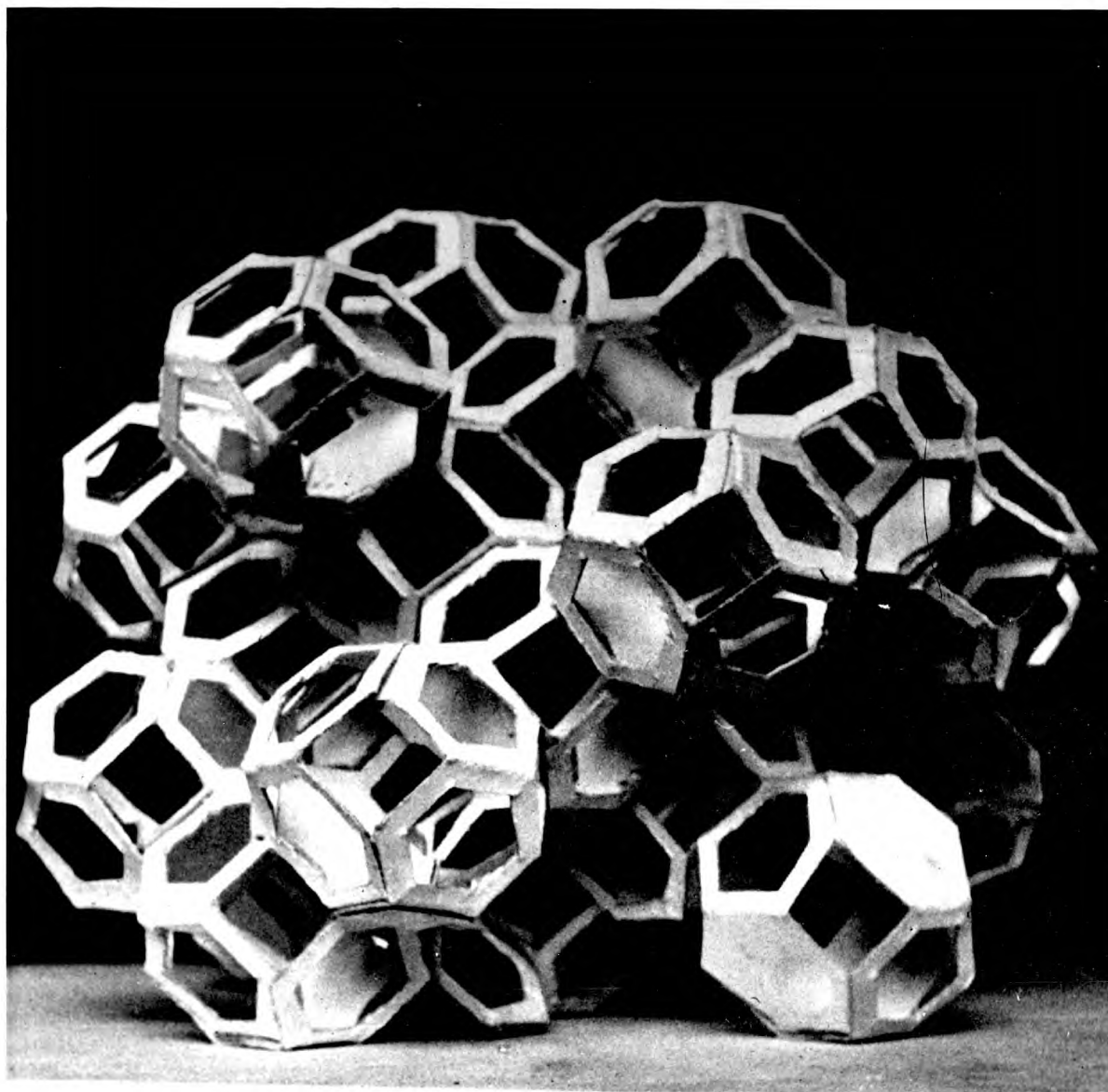


Fig. 2
Sodalite Structure

cage per unit cell, each cage having six octagonal, two hexagonal and twelve quadrilateral faces. Each central cage is connected to six neighbouring cages by eight membered rings^(5,6).

2. In the second structural type⁽⁷⁾ each polyhedron is joined to six others by union of their 6 x four-membered rings with one such ring in another polyhedron, i.e. six-fold co-ordination. The union occurs through oxygen bridges. This mode of linkage creates additional very small cages besides the large supercages. This type of framework occurs in the synthetic zeolite (Linde Sieve A), which has no natural counterpart.

3. In the third structural type the polyhedra are stacked in four-fold co-ordination, by union through oxygen bridges of four of the 8 x six-membered rings of a central polyhedron to one such ring in each of four other polyhedra. This arrangement of the large polyhedra thus creates additional small cages formed by the union of 2 x six-membered rings through six oxygen atoms. The large polyhedra are arranged like the atoms in diamond, and they enclose very large supercages of free diameter ca. 12 Å. This form occurs in faujasite-like crystals which have been synthesised by R. M. Barrer and his co-workers.

1.1.2 Structure of zeolites used in our investigation.

1.1.2a The structure of chabazite.

The new structure for chabazite proposed by Dent and Smith⁽⁶⁾ and by Nowacki, Koyama and Mladek⁽⁵⁾ is shown in fig. 3. The framework is built up of eight-double six-membered rings joined together with each other through oxygen bridges in six-fold co-ordination. They

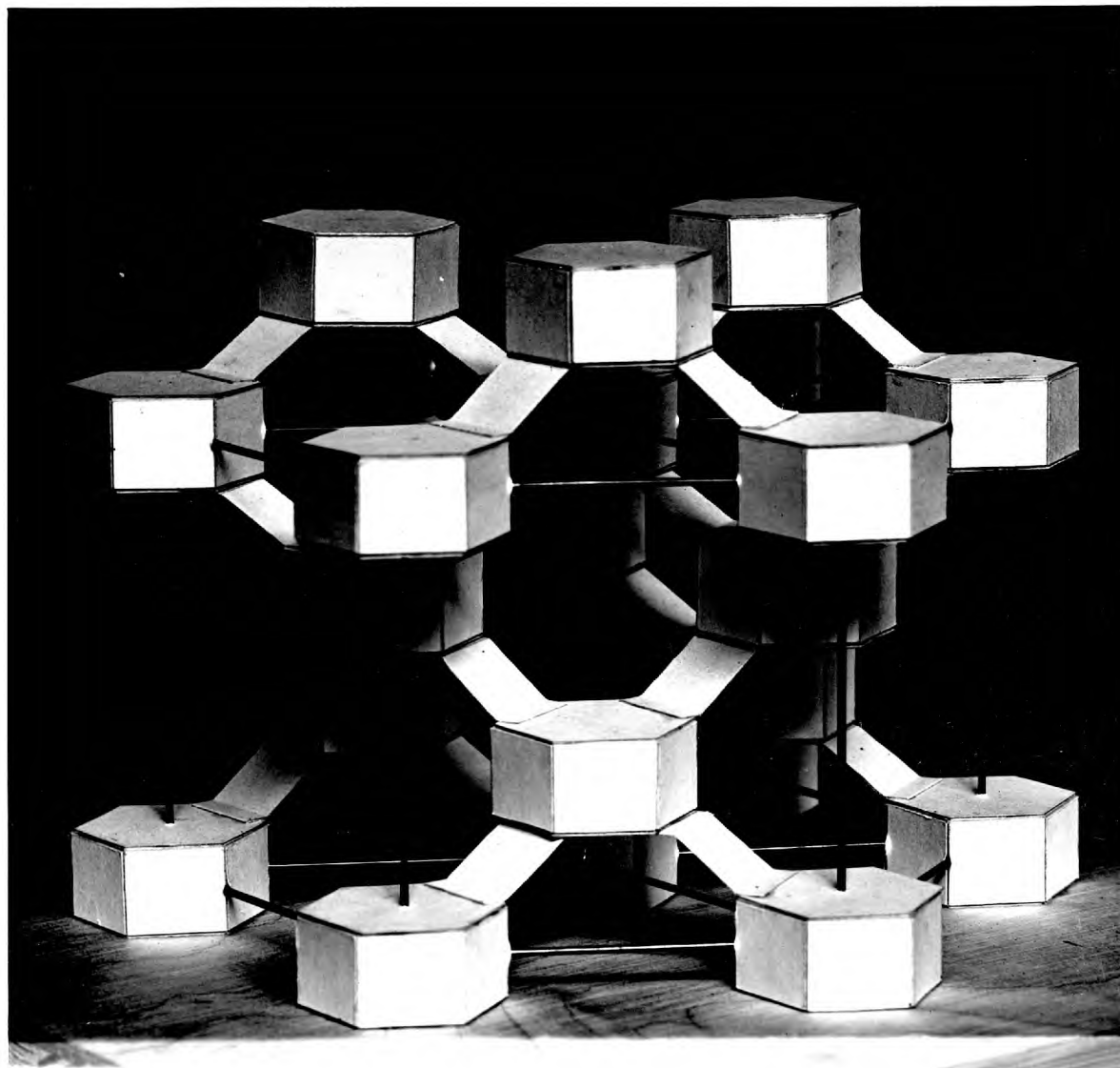


Fig. 3
Chabazite Structure

thus enclose one large cage, of free diameter ca. $9 \times 6.6 \text{ \AA}$ per unit cell. Each cage has six octagonal, two hexagonal and twelve quadrilateral faces, and is connected to the six neighbouring cages by eight-membered rings. One six-membered ring is shared between two cages. This arrangement permits sorption in all directions, but limits it by the octagonal, non-planar, apertures of minimum width about $3.9 \text{ \AA}$.

In the natural state the cavities are filled with water molecules and calcium ions. The water can be removed by heat and evacuation thus giving room for sorption of other molecules.

Chabazite contains one unit of $(\text{Ca}_{1.8} \text{Na}_{0.3})(\text{Si}_{8.1} \text{Al}_{3.9})\cdot\text{O}_{24}\cdot 12\text{H}_2\text{O}$, in a trigonal cell of symmetry $R \bar{3} m$; $a = 9.40 \text{ \AA}$, $\alpha = 94^\circ 18'$.

1.1.2b The structure of synthetic zeolite NaA.

NaA is a synthetic zeolitic aluminosilicate, of which no naturally-occurring counterpart is known. Neglecting the water content, the unit cell composition is given by $\text{Na}_{12}(\text{Al}_{12} \text{Si}_{12} \text{O}_{24})\text{NaAlO}_2$. The structure of this zeolite was determined independently by Reed and Breck (1956) and by Barrer and Meier (1956).

The framework is illustrated in fig. 4 and it is formed by assembling the previously mentioned 'sodalite cages' in six-fold co-ordination, by union of each of their 6 x four-membered rings with one such ring in another polyhedron. The union occurs through oxygen bridges.

By assembling the 'sodalite cages' in this way, very large cages are formed of free diameter ca. $11.8 \text{ \AA}$. (By "free" diameter is meant the distance not occupied

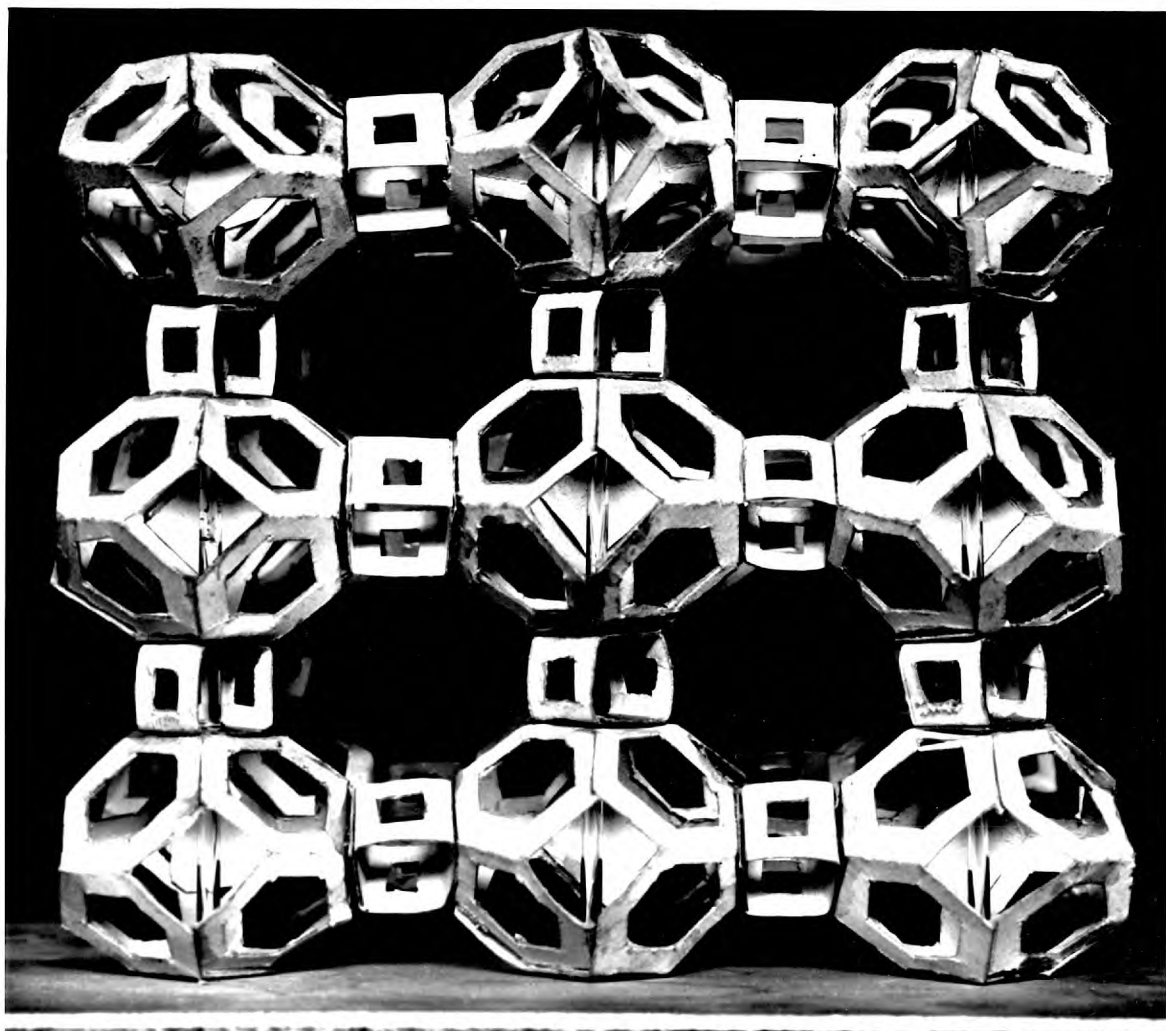


Fig. 4

Linde Sieve A Structure

even by the peripheries of the framework of oxygen atoms). The unit cell is cubic, of unit cell edge $12.27 \text{ \AA}$, and it contains one large and one small sodalite cage per unit cell. The smaller 'sodalite cages' have free diameter of ca. $6.6 \text{ \AA}$ and these in our sample are occupied by sodium aluminate. The smallest cages, which are made up entirely of four-membered rings, are too small to be of interest.

The large cages are bounded by six octagonal windows of free diameter $4.2 \text{ \AA}$, by eight hexagonal windows of free diameter $2.4 \text{ \AA}$ (as the six-membered ring is deformed therefore it gives the minimum free diameter as about $2 \text{ \AA}$), and by twelve quadrilateral windows. In this way the large cages are mutually interconnected to form a series of intersecting channels (at right angles to each other), while the small cages can only be entered from the large ones. While the free diameters of the six- and eight-membered rings will limit the size of the molecules which can enter the small and the large cages respectively, the free volumes of these cages will limit the number of molecules of any one type which can be contained in each cage. In our investigation Ca-form has been used. The Na^+ ions were exchanged for Ca^{++} ions.

1.1.2c The structure of faujasite (NaX).

Faujasite, which occurs rarely in nature, has been synthesised in these laboratories⁽⁸⁾ and by Linde Air Products Co. In our study a synthetic sample supplied by Linde Air Products Co. was used.

The sodalite cages in faujasite are assembled in four-fold co-ordination by union through oxygen bridges of four of the 8 x six membered rings of a central polyhedron to one such ring in each of four other polyhedra. The large polyhedra are arranged like the

atoms in diamond, and they enclose very large cages of free diameter ca. $12 \text{ \AA}$. The large cages are connected through twelve-membered rings (windows) of free diameter $8 - 9 \text{ \AA}$, four such windows to each large cage disposed tetrahedrally.

The framework of faujasite is shown in fig. 5. A unit cell of faujasite contains eight sodalite cages of free diameter $6.6 \text{ \AA}$, and eight large cages of free diameter ca. $12 \text{ \AA}$. The large cages are interconnected by windows of free diameter $8 - 9 \text{ \AA}$ and these limit the size of any kind of molecules that can be occluded by the crystal.

Barrer and Bultitude⁽⁸⁾ obtained good yields of sodium faujasite (NaX), by heating slowly with agitation in an autoclave, a gel of the approximate composition $4\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2$ to a final temperature of $70 - 80^\circ\text{C}$. Appreciable amounts of mineral species NaA was obtained if the heating rate was increased, and if in addition no agitation was allowed only species NaA was formed. If species NaA is heated with caustic soda in excess, a more compact zeolite harmotome is formed. This suggests that neither faujasite nor species NaA are stable materials.

Faujasite structures can be synthesised with Al/Si ratios of between 1:2.68 and 1:3.26 depending upon the composition of starting gel. This gives rise to a varying number of cations per unit cell. However, the differences in properties of faujasites of differing Al/Si ratios are very small. Synthetic faujasite differs from the natural variety in that Al/Si ratio is different and thus having different number of cations per unit cell, some of these being calcium ions in the case of the natural mineral.

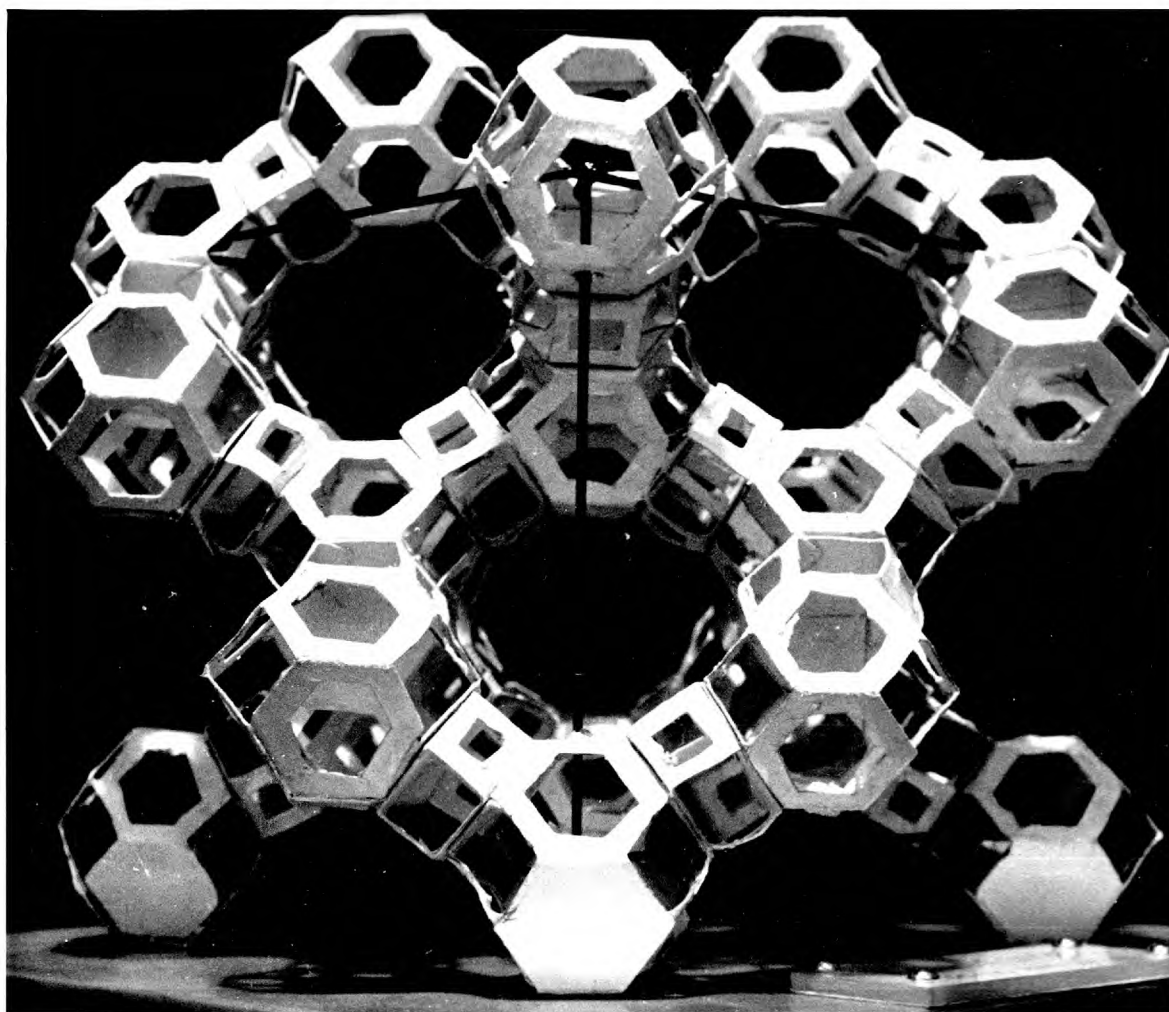


Fig. 5
Faujasite Structure

The unit cell formula of the sodium faujasite sample used in our study is: $\text{Na}_{82.82}\text{AlO}_2.110 \text{ SiO}_2.240-260 \text{ H}_2\text{O}^{(9)}$. The actual positions of cations and water molecules within the intracrystalline channels is still unknown, although Bergerhoff et al⁽¹⁰⁾ have suggested that the alkali ions in natural faujasite lie within the sodalite cages, on the walls of these cages and in the large channels.

In all the three zeolitic crystals mentioned in this chapter, the sodium ion can be readily exchanged for other ions providing that the windows are large enough for the new ion to enter. For example in the case of faujasite, with the largest openings of the three, the exchange becomes progressively less complete as the size of ion increases, the cation $(\text{NEt}_4)^+$ not exchanging at all as the size of this cation is too large to pass through the twelve-membered silicate rings.

As a result of the openness of the structure of these three zeolites, the intracrystalline volume is accessible to small molecules such as O_2 , N_2 , A , H_2O , CH_4 , and to large molecules such as iso-octane in the case of faujasite.

Table 1 summarises some characteristics of the three zeolites. The interstitial volume has been determined by determining the volume of liquid water required to fill the crystal. Hence this volume may not be the absolute value.

Table 1.

Some properties of robust three-dimensional zeolites used
in our investigation.

Struc- tural type	Unit cell edge Å	Free diameter of largest cage Å	Type of window joining largest cages into channels	Largest molecules admitted to dehydrated crystals	Number of molecules needed to fill the largest cages	Inter- stitial volume in cm ³ per cm ³ of crystal
1. (Fig.3) Chaba- zite Ca-form	$a_{hex}=13.74$ $c_{hex}=14.83$ $a_{rho}=9.35$ $\alpha=94^{\circ}37'$	$\sim 9 \times 6.6$	8- membered rings (six in number)	n- paraffins (cross- sectional diameter 4.9 Å)	2 I ₂	0.46
2. (Fig.4) Syn- thetic zeolite Ca-form	12.27	~ 11.8	8- membered rings (six in number)	n- paraffins	~ 29 H ₂ O, 12-14 Å, N ₂ or O ₂ 5.5 I ₂	0.46
3. (Fig.5) Syn- thetic fauja- site Na-form	24.8	~ 12	12- membered rings (four in number)	n-, iso-, and neo- paraffins and aroma- tics readily occluded. Largest molecules not yet determined	~ 32 H ₂ O 17-19 Å, N ₂ , O ₂ 4.5 n-C ₈ H ₁₈ 3.5 n-C ₇ H ₁₆ 2.8 iso-C ₈ H ₁₈ 7.5 I ₂	0.53

1.1.3 Molecular sieve behaviour of zeolites.

The occlusion of small enough molecules in an outgassed zeolitic framework is governed in part by the free interstitial volume. For larger molecules the chief limiting factor may be the minimum diameter of the intracrystalline channels. A molecule, depending upon its dimensions, may diffuse into or be totally excluded from the crystal interior, and thus separation of gases and vapours may be achieved^(11,12,13,14).

Barrer⁽¹⁴⁾ has classified zeolitic molecular sieves on the basis of their ability or non-ability to occlude certain molecules. This classification is not rigid and the molecular sieve properties of a particular zeolite can be considerably modified by the preadsorption of polar molecules or by cation exchange.

Barrer and Rees⁽¹⁵⁾ have studied the effect of preadsorption of polar molecules such as H_2O , NH_3 and CH_3NH_2 on the molecular sieve properties of mordenite and chabazite. In particular they investigated the occlusion of non-polar gases such as H_2 , O_2 , N_2 , A and ethane in the presence of progressively increasing amounts of the modifier molecules present interstitially. They were able to establish that oxygen should be readily separated from argon and nitrogen at 90°K by modifying the intracrystalline channels of chabazite with 90 cc of NH_3 at N.T.P./gm.

Lamb and Woodhouse⁽¹⁶⁾ studied the occlusion of O_2 , H_2 and CO_2 in partially dehydrated chabazite. They observed that occlusion of CO_2 took place after 5% dehydration; occlusion of oxygen required at least 17% dehydration, and occlusion of hydrogen occurred only after 50% removal of the intracrystalline water.

Table 2.
Molecular Sieve Classification.

Characteristics	Examples
<u>Class I.</u> Do not occlude aromatics, naphthenes or iso-paraffins. Occlude n-paraffins slowly at or above room temperature. Occlude C_2H_6, CH_4 and molecules of smaller cross-section, rapidly at or below room temperature.	Chabazite Gmelinite Synthetic zeolite - ($BaAl_2Si_4O_{12} \cdot nH_2O$).
<u>Class II.</u> Do not occlude n-paraffins, iso-paraffins, naphthenes or aromatics. Occlude CH_4 and C_2H_6 slowly. Occlude N_2, O_2 and molecules of smaller cross-section rapidly.	Mordenite (rich in Na)
<u>Class III.</u> Do not occlude aromatics, iso-, n-paraffins, C_2H_6 or CH_4. Occlude A, N_2 and molecules of smaller cross-section.	Ca- and Ba-rich mordenites (prepared hydrothermally by cation exchange).
<u>Class IV.</u> Occludes aromatics, paraffins, O_2 and N_2 rapidly.	Faujasite.

Chabazite can thus be modified to an extreme class III zeolite and separation of mixtures of O_2 , H_2 and CO_2 may be achieved by exposing them to chabazite of the appropriate water content.

During our study it has been observed that the sodium form of the synthetic zeolite A adsorbs iodine only on the external surface, whereas Ca-form of this zeolite sorbs iodine freely.

If two molecules have different rates of diffusion into the crystal a partial separation may be achieved. Cation exchange can influence this by modifying the size of the potential barriers encountered by a diffusing species⁽¹⁷⁾. This may happen because the position occupied by the cation within the lattice may change with its size and valency or purely as a result of the changed size of cation. Cation exchange thus provides a useful method of modifying the sieve properties of a mineral. For example, in cation exchanged mordenites appreciable differences in sorption velocities of He, H_2 , Ne, O_2 , N_2 and A, were observed suggesting that their mixtures should be readily resolvable.

Whereas in some cases it is possible to increase the accessibility of the crystals to sorbate molecules by converting the zeolite to the H^+ -form⁽¹⁸⁾, in other zeolites the presence of cations may prevent the diffusion of certain molecules through the channels. Replacement of sodium ions by calcium ions in the synthetic zeolite NaA effectively enlarges the pore openings so that straight chain hydrocarbons are readily adsorbed and the occlusion of N_2 , which is negligible in the sodium forms at 90°K, becomes rapid and copious. Breck et al⁽¹⁹⁾ explain this by assuming that blockage of the intracrystalline channels

occurs when sodium ions are present. The sorptive capacity of chabazite is also considerably reduced when Na^+ and K^+ ions are present⁽²⁰⁾. Presumably this can also be attributed to the blocking effect of these cations.

The kinetics of molecular sieve action have been investigated for nitrogen-methane mixtures in contact with the Na-form of Linde Molecular Sieve A⁽²¹⁾. It has been found that methane is preferentially sorbed at equilibrium due to its higher affinity for the sorbent, while nitrogen diffuses through the crystal more rapidly and is thus preferentially taken up during the early stages of sorption. In consequence of this the sorbed phase shows an initial enrichment in nitrogen but an equilibrium enrichment in methane. Thus this system illustrates "partial molecular sieve action".

The use of molecular sieves is becoming of increasing importance in the separation and purification of materials and resolution of azeotropic mixtures. The scope of molecular sieve action is continually being widened by the synthesis of new zeolite materials and the modification of their sorptive properties.

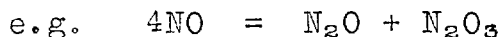
1.1.4 Chemical reactivity of sorbates in zeolites.

With certain sorbates some zeolites give irreversible occlusion isotherms. This, taken in conjunction with subsequent X-ray examination, is attributed to chemical reactivity of the occluded species within the intracrystalline channels. This effect was first observed by Grandjean⁽²²⁾ and Wyart⁽²³⁾ for mercury sorbed on chabazite in the presence of oxygen. Barrer and Woodhead⁽²⁴⁾ in their investigation were able to show that, under high vacuum conditions, reversible sorption of mercury took place but in the presence of oxygen an

irreversible process occurred, turning the chabazite a deep bronze colour, which turned black on exposure to air. A lattice of mercury and oxygen ions within the zeolite was suggested to explain this phenomenon. Many other molecules have been observed to discolour chabazite on being occluded. It has been found, for instance, that carbon disulphide turns chabazite yellow with the liberation of hydrogen sulphide, presumably due to reaction between carbon disulphide and residual water in the crystal⁽²⁵⁾. Occlusion of thiophene and pyridine in chabazite causes the crystals to darken when they are heated to relatively low temperatures, whilst bromine and iodine are liberated when alkyl halides are sorbed in chabazite⁽²⁶⁾. Chabazite has also been observed to remove hydrogen chloride from tert-butyl chloride although this molecule is itself too large to enter the crystals; the remaining olefin polymerised to give oils and the hydrogen chloride liberated interstitial calcium chloride. An X-ray examination, however, showed no structural change of the lattice⁽²⁷⁾.

It must be mentioned, however, that the change in colour of the crystals does not necessarily imply chemical reactivity. For example, during our study of sorption of iodine and bromine on chabazite, faujasite and synthetic zeolite CaA all three forms of crystals changed colour progressively from white, through yellow, brown to black as the amount of occluded sorbate increased, but the sorption was completely reversible and after desorption the original white colour of the crystals was restored.

Recently Barrer and Addison⁽²⁸⁾ observed that in contrast to the stability of sorbed nitrous oxide, nitric oxide underwent a disproportionation reaction



when it was occluded in Ca- and Na-rich faujasites and chabazites. The reaction was usually fast and went nearly to completion. In porous glass, sodium aluminosilicate gel, and silica gel, on the other hand, sorption of NO was less copious and only in the first two sorbents at 0°C was a limited disproportionation observed. This demonstrates the wide difference between the catalytic activity of the amorphous and the crystalline sorbents.

Barrer and Brook⁽²⁷⁾ in their study of sorption of CHF_3 and CClF_2H have found that the occlusive power of the crystal was destroyed and by X-ray diffraction have shown that the sample was changed to amorphous form. Subsequent hydrothermal extraction of the sorbent showed the presence of flourspar. Also the solid evolved hydrofluoric acid when treated with concentrated sulphuric acid. Since the molecules CH_3Cl and CH_2Cl_2 did not react with the mineral it was concluded that the reaction with CHF_3 and CClF_2H must have been associated with the fluorine, and that most likely hydrofluoric acid was liberated. This reaction appears limited to fluoromethanes located interstitially within the chabazite since molecules which could not penetrate into the sorbent showed no measurable interaction. The available information seems to indicate that in the case of fluorocarbons their decomposition is catalysed by zeolites only if a fluorocarbon molecule contains both hydrogen and fluorine atoms; molecules containing fluorine only or fluorine and chlorine only, are sorbed reversibly. However, Cannon⁽¹⁵⁵⁾ reports that evolution of carbon dioxide takes place when chlorodifluoromethane is sorbed on Linde Sieve 5A.

1.2 Sorbates.

As our study here was mainly concerned with the sorption of iodine by three different forms of zeolitic crystals (chabazite, faujasite and synthetic zeolite CaA) therefore, although some information has been obtained about other sorbates, only iodine will be considered in this paragraph.

Iodine.

Iodine is a well known element and most of the general information about it can be found in any advanced textbook on chemistry. Here, a short account will be given of its physical properties.

At room temperature iodine is a black crystalline solid. The crystal is rhombohedral and contains four iodine molecules per unit cell. The I-I separation within the molecule is 2.70 Å, and between molecules ca. 3.54 Å⁽²⁹⁾. The intramolecular separation of iodine atoms in the solid state are almost identical with the separation in vapour phase which is 2.65 Å.

The atomic no. of iodine is 53 and its electron configuration is: 2 . 8 . 18 . 18 . 7 .

Melting point is 113.7°C.

Boiling point is 184.35°C.

Density of solid iodine at 20°C = 4.94.

Critical temperature = 553°C.

The molecular radius of iodine molecule is 2.923 Å.

The density of liquid iodine is given by:
 $3.94916 + 0.003267(120 - t)^{(30)}$, where t is temperature in degrees centigrade.

Specific volume at 120°C = 0.2532 ml.

Coefficient of cubical expansion of solid iodine is $2.64 \times 10^{-4} \text{ cc } ^\circ\text{C}^{-1}$ ⁽³¹⁾.

Coefficient of cubical expansion of liquid iodine is $8.54 \times 10^{-4} \text{ cc } ^\circ\text{C}^{-1}$.

The energy of dissociation of molecular iodine into atoms, i.e. $\text{I}_2 \rightleftharpoons 2\text{I}$ is given as⁽³²⁾

$$\Delta H^\circ_{298.1^\circ\text{K}} = 36,057 \pm 50 \text{ g.cal.mole}^{-1},$$

from spectroscopic data:

$$\Delta H^\circ_{298.1^\circ\text{K}} = 36,341 \pm 100 \text{ g.cal.mole}^{-1},$$

$$\Delta G^\circ_{298.1^\circ\text{K}} = 28,882 \pm 50 \text{ g.cal.mole}^{-1}.$$

The change in volume on fusion of iodine is 2.04%⁽³³⁾.

The latent heat of fusion of iodine is $3,740 \pm 20 \text{ g.cal.mole}^{-1}$ ⁽³⁴⁾.

The latent heat of vaporisation is 14,800.7 g.cal.mole⁻¹ ⁽³⁵⁾.

The heat capacity of iodine at constant pressure for solid iodine can be expressed by the following equation:

$C_p = 13.07 + 3.21 \times 10^{-4} (t - 25)^2 (\pm 5\%) \text{ g.cal.mole}^{-1}$,
where t is the temperature in $^\circ\text{C}$.

Above the melting point the heat capacity has the following values:

Temp. $^\circ\text{C}$	389.4	398.8	413.2	431.9	432.7
$C_p \text{ g.cal.mole}^{-1}$	20.00	19.72	19.00	18.7	18.02

From the melting point of iodine (113.6°C) to 160°C C_p is constant for iodine and equal to $19.5 \pm 0.3 \text{ g.cal.mole}^{-1}$. At 389.4°C $C_p = 20.00 \text{ g.cal.mole}^{-1}$ ⁽³⁶⁾.

Standard entropy of solid iodine at 298.16°K is $27.9 \text{ g.cal.deg}^{-1}\text{mole}^{-1}$.

Standard entropy of gaseous iodine at 298.16°K is $62.28 \text{ g.cal.deg}^{-1}\text{mole}^{-1}$ ^(37,38,39). (The statistical mechanics method gives $61.81 \text{ g.cal.deg}^{-1}\text{mole}^{-1}$).

Chemical constant of molecular iodine is 3.91.

Standard entropy of gaseous monatomic iodine is 43.18 g.cal.deg⁻¹mole⁻¹ (37,40).

Its chemical constant is 2.00.

For the electron affinity of an iodine atom, calculated using the Born cycle, from the lattice and hydration energies of alkali iodides, the following values have been recorded:

69.9; 72.4; 73.6 and 76.3 kcal.g.atom⁻¹.

Polarisation of iodine vapour is given as 32.2 cc⁽⁴¹⁾. Therefore the polarizability of iodine molecule in the gaseous state is 12.763 x 10⁻²⁴ cc.

Molecular iodine is diamagnetic and has no permanent dipole moment.

The diamagnetic specific susceptibility χ , measured for cyclohexane solution is given as -0.35 x 10⁻⁶ c.g.s. units. Using other solvents somewhat higher values were obtained.

The most probable value for diamagnetic susceptibility of iodine ion is -57 x 10⁻⁶ c.g.s. units per g. ion, in the vapour state and in aqueous solution^(42,43,44).

Imam and Khastgir⁽⁴⁵⁾ gives the value for the dielectric constant for ionised iodine as K = 0.987, and the electron density of iodine ion as N = 1.94 x 10⁸

where $K = 1 - \frac{4\pi N e^2}{m(\omega^2 + \nu^2)}$ - Eccles-Larmor equation.

According to the authors the dielectric constant of iodine as opposite to that of Br and Cl, is independent of ionic concentration.

The table below gives the most important physical constants for iodine, bromine and aluminium chloride.

Physical constant	Iodine	Bromine	Aluminium chloride	Ref.
Physical state at room temp.	solid	liquid	solid	
Melting point	113.7°C	-7.2°C	-	
Boiling point	184.35°C	58.8°C	183°C	
Density	4.94 ²⁰ _s	3.10 ²⁵	2.4 ²⁰ _s	157
Coeff. of cubical expansion - solid	2.64x10 ⁻⁴	-	-	31
Coeff. of cubical expansion-liquid	8.54x10 ⁻⁴	-	-	31
L. heat of fusion	3.74 kcal/mole	2.53 kcal/mole	-	34
L. heat of vaporis.	14.88 kcal/mole	7.24 kcal/mole	-	35
S ^o _{298.16°K} vapour	62.28 e.u.	58.64 e.u.	-	37,38,39
Polarisability of vapour	12.763 x 10 ⁻²⁴ cc	-	-	41
T _c	553°C	575°C	629.5°C	
P _c	-	-	-	
Molecular radius	2.923 Å	2.30 Å	-	156
Vap. press. of 1 mm	38.7°C	-15°C	100.0°C	

1.3 Sorption.

Sorption occurs when gas molecules come in contact with the attractive field of a solid and become removed from the gas phase to form a sorbed phase, which is usually located either on the external surface of the solid or in the interstices of the solid as is the case with our sorbents.

The terms sorption, adsorption, occlusion and inclusion, in the case of porous sorbents, can be used interchangeably. Usually, sorption is divided into two categories: physical sorption and chemisorption, although in an actual system they may occur together and very often it is difficult to decide to which category a particular system belongs.

In physical sorption the forces between sorbent and sorbate molecule are physical in nature and are similar to the forces concerned in condensation phenomena, interaction between ions, dipoles and induced dipoles, and dispersion forces.

Chemisorption, on the other hand, involves forces of a chemical nature, and activation energy is required for the process to take place.

The rate of physical sorption is limited only by the rate at which the sorbate molecules can reach the sorbent surface and thus the equilibrium is usually attained rapidly.

In chemisorption, on the other hand, an energy of activation, small or large, must be supplied before the sorbed phase can form. The rate of chemisorption, like that of a chemical reaction increases exponentially with temperature.

Chemisorption is generally unimolecular, whereas physical sorption may be multimolecular. The heat of sorption of a gas or vapour physically sorbed on a solid is generally of the same order as its heat of condensation, whereas with chemisorption the heat of sorption may be much greater.

In the case of sorption in zeolitic crystals, the process is usually discussed in terms of physical sorption

although in certain cases the magnitude of the heat of sorption suggests that chemisorption cannot be ruled out.

1.3.1. Theories of sorption.

A large amount of work has been done on adsorption during the last fifty years and various isotherm equations have been suggested. Some of them, considered to be more important, will be briefly described. Sorption data are usually expressed as isotherms, i.e. as plots of amount sorbed versus the equilibrium pressure, of the sorbed gas or vapour, at constant temperature.

A successful equation should describe the whole isotherm and, after evaluating appropriate constants, allow the prediction of isotherms at other temperatures. The constants of the equation, representing independently measurable physical quantities, must have reasonable values. Hill (1949) pointed out that the coincidence of the theoretical and experimental isotherms is not sufficient for the theory to be valid as the isotherms are only comparisons of Gibb's free energies. For the theory to be valid it must also predict correctly the entropy of the system.

At low pressures or sufficiently high temperatures the amount sorbed (α) is frequently proportional to the pressure (p). From this consideration Freundlich⁽⁴⁶⁾ suggested the empirical equation for isotherm

$$\alpha = k p^{\frac{1}{n}}$$

where k and n are constants and $n > 1$. This is similar to Henry's law of solution where $n = 1$ but is valid only over a limited range.

The first isotherm based on a physical picture is due to Langmuir⁽⁴⁷⁾. He assumed that adsorption was

restricted to monolayer, and that the forces responsible for adsorption were negligible after the first layer. Up to his time the large surfaces of sorbents had not been realised and the adsorbed films were thought to be thick. Langmuir considered the sorbent surface to be composed of sites onto which the sorbate molecules can be sorbed. If there are N_s sites and N sorbed molecules then the fraction, θ , of the sites occupied by the sorbed molecules is given by $\theta = N/N_s$. The sites are assumed to have equal attraction for the gas molecules and the interaction between sorbed molecules is ignored. It follows that:

$$\text{the rate of adsorption} = k_1 p(1 - \theta)$$

$$\text{the rate of desorption} = k_2 \theta$$

$$\therefore \text{at equilibrium } k_1 p(1 - \theta) = k_2 \theta$$

$$\text{and } \theta = \frac{k_1 p}{k_1 p + k_2} = \frac{\frac{k_1}{k_2} p}{1 + \frac{k_1}{k_2} p} = \frac{ap}{1 + ap}$$

Also $\theta = x/x_m$, where x_m is the amount of gas to give complete monolayer coverage, and x is the amount of gas sorbed.

$$\text{So, } \frac{p}{x} = \frac{1}{x_m a} + \frac{p}{x_m}$$

In the above equations, both x_m and "a" are temperature dependent. "a" can be expressed statistically and then it is possible to calculate x_m and "a" for another temperature and the isotherm can be predicted.

The Langmuir isotherm has been derived thermodynamically and statistically. The main defects of the theory lie in its assumptions that:

- (a) the sorption is restricted to a monolayer;
- (b) the sites are equal, i.e. the surface is

homogeneous as far as sorption is concerned;

(c) there is no interaction between adsorbed molecules.

In his later papers Langmuir⁽⁴⁸⁾ did consider the formation of clusters above the primary monolayer of adsorbed molecules, but did not regard this as true van der Waals' sorption.

The considerable increase in sorption observed in many systems as $p/p_0 \rightarrow 1$ (where p_0 = saturation pressure), was not taken into account by the Langmuir isotherm but was readily explained as being due to condensation. Zsigmondy⁽⁴⁹⁾ and others, using the Kelvin equation⁽⁵⁰⁾, showed that in small capillaries condensation may occur at low values of p/p_0 , and they attempted to explain all sorption, other than monolayer, on this basis. The present general opinion is that capillary condensation becomes important only when the capillaries are at least several molecular diameters in width.

About the same time as Langmuir produced his monolayer theory, Polanyi^(51,52) introduced his potential theory assuming adsorption to be due to long range attractive forces extending from the sorbent surface. His ideas were later modified to be in line with more modern theories of intermolecular forces. Polanyi suggested multilayer sorption, the layers being under compression due to the attractive force of the sorbent surface and the upper layers of sorbate. He also postulated a gradual pressure gradient from the sorbent surface to the gas phase. The adsorbed phase was assumed to obey the same equation of state as the gas phase.

Another theory of multimolecular sorption was that of de Boer and Zwikker⁽⁵³⁾. They proposed that only

the first adsorbed layer was attracted strongly to the sorbent surface, other layers being held by polarisation and the interaction of the induced dipoles. The binding energies decreased exponentially with the number of layers. This was the first theory to account qualitatively for the observed S-shaped isotherms, the high pressure region of which had been explained previously by capillary condensation. However, their postulated energies of attraction, for layers other than the first, of non-polar molecules such as argon were much less than experimental values. More recent theories of adsorption have been based on the assumption that physical sorption is due to the total effect of van der Waals' forces, the London dispersion forces being the most important especially with non-polar sorbates.

Brunauer, Emmett and Teller⁽⁵⁴⁾ postulated an improved theory known as B.E.T. theory of sorption. They assumed that the same forces which produce condensation are responsible for the binding energy of multimolecular sorption. Only the first layer is considered to be attracted strongly by the surface of sorbent, and the evaporation-condensation properties of succeeding layers being assumed to be equal to those of the free gas. Otherwise the model is similar to that of Langmuir. Suppose the sorbent has area:

- S_0 - with no molecules on it,
- S_1 - with a monolayer,
- S_2 - with two layers, etc.

At equilibrium these are constant. Therefore,
 rate of condensation to bare surface = $p a_1 S_0$,
 rate of evaporation from monolayer = $b_1 S_1$

$$= b_1' \left(\exp \frac{-E_1}{RT} \right) S_1,$$

where a , b , are constants, and E_1 is the heat of vaporisation from the monolayer. S_1 is proportional to the number of molecules in the monolayer not covered by any other molecules. Only uncovered molecules are assumed to be able to evaporate, hence for the uncovered first layer the equilibrium is given by:

$$p a_1 S_0 = b_1 S_1 = b_1' \left(\exp \frac{-E_1}{RT} \right) S_1$$

$$\text{Therefore, } S_1 = \frac{a_1}{b_1} p S_0.$$

$$\text{Similarly, } S_2 = \frac{a_2}{b_2} p S_1 = \frac{a_2}{b_2} \cdot \frac{a_1}{b_1} p^2 S_0$$

$$\text{The total surface} = A = \sum_{i=0}^{\infty} S_i = S_0 + S_1 + S_2 + \dots$$

$$= S_0 \left(1 + p \frac{a_1}{b_1} + p^2 \frac{a_1}{b_1} \cdot \frac{a_2}{b_2} + \dots \right)$$

The total volume sorbed (in cc at N.T.P) = v

$$v = v_0 \sum_{i=0}^{\infty} i S_i$$

where v_0 = amount to cover 1 cm² of surface with a complete monolayer (in cc at N.T.P.).

It follows that

$$\frac{v}{A v_0} = \frac{v}{v_m} = \frac{\sum_{i=0}^{\infty} i S_i}{\sum_{i=0}^{\infty} S_i} = \text{the effective no. of layers,}$$

where, v_m = the volume of gas adsorbed when the entire adsorbent surface is covered with a complete unimolecular layer.

This summation is simplified by the assumption mentioned previously that the evaporation-condensation

properties of uncovered molecules in all layers, save the first, are equal to those of the free gas,

$$\text{i.e. } \frac{a_2}{b_2} = \frac{a_3}{b_3} = \frac{a_4}{b_4} = g$$

$$\text{and } E_2 = E_3 = E_4 = \dots$$

Let $\frac{a_1}{b_1} = c_1$, then it can be shown that

$$\sum_{i=0}^{\infty} S_i = S_0 \frac{(1 - gp + c_1 p)}{1 - gp}$$

$$\text{and } \sum_{i=1}^{\infty} i S_i = \frac{c_1 p S_0}{(1 - gp)^2}$$

and therefore

$$\begin{aligned} \frac{v}{v_m} &= \frac{c_1 p S_0}{(1 - gp)^2} \cdot \frac{1 - gp}{S_0(1 - gp + c_1 p)} \\ &= \frac{c_1 p}{(1 - gp)(1 - gp + c_1 p)} \end{aligned}$$

As $p \rightarrow p_0$ capillary condensation occurs with the formation of an infinite number of layers (on a plane surface), therefore $v/v_m \rightarrow \infty$

Therefore the R.H.S. denominator $\rightarrow 0$ and g must equal $1/p_0$.

$$\text{Thus, } \frac{v}{v_m} = \frac{c_1 p}{(1 - \frac{p}{p_0})(1 - \frac{p}{p_0} + c_1 p)}$$

$$\text{Let } c_1 = cg = \frac{c}{p_0}, \text{ then } \frac{v}{v_m} = \frac{c_1 p}{(p_0 - p)[1 + (c - 1)\frac{p}{p_0}]}$$

For the purpose of testing the equation it may be put in the form:

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} = \frac{c - 1}{v_m c} \times \frac{p}{p_0}$$

The plot of $\frac{p}{v(p_0 - p)}$ against $\frac{p}{p_0}$ should give a straight line. The intercept of this line is $\frac{1}{v_m c}$ and its slope $\frac{(c - 1)}{v_m c}$. Thus, it is possible to evaluate the two constants v_m and c from experimental data.

$$\begin{aligned} \text{Also, } c &= \frac{c_1}{g} = \frac{a_1}{b_1} \times \frac{b_2}{a_2} \exp \frac{-(E_1 - E_2)}{RT} \\ &= \frac{a_1 b_2}{b_1 a_2} \exp \frac{-(E_1 - E_L)}{RT} \end{aligned}$$

where E_L is the heat of liquefaction of the gas and therefore of all layers above the first from the assumption.

Assuming that $\frac{a_1 b_2}{b_1 a_2}$ approximates to unity
 $c \simeq \exp \frac{-(E_1 - E_L)}{RT}$. Thus the average heat of sorption of the first layer may be obtained from c .

The formulation of c has been criticised by Kemball and Schreiner⁽⁵⁵⁾ who point out that $\frac{a_1 b_2}{b_1 a_2}$ may vary from 10^{-5} to 10, and therefore the B.E.T. single isotherm method for finding the heat of sorption can only be used when the entropy of adsorption is known. The B.E.T. evaluation of c assumes that the entropy of sorption in layers other than the first is equal to the entropy of liquefaction. It is sometimes found that even when the heat of sorption decreases as more gas is sorbed, the straight line plot is still obtained. Therefore the entropy of sorption must be assumed to change to compensate for the decrease of heat of sorption. Barrer and Riley⁽⁵⁶⁾ interpret $c = - \exp \frac{-\Delta A_0}{RT} \simeq - \exp \frac{-\Delta G_0}{RT}$.

Hill⁽⁵⁷⁾ expresses $\frac{a_1 b_2}{b_1 a_2}$ as a ratio of the partition functions of the molecules in the sorbed and liquid states.

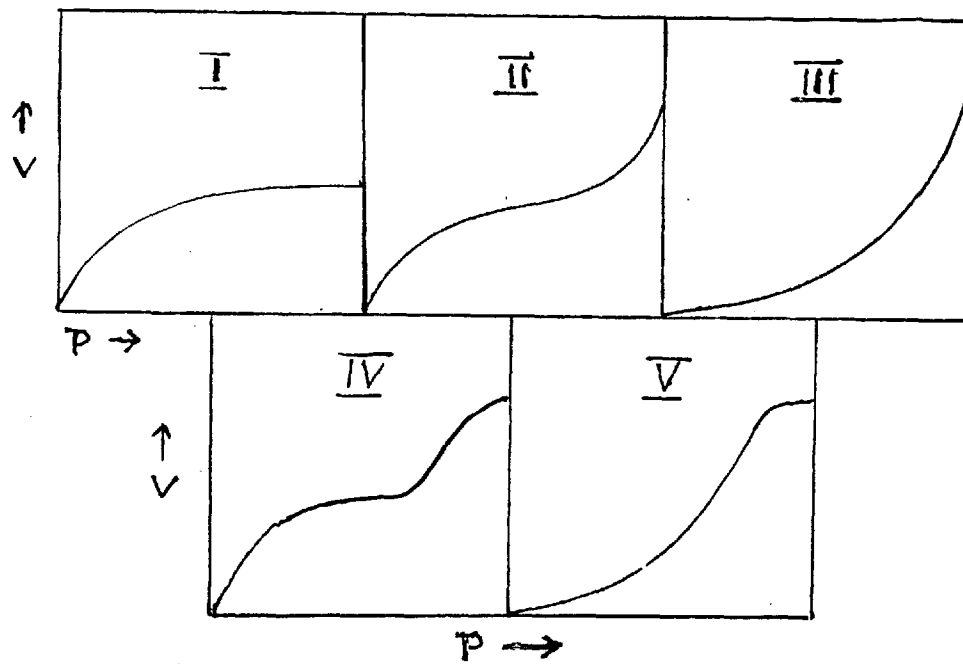
The isotherms experimentally observed in physical sorption have been classified by Brunauer et al⁽⁵⁸⁾ into five types (fig. 6).

Type 1 represents monolayer sorption on plane surface and will also occur in sorbents with very fine pores of molecular dimensions. For monolayer the B.E.T. equation becomes: $\frac{v}{v_m} = \frac{cp}{1 + cp}$ which is identical with the Langmuir form.

Types 2 and 3 represent unlimited sorption, on plane surface, differing in their affinity for sorbate. In type 2, the affinity is large, i.e. c is large and a monolayer forms at low pressures. In type 3 the affinity for sorbate is low (i.e. c is small) and coverage is gradual.

Types 4 and 5 are special cases of 2 and 3. In type 4, although affinity for sorbate is large as in type 2, sorption is restricted to a finite number of layers by some steric consideration such as the size of channels in zeolites. Type 5 is similar to type 4, but the sorbent has low affinity for sorbate. The modification of B.E.T. treatment to deal with finite number of layers of sorbate have been made by Brunauer et al⁽⁵⁸⁾ and Hill⁽⁵⁷⁾.

The B.E.T. equation gives a good fit for most adsorption data in the range of p/p_0 of 0.05 to 0.35, giving good values for the surface areas at monolayer coverage. To calculate surface area from B.E.T., or similar equations, a value must be assigned to the cross-sectional area of the sorbed molecule. Emmett and Brunauer⁽⁵⁹⁾ made the assumption that in the monolayer the molecules are closely packed as in the liquid state, hence the cross-section (δ)

FIG. 6.ISOTHERM TYPES IN PHYSICAL ADSORPTION.

of the molecule is taken as that of the liquid state.

$$= 4(0.866) \left(\frac{M}{4\sqrt{2} N \rho} \right)^{\frac{2}{3}}$$

where ρ = density of liquid sorbate,
 M = molecular weight of sorbate,
 N = Avogadro's number.

The Emmett and Brunauer method of determining δ is found to give inconsistent results with gases other than N_2 ⁽⁶⁰⁾ and generally molecular areas are calculated by experiment on a substance whose specific surface has been found by N_2 sorption or some other method.

Hill⁽⁶¹⁾ suggested an alternative equation

$$\delta = 6.354 \left(\frac{T_c}{P_c} \right)^{\frac{2}{3}}$$

There is good agreement between values calculated from the two equations.

Foster⁽⁶²⁾ gives the molecular diameter as $1.33 \times 10^{-8} \left(\frac{M}{d} \right)^{\frac{1}{3}}$ where d is the normal density of the liquid sorbate.

Knowing the molecular diameter of the sorbate molecule, the surface area apparently covered by sorbate may then be calculated from the relationship:

$$A = \frac{\delta_n}{V_n} \times w_m$$

where V_n is the molal volume of the sorbate,

δ_n is the molecular diameter of the sorbate.

The v_m given by the B.E.T. equation occurs at the point of greatest change of affinity of sorbent for sorbate and this is not well defined in isotherm types 3 and 5, i.e. when c is small. Hill⁽⁵⁷⁾ showed that on the B.E.T.

assumption multilayer formation should begin before the completion of a monolayer.

In the original form of the B.E.T. theory the sorbent surface was assumed to be uniform, that is sorption on all sites was supposed to be energetically identical. Experiments have shown that in numerous cases this is not so. The heat of sorption, due to heterogeneity of the surface, may be maximum during the sorption of initial molecules. The heterogeneity accounts largely for the deviations from B.E.T. observed below, $p/p_0 = 0.05$. McMillan⁽⁶³⁾ has extended the B.E.T. treatment to consider a mixture of two homogeneous surfaces, obtaining a better fit in the low pressure range for N_2 sorption on an inorganic salt. His suggested system is, of course, much less complex than real systems. A similar idea has been elaborated by Zettlemoyer and Walker⁽⁶⁴⁾. Honig and Hill⁽⁶⁵⁾ discuss the determination of the adsorption energy heterogeneity of solid surfaces. Halsey and Taylor⁽⁶⁶⁾ have specified surface heterogeneity in terms of an exponential distribution of sites of different energies. Miller⁽⁶⁷⁾, while agreeing about surface heterogeneity, has pointed out that the B.E.T. treatment ignores lateral interaction between the sorbate molecules, and such an interaction will increase with greater surface coverage. It has been suggested that the heat of sorption will tend to be lowered by repulsions between permanent dipolar molecules, or be increased due to dispersion attractive forces. Theimer⁽⁶⁸⁾ points out that dipolar molecules would generally be oriented so as to attract one another. Conditions for repulsive forces, according to him, would only rarely be fulfilled, e.g. if two molecules were sorbed on sites closer than their normal approach distance in the liquid phase. Hill⁽⁶⁹⁾, Barrer and Robins⁽⁷⁰⁾ and Kiselev⁽⁷¹⁾

have also considered lateral interactions.

Surface forces are neglected after the first adsorbed layer in the simple B.E.T. treatment, the heat of sorption being taken as equal to the heat of liquefaction. Halsey⁽⁷²⁾ has shown that if $E_2 = E_L$ then the B.E.T. hypothesis leads to practically no sorption beyond the first layer, since at least a triangular array of molecules would be required in the first layer before another might be adsorbed in the second layer with a release of energy similar in magnitude to the heat of liquefaction. Also, a stepwise isotherm would be obtained if $E_1 > E_2 \dots E_L$. Attempts to improve upon the B.E.T. treatment were also made by Anderson⁽⁷³⁾, Anderson and Hall⁽⁷⁴⁾, Pickett⁽⁷⁵⁾, Cook⁽⁷⁶⁾ and others. Cassel^(77,78) has pointed out that the B.E.T. treatment also ignores surface tension effects in adsorbed films. But this aspect has been dealt with quantitatively by McMillan and Teller⁽⁷⁹⁾ and by Hill⁽⁸⁰⁾.

Despite all these criticisms the B.E.T. model remains a very useful one. Its simple form can be modified giving accounts for the effects mentioned above, but then the equation becomes very unwieldy and incapable of general application.

There are other isotherm equations, from which surface area may be calculated, but none of them is to be greatly preferred to the B.E.T. Huttig⁽⁸¹⁾ produced an isotherm equation which is similar to B.E.T., except that he considers that any adsorbed molecule may evaporate, whereas the B.E.T. postulates that only uncovered molecules may evaporate. Barrer⁽⁸²⁾ has shown that in this treatment sorbate molecules are considered to be in the potential field of the sorbent and of other

sorbate molecules in a fashion compatible with allowance for lateral interaction between the sorbed molecules but not for vertical interaction. Ross⁽⁸³⁾ has derived the Huttig isotherm using the conventional B.E.T. symbols. It thus becomes:

$$\frac{v}{v_m} = \left(\frac{c \cdot \frac{p}{p_0}}{1 + c \cdot \frac{p}{p_0}} \right) \left(1 + \frac{p}{p_0} \right)$$

or for purpose of testing:

$$\frac{p}{v} \left(1 + \frac{p}{p_0} \right) = \frac{p_0}{c v_m} + \frac{p}{v_m}$$

Thus plot of $\frac{p}{v} \left(1 + \frac{p}{p_0} \right)$ against p should give a straight line of slope $\frac{1}{v_m}$. This isotherm fits well adsorption data from $\frac{p}{p_0} = 0.05$ to 0.5 . Hill⁽⁸⁴⁾ points out that the Huttig model contains the fundamental error of equating the rates of two molecular processes which are not the reverse of each other. Barrer and Ferguson's⁽⁸⁵⁾ statistical treatment of the Huttig equation necessarily contains a similar wrong assumption in equating the chemical potentials of the various layers. None the less the Huttig equation remains a useful empirical isotherm equation. The surface areas calculated from this equation are generally about 10% greater than those from B.E.T. The straight line plots do not necessarily extend over a greater pressure range than for the B.E.T., and for sorbents with low specific surface areas the B.E.T. gives generally more self-consistent area values for different gases on the same solid⁽⁸⁶⁾.

Theimer^(87,88) finding the Huttig assumption of evaporation of a molecule beneath another layer incompatible with the formation of vertical chains, considers multilayer formation to take place around active

sides, at least two molecular diameters apart, in a two dimensional fashion. Only at higher relative pressures do the 'clusters' overlap and grow vertically. The multilayer concept is replaced by that of molecules adjacent to active sites and those further away. Huttig formulation is retained by Theimer giving

$$\frac{v}{v_m} = cx(1 + \infty - x^s)/(1 + cx - x^s)(1 - x^s)$$

where s is a parameter interpreted as the average number of molecules required to envelop entirely a molecule in the first layer. This equation follows some sorption data as far as $p/p_0 = 0.8$; s has to be determined by trial and error. Generally the equation is rather unwieldy for surface area determination. The reciprocal of s is taken to represent the tendency of the 'two dimensional clusters' to grow vertically. $s = 1$ in the B.E.T. model, and ∞ in the Huttig model. Theimer's theory gets over two difficulties. With his sorption centres practically outside the range of mutual attraction and with the rest of the sorbent surface unattractive he excludes two dimensional condensation. Also he does not postulate vertical chains of sorbate molecules which Halsey has criticised.

Harkins and Jura^(88,89) include the sorption of vapours on solids as part of a general treatment of the behaviour of insoluble and adsorbed films on the surfaces of liquids and solids, therefore involving the Gibbs free energy of the surface. This idea seems to have come from the suggestions of Gregg⁽⁹⁰⁾ and Bangham⁽⁹¹⁾ who have produced isotherm equations based on integration of the Gibbs isotherm. Harkins and Jura obtain their expression by combining the differential of the pressure-area relation for condensed monolayers.

$\Pi = b - a\delta$, where Π = pressure, δ = mean area per molecule = Σ/N . With the Gibbs adsorption isotherm:

$a\Pi = \left(\frac{RT}{V\Sigma}\right)\left(\frac{V}{P}\right) dp$. They obtained the following equation:

$$\ln p = B - \frac{\Lambda}{V^2} \quad (92)$$

where $\Lambda = a\Sigma^2 V^2 / 2 NRT$

$B = \ln p_0 + \Lambda/V_0^2$

V_0 = amount of gas sorbed at saturation in cc/g sorbent,

Π = surface pressure = decrease in surface free energy = $-\Delta\gamma$;

Σ = specific area of the solid in cm²/g.

a and b are constants.

Livingstone stresses the fact that this equation is thermodynamic only in that it involves the Gibbs isotherm. It owes its success to the experimental fact that Π is related in a linear fashion to δ over a large pressure range for many systems. The area per molecule of sorbent = $KA^{\frac{1}{2}}$, where K is assumed constant for a given sorbate. Hence from a single isotherm on a sorbent of known surface area, the surface areas of other sorbents may be found from isotherms with the same sorbates at the same temperature. Actually K is found not to be independent of the adsorbent⁽⁸⁶⁾. A is obtained from the plot of $\ln p$ against $1/V^2$. Duncan⁽⁹³⁾ has compared this equation with B.E.T. method of estimating surface area of a particular sorbent-sorbate system. He finds good agreement between these methods.

Fu and Bartell⁽⁹⁴⁾ have produced another method of estimating surface area; this does not involve a knowledge of the molecular area of the sorbate but requires a complete isotherm. In their treatment they make use of

the integrated form of Gibbs isotherm.

Chu Liang⁽⁹⁵⁾ made an attempt to modify the Harkins-Jura equation to express v_m in cc and to convert K into a universal constant. Writing the Harkins-Jura equation in the following form:

$$\ln \frac{p}{p_0} = B' - \left(\frac{k}{v_m} \right)^2 \theta^2$$

where $\theta = v/v_m$, and k is a constant to be determined. The B.E.T. equation expressed similarly is:

$$\frac{p}{(p_0 - p)\theta} = \frac{1}{c} + \frac{(c - 1)p}{cp_0}$$

Using various values of c in the B.E.T. equation to construct hypothetical isotherms and then plotting these in the form of $\ln \frac{p}{p_0}$ against $\frac{1}{\theta^2}$, he obtains linear portion with a slope of -1. Therefore, $\left(\frac{k}{v_m} \right)^2 = -1$, and $k = v_m$.

Thus the Harkins-Jura equation reduces to:

$$\ln \frac{p}{p_0} = B' - \frac{v_m^2}{v^2}$$

or in the original form: $\ln p = B - \frac{v_m^2}{v^2}$. Thus from plot of $\ln p$, against $1/v^2$, we find that $v_m = \sqrt{\text{slope}}$.

Barrer, Mackenzie and MacLeod⁽⁹⁶⁾, in their discussion of the use of adsorption isotherms for measuring surface areas, have put forward several B.E.T. type equations. In these allowance was made for increasing volatility of sorbate molecules in higher layers. This treatment reduces the theoretical amount sorbed at higher relative pressures and partially corrects the B.E.T. model in its allowance of molecular columns of quite different heights. A modification was also introduced for the liquid-like properties of thick films.

1.3.2 Adsorbate-adsorbate interaction.

On entering the adsorption layer, the molecules of the adsorbed substance interact with each other. Generally the influence of this interaction is superposed on the influence of surface inhomogeneity and these factors cannot be separated; this hinders the interpretation of experimental data.

Kiselev⁽⁹⁷⁾ studied the adsorption on carbon black graphitized at about 1500°C, which he claims produces a homogeneous surface. With the aid of experimental data thus obtained he considers the influence of adsorbate-adsorbate interaction on various models of isotherm equation from a purely thermodynamic standpoint, by introducing appropriate constants, the values of which are not calculated theoretically. He concludes that, with the exception of special cases of surfaces bearing charges of the same sign, adsorbate-adsorbate attraction generally predominates over a wide range of θ' where θ' is fraction of monolayer covered.

Fowler and Guggenheim⁽⁹⁸⁾ considered adsorbed layers from the viewpoint of statistical thermodynamics. They derived the following equation for localized sorption with mutual attraction between neighbouring adsorbate molecules:

$$p = \frac{\theta'}{K_1'(1 - \theta')} \exp^{-a\theta'}$$

The advantage of the treatment by means of statistical thermodynamics is that the equilibrium constant K_1' is expressed in terms of the distribution functions of the sorbate in the gas phase and on the surface of adsorbent, so that a theoretical calculation is possible in principle.

Barrer and Stuart⁽⁹⁹⁾ and Barrer and Robins⁽¹⁰⁰⁾ used isotherms derived by statistical thermodynamics to describe the adsorption of vapours on carbon and to make allowance for sorbate-sorbate interaction. The equilibrium equation is of the form:

$$p = \frac{\theta'}{K_1'(1 - \theta')} \left(\frac{2(1 - \theta')}{\beta + 1 - 2\theta'} \right)$$

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

and $2w/z$ is the energy of interaction calculated for a pair of molecules at neighbouring sites. z is the co-ordination number of the sites (usually 4 or 6).

Kiselev⁽¹⁰¹⁾ obtained the following equation:

$$p = \frac{\theta'}{K_1'(1 - \theta')(1 + K_n\theta')}$$

for adsorption in a monolayer with adsorbate-adsorbate interaction approximately taken into account, where

K_1' is the equilibrium constant for adsorbate-adsorbent interaction, and

K_n is the equilibrium constant for adsorbate-adsorbate interaction.

The shape of the adsorption isotherm depends on the magnitude of K_1' and K_n and on the ratio between them. The concave or convex nature of the start of the isotherm is determined by the limiting value ($\theta' = p = 0$) of the second derivative of the isotherm equation.

At high values of the adsorbate-adsorbent equilibrium constant K_1' the shape of the above isotherm approaches that of the Langmuir isotherm.

Kiselev^(102,101) derived an approximate equation for multimolecular adsorption with adsorbate-adsorbate interaction in the first layer taken into account

i.e. Vapour molecules + free sites on horizontal
complexes $\rightleftharpoons$
 $\rightleftharpoons$ binary vertical complexes, etc.

He assumes that in multimolecular adsorption only uncovered unitary complexes take part in the formation of unitary complexes with adsorbate-adsorbate interaction, and he derived the following equation based on B.E.T.

$$p = \frac{\theta(1 - K_{\ell}p)^2}{K_1'[1 - \theta(1 - K_{\ell}p)][1 + K_n\theta(1 - K_{\ell}p)]}$$

In general this equation represents a curve with two points of inflection. In the particular case when K_1' is large, adsorbate-adsorbate interaction is relatively small and the equation approaches the following equation:

$$\theta = \frac{v}{v_m} = \frac{K_1'p}{(1 - p)(1 + K_1'p)}$$

which is convenient for the determination of the capacity of the dense monolayer, v_m , and of specific surface area.

1.3.3 Empirical isotherm equation.

By making the assumption that the sorbed state can be adequately described by a virial equation of state, it is possible to derive an empirical isotherm equation which can be used to describe the shape of an experimental isotherm. This is useful due to the fact that much information can be obtained concerning intermolecular force potentials from second virial coefficients.

Barrer and Rees⁽¹⁰³⁾ have used a modified form of van der Waals equation of state to express isotherms of argon and nitrogen in ion exchanged faujasites. A similar procedure can be followed in order to obtain an isotherm equation in terms of a virial equation of state⁽¹⁰⁴⁾.

The work done in transferring a mole of gas from a gas phase where the pressure is P_g and the molar volume V_g , to a sorbed phase in a uniform field of sorption potential where the pressure is P_s and the molar volume V_s is given by:

$$W = \int_{P_g}^{P_s} V dP + \phi \quad 1.3.3. 1.$$

where ϕ is the sorption energy per mole due to the uniform field of potential. This is the difference in free energy of the sorbate in the two phases. At equilibrium therefore:

$$\int_{P_g}^{P_s} V dP + \phi = 0 \quad 1.3.3. 2.$$

If the sorbed state can be described by a virial equation of the form:

$$PV = RT \left(1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots \right) \quad 1.3.3. 3.$$

where B, C and D are the second, third and fourth virial coefficients, the following isotherm equation can be obtained from 1.3.3. 2. and 1.3.3. 3., by integrating and assuming that $V_g \gg V_s$:

$$P_g = \left[\frac{RT}{b_1} \exp \frac{\phi}{RT} \right] \theta \exp \left[\frac{2B\theta}{b_1} + \frac{3C\theta^2}{2b_1^2} + \frac{4D\theta^3}{3b_1^3} + \dots \right] \quad 1.3.3. 4.$$

where b_1 is the gm molecular co-volume of the sorbed molecules, and

$$\theta = \frac{\text{number of molecules sorbed}}{\text{no. of molecules needed to saturate the intra-crystalline volume}}$$

In the Henry's law region this equation reduces to

$$P_g = K\theta, \text{ where } K = \frac{RT}{b_1} \exp \frac{\phi}{RT} \quad 1.3.3. 5.$$

$$\begin{aligned} \text{and} \left(\frac{\partial \ln P}{\partial T} \right)_{\theta} &= \left(\frac{\partial \ln K}{\partial T} \right) = \frac{\partial}{\partial T} \left(\frac{\phi}{RT} + \ln T + \ln \frac{R}{b_1} \right) \\ &= \frac{RT - \phi}{RT^2} \end{aligned} \quad 1.3.3. 6.$$

$$\text{assuming that } \frac{\partial}{\partial T} \left(\frac{1}{b_1} \right) = 0.$$

From the Clausius-Clapeyron equation

$$\left(\frac{\partial \ln P}{\partial T} \right)_{\theta} = - \frac{\Delta H}{RT^2},$$

$$\text{therefore, } \Delta H = \phi - RT \quad 1.3.3. 7.$$

where ΔH is the limiting value of the isosteric heat of sorption at low values of θ .

The values of ϕ obtained from equation 1.3.3. 5. will be lower than the value predicted from the heat of sorption; this is due to the fact that when molecules are transferred from the gas phase to the intracrystalline cavity, the thermal entropy of the sorbate is changed more than is implicit in equation 1.3.3. 3., and the process of compression. This entropy effect can be allowed for by writing

$$K = \frac{RT}{b_1} \exp \frac{\Delta S_0}{R} \exp - \frac{(\Delta H + RT)}{RT} \quad 1.3.3. 8.$$

Equation 1.3.3. 4 can be written in the following more useful form:

$$\theta = \frac{n_s b_1}{V_i}$$

where n_s = number of molecules sorbed,

b_1 = gm molecular co-volume of molecules,

v_i = interstitial volume of the crystals.

Also $n_s = \frac{V}{22414}$, where V = volume sorbed at N.T.P. per gm of outgassed solid.

Equation 1.3.3. 4 therefore becomes:

$$P_g = \left[\frac{RT}{22414V_i} \exp \frac{\phi}{RT} \right] V. \exp \left[\frac{2BV}{22414V_i} + \frac{3CV^2}{2(22414V_i)^2} + \frac{4DV^3}{3(22414V_i)^3} + \dots \right] \quad 1.3.3. 9.$$

This can be simplified to:

$$P_g = K_T \cdot V \cdot \exp [B'_T V + C'_T V^2 + D'_T V^3 + \dots] \quad 1.3.3. 10.$$

where K_T , B'_T , C'_T , D'_T , etc. are constants for temperature T . K_T can be evaluated by the extrapolation of the Henry's law region of an experimental isotherm, and the remaining constants can be evaluated by substituting three experimental points in the equation and solving the three equations.

1.3.4. Thermodynamics of adsorption.

Thermodynamics may be applied to sorption data in two ways, using

- (1) the method of approach called 'adsorption thermodynamics';
- (2) the procedure of solution thermodynamics.

In adsorption thermodynamics, the sorbate is considered as a one component phase in the potential field of the solid. This approach leads directly to molar thermodynamic quantities. It involves the evaluation of an independent variable characteristic of the sorbate, the spreading pressure, $\phi^{(105)}$. This cannot be directly

evaluated in most sorption systems and its indirect determination usually involves quite considerable errors in the final thermodynamic quantities. However, it is desirable to obtain molar thermodynamic quantities because integral or molar thermodynamic quantities are usually obtained from theoretical models of the sorbed state. Notwithstanding, Garden and Kington^(106,107) and Everett⁽¹⁰⁸⁾ have shown that differential heats and entropies of sorption may be usefully applied to describe the properties of molecules in the sorbed state. In some instances differential functions are to be preferred since they are more sensitive to small differences in energy of the sorbed molecule.

(2) In the solution thermodynamics method, which is used in this work, the system is regarded as a two-component solution of sorbate-sorbent. This approach leads to partial molar thermodynamic quantities. Recent developments in this field have been discussed by Everett^(108,109,110), Kington et al^(106,111), Hill⁽¹¹²⁾ and Drain⁽¹¹³⁾ and therefore here will be given only a very short outline.

In this work the following symbols and thermodynamic functions will be used:

P = pressure,
 T = temperature °K,
 n_A = no. of sorbent molecules,
 n_S = no. of sorbate molecules,
 H_0 = total heat content of pure sorbent in absence of sorbate,
 H_J = total heat content of sorbate and sorbent,
 So $H_S = H_J - H_0$ = total heat content of sorbate,
 and $S_S = S_J - S_0$ = total entropy of sorbate.

$$\bar{H}_S = \left(\frac{\partial H_J}{\partial n_S} \right)_{P, T, n_A} = \text{Partial molar heat content of sorbate} \quad 1.3.4. \ 1.$$

$$\bar{S}_S = \left(\frac{\partial S_J}{\partial n_S} \right)_{P, T, n_A} = \text{Partial molar entropy of sorbate} \quad 1.3.4. \ 1.$$

$$q_{st} = \tilde{H}_g - \bar{H}_S = \Delta H = \text{Isosteric heat of sorption} \quad 1.3.4. \ 2.$$

where $\tilde{H}_g$ = molar heat content of the gas phase.

$$\Delta S = \tilde{S}_g - \bar{S}_S = \text{Differential entropy of sorption} \quad 1.3.4. \ 3.$$

where $\tilde{S}_g$ = molar entropy of the gas phase.

$$\tilde{H}_g - \bar{H}_S = \text{Integral molar heat of sorption, or mean molar heat of sorption.} \quad 1.3.4. \ 4.$$

$$\tilde{S}_g - \bar{S}_S = \text{Integral molar entropy of sorption, or mean molar entropy of sorption.} \quad 1.3.4. \ 5.$$

$$\begin{aligned} \bar{H}_S &= \frac{H_S}{n_S} = \frac{H_J - H_0}{n_S} = \frac{1}{n_S} \int_0^{n_S} \bar{H}_S dn_S \\ &= \text{molar heat content of sorbate} \quad 1.3.4. \ 6. \end{aligned}$$

$$\begin{aligned} \bar{S}_S &= \frac{S_S}{n_S} = \frac{S_J - S_0}{n_S} = \frac{1}{n_S} \int_0^{n_S} \bar{S}_S dn_S \\ &= \text{molar entropy of sorbate} \quad 1.3.4. \ 7. \end{aligned}$$

The isosteric heat may be related to the energy of the sorbed molecules by the equation:

$$q_{st} = \tilde{E}_g - \tilde{E}_S - n_S \left(\frac{\partial \tilde{E}_S}{\partial n_S} \right)_{P, T, n_A} + RT \quad 1.3.4. \ 8.$$

$$\text{also } \frac{1}{n_S} \int_0^{n_S} q_{st} dn_S = \tilde{E}_g - \tilde{E}_S + RT \quad 1.3.4. \ 9.$$

Using the standard methods of solution thermodynamics an equation exactly analogous to the Clapeyron-Clausius equation can be derived⁽¹¹⁴⁾:

$$\text{i.e. } \left(\frac{\partial \ln P}{\partial T} \right)_{n_S} = \frac{\tilde{S}_g - \bar{S}_S}{RT} = \frac{\tilde{H}_g - \bar{H}_S}{RT^2} = \frac{q_{st}}{RT^2} \quad 1.3.4. 10.$$

In the derivation of this equation it is assumed that the gas behaves ideally and that the volume of the gas phase is very much greater than the volume of the same quantity in the sorbed phase. Furthermore, the equation applies regardless of whether the sorbent swells on adsorption or whether the number of sorption sites varies with temperature. The concept of surface area is not involved in this equation.

Evaluation of thermodynamic quantities from experimental data.

Isosteric heats.

From equation 1.3.4. 10:

$$\left(\frac{\partial \ln P}{\partial T} \right)_{n_S} = \frac{q_{st}}{RT^2} = \frac{\Delta H}{RT^2}$$

Integrating $\ln P = A - \frac{\Delta H}{T}$, where A is a constant of integration,

$$\frac{\partial \ln P}{\partial \frac{1}{T}} = \frac{-q_{st}}{R} = \frac{-\Delta H}{R}$$

hence the isosteric heat can be evaluated from a series of isotherms at different temperatures by plotting $\log P$ against $1/T$ for a fixed amount sorbed. The slope of this plot, or the tangent at a certain point if a curve is obtained, gives the isosteric heat of the given system at constant amount sorbed.

Entropy of sorption and partial molar entropy.

The entropy of sorption is related to the isosteric heat of sorption in the following manner:

$$\Delta S = \tilde{S}_g - \bar{S}_S = \frac{\tilde{H}_g - \bar{H}_S}{T} = \frac{q_{st}}{T} = \frac{\Delta H}{T} \quad 1.3.4. \ 11.$$

The molar entropy in this expression is the molar gas entropy at temperature T and a pressure corresponding to an equilibrium pressure on the isotherm. Referred to the entropy $\tilde{S}_{og}$ at a standard pressure p^x (760 cm Hg)

$$\tilde{S}_g = \tilde{S}_{og} + R \ln \frac{p^x}{p} \quad 1.3.4. \ 12.$$

Combining 1.3.4. 11 and 1.3.4. 12 we get

$$\bar{S}_S = \tilde{S}_{og} + R \ln \frac{p^x}{p} - \frac{\Delta H}{T} \quad 1.3.4. \ 13.$$

Moreover the entropy is usually referred to entropy at a standard temperature (i.e. 25°C for gas), then entropy at any other temperature T_2 is for constant C_p given by:

$$\tilde{S}_g = \tilde{S}_{og} + C_p \ln \frac{T_2}{T_1} \quad 1.3.4. \ 14.$$

where, $\tilde{S}_{og}$ = entropy at standard temperature, and

C_p = heat capacity at constant pressure.

Therefore from 1.3.4. 13 and 1.3.4. 14 we get:

$$\bar{S}_S = \tilde{S}_{og} + C_p \ln \frac{T_2}{T_1} + R \ln \frac{p^x}{p} - \frac{\Delta H}{T} \quad 1.3.4. \ 15.$$

Hence the partial molar entropy of the sorbed phase $\bar{S}_S$ can be evaluated for constant amount sorbed from the isosteric heats of sorption.

1.3.5. Thermodynamic properties of the sorbent.

Statistical thermodynamic interpretations of the sorption process often tend to assume that the sorbent

remains rigid and inert during sorption. Any perturbations of the sorbent by the sorbate will appear to an unknown extent in the thermodynamic changes which are experimentally observed and hence the subsequent interpretation of these functions by statistical mechanical methods will be considerably complicated if large perturbations occur. Therefore it is of great importance to investigate the changes in thermodynamic properties of the sorbent which may occur during sorption process.

A method for the investigation of changes in the thermodynamic properties of sorbent due to sorption has been suggested by Barrer.

For the purpose of this consideration a suitable fraction of the zeolite in question is taken as a unit and the change in thermodynamic properties of this unit is considered on sorption. A convenient unit in the case of three-dimensional zeolites (our case under investigation) is a unit containing one silicon or aluminium atom and two oxygen atoms, $-O-Si-O-$, as these zeolites can be considered as a three-dimensional array of these units.

Consider 1 mixed mole of sorbent (A) and sorbate (S) as a solution.

At constant temperature the Gibbs-Duhem equation gives:

$$N_S d\mu_S + (1 - N_S)d\mu_A = VdP \quad 1.3.5. 1.$$

where, N_S = mole fraction of sorbate,

μ_S = chemical potential of sorbate,

μ_A = chemical potential of sorbent,

V = molar volume of the mixed molecule,

but $d\mu_S^g = V_g dP$ for the gas state of sorbate; and at

equilibrium $\mu_S^g = \mu_S$,

therefore $d\mu_S^g = d\mu_S$ 1.3.5. 2.

hence substituting in 1.3.5. 1 we get:

$$N_S d\mu_S^g + (1 - N_S)d\mu_A = VdP \quad 1.3.5. 3.$$

From this we get:

$$d\mu_A = \frac{VdP}{(1-N_S)} - \frac{N_S d\mu_S^g}{(1-N_S)} \quad 1.3.5. 4.$$

but since $d\mu_S^g = RT d \ln a_S^g = RT d \ln P_S^g$ 1.3.5. 5.

that is assuming ideal behaviour, i.e. $a_S^g = P_S^g$,

where P_S^g = gas pressure of sorbate.

Further, assuming that there is no expansion of the lattice on sorption, the volume of the mixed molecule can be taken as the volume of the zeolite lattice containing 1 mixed molecule and so 1.3.5. 5 can be written as:

$$d\mu_A = V_M dP - \frac{MRT\alpha}{m} \cdot \frac{dP}{P} \quad 1.3.5. 6.$$

where, V_M = volume of the unit chosen,

M = molecular weight of the unit chosen,

α = amount sorbed in gm/gm of outgassed sorbent,

m = molecular weight of sorbate.

Equation 1.3.5. 6 can be integrated to give the change of the chemical potential of the solid in terms of isotherm quantities, i.e.

$$\mu_A - \mu_A^o = V_M(P - P_o) - \frac{MRT}{m} \int_{P_o}^P \frac{\alpha}{P} dP \quad 1.3.5. 7.$$

If the amount sorbed is obtained in terms of volume of sorbate at N.T.P. equation 1.3.5. 7 can be written in a more convenient form for that purpose, i.e.

$$\mu_A - \mu_A^0 = V_M(P - P_0) - \frac{MRT}{22414} \int_{P_0}^P \frac{V}{P} dP \quad 1.3.5. 8.$$

where V = amount sorbed in cc at N.T.P. per gm of outgassed sorbent.

Thus from equation 1.3.5. 7 or 1.3.5 8 the chemical potential of the sorbent relative to some standard state can be calculated as a function of amount sorbed.

The corresponding entropy change and enthalpy change can be found by application of Gibbs-Helmholtz equation:

$$\partial \left(\frac{\mu_A - \mu_A^0}{\partial T} \right)_{\infty} = -(\bar{S}_A - \bar{S}_A^0) \quad 1.3.5. 9.$$

That is the slope of the plot of $\Delta\mu_A$ against T gives $-\Delta\bar{S}_A$.

$$\text{Also, } (\mu_A - \mu_A^0) + T(\bar{S}_A - \bar{S}_A^0) = (\bar{H}_A - \bar{H}_A^0) \quad 1.3.5. 10.$$

$$\text{and } \left[\frac{\partial(\Delta\mu_A/T)}{\partial T} \right]_{\infty} = \frac{-\Delta\bar{H}_A}{T^2} \quad 1.3.5. 11.$$

$$\text{hence } \partial(\Delta\mu_A/T) = \frac{-\Delta\bar{H}_A}{T^2} \partial T \quad 1.3.5. 12.$$

Integrating 1.3.5. 12 we get, provided $\Delta\bar{H}_A$ does not depend on temperature

$$\frac{\Delta\mu_A}{T} = \frac{\Delta\bar{H}_A}{T} + \text{constant} \quad 1.3.5. 13.$$

Thus a plot of $\frac{\Delta\mu_A}{T}$ versus $\frac{1}{T}$ serves to give $\Delta\bar{H}_A$.

1.3.6. Models of the sorbed state.

The thermodynamic quantities can only supply useful information about the nature of the sorbed state if they can be related to the thermodynamic properties predicted from statistical models of the sorbed state. These models are simplified descriptions of ideal systems and consequently may not be strictly applicable to real systems. The main deviations from ideal behaviour arise from energetic heterogeneity of the surface, i.e. molecules may be selectively sorbed on particular crystal planes or edges, also multilayer formation and mutual interaction between sorbed molecules have great influence on the energetics of the system. Generally 'intracrystalline sorbed phases, such as are found in zeolites, are more suitable for this type of approach since multilayer formation does not occur, although sorbate-sorbate interaction will have its effect. Sometimes the intracrystalline sorption sites prove to be more energetically homogeneous than do those on external surfaces of gels and oxides.

Models of the sorbed phase can be divided into two main groups:

(1) A localised model in which molecules are sorbed on localised sites and do not have thermal energy sufficient to overcome potential barriers between sites. In this case the sorbed molecules are assumed to vibrate about mean positions in the intracrystalline channels.

(2) A mobile model in which the thermal energy is large enough to permit passage over these energy barriers and translational degree of freedom may be retained.

These are the extreme models but there is a possibility of transition occurring between these two

extreme models with the change in temperature or the degree of filling. Hill^(115,116) and Morrison⁽¹¹⁷⁾ have discussed the transition from a localized phase to a mobile phase as the temperature increases, and this type of transition has been demonstrated in the sorption of argon on rutile. Kington et al⁽¹¹¹⁾ have shown that argon in chabazite probably changes from a mobile phase to a localized phase as the degree of filling of the cavities in crystals approaches saturation, presumably due to the mutual caging effect of occluded argon atoms.

The two main models of sorbed state discussed above can be further refined into the following groups:

(a) a localized model based on the Langmuir isotherm without sorbate-sorbate interaction. This gives:

$$\Delta A^\circ = RT \ln \frac{p(1 - \theta)}{\theta} \quad 1.3.6. 1.$$

$$\text{and } K_1 = \frac{\theta}{p(1 - \theta)}$$

$$\text{where } K_1 = kT \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{j(T)}{a(T)} \quad 1.3.6. 2.$$

ΔA° = standard free energy of sorption,

$j(T)$ = the partition function for rotations, vibrations and electronic state of molecule,

$a(T)$ = the partition function for a sorbed molecule including its degrees of freedom relative to its intracrystalline environment.

This model can be tested by plotting $\ln \frac{p(1 - \theta)}{\theta}$ against θ ; a horizontal straight line should be obtained if the model is valid.

(b) A localized model with interaction between adjacent pairs of occluded molecules. This gives:

$$K_2 = \frac{\theta}{p(1-\theta)} \left(\frac{2-2\theta}{\beta+1-2\theta} \right)^z \quad 1.3.6. 3.$$

where β and z have the same meaning as in section 1.3.2.

These two models take no account of a possible variation of the entropy of sorption with θ other than variation that arises from the change in configurational entropy with θ .

Everett⁽¹⁰⁹⁾ has included the change in entropy in the following equation:

$$P = \exp\left(\frac{-\Delta H + T\Delta S}{RT}\right) \frac{\theta}{1-\theta} \quad 1.3.6. 4.$$

where, ΔH = isosteric heat of sorption,

ΔS = entropy of sorption leaving out the contribution from the configurational entropy.

The partial molar entropy $\bar{S}_S$ of a localized phase may be separated into thermal entropy, $\bar{S}_{Th}$, and configurational entropy, $\bar{S}_C$,

$$\text{i.e. } \bar{S}_S = \bar{S}_C + \bar{S}_{Th} \quad 1.3.6. 5.$$

In the case of diatomic or polyatomic molecules the partial molar thermal entropy, $\bar{S}_{Th}$, will be composed of contributions due to vibrations about chemical bonds, vibrations of the molecules in the intracrystalline channels and rotational (or librational if there is any rotational restriction) degrees of freedom and any internal degrees of freedom,

$$\text{i.e. } \bar{S}_{Th} = \bar{S}_V + \bar{S}_R + \bar{S}_I \quad 1.3.6. 6.$$

The configurational entropy arises from the number of distinguishable arrangements of N molecules on N_A sites and is given by:

$$\bar{S}_C = R \ln\left(\frac{1}{\theta} - 1\right) = R \ln\left(\frac{1 - \theta}{\theta}\right) \quad 1.3.6. 7.$$

Allowing for the mutual interaction between sorbed molecules this becomes:

$$\bar{S}_C = R \ln\left(\frac{1 - \theta}{\theta}\right) - zR \ln \frac{2(1 - \theta)}{(\beta + 1 - 2\theta)} + \frac{w}{T} \frac{(\beta - 1 + 2\theta)}{\beta} \quad 1.3.6. 8.$$

The meaning of the symbols is the same as given in section 1.3.2.

A sorbed phase will fit perfectly a localized model if:

- (1) experimental isotherm data gives a constant value of K , the isotherm constant;
- (2) the thermal entropy does not vary with θ ;
- (3) the value of residual entropy $\bar{S}_S - \bar{S}_C$ must be compatible with reasonable values of the vibrational frequency of the molecules in the channels.

(c) A mobile model without sorbate-sorbate interaction. In this the occluded molecules are assumed to have translational degrees of freedom. One, two, or possibly in exceptional structures such as faujasite, even three translational degrees of freedom might be envisaged with the appropriate molecular co-length, co-area, or co-volume of the sorbate, corresponding to the Volmer equation of state. In this case the isotherm takes the following form⁽¹¹⁸⁾:

$$K_3 = \frac{\theta}{p(1 - \theta)} \exp \frac{\theta}{1 - \theta} \quad 1.3.6. 9.$$

(d) A mobile model with interaction between sorbed molecules. This is obtained by using the equation of state for the occluded sorbate which is a one, two or three dimensional analogue of the van der Waals equation. In this case we get⁽¹¹⁹⁾:

$$K_4 = \frac{\theta}{p(1 - \theta)} \exp \left(\frac{\theta}{1 - \theta} - \alpha\theta \right) \quad 1.3.6. 10.$$

where α is a constant, and is a measure of the interaction potential.

A careful examination of equations 1.3.6. 1, 1.3.6. 3, 1.3.6. 9 and 1.3.6. 10 was made by Kington et al^(111,106,107) for O_2 , A and N_2 on chabazite at liquid air temperature.

The models discussed above require that the isotherm constants, K_3 , K_4 , should be independent of θ . Therefore calculation of these constants from experimental data provides a test of the validity of a particular model.

If a molecule has translational degrees of freedom in the sorbed state, the partial molar entropy of the sorbed phase will be given by the following contributions:

$$\bar{S}_S = \bar{S}_T + \bar{S}_V + \bar{S}_R + \bar{S}_I \quad 1.3.6. 11.$$

where T may denote one or possibly two translational degrees of freedom and as a result the vibrational degrees of freedom, V will be $(3 - x)$ where $x = 1$ or 2.

The possibility that a particular model is valid depends inter alia on whether the experimental vibrational entropy gives a reasonable value of the vibrational frequency ν . If $\bar{S}_S - \bar{S}_T$ is a constant with θ , and $\bar{S}_R$ and $\bar{S}_I$ are assumed to be equal to their gas state values, the vibrational frequency can be calculated,

(assuming that the vibration is simple harmonic and that a mean frequency can be used to represent vibrations in different directions), from the following equation (for one vibrational degree of freedom):

$${}_1S_V = R \left[u(e^u - 1)^{-1} - \ln(1 - e^{-u}) \right] \quad 1.3.6. 12.$$

where $u = \frac{h\nu}{RT}$,

ν = the vibrational frequency.

A value of ν , the vibrational frequency, must be found from some other sources to compare with the value derived from the partial molar entropy of the sorbed state. Unfortunately very little experimental data is available concerning the vibrational frequencies of molecules in the sorbed state. Orr⁽¹²⁰⁾ has computed a value of $1 \times 10^{12} \text{ sec}^{-1}$ for argon sorbed on potassium chloride when the energy of sorption was 1.5 kcal/mole. Assuming simple harmonic vibration the frequency is given by:

$$\nu = \frac{\pi}{2} \sqrt{\frac{f}{m}} \quad 1.3.6. 13.$$

where f = restoring force,

m = mass of the vibrating particle.

Hill⁽¹¹²⁾ has suggested that as a reasonable assumption the restoring force is proportional to the energy of sorption. Therefore:

$$\nu = K \left(\frac{\Delta E}{m} \right)^{\frac{1}{2}} \quad 1.3.6. 14.$$

Kington⁽¹¹¹⁾ suggested that ν may be estimated for a molecule from its energy of sorption and mass, using the value of K derived from Orr's data for argon on potassium chloride. The value of ν thus derived is far from satisfactory but is probably within the error of other

theoretical approximations.

The above procedure can be considered to be adequate only for simple monatomic molecules such as argon. In the case of di- and poly-atomic molecules the hindered rotational entropy and change of vibrational frequency with coverage (θ) have to be considered as well and therefore often it is impossible to give a complete unambiguous picture of the physical state of the sorbed molecule.

To sum up, Table 3 gives the values of equilibrium constants, K , for different degrees of freedom of sorbate molecules.

Table 3.

Degrees of freedom of occluded molecules relative to its environment	Equilibrium constants, K	Relevant isotherms
(i) 3T, 3R	$\frac{1}{kT} \cdot \frac{1}{N'_S} \exp \frac{x}{RT}$	$K_3 = \frac{\theta}{p(1-\theta)} \exp \frac{\theta}{1-\theta}$ or $K_4 = \frac{\theta}{p(1-\theta)} \exp \left(\frac{\theta}{1-\theta} - \alpha\theta \right)$
(ii) V, 2T, 3R	$\frac{1}{kT} \cdot \frac{1}{N''_S} \left(\frac{kT}{2\pi m} \right)^{\frac{1}{2}} \cdot \frac{1}{V} \exp \frac{x}{RT}$	
(iii) 2V, T, 3R	$\frac{1}{kT} \cdot \frac{1}{N''_S} \cdot \frac{kT}{2\pi m} \cdot \frac{1}{V^2} \exp \frac{x}{RT}$	
(iv) 3V, 3R	$\frac{1}{kT} \cdot \left(\frac{kT}{2\pi m} \right)^{\frac{3}{2}} \cdot \frac{1}{V^3} \exp \frac{x}{RT}$	$K_1 = \frac{\theta}{p(1-\theta)}$ or $K_2 = \frac{\theta}{p(1-\theta)} \left(\frac{2-2\theta}{\beta+1-2\theta} \right)^z$
(v) 4V, 2R	$\frac{1}{kT} \cdot \left(\frac{kT}{2\pi m} \right)^{\frac{3}{2}} \cdot \frac{1}{V^4} \cdot$ $\left(\frac{kT}{8\pi^3 I_1} \right)^{\frac{1}{2}} \exp \frac{x}{RT}$	
(vi) 5V, R	$\frac{1}{kT} \cdot \left(\frac{kT}{2\pi m} \right)^{\frac{3}{2}} \cdot \frac{1}{V^5} \cdot \frac{kT}{8\pi^3} \cdot$ $\frac{1}{(I_1 I_2)^{\frac{1}{2}}} \cdot \exp \frac{x}{RT}$	
(vii) 6V	$\frac{1}{kT} \cdot \left(\frac{kT}{2\pi m} \right)^{\frac{3}{2}} \cdot \frac{1}{V^6} \cdot \left(\frac{kT}{8\pi^3} \right)^{\frac{3}{2}} \cdot$ $\frac{1}{(I_1 I_2 I_3)^{\frac{1}{2}}} \cdot \frac{\delta}{\pi^{\frac{1}{2}}} \cdot \exp \frac{x}{RT}$	

where x = the least energy required to remove a mole of sorbate from infinite amount of zeolite + sorbate into the gas phase,

N'_S = number of molecules required to fill completely 1 cm³ of intracrystalline volume,

N''_S = number of molecules required to fill completely 1 cm² of intracrystalline area,

N'''_S = number of molecules required to fill completely 1 cm of intracrystalline length,

ν = vibrational frequency,

$\bar{\nu}$ = mean vibrational frequency,

δ = symmetry number of occluded molecule.

1.4 Intra-molecular Forces.

Information on the nature of interaction between molecules has been obtained by:

- (1) using the method of quantum mechanics;
- (2) observations of the macroscopic behaviour of physical systems.

The quantum mechanical approach may be used to suggest the general form of intermolecular potential functions, and the properties of macroscopic systems may be used to evaluate the parameters contained in these functions; such properties are the virial coefficients of gases and vapours, viscosity of dense gases and vapours, sublimation energies and thermal diffusion in gaseous mixtures. A review of present theories of intermolecular forces is given by Hirschfelder et al⁽¹²¹⁾.

In general, forces which contribute to the interaction of physically adsorbed molecules with a solid surface are:

- (1) dispersion forces;
- (2) polarization interaction;

- (3) interaction of the permanent dipole moment of a molecule with the electric field of a solid;
- (4) quadrupole moment interacting with field gradient;
- (5) short range forces of repulsion.

In the case of non polar molecules such as iodine, the forces which contribute towards the interaction between the sorbed molecule and the solid will be mainly (a) dispersion and repulsion forces (b) forces due to polarization interaction. Quadrupole moment interaction may contribute as well but as there are no data available for the quadrupole moment of iodine, these will not be considered here.

Dispersion forces.

The concept of dispersion forces was evolved by the quantum mechanical approach of London^(122,123) who showed that these forces give an adequate explanation of the non ideal behaviour of gases and vapours. Previous to the formulation of London's theory, Debye⁽¹²⁴⁾ and Keesom⁽¹²⁵⁾ attempted to explain these physical phenomena in terms of dipole, induced-dipole and quadrupole interactions.

Debye and Keesom forces are important in the case of highly polar molecules, but they fail to explain the condensation of non-polar gases such as argon and krypton, or the persistence of van der Waals forces at high temperatures.

London and Eisenschitz⁽¹²⁶⁾ have shown that the dispersion energy of two spherical molecules is approximately given by:

$$\phi_{\text{disp.}} = -A/r^6 \qquad 1.4. 1.$$

$$\text{where } A = \left[3ha_1a_2\nu_1\nu_2 / 2(\nu_1 + \nu_2) \right]$$

and a_1 a_2 are the polarisabilities of these two molecules,
 ν_1 and ν_2 are constants which depend upon the nature
of the molecules.

This equation is an approximation and $\phi_{\text{disp.}}$ may be represented more exactly by a series in ascending inverse powers of r , the intermolecular distance. However, the first term of the series, as given by 1.4. 1, makes the most important contribution to the dispersion energy.

Evaluation of the constant A , using London's equation is often difficult. Slater and Kirkwood⁽¹²⁷⁾ using a more approximate approach have evolved the following equation for A :

$$A = \frac{3}{4\pi} \cdot \frac{eh}{m^{\frac{1}{2}}} \cdot \frac{a_1 a_2}{(a_1/n_1)^{\frac{1}{2}} + (a_2/n_2)^{\frac{1}{2}}} \quad 1.4. 2.$$

where e = the electronic charge,

h = Planck's constant,

m = mass of the electron,

n_1 and n_2 = the number of electrons in the outer
shell of the molecule.

Values of the interaction energy obtained using this formula are generally higher than the equivalent values obtained from the London expression.

Müller⁽¹²⁸⁾ derived a third method for evaluating A using an adaptation of Slater-Kirkwood approach,

$$\text{e.g. } A = 6 m c^2 \frac{a_1 a_2}{(a_1/\chi_1)^{\frac{1}{2}}(a_2/\chi_2)^{\frac{1}{2}}} \quad 1.4. 3.$$

where χ_1 and χ_2 are the diamagnetic susceptibilities of
the two molecules, and

c = velocity of light.

The use of diamagnetic susceptibilities in the calculation of dispersion energy is questionable; the behaviour of a molecule in the oscillating electric field of another may differ from its behaviour in a magnetic field. For this reason the Müller expression can be regarded only as semi-empirical. Nevertheless, it may be used to give qualitative agreement with experimental data. Lennard-Jones⁽¹²⁹⁾ has shown that the Kirkwood-Müller equation will account for the dispersion energy between rare gases to within 15%.

Dispersion forces have two important properties:

- (a) they are additive;
- (b) they are independent of temperature.

The condition of additivity allows one to express the dispersion energy of interaction of a molecule with a solid as a simple summation of all the interactions with individual atoms, provided that the structural characteristics of the solid are accurately known. Positions of potential energy minima can be compared with experimental heats of sorption.

Short range repulsion forces.

These forces are significant at small inter-molecular distances where overlapping of electron clouds occurs. The overlapping may result in attraction, but in many cases, and certainly in physical adsorption, it results in repulsion as would be expected from the application of Pauli exclusion principle.

The interaction of two symmetrical non-polar molecules is described reasonably well by Lennard-Jones' 6-12 potential function⁽¹³⁰⁾:

$$\phi = 4\epsilon \left[-\frac{\epsilon}{r^6} + \frac{\epsilon}{r^{12}} \right] \quad 1.4. 4.$$

The second term in the bracket represents energy of repulsion; it is significant only at small intermolecular distances and falls off rapidly as r increases.

However, quantum mechanical calculations suggest that intermolecular repulsion-potentials are best described by an exponential function which has the form:

$$\phi_{\text{rep.}} = P(r) \exp(-\beta/r) \quad 1.4. 5.$$

where $P(r)$ is a polynomial in positive and negative powers of r .

Nevertheless, for small values of r , the exponential form of the repulsion potential is not accurate and in this respect has no great advantage over the Lennard-Jones expression which is much more easy to use.

Polarization.

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

$$\mu_{\text{ind.}} = \alpha F \quad 1.4. 6.$$

where F = field strength,

α = polarisability of the molecule.

The energy of the induced dipole in the electric field, F , is given by:

$$\phi_{\text{ind.}} = \int_0^F \mu_{\text{ind.}} dF = -\frac{1}{2} \alpha F^2 \quad 1.4. 7.$$

The polarisability of a molecule is directional and usually it has three different components along the three axes.

However, for the purpose of calculation of ϕ_{ind} , the mean value suffices as a first approximation.

The electrostatic field, F , is a vector quantity and therefore the contributions of polarization to the total energy of interaction of molecules with a solid will be expressed as a vector sum. Usually, except at a very small distance from the surface, the polarization energy is small.

In the intracrystalline channels of a zeolite, the net electrostatic field may be reduced, not only by the opposing effects of cationic and anionic charges, but also by the three-dimensional array of like charges. However, although the electrostatic field towards the centre of cavity may be small, in a close proximity of the walls of the intracrystalline channel it may have quite a significant value especially when the sorbate molecules come close to the two π electrons on the oxygen atom of the anionic framework.

Summing up, the energy of interaction of a non-polar molecule with a solid can be written as the sum of contributions of dispersion energy, Q_D , plus repulsion energy, Q_R , plus polarization energy, Q_P ,

$$\text{i.e.} \quad Q = Q_D + Q_R + Q_P. \quad 1.4. 8.$$

neglecting Q_Q , the quadrupole moment energy of interaction contribution.

Chapter II.

2. Experimental Methods, Materials and Apparatus.

2.1 Materials.

2.1.1 Sorbents.

Three sorbents were used in this study:

(1) Sodium faujasite (NaX), a synthetic zeolitic species, which is described by the formula: $\text{Na}_{82}[(\text{AlO}_2)_{82}(\text{SiO}_2)_{110}] m \text{H}_2\text{O}$, where $m \simeq 260$. The sample was supplied by Linde Air Products Co. The structure of the synthetic species is almost identical with that of the natural mineral faujasite, the difference being only in the nature and number of cations present interstitially. The natural mineral contains sodium and calcium ions, while only sodium ions are present in the synthetic zeolite.

(2) Linde Sieve A - calcium form (CaA). This synthetic zeolite which has no counterpart in nature was supplied, in its sodium form, by Linde Air Products Co.; the sodium ions were then exchanged for calcium.

The sodium form is described by the formula: $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 0.14\text{NaAlO}_2 \cdot 4.77\text{H}_2\text{O}$. The unit cell formula for the calcium form being: $\text{Ca}_6[12\text{AlO}_2 \cdot 12\text{SiO}_2] \cdot \text{NaAlO}_2$ in its anhydrous form. The sodium aluminate molecule is located in the small cages.

(3) Chabazite. This natural mineral of the unit cell formula: $(\text{Ca}_{1.8}\text{Na}_{0.3})(\text{Si}_{8.1}\text{Al}_{3.9})\text{O}_{24} \cdot 12\text{H}_2\text{O}$ was obtained in rock form from Nova Scotia, Canada. Crystals free from impurities were hand picked, washed several times with hot water, then crushed and ground in a mortar, graded through 200 mesh sieve and again washed several times with hot water.

Ion exchange of synthetic Linde Sieve A.

The sodium form of Linde Sieve A, in powder form, as supplied by Linde Air Products Co., was treated with concentrated solution of $\text{Ca}(\text{NO}_3)_2$ (50%) and digested in a covered beaker for 24 hours on a hot water bath. This procedure was repeated thrice. To ensure full exchange the exchanger was next subjected to percolation using a moderately concentrated salt solution of $\text{Ca}(\text{NO}_3)_2$ (30%). The percolation was carried out in an apparatus surrounded with a steam bath for about 3 - 4 days. Then the filtered product was washed several times with hot distilled water until no nitrate was present and then dried in an oven at 120°C .

Preparation of sorbents for sorption.

All the sorbents, in the form described in the previous section, were ground in an agate mortar, graded through 200 mesh sieve, washed four to five times with hot distilled water, dried under suction and then stored in a constant humidity chamber over a saturated solution of ammonium chloride.

An X-ray photograph of each one in the outgassed state was taken.

2.1.2 Sorbates.

Sorbates used in this research were iodine, bromine and aluminium chloride.

2.1.3. Preparation and purification of sorbates.

Iodine. AnalaR grade iodine was dissolved in a concentrated solution of potassium iodide (AnalaR)^(131,132) and distilled. The product was redistilled with steam, and washed with pure distilled water. Then it was three

times steam distilled from a concentrated solution of AnalaR potassium iodite (KIO_3). The removal of organic matter was effected by sublimation in a current of oxygen over platinum at about 700°C . This was done in a quartz tube divided into three compartments by constrictions (quartz tube about 2 cm diameter; constrictions about 1 cm diameter, 2 - 3 cm long). In each constriction was placed a platinum spiral and it was heated to ca. 700°C . The iodine was then slowly distilled from compartment to compartment in a current of pure oxygen.

Pure iodine thus obtained was then twice fractionated in vacuo, the end product was sealed under vacuum in a specially designed tube with break-off at the top.

Bromine. AnalaR grade of bromine was twice fractionated in vacuo and stored in vacuum sealed tubes as for iodine.

Aluminium chloride. Fragments of pure, dry aluminium foil were placed in a pyrex tube, 50 cm long, 3 cm diameter, fitted at both ends with ground glass joints. This was connected to three other similar tubes and both ends of this apparatus were connected to bubble flasks with pure concentrated sulphuric acid to exclude moisture. One of these flasks was connected to a cylinder with pure chlorine. The rate of the current of chlorine was adjusted and the reaction was initiated by slightly warming the tube containing aluminium foil with a bunsen burner. Once started, the reaction, being exothermic, proceeded on its own, the rate being controlled by the rate of flow of chlorine. The foil burned briskly emitting ultra-violet radiation and the anhydrous aluminium chloride sublimed into the next tube. This dry aluminium chloride was resublimed three times in a stream of dry chlorine in the same

apparatus. The end product was quickly transferred to glass tubes which were then sealed. The tube with the aluminium chloride was then placed in a vacuum distillation apparatus, the tube was broken with a magnetic hammer and the whole apparatus was then evacuated, the limb containing the sample being immersed in liquid oxygen. After evacuation was complete the distillation part was sealed off and the aluminium chloride was fractionated three times; the end product being stored in vacuum sealed tubes as for iodine.

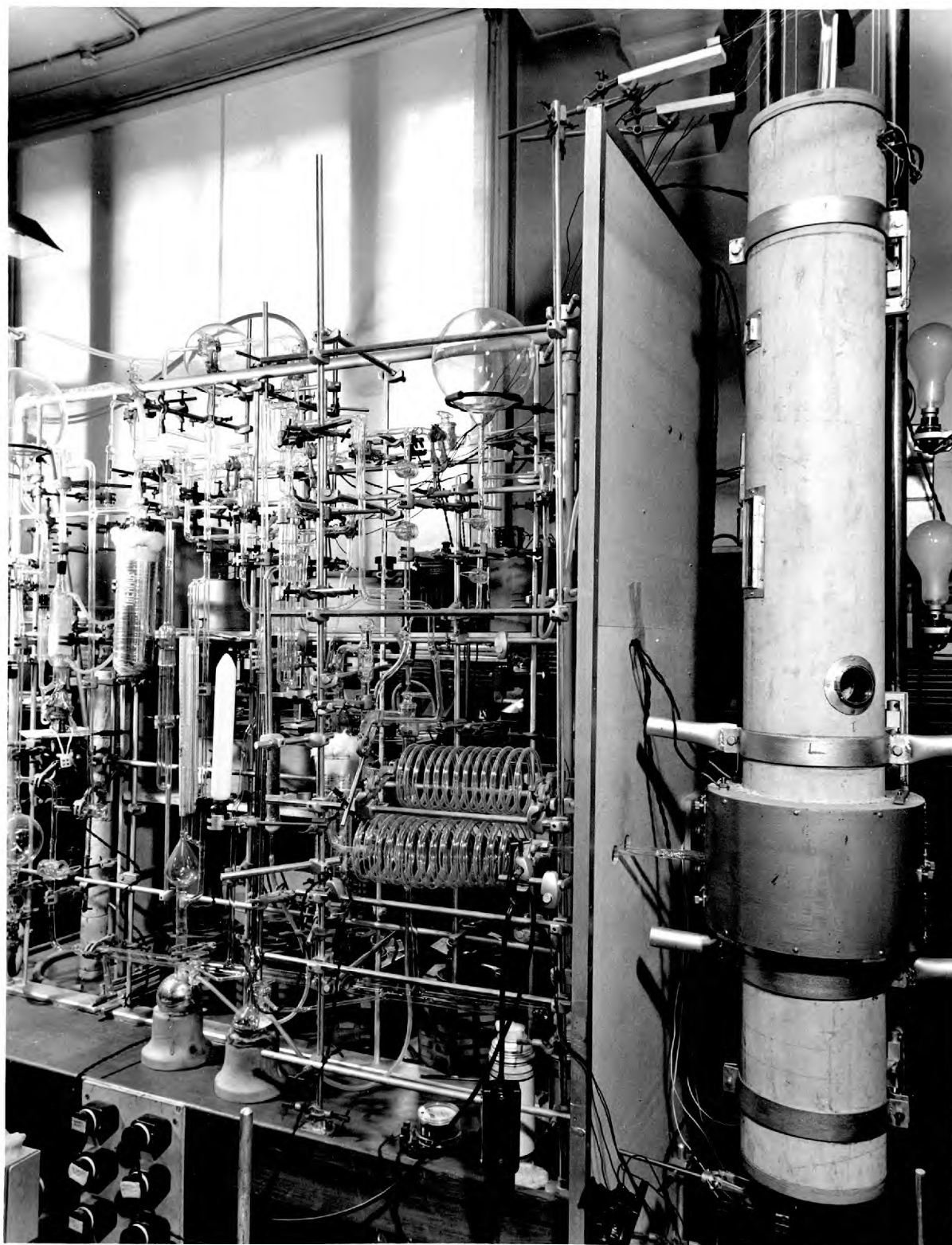
2.2 Apparatus.

Since its introduction by McBain and Bakr⁽¹³³⁾ the silica spring balance has been an important means of studying the sorption of gases and vapours by solids. It has been used successfully not only at ordinary temperatures and pressures but also at high pressures and at low temperatures. During our study of sorption equilibria we had to make measurements under exacting conditions which led us to develop the apparatus, involving the silica spring balance, described below. Accurate sorption isotherms were required under the following conditions:

- (i) the sorbate was not readily volatile (e.g. I_2 , S, $AlCl_3$, $FeCl_3$, $HgCl_2$), or was corrosive towards mercury or tap grease (I_2 , Br_2 , S);
- (ii) the sorption studies were to be conducted up to about $350^\circ C$, at pressures up to one atmosphere.

The apparatus (Fig. 7) comprised the following main component parts:

- (i) pumping system;
- (ii) the balance system;
- (iii) sorbate reservoir;

FIG. 7.THE APPARATUS.

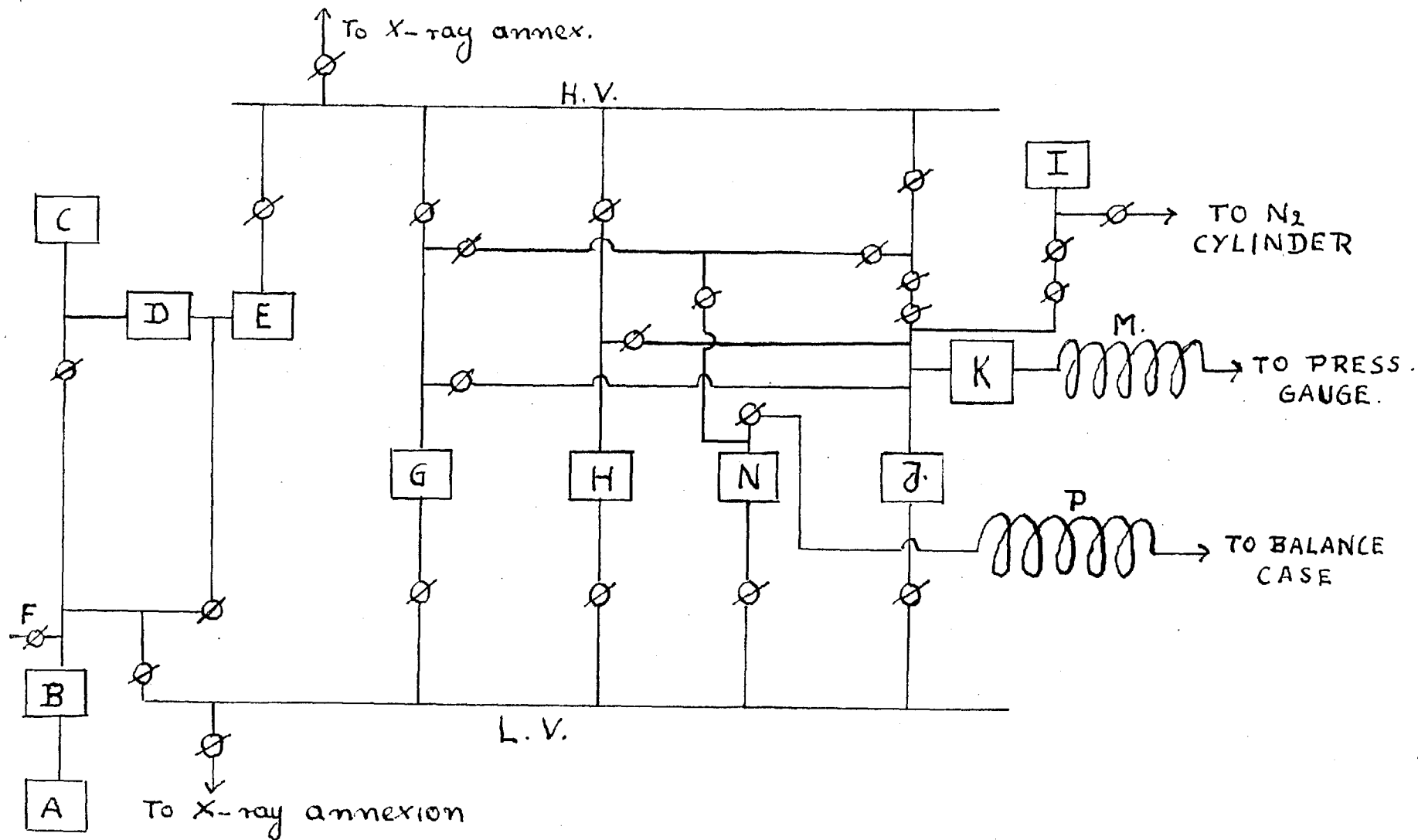
- (iv) pressure measuring devices;
- (v) furnaces;
- (vi) temperature measuring and control devices;
- (vii) extension for the preparation of samples for X-ray analysis.

These will be briefly described.

2.2.1 Pumping system.

The pumping system, shown diagrammatically in fig. 8, was made wholly from pyrex glass (except oil rotary pump) and comprised the following component parts: an Edwards 'Speedivac' single stage rotary oil pump (A) capable to produce vacuum up to 10^{-3} cm Hg, backed by a single stage umbrella type silica Hg-diffusion pump (D) to give a vacuum of the order of 10^{-7} cm Hg. An oil trap was placed at (B) to prevent oil entering the apparatus in the event of a power failure. A buffer volume of 5 l. capacity at (C) allowed the diffusion pump to run for long periods without the backing of the oil pump. Pressure measuring devices could thus be operated by the oil pump without disturbing the high vacuum. A cold trap (E) at liquid oxygen temperatures, between the high vacuum line (H.V.) and the diffusion pump (D) served two purposes. It prevented any vapours reaching the oil pump, and mercury vapour from the diffusion pump reaching the high vacuum line. A McLeod gauge at (G) can be connected to the pressure gauge or any other part of the apparatus. An air leak at (F) allowed air into the apparatus if necessary. A vacuum of at least 10^{-3} cm Hg could be obtained in the low vacuum line (L.V.) by using the rotary pump without the diffusion pump. A manometer at (H) can be connected to the pressure gauge in the sorption vessel to read pressures between 0.5 and 76 cm Hg.

FIG. 8.
PUMPING SYSTEM.



Storage bulb at (I) containing dry pure nitrogen can be connected to the McLeod gauge or manometer and in conjunction with them the spiral gauge to read the null point of pressure. The cold trap at (J) was a safeguard against any vapour diffusing to the pumping system and other parts of the apparatus should the pressure gauge be not completely vacuum proof at any time during the experiment. Magnetic tap at (K) separated the spiral pressure gauge from the apparatus when readings were not being taken. The cold trap at (N) prevented any vapours entering the apparatus during outgassing of the balance case and the sorbent. Hollow glass spirals at (M) and (P) provided elastic connection between the pumping system mounted on one base and the balance case mounted externally.

2.2.2 The balance system.

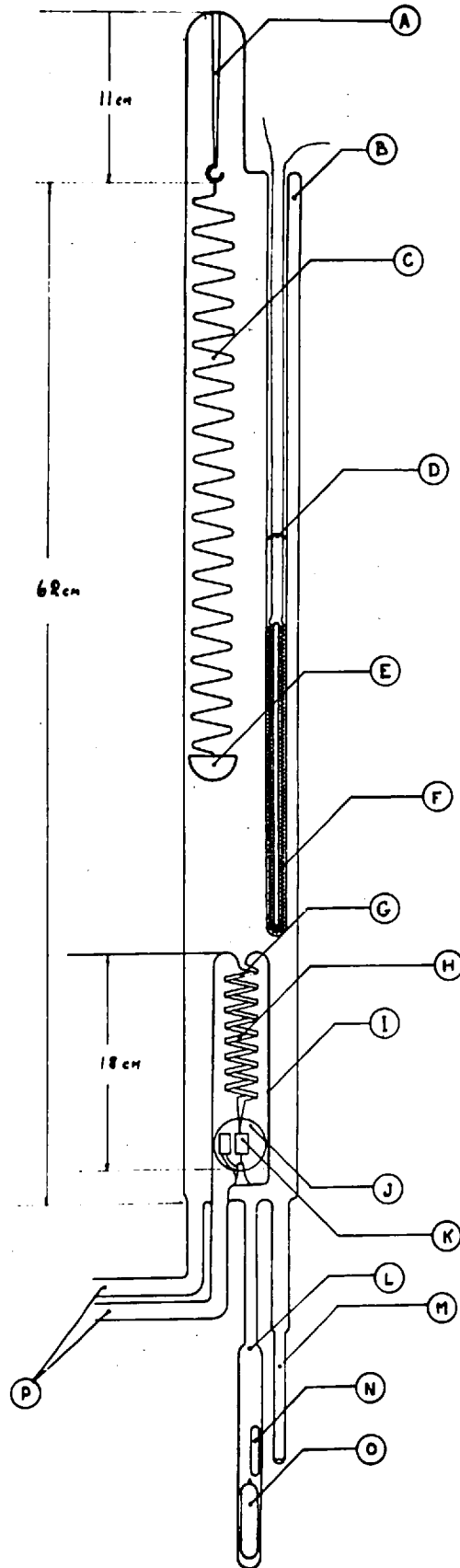
As mentioned previously accurate isotherms were required under the following conditions:

- (i) the sorbate was not readily volatile or was corrosive towards mercury or tap grease;
- (ii) the sorption studies were to be conducted up to about 350°C at pressures up to one atmosphere.

The conditions (i) and (ii) were met, as in Fig. 9 by constructing a wholly enclosed pyrex glass balance system, consisting of an upper section, in which was suspended the spring (C) carrying a small bucket of sorbent (E), and a bottom reservoir (L), containing the sorbate in a sealed tube (O), and magnetic hammer (N). The bottom reservoir was joined to the upper section by a narrow tube of 8 mm diameter.

In-sealed into the balance case was platinum resistance thermometer (F) appropriately placed in relation to the bucket carrying the sorbent. A pyrex glass spiral

FIG. 9.
THE BALANCE CASE.



Description of Fig. 9.

- (A) Glass hook.
 - (B) Balance case.
 - (C) Silica spring.
 - (D) In-seal.
 - (E) Glass bucket with sorbent.
 - (F) Platinum resistance thermometer.
 - (G) Spiral gauge.
 - (H) Hollow spiral.
 - (I) Outer wall of spiral gauge.
 - (J) Optical flat.
 - (K) Platinised mirror.
 - (L) Reservoir for sorbate.
 - (M) Device for admitting air.
 - (N) Magnetic hammer.
 - (O) Sealed tube with sorbate.
 - (P) Connection tubes to pumping system and pressure levelling and measuring devices.
-

gauge (H) was used for pressure measurement, this gauge being in-sealed into a glass tube (I) which in turn was in-sealed into the bottom of the upper balance case. A second side-arm (P) passing through a small opening in the furnace served to evacuate the balance case, and to outgas the sorbent. When outgassing was complete this side-arm was sealed off, completing the isolation of the sorption system. Additional side-arm (M) served for

careful admission of air to the system when, after completion of a series of experiments, it was desired to change either sorbate or sorbent. This was a glass tube, very narrow at the end, which could be broken after covering by a rubber tube closed by a screw clip. A window (J) made of optical flat 5 cm diameter was sealed-in onto the balance case to allow a light beam from a telescope projector to be reflected from the mirrors (K) of the spiral gauge, and to avoid parallelism. The balance case was suspended inside furnaces from the top of a stainless steel tube shown in Fig. 10(10).

2.2.3 Pressure measuring devices.

A pyrex glass hollow spiral gauge, Fig. 9 (G), was used as a pressure measuring device in connection with a McLeod gauge and a mercury manometer placed externally. The connection was through a glass tube (P) to the external part of the spiral gauge.

The glass spiral gauge manometer (G) (Fig. 9), consisted of a cylindrical glass jacket (I), about 15 cm long and 2 cm diameter. At one end was in-sealed a hollow glass spiral (H), made of extremely thin glass and consisting of about 12 turns. The lower part of this spiral was closed and was sealed to a small platinised glass mirror (K), (5 x 3 mm) terminated with a glass pointer which rotated in a glass sleeve to keep the mirror in position. A second mirror was permanently fixed by the side of the first and served as a reference. Onto the jacket, in front of the mirrors, was in-sealed an optically flat plane window (J) (2 cm diameter) to avoid parallelism of the reflected beam.

The inside of the spiral (H) had then direct contact with the vapour in the balance case, while the

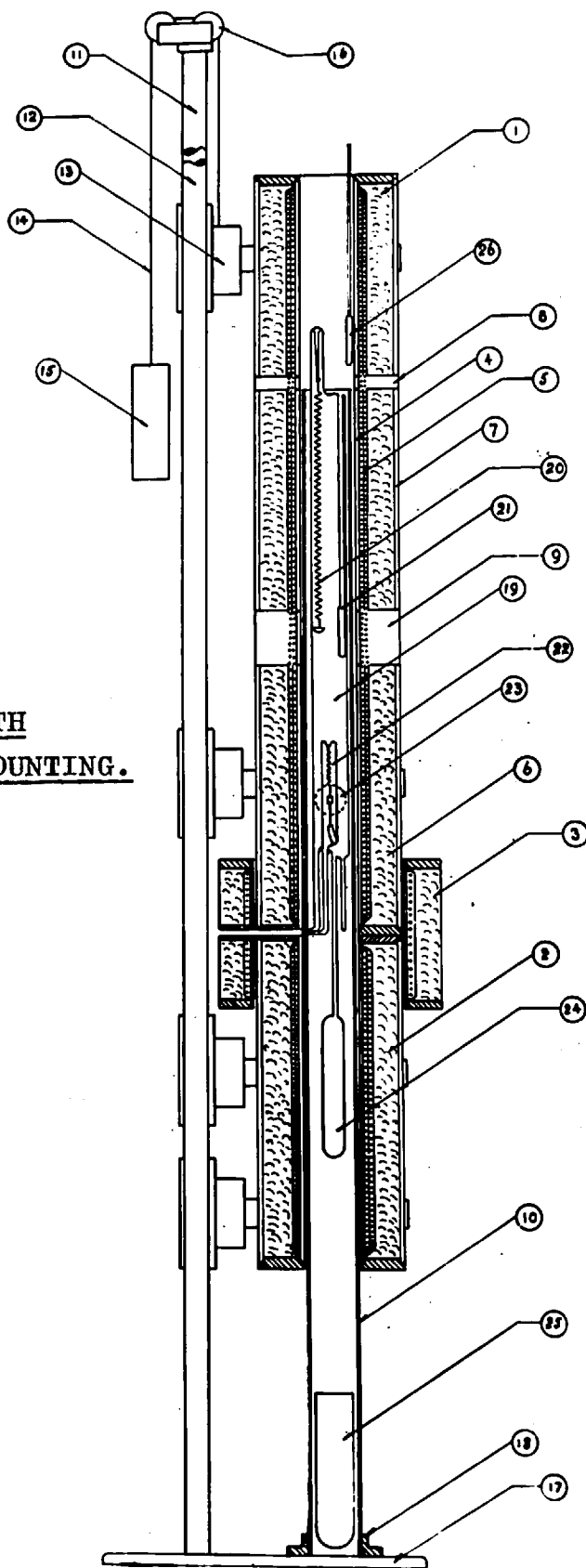
outside surface was in contact with nitrogen gas, introduced at regulated pressures through a tube (P) entering by way of a suitable small aperture in the surrounding furnace. By adjusting the nitrogen pressure the gauge could always be brought to zero deflection and the nitrogen pressure then equalled the pressure of sorbate vapour in equilibrium with the sorbent and this could be read either on the McLeod gauge or the mercury manometer. Movement of the spiral gauge was registered by the movement of platinum-coated mirror (K), attached to the spiral, which reflected a beam of light through optically flat glass windows on to a galvanometer scale.

2.2.4 The furnaces.

Three furnaces were used. They are shown with mounting on fig. 10. The top-most furnace (1) heated the upper chamber of the balance case; the bottom furnace (2) heated the sorbate reservoir (24). The middle furnace (3) was designed to eliminate any temperature drop at the junction between the upper furnace (temperature T_1) and the lower furnace (temperature T_2). It is essential that no part of the system should fall below T_2 in temperature since otherwise distillation of sorbate out of the reservoir would occur.

The first furnace (1) was mounted on steel railings (11, 12) by means of sliders (13) and was counter weighed (15) so that it could be moved in vertical directions, and then rotated sideways to give easy access to the balance case. The second furnace (2) was also mounted similarly but not counter weighed. The third furnace (3) was in the form of two semi-circular segments which could be removed separately. To ensure the most even temperature distribution the inside cores of the furnaces were made of stainless steel tube.

FIG. 10.
THE FURNACES WITH
BALANCE CASE AND MOUNTING.



Description of Fig. 10.

1. Furnace No. 1.
2. Furnace No. 2.
3. Furnace No. 3.
4. Stainless steel tube.
5. Heating wire and insulating material.
6. Asbestos wool.
7. Asbestos tube.
- 8, 9, 23. Windows.
10. Stainless steel tube supporting balance case.
- 11, 12. $1\frac{1}{2}$ " diameter steel rods, 11 feet high.
13. Sliding clamps.
14. Steel cord.
15. Counter-weight.
16. Pulleys.
17. Cast-iron base.
18. Independent support for (10) with levelling device.
19. Balance case.
20. Quartz spring.
21. Platinum resistance thermometer for measuring temperature.
22. Pressure gauge.
23. Optical window.
24. Vessel for sorbate.
25. Dewar flask.
26. Platinum resistance thermometer for temperature control.

The main furnace (1).

In this furnace the inner steel tube was 110 cm long and 3 $\frac{3}{8}$ " diameter, and was fitted with five quartz windows, 8, 9, 23, to allow measurements of the length of the silica spring and observation of the mirror attached to the spiral gauge. The steel tube was covered with asbestos or silica cloth and on it the heating wire (Nicalloy A) of total resistance 270 ohms (7.16 ohms per yard) was wound in such a way as to secure uniform heat distribution along the tube. The heating wire was fixed in position by alumina cement and covered with asbestos or silica cloth. On it was wound the main heating element (Kanthal wire of resistance 0.66 ohms per yard and of total resistance 27 ohms). It was secured in position and covered as for the inner winding. The resultant furnace core was placed inside the asbestos tube (7) of 1-foot diameter, fitted with five pyrex windows (8, 9, 23). The free space between the tubes, except for that of the windows, was packed with asbestos wool. The two tubes were held in position at both ends by asbestos rings which were bound together by two steel rods diametrically spaced inside the furnace.

The lower furnace (2) 40 cm long, was constructed in the same way as the furnace (1), but it had no windows. The total resistance of the main heating element was 36 ohms (1.60 ohms per yard), and that of the subsidiary element was 250 ohms (10.8 ohms per yard).

Each semi-circular part of the central furnace (3) had windings of resistance 30 ohms (0.835 ohms per yard) in a form of a uniform wire coil 0.5 cm diameter. The windings were uniformly and vertically distributed along the inner wall and secured in position by Pyruma cement; the inner wall was first covered with asbestos cloth.

The free space inside was closely packed with asbestos wool.

A one inch diameter hole passed through all the three furnaces (at right angles to the wall) to allow for the glass connection between the balance case and the pumping system.

2.2.5 Temperature measuring and control devices.

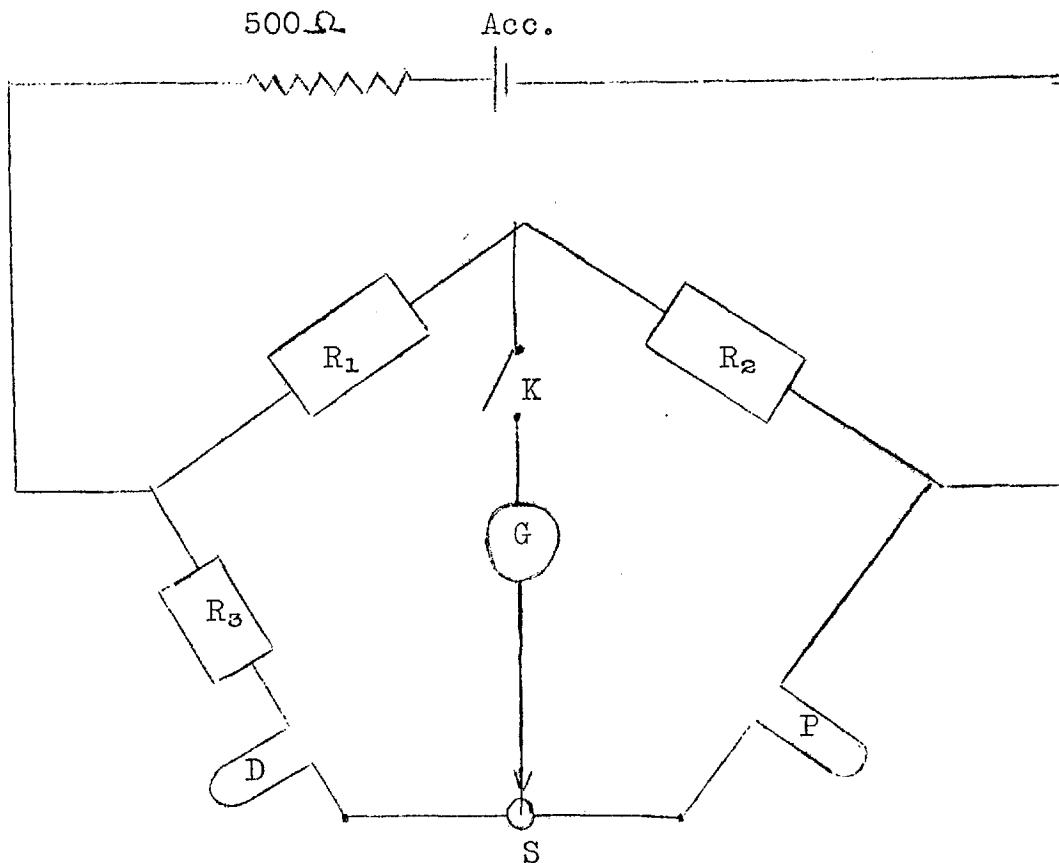
Temperature measurement.

The temperature inside the sorption balance case was measured by means of a platinum resistance thermometer (F) (Fig. 9). This thermometer was specially designed and constructed for this apparatus. The U-tube containing the platinum coil (made of thermally pure platinum wire 0.004" diameter and of total resistance about 10 ohms at 0°C), was made of glass tubing 3 mm diameter, the walls of which were less than 0.1 mm thick to minimise the time lag in heat conduction. The leads and compensating leads were 0.01" diameter. The thermometer was filled with pure helium at $\frac{1}{3}$ atmosphere. It responded to temperature variations of less than 0.001°C. The resistance was read on a low resistance bridge in conjunction with a mirror-galvanometer of sensitivity 740 mm per micro amp.

The low resistance bridges (two of them) were constructed to suit best our thermometers. They were a modified form of Callendar-Griffiths bridge⁽¹³⁴⁾ and were constructed as follows:

Fig. 11.

Circuit diagram of bridge used for measurement and control of temperature.



R_1 and R_2 constituted the ratio arms and each were 20 ohm standard non-inductive resistors of 0.02% accuracy.

R_3 consisted of 3-decade non-inductive resistors reading in 10, 1 and 0.1 ohms of accuracy 0.05%.

S is a platinum slide wire reading in 0.001 ohms and of accuracy better than 0.1%.

P is a platinum thermometer;

D - dummy leads.

G - a sensitive mirror galvanometer of sensitivity 740 mm per micro-amp.

K is an all copper knife switch free of thermo-electric current.

A 2 volt accumulator was used, the current being reduced by 500 ohm resistor in series to safeguard the bridge.

The terminals and connections were made of thermally pure copper rods (conductivity copper) of $\frac{1}{8}$ " diameter.

These bridges were checked on a new type of Smith difference bridge⁽¹³⁵⁾, as supplied by the Cambridge Instrument Co., which had an accuracy of 0.000001 ohms, and the accuracy was found to be to better than 0.00001 ohm.

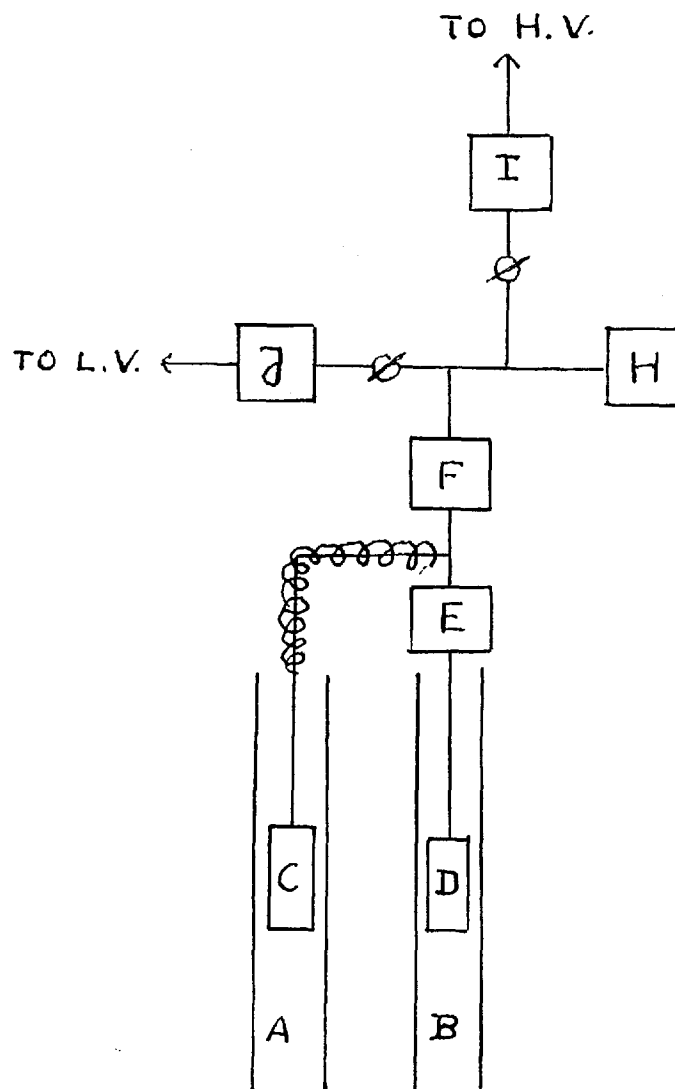
Temperature control devices.

The control of temperature was effected by a platinum thermometer (26) Fig. 10, placed in a close proximity to the inner metal wall of the furnace, in conjunction with the modified form of Robert's controller⁽¹³⁶⁾ across the switch of which a variable resistor was connected. By adjusting the resistance of this resistor an optimum value for the decrease of heat supply to the furnace, on the opening of the switch, can be obtained.

2.2.6 Extension for the preparation of samples for X-ray analysis.

This is shown diagrammatically in fig. 12.

(A) and (B) are two furnaces; (C) is a reservoir with sorbate; (D) are tubes with sorbent; (E) and (F) are magnetic taps; (G) a heating coil; (H) is a buffer volume, while (I) and (J) are cold traps.

FIG. 12.

A & B - FURNACES.

C - RESERVOIR WITH SORBATE.

D - X-RAY SAMPLES WITH SORBENTS.

E & F - MAGNETIC TAPS.

G - HEATING COIL.

H - BUFFER VOLUME.

I & J - COLD TRAPS.

2.3 Experimental procedure.

2.3.1 The control of temperature.

As has been mentioned in the previous section the two furnaces, which surrounded the balance case and the sorbate vessel, had two heating elements, an inner (control) of about 250 watts, and an outer (main) of about 2 k.watts. The control of temperature was effected by a modified form of Roberts' controller⁽¹³⁶⁾, which was operated by a sensitive platinum resistance thermometer (10 ohms at 0°C) placed in a close proximity to the inner metal wall of the respective furnace. Furnaces (1) and (2) (fig. 10) were first heated by the main heating element to a temperature a few degrees below that required, the voltage being maintained constant by a constant voltage regulator and adjusted by an 8 amp. Variac. Fine control was then obtained by switching on the auxiliary heating element, the current of which passed through the switch of the Roberts' controller. Across the switch of the controller a variable resistor was connected, so that in effect the current through the auxiliary heating element was automatically decreased or increased, as the switch opened or closed, so as to keep the temperature constant.

The temperature being recorded by the platinum resistance thermometer inside the balance case (26) (fig. 10) was indicated on a galvanometer scale so that check on temperature was constantly maintained. With this equipment the temperature inside the sorption vessel and sorbate vessel was maintained constant to better than $0.1^{\circ}\text{C} \pm 0.05^{\circ}\text{C}$. The temperature of the third furnace (3) (fig. 10) was regulated by means of a Variac.

It is worth while to mention that at first the

control of temperature was intended to be made by means of a photo-electric cell and photo-electric relay in conjunction with a platinum resistance thermometer. The circuit was designed and the relay was operated by every second pulse from the photo-electric cell. By this means the control of temperature was effected to better than 0.005°C . However, it was not 100% proof due to the fact that sometimes two pulses were given by one passage of the galvanometer reflected beam of light, across the photo-electric cell. Due to the pressure of time this method has been abandoned in favour of the simpler but not so efficient one. Nevertheless, the photo-electric method of temperature control is a better one and time saving, provided that the technicalities of it can be solved.

2.3.2 The measurement of temperature.

Temperature inside the balance case was measured by means of a sensitive platinum resistance thermometer described in section 2.2.5. The bridge read to 0.001 ohm and the variation in temperature was continuously indicated on a galvanometer scale by beam of light reflected from its mirror.

2.3.3 The introduction of vapours of sorbates to the balance case.

The pure sorbate after being fractionated in vacuo was vacuum sealed in a pear shaped glass bulb with a break-off at the top. This was then in-sealed into the balance case. After the evacuation of the balance case and the outgassing of the sorbent was completed the balance case was sealed off from the rest of the apparatus and the tip of the sorbate reservoir was broken with a magnetic hammer thus allowing the vapour to enter the balance case.

2.3.4 Measurement of pressure.

Pressure was measured by means of a glass spiral gauge manometer, described in section 2.2.3, in conjunction with a McLeod gauge and a mercury manometer. Before the commencement of pressure measurement the sorbate was frozen in the sorbate reservoir by immersing the reservoir in liquid oxygen contained in a dewar flask. The casing containing the pressure gauge was completely evacuated so that there was a complete vacuum on both sides of the spiral gauge, and the zero reading on the galvanometer scale was taken. Then the dewar flask, with liquid oxygen, was removed, furnace no. 2 put in position, and its temperature was adjusted to give the required vapour pressure. Dry nitrogen was then let into the outer compartment containing the pressure gauge so as to bring the reflected beam to zero point. The pressure of nitrogen equalled then to the vapour pressure of the sorbate and it was read either on the McLeod gauge, if the pressure was very low, or on the mercury manometer if the pressure was above 5 mm Hg. The height of the mercury column was read by means of a cathetometer reading to 0.001 cm. The meniscus correction was applied.

The spiral gauge manometer already referred to gave a 1 mm deflection on the galvanometer scale for 0.1 mm pressure difference, so that in a pressure range 1 mm to 760 mm Hg, the pressure could be read to at least 0.05 mm. Since the counter-balancing nitrogen pressure was read by cathetometer in a manometer at room temperature, the connecting tube was made not less than 1 cm diameter, to avoid thermomolecular pressure effects^(137,138).

After the completion of each isotherm, the sorbate was frozen out in the sorbate vessel and the zero pressure

reading was checked at the temperature of the experiment. Before the commencement of each experiment the pressure gauge was annealed for two days at the temperature of the required isotherm and the zero pressure was read on the galvanometer scale; due to the thermal properties of the glass, these readings need not to be the same for different temperatures.

The advantage of this pressure gauge is that pressure is read at the temperature of the experiment, but care must be taken to construct such a spiral so that a spiral of 12 turns will give no more than 170° - 180° deflection for one atmosphere pressure difference at temperatures up to 300° - 350°C .

2.3.5 The measurement of sorption.

The amount sorbed was measured on a 60 turns silica spring, sensitivity ca. 36 cm per gm, used as microbalance. As the distance, over which the silica spring extended was limited by its maximum allowed load and the length of windows in the furnace, the amount of zeolite to be used for sorption measurements was pre-calculated from the knowledge of its free internal volume and the density of the sorbate.

The zeolite was weighed carefully on a balance in a small glass bucket of about 0.2 gm weight, then suspended from the silica spring and in-sealed to the balance case. The balance case was then evacuated and the sorbent outgassed for at least 48 hours at 350°C with continuous evacuation. The balance case was then sealed-off from the pumping system; zero point pressure reading was taken and the spring length was read with cathetometer; the break-off to the sorbate reservoir was then broken with a magnetic hammer, the vapour pressure of the sorbate

was adjusted approximately to the required value and the pressure and the length of the silica spring was read after equilibrium had been reached. It took about six hours on the average for the equilibrium to be established. The procedure was repeated for different vapour pressures of the sorbate. After the sorption isotherm was completed desorption readings were taken in a similar manner by lowering the temperature of the sorbate reservoir. Then the sorbate was frozen out as described in section 2.3.4, and the zero point pressure reading was checked. The temperature of the balance case was then adjusted to the value required for the next isotherm, left at this temperature for 48 hours and the zero pressure reading was noted. The procedure was repeated as for the first isotherm. The amount sorbed, for each equilibrium pressure, was read from the calibration graph (extension against weight) for the spring at the particular temperature.

After the completion of a series of experiments for one sorbate and sorbent an isotherm, at the other extreme temperature range, was repeated to check the accuracy of readings and temperature measurement.

2.3.6 Calibration of silica-spring.

It has been found necessary to anneal the silica-spring, before reproducible results could be obtained, over the temperature range used in this study. The annealing was done by repeatedly and slowly heating and cooling the spring over the temperature range 20 - 350°C. Care must be taken not to heat the spring to a higher temperature than 350°C, as thermal hysteresis was then found to occur. This property of these springs limits the range of temperature for which they can be used with any accuracy.

The spring was then calibrated at different

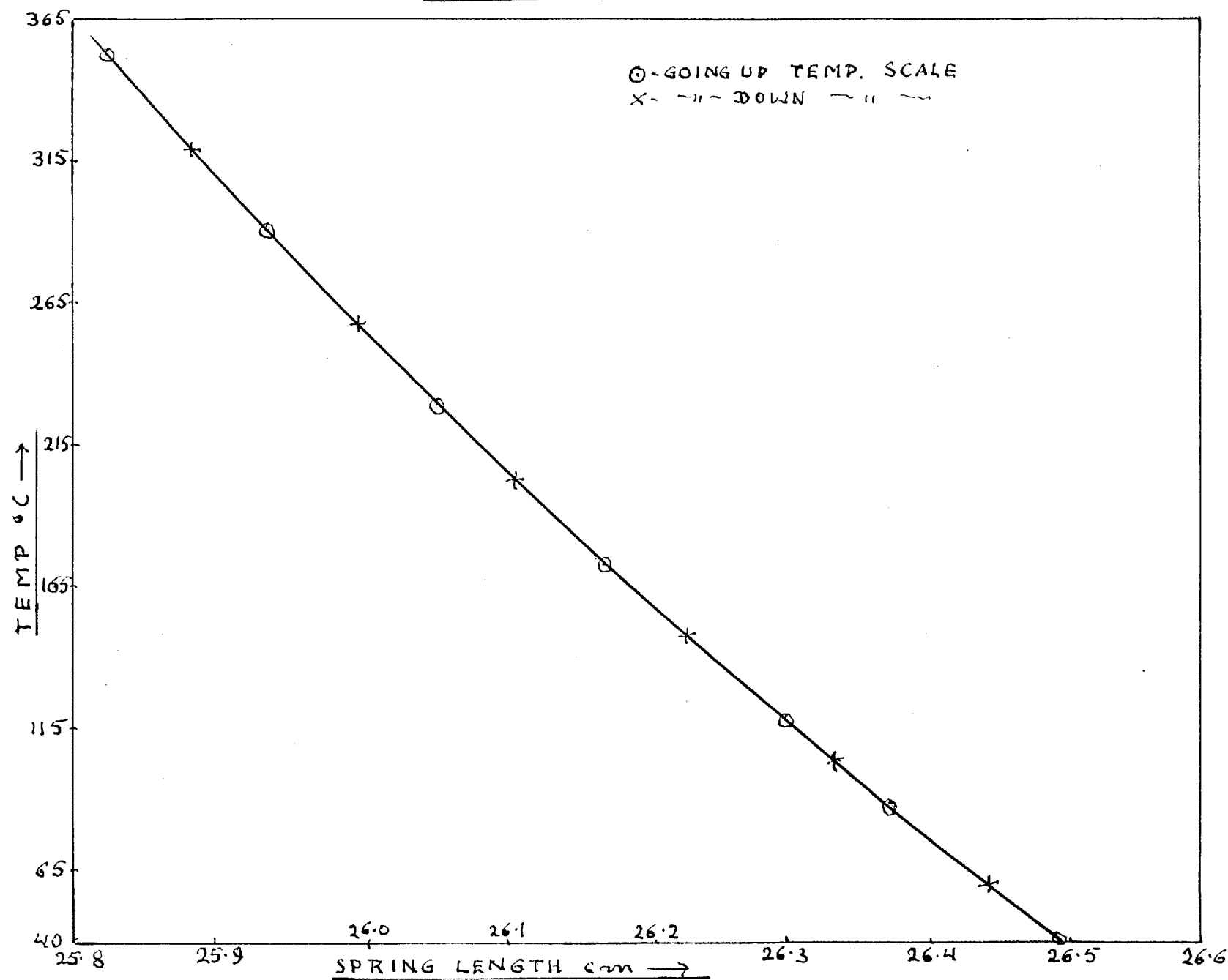
temperatures using small glass weights. A typical calibration curve is shown on fig. 13. These curves were used to read off the amount sorbed.

2.3.7 Construction and calibration of platinum resistance thermometers.

The platinum resistance thermometers were constructed according to the requirements of the National Bureau of Standards^(139,140,134). Thermally pure platinum was used. The coil and leads were annealed over the temperature range up to 700°C. They were then cleaned in hot pure concentrated nitric acid, washed, dried and in-sealed in a glass jacket made of very thin pyrex glass of less than 0.1 mm wall thickness. The jacket was filled with pure helium at $\frac{1}{3}$ atmosphere pressure, sealed, annealed at 500°C and then calibrated at ice point, boiling point of water and boiling point of sulphur, using pyknometers specially made for that purpose. For the calibration, pure distilled water and ice made of distilled water saturated with air, were used. Sulphur was purified in the following manner.

Flowers of sulphur were dissolved in carbon disulphide and the solution was treated with concentrated sulphuric acid, to which a little of concentrated nitric acid was added, with constant stirring^(141,142). The solution of sulphur in carbon disulphide was separated from the sulphuric acid mixture and evaporated to dryness. Before evaporation it was filtered through calcium oxide to remove traces of acid. After evaporation it was crushed, transferred to a distillation apparatus, and distilled three times in an atmosphere of carbon dioxide⁽¹⁴³⁾, the first and last fraction being rejected. The final stage of fractionation was carried out in vacuum.

FIG. 13.



2.3.8 Accuracy of results.

Temperature was kept constant to $0.1 \pm 0.05^\circ\text{C}$. Pressure was read to 0.1 ± 0.05 mm Hg. The length of the spring was read using the cathetometer and successive readings agreed to ± 0.001 cm, so that the amount sorbed was accurate to ± 0.03 mgm. The accuracy of the isotherm determination varied depending on the region considered, the main error being at low pressures and due to pressure measurement.

The accuracy of the isosteric heats can be obtained from the deviation of points from a mean curve of isosteric heat versus amount sorbed. This varied slightly with the sorbate, e.g. the maximum deviation for iodine in faujasite was 0.2 kcal/mole; on CaA, 0.1 kcal/mole; and on chabazite, 0.15 kcal/mole. However, in all cases the mean deviation was better than 50 kcal/mole. This can be seen from the entropy curves (figs. 23, 24, 25), from which the points fall exactly on the curve.

2.3.9 X-ray diffraction technique.

2.3.9.1 Equipment.

This section will deal only with powder photographs since the powder technique was used in this work.

X-rays were generated by means of a Hilger H-R-X research unit supplied by Hilger and Watts Ltd. This was fitted with demountable copper target which, bombarded with electrons under a potential difference of 39-40 K.V., emitted a characteristic copper radiation, $\text{Cu } K_\alpha$ and $\text{Cu } K_\beta$. The $\text{Cu } K_\beta$ radiation was filtered out by means of nickel foil placed in the aperture of the X-ray unit, so that only $\text{Cu } K_\alpha$ radiation was used.

The cameras used were the 9 cm Debye-Scherrer cameras.

2.3.9.2 Preparation of specimens.

The powder was introduced into pyrex-glass tubes specially drawn for that purpose, of about $1/3$ mm external diameter and about $1/50$ mm wall thickness. These tubes were drawn in the following manner. A clean tube of 3 cm diameter was first drawn into a thin walled tube of 4 - 5 mm diameter and from it the final tube was drawn using this time the oxygen brush flame. These tubes after being filled with the powder (200 mesh) under investigation, were in-sealed into the apparatus described in section 2.2.6, fig. 12, and after outgassing or sorption the tubes were vacuum sealed and detached from the apparatus ready for investigation.

2.3.9.3 Mounting of specimens.

The tube containing the specimen was accurately centred in the camera in a vertical manner so that it showed no lateral movement on rotation, i.e. the axis of rotation coincided with that of the cylindrical film. During exposure the sample was rotated at the rate of one revolution per minute. 39 - 40 K.V. potential difference was used and the filament current was 55 m.amps. To get a good photograph 12 hours' exposure was necessary, using a collimator with an aperture of about 0.2 mm.

2.3.9.4 Measurement of "d" spacings.

The cones of diffraction pattern produced when X-rays are diffracted by powder appear as a series of arcs when recorded on a cylindrical film, each cone giving two arcs at equal angles on either side of the incident beam. Each of these cones is produced by diffraction from planes of equal "d" spacing, this being the normal between a set

of equivalent planes.

In the 9 cm diameter cameras the film was mounted after the method of van Arkel⁽¹⁴⁴⁾ and so lines of large "d" spacings were produced near the ends of the film. "d" spacings can be readily calculated from a knowledge of the geometry of the camera (fig. 14). The distance D between two equivalent powder lines can be measured to 0.005 cm by means of a film measuring rule, fitted with a Vernier scale. The distance D₀ between the shadows cast by the knife edges can be also measured, and from the known distance between the knife edges on the camera, a correction factor could be applied to D to allow for any alteration in length which had occurred during processing.

It can be seen from fig. 14 that:

$$\frac{D}{2\pi R} = \frac{2\pi - 4\theta}{2\pi}$$

$$\text{therefore, } \frac{D}{4R} = \frac{\pi}{2} - \theta \quad 2.3.9.4. 1.$$

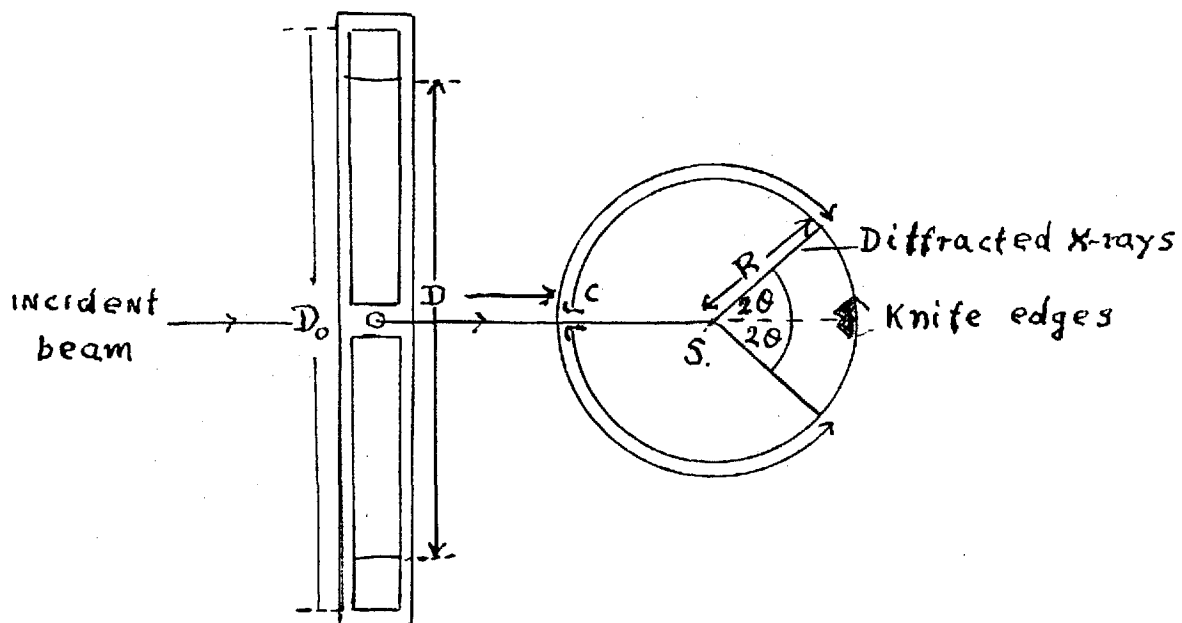
The Bragg equation relating "d", the wavelength of the X-rays, λ , and the angle θ between the incident beam and the reflecting plane, gives:

$$\lambda = 2 d \sin \theta$$

$$\text{therefore, } d = \frac{\lambda}{2 \sin \theta} = \frac{\lambda}{2 \cos (\pi/2 - \theta)} \quad 2.3.9.4. 2.$$

Substituting from 2.3.9.4. 1 for $(\pi/2 - \theta)$ we get

$$d = \frac{\lambda}{2 \cos \frac{D}{4R}} \quad 2.3.9.4. 3$$

Fig. 14.

GEOMETRY OF X-RAY POWDER CAMERA.

C-Collimator.

S-Specimen.

The calculation of "d" can be facilitated by plotting values of "d" against D for a given camera.

2.3.9.5 Interpretation of powder photographs.

Once the "d" spacings had been determined, the lines on the photograph can be indexed. If the unit cell parameters are known the indexing is a relatively simple matter. Equations relating the unit cell parameters, d and hkl indices for different crystal classes have been calculated⁽¹⁴⁵⁾. From these equations the "d" spacings can be obtained for various hkl values and by inspection, observed values of "d" can be indexed.

For cubic cell:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

For tetragonal cell:

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}}}$$

For hexagonal cell:

$$d_{hkl} = \frac{1}{\sqrt{\frac{4}{3} \frac{(h^2 + hk + k^2)}{a^2} + \frac{l^2}{c^2}}}$$

For rhombohedral unit cell:

$$d_{hkl} = \frac{a}{\sqrt{\left\{ \frac{1 + 2 \cos^3 \alpha - 3 \cos^2 \alpha}{(h^2 + k^2 + l^2) \sin \alpha + 2(hk + kl + lh)(\cos^2 \alpha - \cos \alpha)} \right\}}}$$

where α = interaxial angle.

When the unit cell is unknown the problem of indexing is much more difficult. The method found most convenient is a graphical one due to Björström and modified by Bunn⁽¹⁴⁵⁾. In this chart values of $\log(h^2 + k^2)$ are plotted on the left hand side, and values of $\log l^2$ on the right hand side along perpendicular axis; these are joined by logarithmic curves, the values of the axial ratios c/a being plotted along the base line starting from zero at the right hand side. For the interpretation of this chart values of l/d^2 are determined from the photograph and a correction factor applied to them so that the smallest has a value of unity. These values are then plotted, on the same logarithmic scale as the chart, on a strip of paper. The strip is then moved over the graph, with its edge parallel to the vertical axis, until a point is reached where the plots on the paper strip coincide with lines on the graph. This chart can be used for indexing hexagonal or trigonal crystals.

For orthorhombic, monoclinic and triclinic systems, the indexing of lines and determination of unit cell parameters from powder photographs is almost impossible.

For hexagonal or trigonal crystal symmetry, the lines having been indexed from the Björström chart, the unit cell parameters are determined by means of the equations given above. Theoretical d_{hkl} values should be calculated and compared with the experimental values, and only if there is a good agreement between the two could the lattice constants be said to have been determined correctly.

All experimental reflections had to be accounted for but, unless the space group of the crystal is known, some reflections which might have been expected may be

missing due to operation of symmetry elements in the structure, while others may be too weak to be observed.

Chapter 3.

3. Results and Discussion.

3.1 General.

All isotherms measured for iodine on the three sorbents chabazite, Linde sieve A, and faujasite were reversible over all the temperature ranges studied, and it was possible to evaluate thermodynamic quantities for all these systems, over most of the range of filling of the interstitial volume.

On the other hand sorption of aluminium chloride was irreversible and therefore chemisorption, or reaction of the aluminium chloride with the residual intracrystalline water or perhaps catalytic decomposition cannot be ruled out.

In this study each sample was removed after the sorption and desorption study and examined by X-ray diffraction. No detectable decomposition was observed, the diffraction pattern being exactly that of the outgassed sample before sorption.

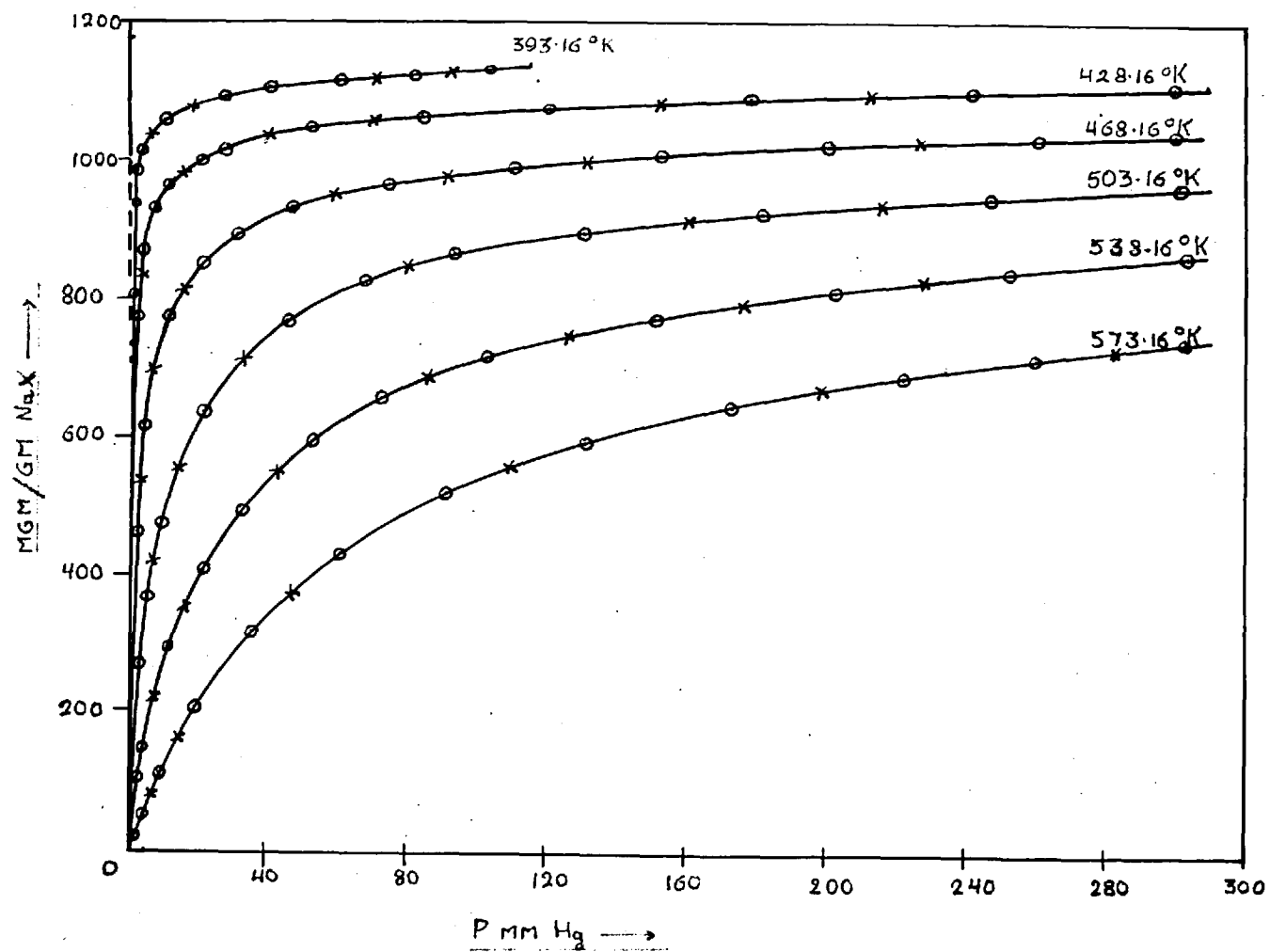
All isotherm results were expressed in mgm of sorbate per gm of outgassed sorbent. Typical families of isotherms are shown in fig. 15. Numerical values of all isotherms measured are given in the appendix.

3.2 Comparison of sorbents.

The frameworks of all the three zeolites used in this study have very similar chemical composition, the ultimate building unit, in each case, being - O - Si - O - or - O - Al - O - . In the samples used the silicon: aluminium ratio in the framework varies:

FIG. 15.

FAMILY OF ISOTHERMS FOR I_2 IN FAUJASITE.

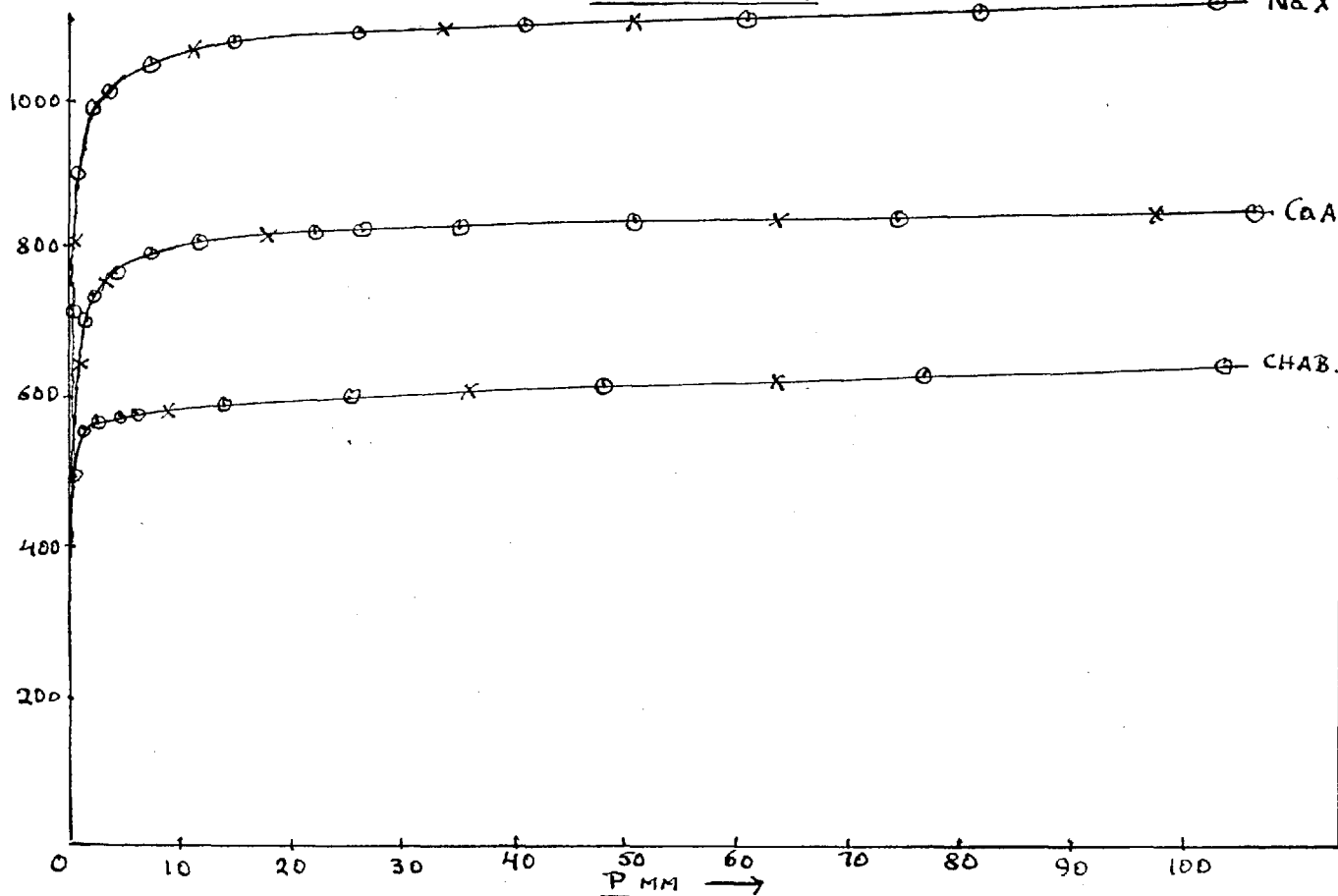
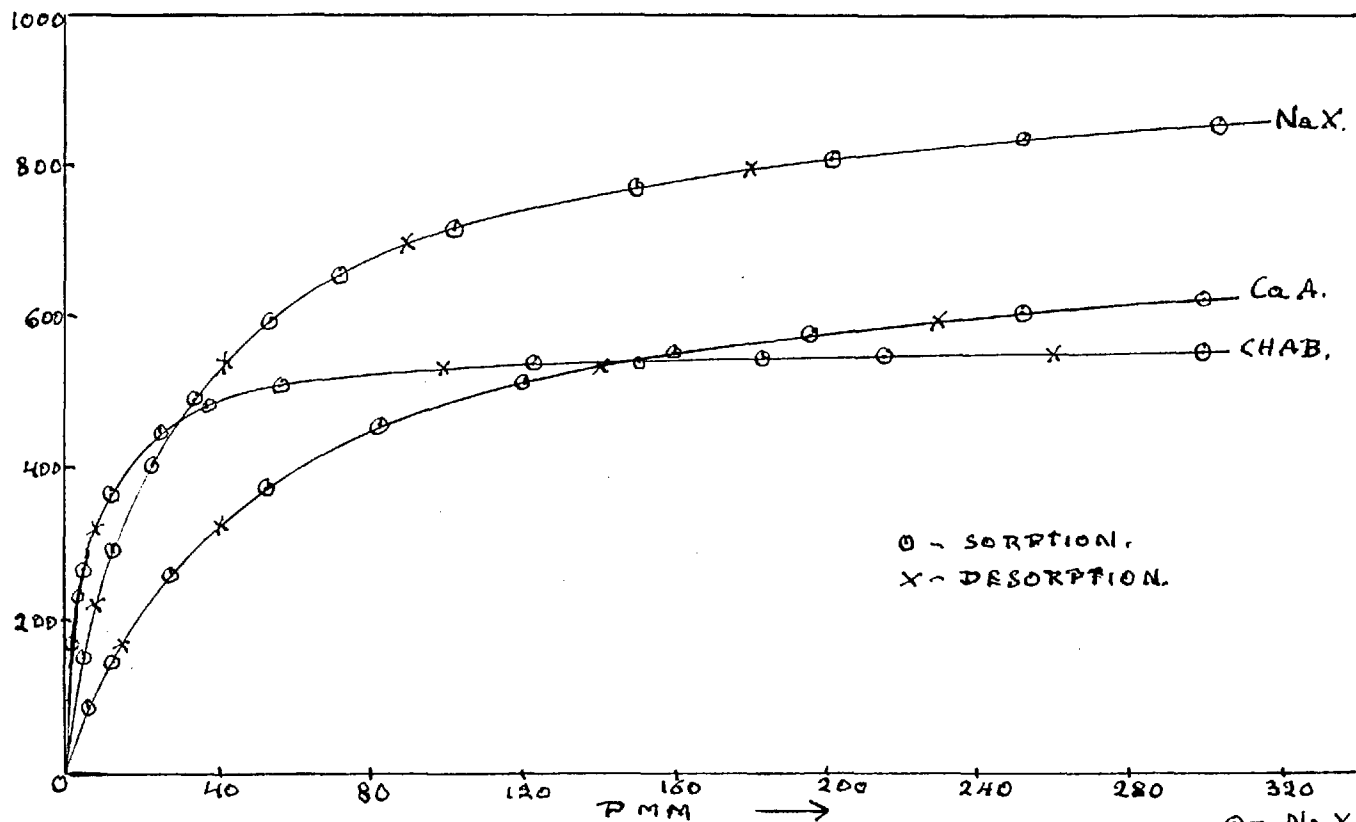


e.g. in chabazite it is $\sim 2 : 1$,
in CaA it is $\sim 1 : 1$,
in faujasite it is $\sim 1.33 : 1$.

This, however, will not influence the sorptive properties of the sorbents to any significant extent as the silicon and aluminium ions are almost completely surrounded by oxygen anions and thus the force field inside the cages and channels will be mainly due to the anionic oxygen of the framework. Therefore, in the case of physical sorption, the amount sorbed will be determined by the interstitial volume available and by steric factor in the case of large asymmetric molecules.

120°C-isotherms, shown in fig. 17, give the maximum amount of intracrystalline sorption at that temperature. Therefore, we can use these isotherms for the determination of the ratio of intracrystalline free volume available to the sorbed molecules at 120°C. This was found from the isotherms to be approximately $1 : 0.755 : 0.555$ (NaX : CaA : chabazite). Naturally, these ratios are not exact, as these were calculated using iodine as sorbate and we have to make allowance for the finite dimensions of the sorbate molecules. The total pore volume as found from sorption of water is approximately $0.53 : 0.46 : 0.46$ per cm^3 of crystal for these sorbents. These free volumes are different to those found from sorption of iodine probably due to operation of steric factor in the packing of iodine molecules in the cages.

Fig. 16 shows the sorption of iodine in the three sorbents at 265°C. Here the isotherm for Linde sieve A (CaA) falls all along below that of faujasite (NaX), but the isotherm for chabazite rises initially above the other two then, close to the saturation value, at that temperature, it falls below. This behaviour results

SORPTION OF I_2 AT $265^\circ C$.FIG. 17. - SORPTION OF I_2 AT $120^\circ C$.

from the differing affinity of the sorbents for the sorbate and could be expected from the consideration of the shapes of the cavities in the three sorbents and dispersion and polarization forces. In the case of faujasite and Linde sieve A, the cavities are approximately spherical and differ only slightly in their free diameter, therefore the force of attraction for sorbate molecules (excluding contribution due to cations) will be approximately the same and the amount sorbed at a given pressure will almost entirely depend on the free volume available and so the CaA isotherm falls all the time below that of NaX. In the case of chabazite, however, the cages are of elliptical shape of 6.6 Å width, which is of the same order as the molecular diameter of the iodine molecule and therefore the force of attraction for iodine molecule is much greater in the case of chabazite and hence we should expect that more iodine molecules should be sorbed by chabazite than by the other two sorbents at a given pressure not too close to saturation value. This we find in practice as can be seen from fig. 16.

3.3 Saturation values and number of molecules occluded per cage.

All substances studied gave almost rectangular isotherms at lower temperatures, from which saturation values (i.e. amounts of sorbate required to fill the intracrystalline volume of the crystals) were calculated. This was done by plotting p against p/a for near saturation region of each isotherm, where p = pressure, a = amount sorbed. All these plots gave straight lines from the slopes of which a_{sat} was estimated.

From the saturation values the maximum number of iodine molecules capable of being occluded per cage by

the given sorbent were calculated. These are as follows:

faujasite	= 7.5 molecules of I ₂ ;
Linde sieve 5A	= 5.5 " " ";
chabazite	= 2 " " ".

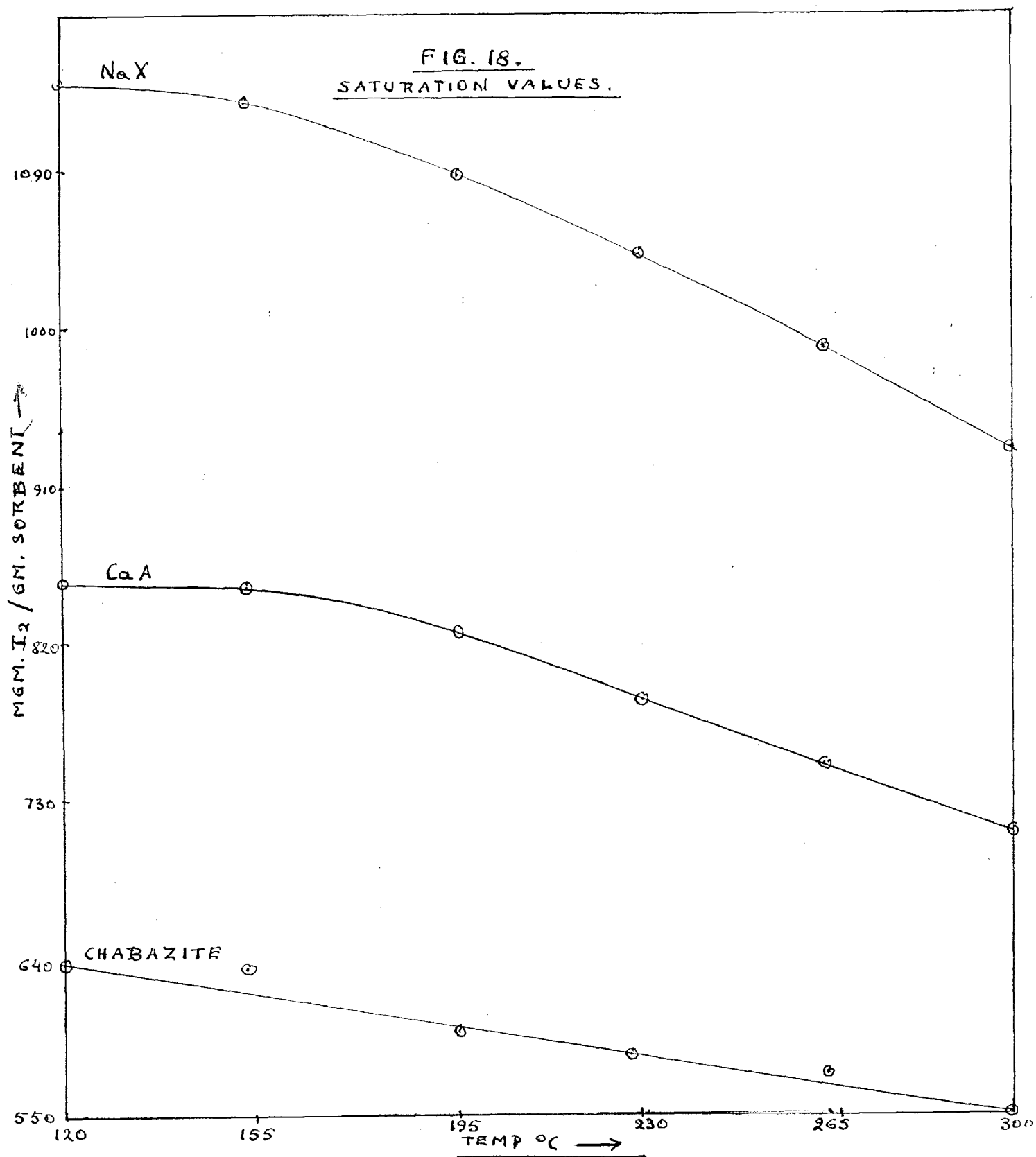
Graphs showing the saturation values for each sorbent at different temperatures are shown in fig. 18. It is seen that as the temperature rises the saturation value decreases. The behaviour of the sorbed substance at saturation can therefore be compared with that of a substance expanding with rising temperature. As the expansion of sorbent is negligible over the range of temperature studied, an approximate coefficient of cubical expansion of the sorbate can be calculated from the straight portion of the graph in fig. 18. In this way the mean coefficient of cubical expansion of iodine was found to be 2.785×10^{-4} between the temperature range 195 - 300°C. This is in good agreement with the coefficient of cubical expansion of solid iodine as given in the literature (i.e. 2.64×10^{-4}).

3.4 Thermal expansion of sorbed substance.

It has been shown in the previous section that the coefficient of cubical expansion of sorbed iodine as calculated from the saturation values is almost identical with that of solid iodine. The thermal behaviour of the sorbed material can be examined further in terms of its thermal expansivity using the process outlined by Barrer and Sutherland⁽¹⁴⁶⁾.

The free energy of sorption, ΔG , is given approximately by the expression:

$$-\Delta G = \epsilon = -RT \ln \frac{p}{p_0} \quad 3.4. 1.$$



where P_0 is the saturation vapour pressure of the sorbate, and P is the isotherm pressure. If V_i is the interstitial volume of the crystals, α the mass sorbed, and δ the density of the interstitial substance, then

$$\alpha = V_i \delta \quad 3.4.22.$$

At constant free energy of sorption

$$\left(\frac{d\alpha}{dT}\right)_\epsilon = V_i \left(\frac{d\delta}{dT}\right)_\epsilon + \delta \left(\frac{dV_i}{dT}\right)_\epsilon \quad 3.4.3.$$

The thermal expansion coefficients of the intracrystalline substance " α " and the intracrystalline volume α_i at constant ϵ , are given by:

$$\alpha = -\frac{1}{\delta} \left(\frac{d\delta}{dT}\right)_\epsilon, \quad \alpha_i = \frac{1}{V_i} \left(\frac{dV_i}{dT}\right)_\epsilon \quad 3.4.4.$$

Dividing 3.4.3 by $V_i \delta$ and substituting from 3.4.4., we get:

$$-\frac{1}{\alpha} \left(\frac{d\alpha}{dT}\right)_\epsilon = (\alpha - \alpha_i) \quad 3.4.5.$$

If ΔG is plotted as a function of the amount sorbed to give a family of affinity curves for various temperatures, $(\alpha - \alpha_i)$ can be evaluated for each value of ΔG .

However, the error in determination of $(\alpha - \alpha_i)$ by this method is large (about 10%) and the value of $(\alpha - \alpha_i)$ does not differ widely from that obtained in the previous section.

It can be concluded from paragraph 3.3 and 3.4 that the expansivity of iodine in the sorbed state near saturation are not greatly different from the bulk solid. In the case of hydrocarbons and fluorocarbons sorbed in zeolites and for zeolitic water, it was also found that $(\alpha - \alpha_i)$ was not very different from that for the bulk liquids^(104,158).

3.5 Occlusion isotherms.

All isotherms obtained in this work correspond to type I of Brunauer's classification⁽⁵⁸⁾ as shown in fig. 6. This means that nothing to correspond with multilayer formation is found, as might be expected from the dimensions of the intracrystalline cavities. Typical family of occlusion isotherms is shown in fig. 15, and a comparison of sorbents at one temperature is shown in figs. 16 and 17.

All these isotherms, qualitatively at least, obey the Langmuir isotherm equation for the localised model over the range of filling $0.2 - 0.8 \theta$ as can be seen from figs. 29, 30, 31. The departure from the localised model at low values of θ may be due to the trend in sorption heat, ΔH , with θ , so that all the sides are not homogeneous or partly due to solution of iodine in the residual intracrystalline water. The departure from the Langmuir localised model at high values of θ is due to the increasing sorbate-sorbate interaction. The greater deviation at large values of θ exhibited by isotherms at lower temperature range is due to the beginning of capillary condensation on the outer surfaces of the crystals.

It can be seen also that at high values of θ the slope of the curves of $\log p(1 - \theta)/\theta$ against θ are positive, figs. 29, 30, 31. This is required if the deviation from the ideal Langmuir equation is dominated by losses in thermal entropy on tightly packing the I_2 molecules within the structure (see Sections 3.8.2. and 3.9).

3.6. Inter-molecular Forces (Sorbate-Lattice Interaction).

This section will deal with the aspect of inter-molecular forces concerning mainly sorbate-lattice interaction, as this gives the main contribution to the heats of sorption (see section 3.7). The theory of inter-molecular forces has been reviewed in section 1.4.

The potential energy of a non-polar, spherically symmetrical molecule can be expressed as:

$$Q = Q_D + Q_R + Q_P \quad 3.6. 1.$$

where Q_D = dispersion energy

Q_R = repulsion energy

Q_P = polarisation energy.

Quadrupole moment interactions will also give some contribution, Q_Q , but in this treatment such a contribution cannot be evaluated since the quadrupole moment of I_2 is unknown.

The polarisation energy seems to be important only at small coverages ($\theta \leq 0.3$) and as the position and number of polarizing centres is unknown it will not be considered here.

Dispersion and repulsion energy.

The main contribution to dispersion energy will come from the oxygen atoms of the alumino-silicate framework. The smaller number of cationic silicon and aluminium atoms are almost completely screened by the large oxygen atoms and they have small polarisabilities and hence their contribution to dispersion energy interaction of sorbate molecules will be small and will be considered to be negligible. A calculation of this contribution carried out for argon⁽¹⁴⁷⁾ using the method of integration was shown to be 0.1 kcals. Some

contribution will come from cations located in the cavities of the zeolitic crystals, but their position is uncertain and number relatively small, and therefore the contribution due to their interaction will be omitted. The large oxygen atoms will contribute the major part to this interaction since:

1) the sorbate molecules will approach nearer to oxygen atoms than any other atom (with the possible exception of cations);

2) the oxygen atoms are far more numerous than cations;

3) the oxygen atom has a large polarisability.

Excluding the polarisation and quadrupole interaction, the interaction energy of a spherically symmetrical molecule with a single oxygen atom can be represented by a Lennard-Jones potential energy function.

$$\text{i.e. } Q = \frac{-A}{r^6} + \frac{B}{r^{12}} \quad 3.6. 2.$$

where A is the dispersion constant; B is the repulsion constant, and r is the distance between the centres of the two molecules. We may consider I₂ as behaving approximately as though spherical, especially if rotating.

A was evaluated from the Slater-Kirkwood equation (see section 1.4, equation 1.4. 2). Also equation 3.6. 2. can be rewritten as:

$$Q = \frac{-A}{r^6} \left(1 - \frac{r_e^6}{2r^6}\right) \quad 3,6, 3,$$

where r_e is the distance between the centres of the two molecules at which the potential energy is a minimum. It is assumed to be the sum of half the equilibrium separation of two sorbate molecules and the ionic radius of an oxygen ion. The total dispersion energy interaction

with an array of oxygen atoms can then be found by a summation of the individual interactions given by equation 3.6. 3.

It is of interest to consider the potential energy of interaction of a sorbate molecule situated in different positions in the large cages and in the windows. The following positions of a sorbate molecule will be considered:

- 1) in the large cavities and on approaching a 12-membered ring;
- 2) in the plane of a 12-membered ring;
- 3) on approaching an 8-membered ring;
- 4) on approaching a 6-membered ring.

Physical constants used in the evaluation of Q are given in Table 4.

Table 4.

Molecule	Radius Å	Polarisability $\times 10^{24} \text{ cm}^3/\text{molecule}$	$A \times 10^{65}$ cals.	No. of electrons in outer shell
I_2	2.923 (rotating) 2.15 (perpen- dicular)	12.763	1.12894	8
Frame- work Oxygen	1.40	3.916		2

3.6.1. Interaction in large cavities.

The energy of interaction of iodine molecule, in the large cavity in faujasite with the oxygen atoms of the framework was obtained by summation of individual

interactions using equation 3.6. 3. The positions of centres of oxygen atoms in a large cavity of faujasite, relative to a line through the centre of the 12-membered ring (window) and joining the centres of two neighbouring cavities, are shown to scale in Fig. 45, and the values are given in appendix. The oxygen atoms do not necessarily lie in the plane of the diagram their position being only true with respect to the above mentioned line and the centre of the cage. The number of atoms in equivalent positions is tabulated below.

Atom	ia	ib	ic	iib	iic	iiia	iiib	iiic	iiid
No. of positions	3	3	6	3	6	6	6	6	6

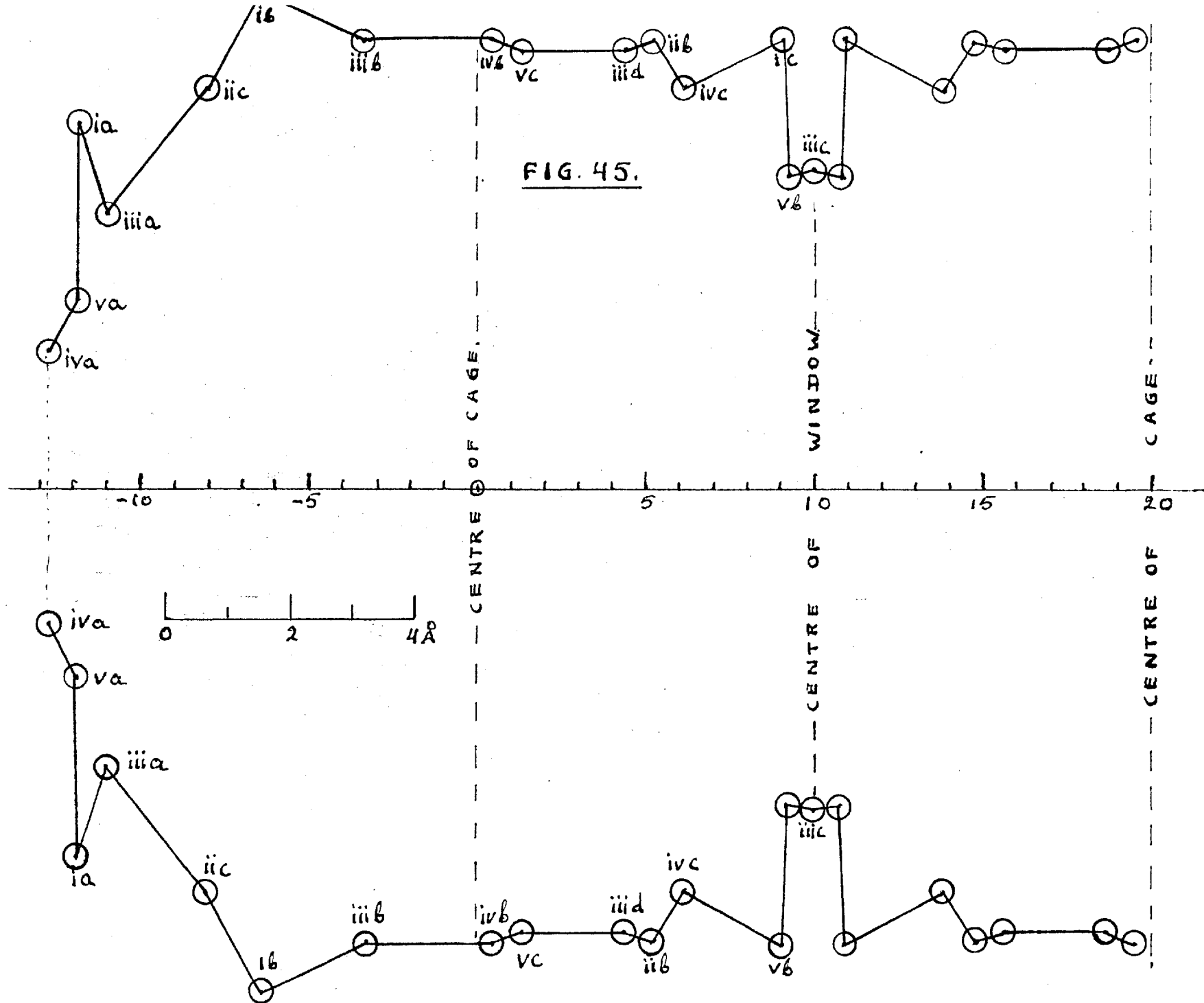
Atom	iva	ivb	ivc	va	vb	vc
No. of positions	3	3	6	3	3	6

A similar calculation of the energy of interaction using the method of integration previously used by Barrer⁽¹⁴⁷⁾

$$\text{i.e. } Q_D + Q_R = \pi N A \left[-\frac{P(x)}{R^3} + \frac{r_e^6 \cdot Q(x)}{5R^9} \right]$$

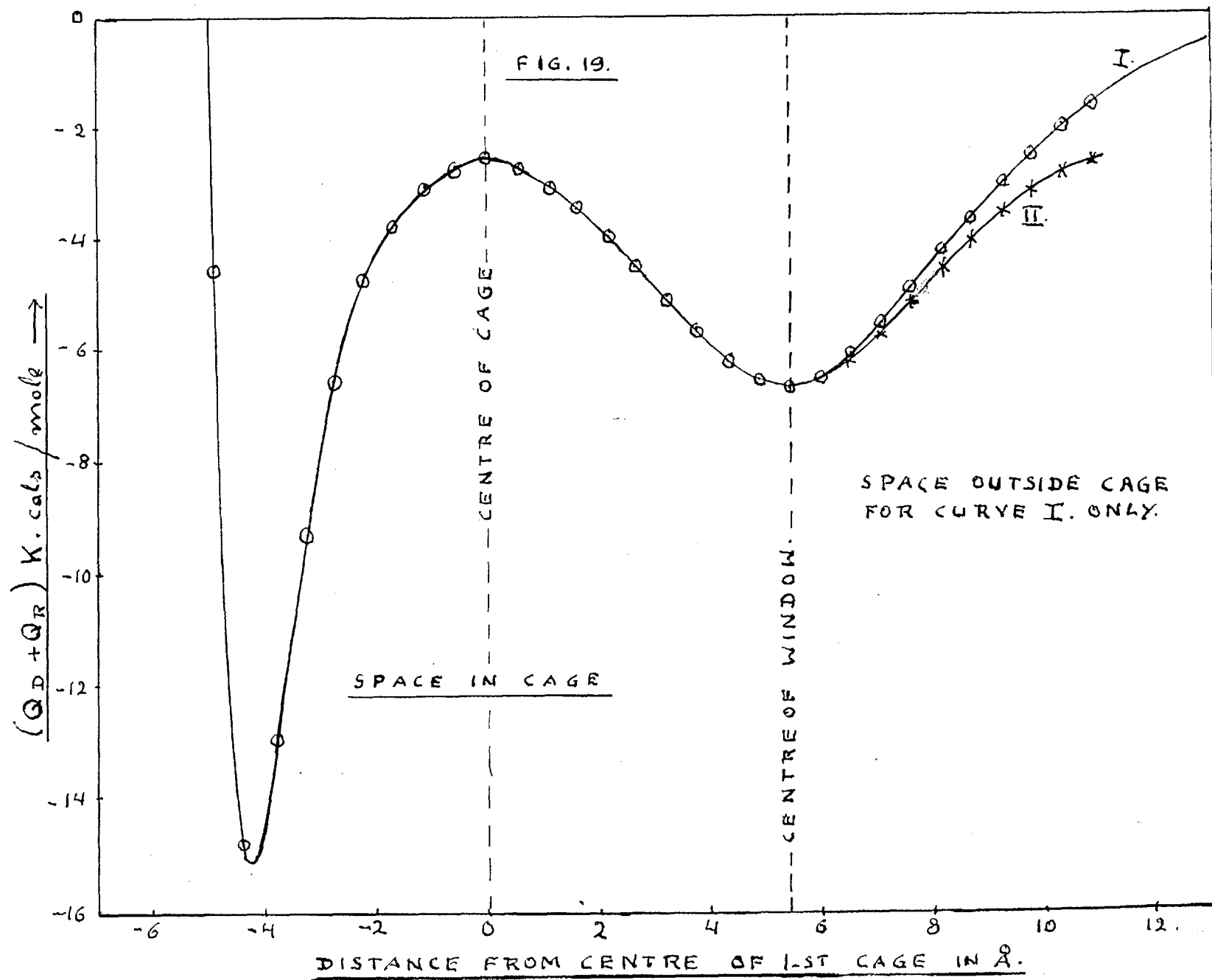
gives the values of the energy of interaction much too small. This is due to the fact that over 95% of the energy comes from contribution from the first shell of oxygen atoms, while in the method of integration all the oxygen atoms are assumed to be uniformly distributed throughout the whole volume of the crystal outside the cage in consideration. Thus the first shell will appear to contain a much smaller number of oxygen atoms than it actually does.

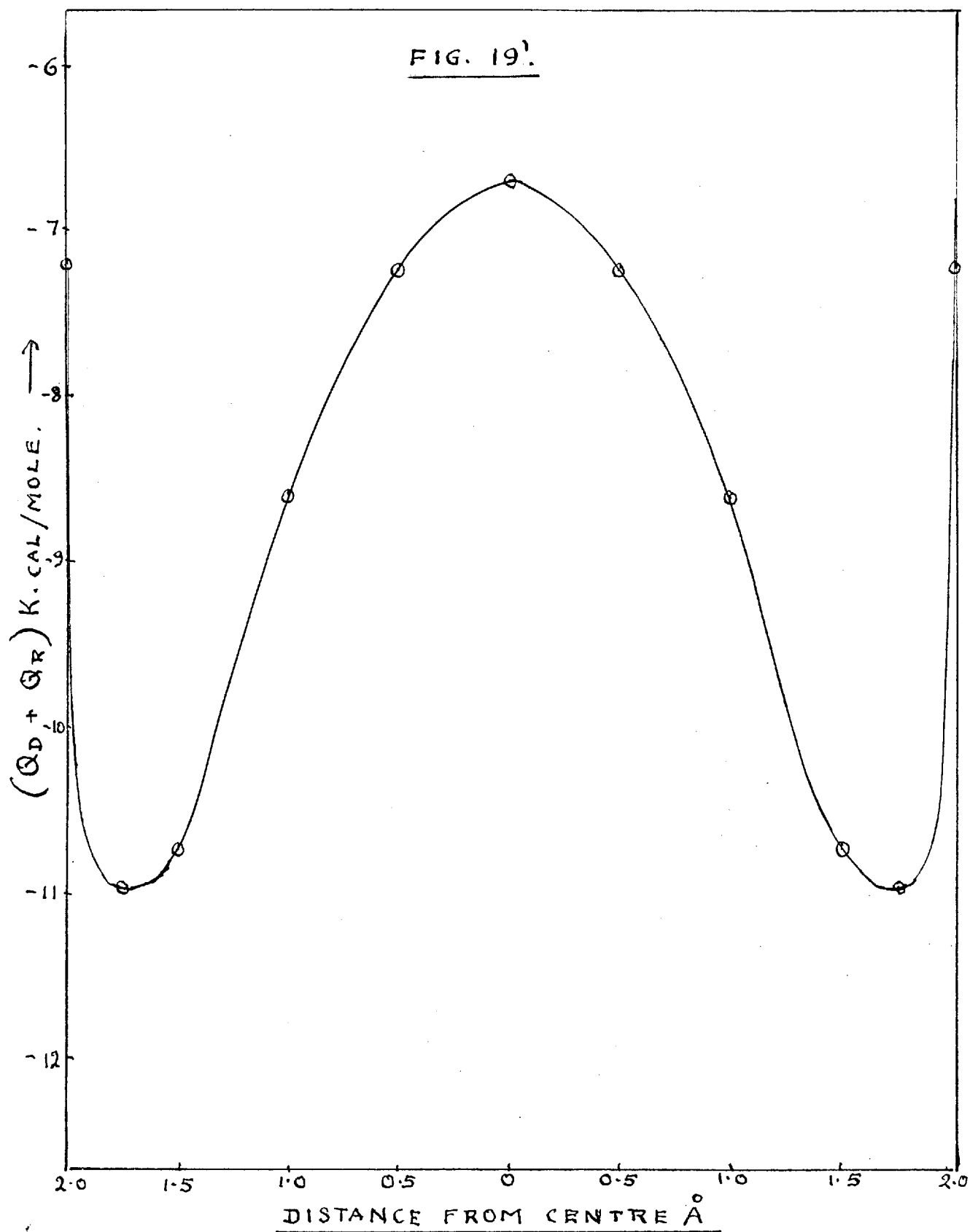
The values of the potential energy of an iodine molecule (obtained by the method of summation of



individual interactions), inside the large cage in faujasite, as it moves from the centre of one cage along a line perpendicular to the plane of a 12-membered window and through its centre towards the centre of neighbouring cavity, and then to its wall, i.e. to the centre of a six membered ring, is shown in Fig. 19, curve II. Curve I shows the potential energy as an iodine molecule moves along the same path but starts from a point outside the crystal. As the I_2 molecule will, preferentially, take up a position at which its potential energy is a minimum hence it follows from Fig. 19 that at equilibrium it will be situated near the wall of the cavity. The difference in energy between an equilibrium position near the wall of the cavity and its centre being 12.5 kcals/mole. The potential energy well is a narrow one, hence the I_2 molecule will not easily escape once it has gone there. At its minimum the potential energy of interaction is -15.1 kcals/mole. At other points along the wall the energy of interaction, from consideration of the crystal structure, will have almost the same value although it may be at some points slightly less than 15.1 kcals/mole.

The I_2 -molecule is not spherical but ellipsoidal (or some prefer to see it as dumb-bell shaped). The above energy of interaction was calculated assuming that I_2 will adhere to the wall with its longer diameter parallel to the wall. Should it take up a position with its shorter diameter parallel to the wall or should it rotate, the minimum energy at its equilibrium position near the wall would be ~ -9 kcals/mole. The difference in energy is 6 kcals/mole; this is large enough to prevent the molecule from rotating in such a manner, and so it is obvious that the I_2 molecule will take up position near the wall with its longer diameter parallel to the wall.





The relation between the differential heat $\Delta\bar{H}$ and Q is considered in section 3.7.

3.6.2. Interaction in the plane of 12-membered ring.

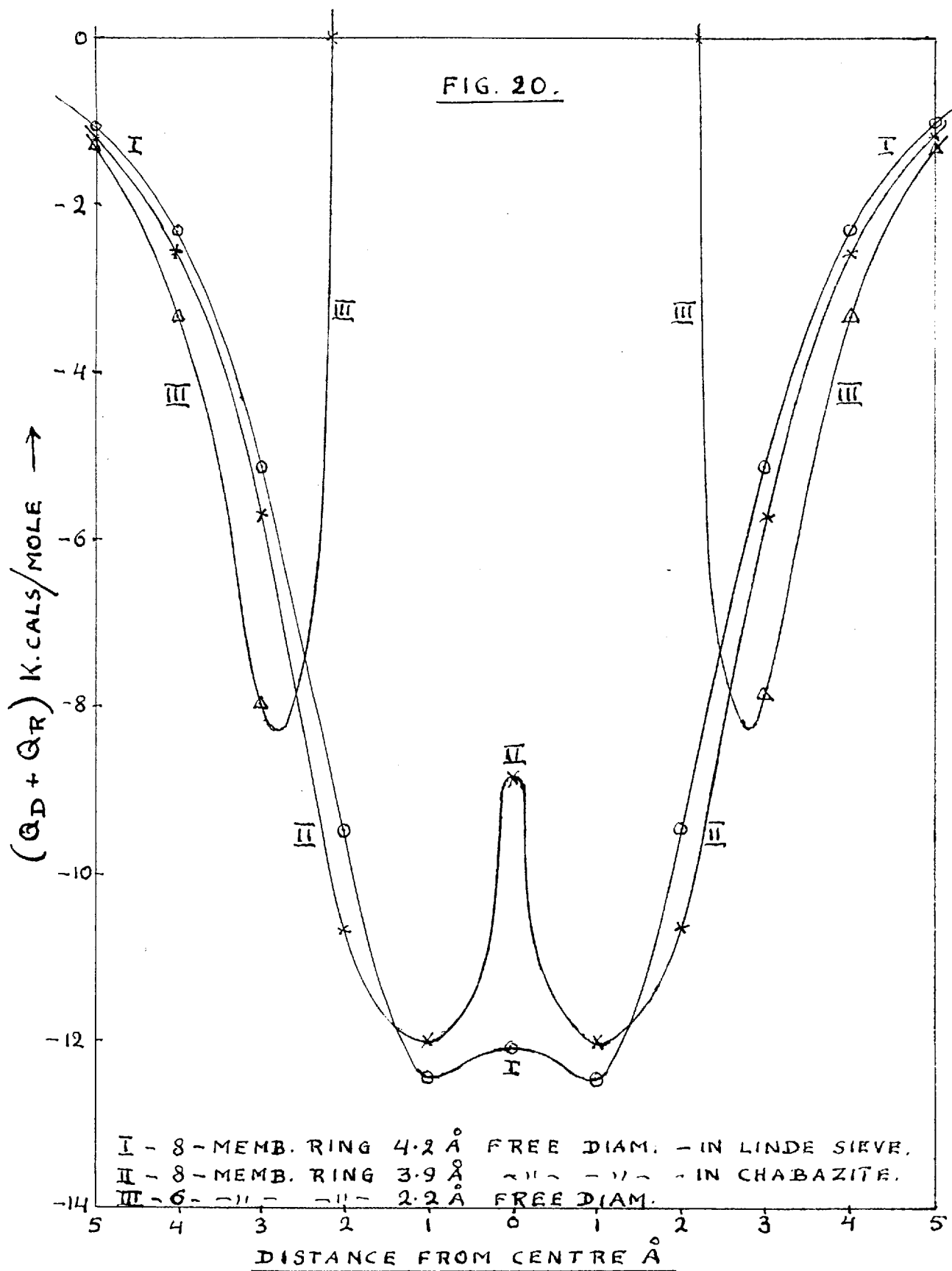
The interaction energy for different position in the plane of a window, joining two neighbouring cavities in faujasite, along a line joining the centre of the window to oxygen atom, iiic, (see Fig. 45), has been calculated using equation 3.6. 3. This has been done for only 5 rings of oxygen atoms nearest to the central plane of the window, i.e. atoms iiic, vb and ic, total 24 atoms. The more distant atoms are distributed symmetrically with respect to the plane of the window. To account for their contribution to the interaction energy the value of the energy obtained, for the centre of the window, in the previous paragraph (3.6.1.) was divided by the value of energy obtained in this section for the same position and the energies at all points were multiplied by this quotient. The energies thus obtained are equal, to the first approximation, to energies which would be obtained by summation of contributions from all the atoms in the two neighbouring cages. The plot of the energy of interaction against distance from the centre of the window (in its plane) is shown in Fig. 19'. The difference in energy of interaction for a sorbate molecule placed in the centre of the window and near its periphery is ~ 4.3 kcals per mole, a difference large enough to ensure that the molecule will preferentially enter the cage by way of a path near the frame of the window.

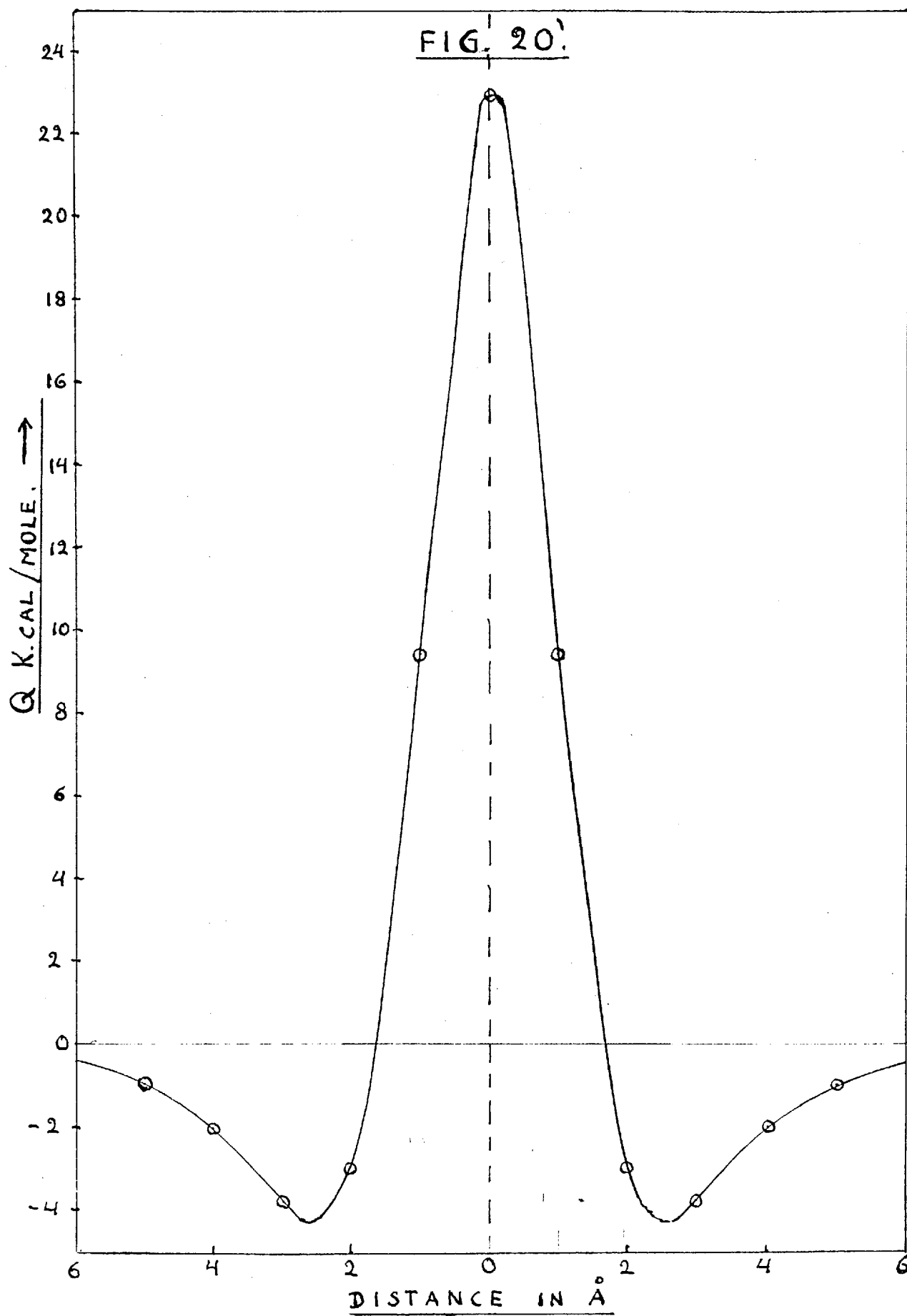
The difference in energy between an equilibrium position in the plane of the window and an equilibrium position near the wall of a cage where the potential energy is a minimum is ~ 4.0 kcals/mole. The potential energy calculated for the plane of the window was along a line

joining the centre of the window to centre of the nearest oxygen atom, the potential energy at a point near the periphery of the window along a line joining the centre of the window to a point mid-way between two oxygen atoms should be still less than -11.0 kcals/mole, but it will be greater than -15.1 kcals/mole which is the potential energy near a wall inside the cage. Hence the sorbate molecule will diffuse, along the ribs in the cage, towards a point inside the cage where its potential energy is a minimum, that is near the wall of the cage.

3.6.3. Interaction on approaching 8-membered ring.

As the windows connecting the large cavities in Linde Sieve A and chabazite are 8-membered rings of free diameter 4.2 Å and 3.9 Å respectively, it is of an interest to calculate the energy of interaction of an iodine molecule with the oxygen atoms of this ring when the molecule approaches the 8-membered ring along the axis through the centre and perpendicular to the plane of the ring. The potential energy plots as a function of distance from the centre of the ring are shown in Fig. 20, (curve I for Linde Sieve A; curve II for chabazite). The calculation was made assuming that the I_2 molecule approaches the ring oriented with its longer diameter perpendicular to the plane of the ring. Fig. 20' shows a similar plot for rotating I_2 molecule in the case of the 8-membered ring 4.2 Å free diameter (i.e. for Linde Sieve A). It follows from Figs. 20 and 20' that an I_2 molecule must be oriented with its longer axis perpendicular to the plane of the 8-membered ring to be able to pass through the ring. In the case of a rotating I_2 molecule ~37 kcals/mole activation energy would be required for the molecule to be able to pass through the window to the next cavity.





Further it can be seen from Fig. 20 that an oriented I_2 molecule can pass easily through the 8-membered window in the case of Linde Sieve A, whereas 3 kcal/mole activation energy is required in the case of chabazite.

3.6.4. Interaction with 6-membered ring.

Using the same assumptions as in the previous section, the energy of interaction of an I_2 molecule with the oxygen atoms of a six-membered ring of 2.2 Å free diameter was calculated for different points along a line perpendicular to the plane of the ring and passing through its centre. This is of interest because the large cavities in faujasite and Linde Sieve A on their peripheries have cubo-octahedra (sodalite type cages) as structural units, with 6- and 4-membered rings as faces, and 6.6 Å free diameter. The 6-membered rings have free diameter of 2.2 Å. The free space inside these cubo-octahedra is sufficient to accommodate one I_2 molecule. However, the molecule must first be able to pass through the window to enter the small cavity. Curve III, Fig. 20, shows the potential energy plot of an oriented I_2 molecule as a function of distance from the centre of the six-membered ring. It is seen from this curve that the potential energy minimum is at a point of ~ 3 Å from the plane of the ring; at smaller distances the repulsion energy increases rapidly to $\sim +600$ kcal/mole. Therefore, I_2 cannot find its way into the small cavities and so all the sorbate molecules will be located in the large cavities.

3.6.5. Normal vibration frequency of an I_2 molecule occluded in faujasite.

Considering attraction and repulsion energy only we can write:

$$Q_{\text{Tot}} = Q_A + Q_R \quad 3.6.5. 1.$$

Rewriting equation 3.6.2. as

$$Q_{\text{Tot}} = -Ar^{-n} + Br^{-m} \quad 3.6.5. 2.$$

we get the general energy equation where r is the separation distance between two molecules and n and m are indices; in our case 6 and 12. When interaction energy is at its minimum, the force exerted between the molecules is zero; hence

$$-\left(\frac{dQ}{dr}\right)_{r=r_e} = 0 \quad 3.6.5. 3.$$

$$\therefore r_e^{m-n} = \frac{mB}{nA} \quad 3.6.5. 4.$$

and the energy Q_e , corresponding to the equilibrium separation is:

$$Q_e = Ar_e^{-n} \left(\frac{n}{m} - 1\right) = Ar_e^{-m} \left(1 - \frac{m}{n}\right) \quad 3.6.5. 5.$$

Eliminating A and B we write Mie's equation as follows:

$$Q = Q_e \frac{1}{(n-m)} \left[n \left(\frac{r_e}{r}\right)^m - m \left(\frac{r_e}{r}\right)^n \right] \quad 3.6.5. 6.$$

Neglecting the zero point energy correction the energy required to remove the adsorbed molecule to infinite distance, that is outside the crystal, is

$$D_e = Q_{r=\infty} - Q_{r=r_e} = -Q_e \quad 3.6.5. 7.$$

and the excess energy a separation r over that at the separation r_e , is

$$w = Q_{r=\infty} - Q_e = \frac{-Q_e}{m-n} \left\{ m \left[1 - \left(\frac{r_e}{r}\right)^n \right] - n \left[1 - \left(\frac{r_e}{r}\right)^m \right] \right\} \quad 3.6.5. 8.$$

In order to see how this displacement energy, w , varies as the molecule is displaced slightly from its equilibrium

position, we substitute

$$x = \frac{r - r_e}{r_e} \quad 3.6.5.9.$$

so that $\frac{r_e}{r} = \frac{1}{1+x},$ 3.6.5.10.

and on substituting in 3.6.5. 8. we get:

$$w = \frac{-Q_e}{m-n} \left\{ m \left[1 - (1+x)^{-n} \right] - n \left[1 - (1+x)^{-m} \right] \right\} \quad 3.6.5.11.$$

On expanding the terms in the small brackets by means of the binominal expansion, and ignoring powers of x greater than the second, we obtain the expression:

$$w = -\frac{1}{2} mn Q_e x^2 = -\frac{1}{2} \frac{mn Q_e}{r_e^2} (r - r_e)^2 \quad 3.6.5.12.$$

Hence for a small displacement the displacement energy is proportional to the square of the displacement, and therefore the motion is simple harmonic with frequency

$$\nu_e = \frac{1}{2\pi r_e} \sqrt{\frac{mn Q_e}{\mu}} \quad 3.6.5.13.$$

where μ is the reduced mass.

In the large cages in faujasite the largest difference in energy is that between r_e and the centre of the cage, i.e. 12.5 kcals/mole and hence the normal vibrational frequency corresponding to a small displacement of an I_2 molecule from its equilibrium position towards the cage centre is (using equation 3.6.5.13. with $m = 12$ and $n = 6$; μ = mass of I_2 molecule; $r_e = 3.5_5^{\circ} \text{ \AA}$),
 $\nu_e = 1.735 \times 10^{12} \text{ sec}^{-1}.$

This can be compared with the mean vibration frequency of I_2 obtained from thermal entropy considerations (see section 3.8.3) which was found to be $\sim 7.4 \times 10^{11} \text{ sec}^{-1} = \bar{\nu}.$

This gives quite a good agreement as it is expected that the normal vibration frequency, ν_e , should be greater than the mean vibrational frequency, $\bar{\nu}$.

3.6.6. Summary of Section 3.6.

The calculations and considerations of inter-molecular forces have thrown light on the behaviour of occluded iodine in faujasite and on the probable mechanism of intracrystalline diffusion of this sorbate.

The following conclusions were arrived at:

- 1) All the occluded iodine will be located in the large cavities and 12-membered ring windows, none being present in sodalite cages.
- 2) I_2 will easily diffuse into the crystal through the 12-membered ring in faujasite and the 8-membered ring in Linde Sieve 5A, but a small activation energy may be required in the case of diffusion through the 8-membered ring in chabazite.
- 3) The I_2 molecule has to be oriented with its longer diameter perpendicular to the plane of the 8-membered ring to be able to pass through it.
- 4) The occluded I_2 molecule will be located at equilibrium near the wall of the cage at approximately its equilibrium distance of separation and will take up position with its longer diameter parallel to the wall of the cage. This will tend to apply also to other non-polar diatomic molecules.
- 5) The diffusing molecule will not enter through the centre of the 12-membered ring (window) and then diffuse from the centre of one cage to another, but once the entering molecule will come into attractive field of the crystal it will be attracted towards the frame of the

window and then it will diffuse towards the inside of the crystal by moving or rolling, from one sorption site to a neighbouring one, along the walls of the cages.

3.7. Heats of Occlusion.

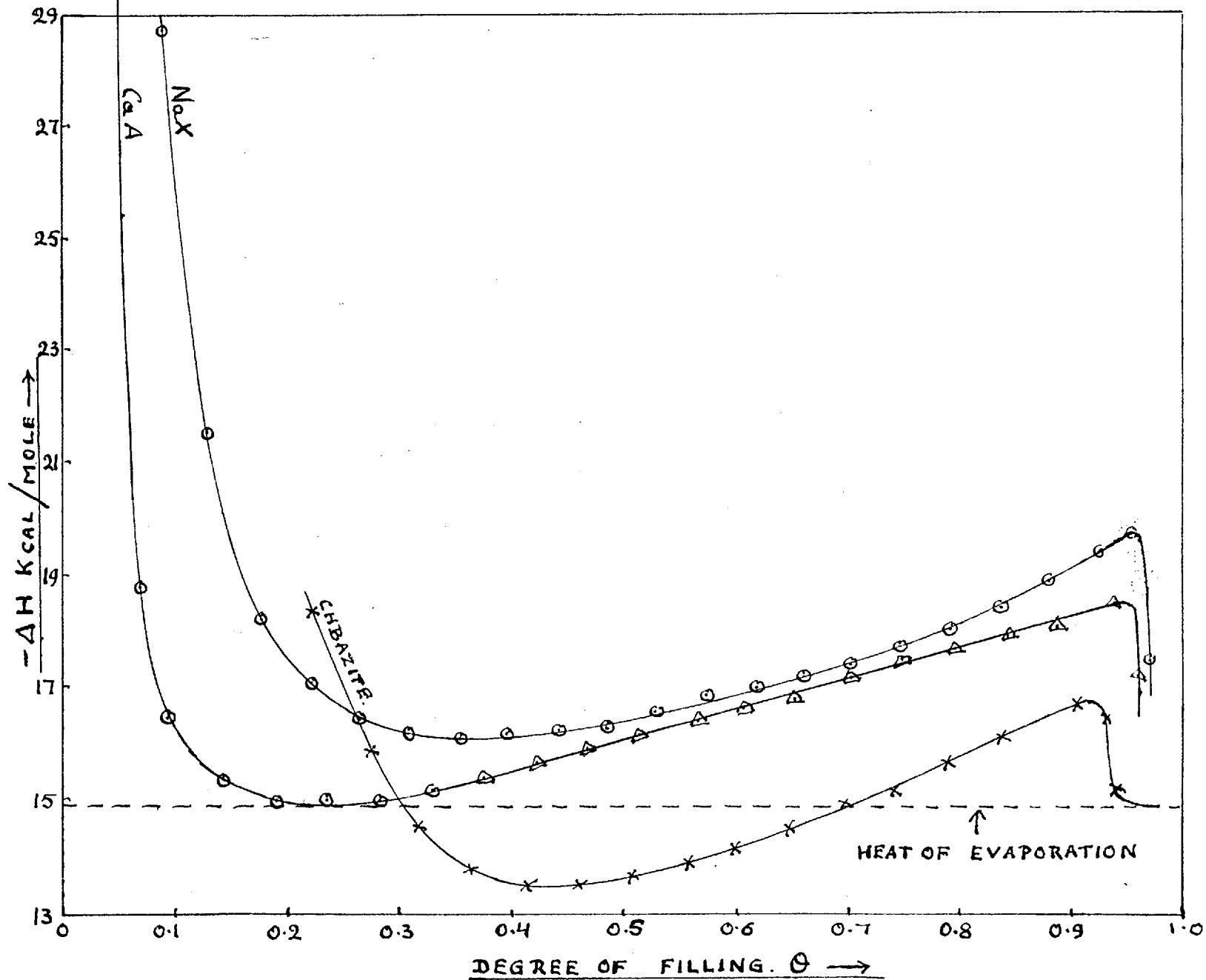
3.7.1. General Discussion of Heat Data.

The isosteric heats of occlusion were obtained from the slope of plots of $\log P_{\text{equil.}}$ against $1/T$ for constant amount sorbed. Linear plots were obtained in all cases within experimental error. These gave the mean isosteric heats over the temperature range studied. There is probably a small change in the isosteric heat with temperature, but this was impossible to estimate with any accuracy. Plots of the mean isosteric heats against amount sorbed are shown in Fig. 21, for the three sorbents studied.

For all the three systems it was possible to evaluate heats from $\Theta \sim 0.1$ to near saturation. The values at both extremes cannot be considered to be very accurate although they follow the general trend in the heat curve.

As can be seen from Fig. 21, there is in all these zeolites an initial sharp drop in the heat curve at very low coverages up to $\Theta \sim 0.3$. It seems that there are a few sites which give high value for the isosteric heat of sorption. This phenomenon has been observed by other workers^(148,149) for polar molecules. Very little energetic heterogeneity has however been observed by Barrer and Stuart⁽¹⁴⁷⁾ in the sorption of argon, and by Reucroft⁽¹⁵⁰⁾ in the sorption of fluorocarbons in faujasite. From the information so far available high isosteric heats of sorption at low coverage may be ascribed to dipole-field interactions. Iodine, with a very high polarisability, may fall into the same group, having polarity induced by the field.

FIG. 21.



MEAN ISOSTERIC HEAT OF OCCLUSION OF I_2 IN ZEOLITES.

From degree of coverage of $\theta \sim 0.3$ there is a gradual increase in the magnitude of the isosteric heat until condensation of iodine on the outside of the crystals begin to occur. Then the isosteric heat drops sharply to a value near to the heat of condensation of iodine. The gradual increase in isosteric heat with increasing θ , at values of $\theta > 0.3$, can be attributed to intermolecular interaction between the sorbed molecules inside the crystals. This is discussed in a later section.

3.7.2. Sorbate-Lattice Interactions.

Since at values of θ of about 0.3, the mutual interaction between sorbed molecules is still small, the heat of occlusion may here reasonably be interpreted in terms of the interaction of an isolated molecule with the oxygen atoms of the lattice, the contribution from aluminium and silicon atoms being neglected as discussed in section 3.6.

The isosteric heat at temperature T is defined by⁽¹⁵¹⁾

$$q_{st}^T = \widetilde{E}_g - \overline{E}_s + RT = \widetilde{E}_g - \widetilde{E}_s - n_s \left(\frac{\partial \widetilde{E}_s}{\partial n_s} \right)_{P, T, n_A} + RT$$

where $\widetilde{E}_g$ and $\widetilde{E}_s$ are molar energy contents of gaseous and sorbed molecules respectively, and $\overline{E}_s$ is the partial molar energy of the sorbed molecules. There are n_s moles of sorbate and n_A moles of zeolite in the mixture. If q_{st}^T is independent of amount sorbed then either there is compensation between the concentration dependence of $\widetilde{E}_s$ and $n_s \frac{\partial \widetilde{E}_s}{\partial n_s}$, or else, as seems likely, $\widetilde{E}_s$ is independent of n_s . In this event, at the minima in the curves of q_{st}^T versus amount sorbed

$$q_{st}^T = \widetilde{E}_g - \widetilde{E}_s + RT.$$

At 0°K the isosteric heat is then, neglecting zero point energy, given by:

$$q_{st}^0 = -Q \quad 3.7.2. 1.$$

Q being the potential energy of the occluded molecules.

The isosteric heat at temperature T is:

$$q_{st}^T = q_{st}^0 - \int_0^T \Delta C_p \, dT \quad 3.7.2. 2.$$

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

The molar heat capacity of gaseous sorbate ($\tilde{C}_g$) is known but unfortunately the partial molar heat capacity ($\bar{C}_s$) of occluded sorbate is not. In order to compare q_{st} at temperature T , rigorously with the potential energy of the sorbed molecules, a knowledge of $\tilde{C}_g$ and $\bar{C}_s$ is required. However, Orr⁽¹²⁰⁾ has concluded that the variation of heat capacity of sorbed argon is not great and that the isosteric heat at temperature T may be directly compared with Q within experimental error. Assuming that this argument is valid also for iodine, the experimental isosteric heats at coverage of $\theta \sim 0.3$ can be directly compared with the potential energy of a sorbed molecule in the intra-crystalline environment, i.e.

$$Q = -q_{st} + RT \quad 3.7.2. 3.$$

The potential energy of a non-polar, spherically symmetrical molecule (see section 3.6) is:

$$Q = Q_D + Q_R + Q_P,$$

neglecting quadrupole interaction. Making the reasonable assumption that at the degree of coverage $\theta \approx 0.2 - 0.3$, that is at the point of minimum in the isosteric heat curve, the polarisation energy has completely died out, therefore the value of isosteric heat at that point is

due to $(Q_D + Q_R)$.

It has been shown in section 3.6.1. that the maximum value of $(Q_D + Q_R)$ for the iodine molecule is -15.1 kcals per gm molecule in the case of iodine occluded in faujasite (see Fig. 19). This can be compared with the value of isosteric heat at the minimum of isosteric heat curve plus the factor RT . For iodine occluded in faujasite q_{st} at its minimum is +16 kcals/mole (see Fig. 21). Taking into account the approximations involved in the calculation of $(Q_D + Q_R)$ and the fact that the isosteric heat is a mean isosteric heat value over large range of temperature, this is a good agreement, qualitatively at least.

If we assume that localised model is valid for the sorption (see section 3.7.3) then small amount of energy due to sorbate-sorbate interaction has to be subtracted from q_{st} at $\theta = 0.3$ to allow for the linear increase of the energy due to sorbate-sorbate interaction with θ the degree of coverage.

3.7.3. Sorbate-Sorbate Interaction.

From Fig. 21 it can be seen that after the degree of filling of intracrystalline volume of $\theta \sim 0.3$ the isosteric heat increases with increasing amount sorbed. This increase is thought to be due to the increasing contributions to the isosteric heat from sorbate-sorbate interactions as the number of occluded molecules increases.

A close inspection of the structure of the zeolites (faujasite, Linde Sieve A and chabazite) suggests, with large sorbed molecules such as iodine, that in the consideration of sorbate-sorbate interaction the large cages, in which the sorbate molecules are

occluded, cannot be considered as isolated units. Rather the crystal has to be regarded as a whole for that purpose. When the crystal is saturated with sorbate molecules, a molecule in one cage has as its neighbours some of those in adjoining cages. Consideration of the saturated crystals in terms of space models showed that in all the three zeolites, mentioned above, iodine has a co-ordination number 4 with respect to other iodine molecules occluded in these crystals.

Assuming that at $\theta > 0.3$ the energy of sorption, at a given value of θ , can be split up into a contribution from the interaction of sorbate molecules with the aluminosilicate framework and a contribution from mutual interaction between sorbate molecules we can write:

$$\bar{E}_s - \widetilde{E}_g = \Delta\bar{E} = \Delta E_L + f(n_s) \quad 3.7.3. 1.$$

where $\bar{E}_s$ = partial molar energy of sorbate in sorbed phase,

$\widetilde{E}_g$ = molar energy of sorbate in gaseous phase,

$\Delta\bar{E}$ = energy given out on sorption,

ΔE_L = energy given out due to sorbate-lattice interaction, assumed independent of θ for $\theta > 0.3$,

$f(n_s)$ = contribution to $\Delta\bar{E}$ from mutual interaction between sorbed molecules, assumed to be a function of the number of molecules occluded (n_s).

$$\begin{aligned} \text{Also } q_{st} &= -\Delta\bar{H} = -(\Delta\bar{E} - RT) \\ &= -(\Delta E_L + f(n_s) - RT) \end{aligned} \quad 3.7.3. 2.$$

We can also write $\bar{E}_s$ in equation 3.7.3. 1. as

$$\bar{E}_s = \frac{\partial}{\partial n_s}(n_s \widetilde{E}_s) \quad 3.7.3. 3.$$

so that

136.

$$\Delta \bar{E} = \left[\bar{E}_s + n_s \left(\frac{\partial \bar{E}_s}{\partial n_s} \right)_{P,T,n_A} \right] - \bar{E}_g \quad 3.7.3. 4.$$

where $\bar{E}_s$ = molar energy of sorbate in sorbed phase

n_A = moles of zeolite in the mixture.

$$\text{But } \bar{E}_s = \bar{E}_{I_2-L} + \bar{E}_{I_2-I_2} \quad 3.7.3. 5.$$

where $\bar{E}_{I_2-L}$ = molar energy of sorbate in sorbed phase

due to I_2 -lattice interaction,

$\bar{E}_{I_2-I_2}$ = ditto, due to I_2 - I_2 interaction.

$$\begin{aligned} \therefore \Delta \bar{E} &= (\bar{E}_{I_2-L} + \bar{E}_{I_2-I_2}) + n_s \frac{\partial (\bar{E}_{I_2-L} + \bar{E}_{I_2-I_2})}{\partial n_s} - \bar{E}_g \\ &= \bar{E}_{I_2-L} + \bar{E}_{I_2-I_2} + n_s \frac{\partial \bar{E}_{I_2-I_2}}{\partial n_s} - \bar{E}_g \end{aligned} \quad 3.7.3. 6.$$

if $\bar{E}_{I_2-L}$ does not vary with amount sorbed (assumption made for $\theta >$ about 0.3). If we now consider localised sorption we may set

$$\bar{E}_{I_2-I_2} = \frac{1}{2} (u) \theta \cdot z \quad 3.7.3. 7.$$

where z = co-ordination number of sorbed I_2 ,

u = energy of interaction per Avogadro no. of bonds at distance corresponding to separation of adjacent sites.

From 3.7.3. 7.

$$n_s \frac{\partial \bar{E}_{I_2-I_2}}{\partial n_s} = \theta \cdot \frac{\partial \bar{E}_{I_2-I_2}}{\partial \theta} = \frac{1}{2} (u) \theta \cdot z \quad 3.7.3. 8.$$

$$\text{Also, } \bar{E}_{I_2-I_2} = \frac{\partial}{\partial n_s} (n_s \bar{E}_{I_2-I_2})_{P,T,n_A} = f(n_s)$$

$$= \bar{E}_{I_2-I_2} + \left(n_s \frac{\partial \bar{E}_{I_2-I_2}}{\partial n_s} \right)_{P,T,n_A} \quad 3.7.3. 9.$$

$\therefore$ from 3.7.3. 7. and 3.7.3. 8.

$$\bar{E}_{I_2-I_2} = (\bar{E}_{I_2-I_2} + n_s \frac{\partial \bar{E}_{I_2-I_2}}{\partial n_s} = (u) \theta. z \quad 3.7.3.10.$$

where $\bar{E}_{I_2-I_2}$ = contribution to isosteric heat from mutual interaction due to iodine.

At the maximum in the isosteric heat curve, $\theta \sim 1$, and so

$$\bar{E}_{I_2-I_2} = uz = 4u \quad 3.7.3.11.$$

Also, $\bar{E}_{I_2-I_2}$ should increase linearly with amount sorbed.

The potential energy of interaction per Avogadro no. of bonds, u , for I_2 was obtained from the potential energy plot Fig. 22 (curve I), which was calculated using the Lennard-Jones potential energy function, i.e.

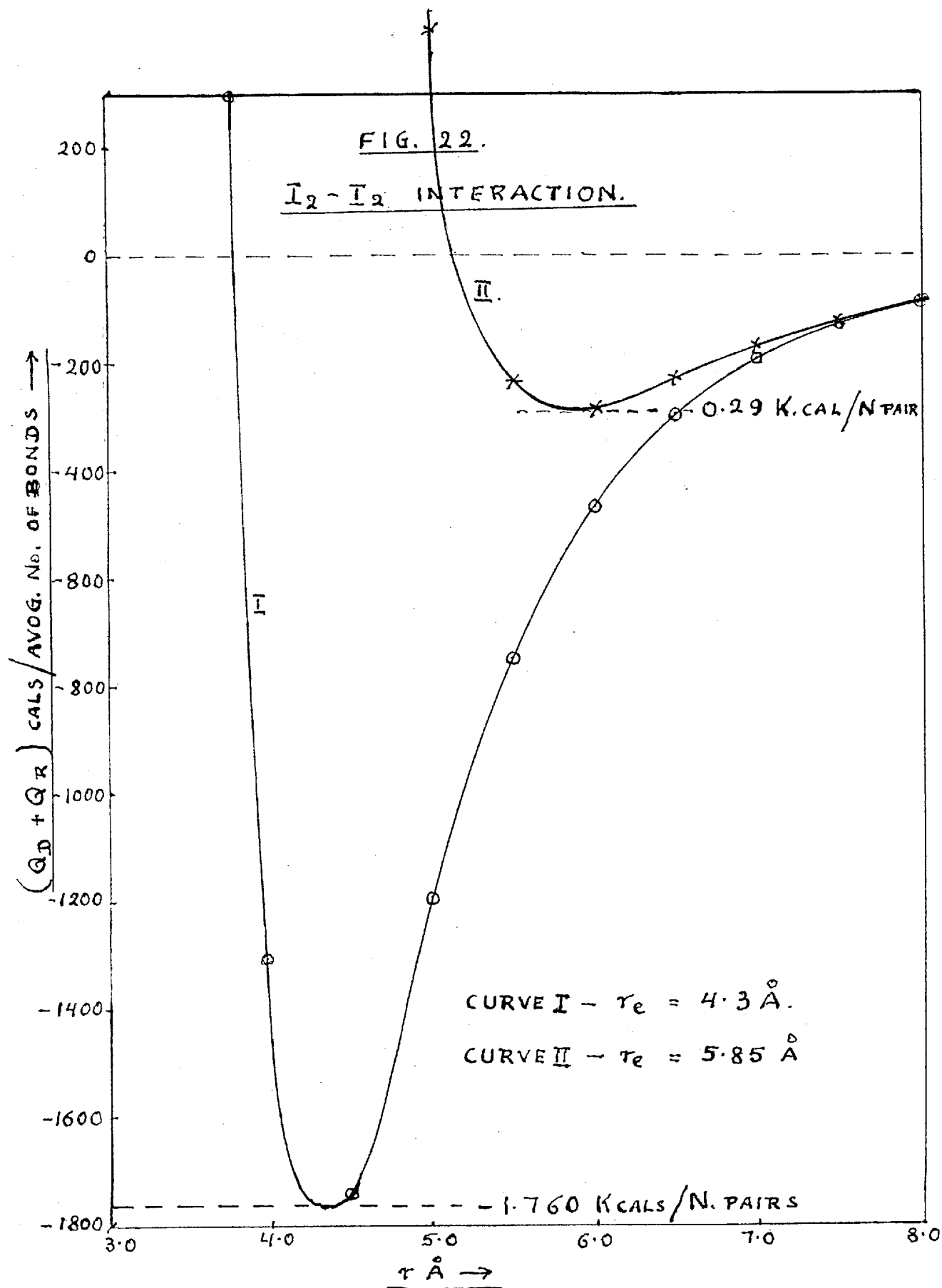
$$Q = \frac{-A}{r^6} \left(1 - \frac{r_e^6}{2r^6} \right)$$

The meaning of the symbols in this equation has been explained in section 3.6. It was assumed that the distance between sites in the crystal is the equilibrium distance corresponding to orientation (i) shown overleaf.

From Fig. 22, the potential energy of interaction between two isolated iodine molecules at this equilibrium separation is $(u) = -1.76$ kcals/Avogadro No. of bonds. The value obtained from latent heat of sublimation is -1.79 kcals/Avogadro No. of bonds. For I_2 in faujasite (see Fig. 21) the minimum in isosteric heat curve is at $\theta = 0.35$. The difference between maximum and minimum in the isosteric heat curve is -3.7 kcals/mole, therefore, to compare this value with that obtained from equation 3.7.3.11. we have to subtract value for $\bar{E}_{I_2-I_2}$ at $\theta = 0.35$, i.e.

$$(\bar{E}_{I_2-I_2})_{\text{Max-Min}} = (\bar{E}_{I_2-I_2})_{\theta=1} - (\bar{E}_{I_2-I_2})_{\theta=0.35}$$

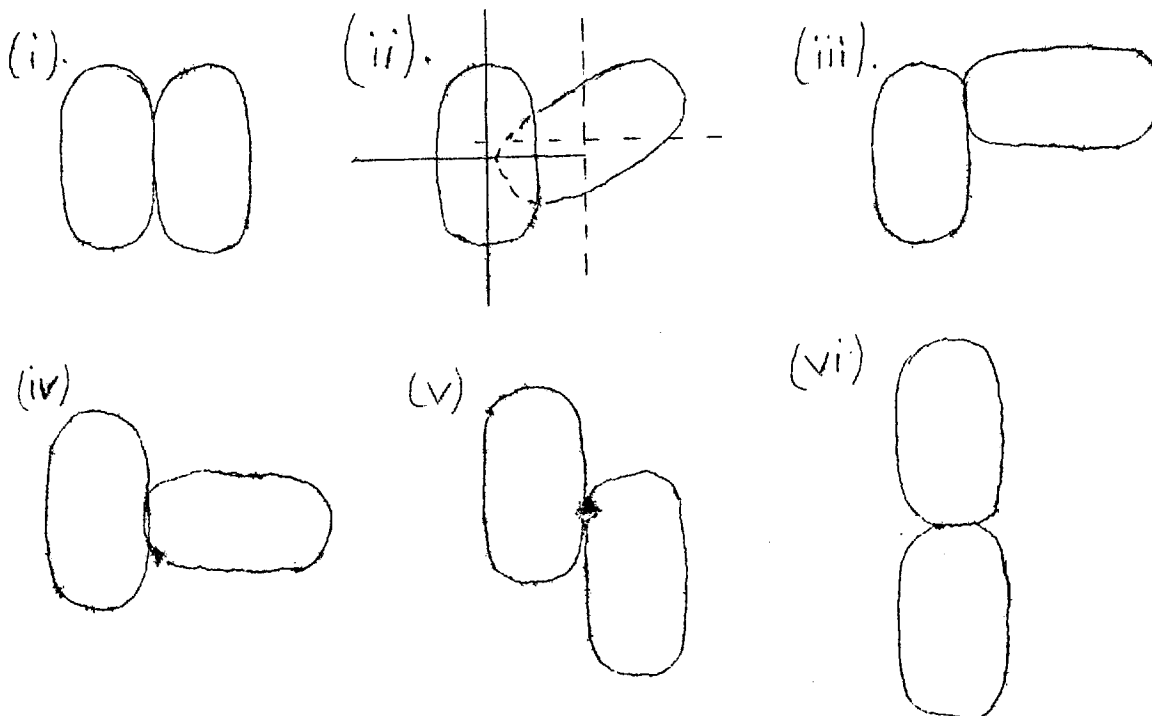
$$\begin{aligned} \text{from 3.7.3.11.} &= 4u \times 0.65 \\ &= \underline{4.6 \text{ kcals/mole.}} \end{aligned}$$



Values of $(\Delta H_{\text{Max}} - \Delta H_{\text{Min}})$ and the calculated values of contribution to ΔH from sorbate-sorbate interaction are given in the table below for the three zeolites.

Zeolite	$-(u)$ kcal/ Avog. No. of bonds	c =co-ordi- nation number	$(\bar{E}_{\text{I}_2-\text{I}_2})_{\text{Max}} -$ $(\bar{E}_{\text{I}_2-\text{I}_2})_{\text{Min}}$ kcal/mole	$-(\Delta H_{\text{Max}} - \Delta H_{\text{Min}})$ kcal/mole
Faujasite	1.76	4	4.6	3.7
Linde Sieve 5A	1.76	4	4.9	3.6
Chabazite	1.76	4	4.2	3.3

In the calculation of the energy of interaction between I_2 molecules, the equilibrium separation was, as noted, taken corresponding to case (i) below, whereas in the crystal they might be arranged in different ways such as are given below:



Thus, the average energy of interaction per "bond" may be less than (u). The energy of interaction for the extreme case (vi) is shown in Fig. 22 (curve II) and is only -0.29 kcal/Avogadro No. of bonds. Therefore the values of $(\bar{E}_{I_2-K_2})_{\text{Max}} - (\bar{E}_{I_2-I_2})_{\text{Min}}$ may be less than those given in the table. It can be concluded that this treatment of sorbate-sorbate interaction gives reasonable correspondence with experimental observations. It also follows that the treatment of sorbate-sorbate interaction as given by Reucroft (1959) is less satisfactory as it gives much too low values for I_2-I_2 interaction in chabazite.

Summing up section 3.7, it can be concluded, taking into account the approximations and assumptions involved in assessing inter-molecular forces, that the experimental heats of occlusion, observed in this study, can be adequately explained in terms of:

- a) surface heterogeneity at lower coverage ($\theta < \text{about } 0.3$);
- b) interaction of sorbate molecules with the oxygens of crystal lattice, which remains independent of the amount sorbed for higher coverages ($\theta > 0.3$);
- c) mutual interaction between the sorbed molecules, this being a function of the number of molecules sorbed.

3.7.4. Comparison between sorbents.

The isosteric heat curves for the three sorbents have similar shape (Fig. 21) but they are displaced laterally in the following order:

Faujasite $>$ Linde Sieve 5A $>$ Chabazite.

This observation is in the order of the size of the cages of these sorbents. The curves (except at initial values) for faujasite (NaX) and Linde Sieve 5A (CaA) are very close together, whereas the chabazite curve falls much lower. The sequence may be determined by several factors:

- i) the size of cavity (for Q_D , Q_R and Q_P);
- ii) the number and the detailed arrangement of the polarizing centres relative to I_2 molecule (for Q_P at $\theta < 0.3$);
- iii) the total number of oxygen atoms in the first shell (for Q_D and Q_R).

There is also the question of field gradients between cations and anionic centres, important if the I_2 molecule proves to have a quadrupole moment. At present no detailed discussion of the relative importance of these factors is warranted.

3.8. Entropy of Occlusion.

3.8.1. Discussion of Entropy.

The partial molar entropies of the sorbed molecules were evaluated from the isosteric heat data and standard gas state entropies, using the relationship

$$\bar{S}_s = \tilde{S}_{og} + C_p \ln \frac{T_2}{T_1} + R \ln \frac{p^\#}{p} + \frac{\Delta \bar{H}}{T} \quad 3.8.1. 1.$$

where $\bar{S}_s$ = partial molar entropy of the sorbate,
 $\tilde{S}_{og}$ = standard entropy of gaseous phase at 25°C,
 C_p = heat capacity of sorbate at constant pressure,
 $p^\#$ = standard pressure (760 mm Hg),
 p = equilibrium pressure.

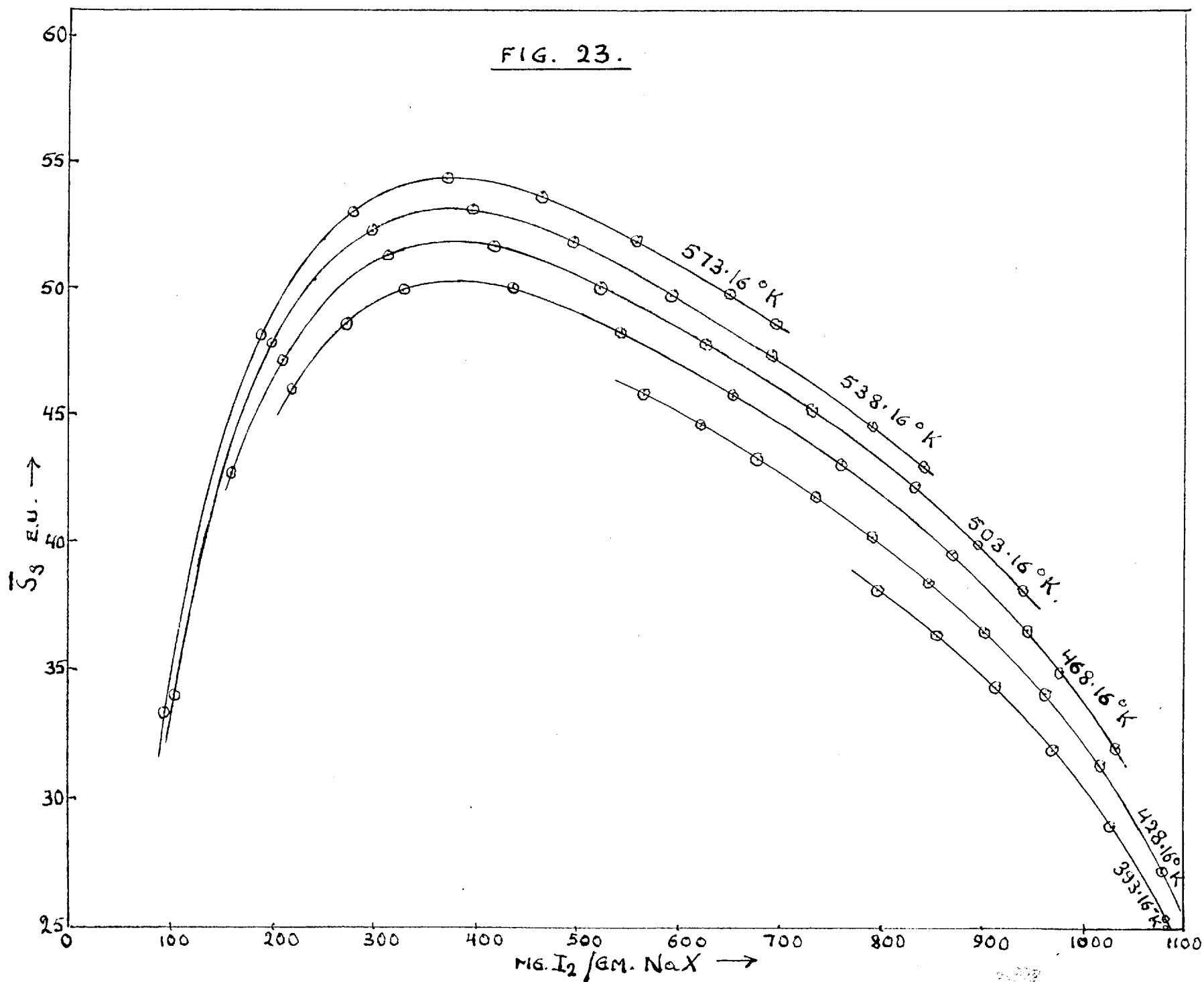
The plots of $\bar{S}_s$ against amount sorbed for the three

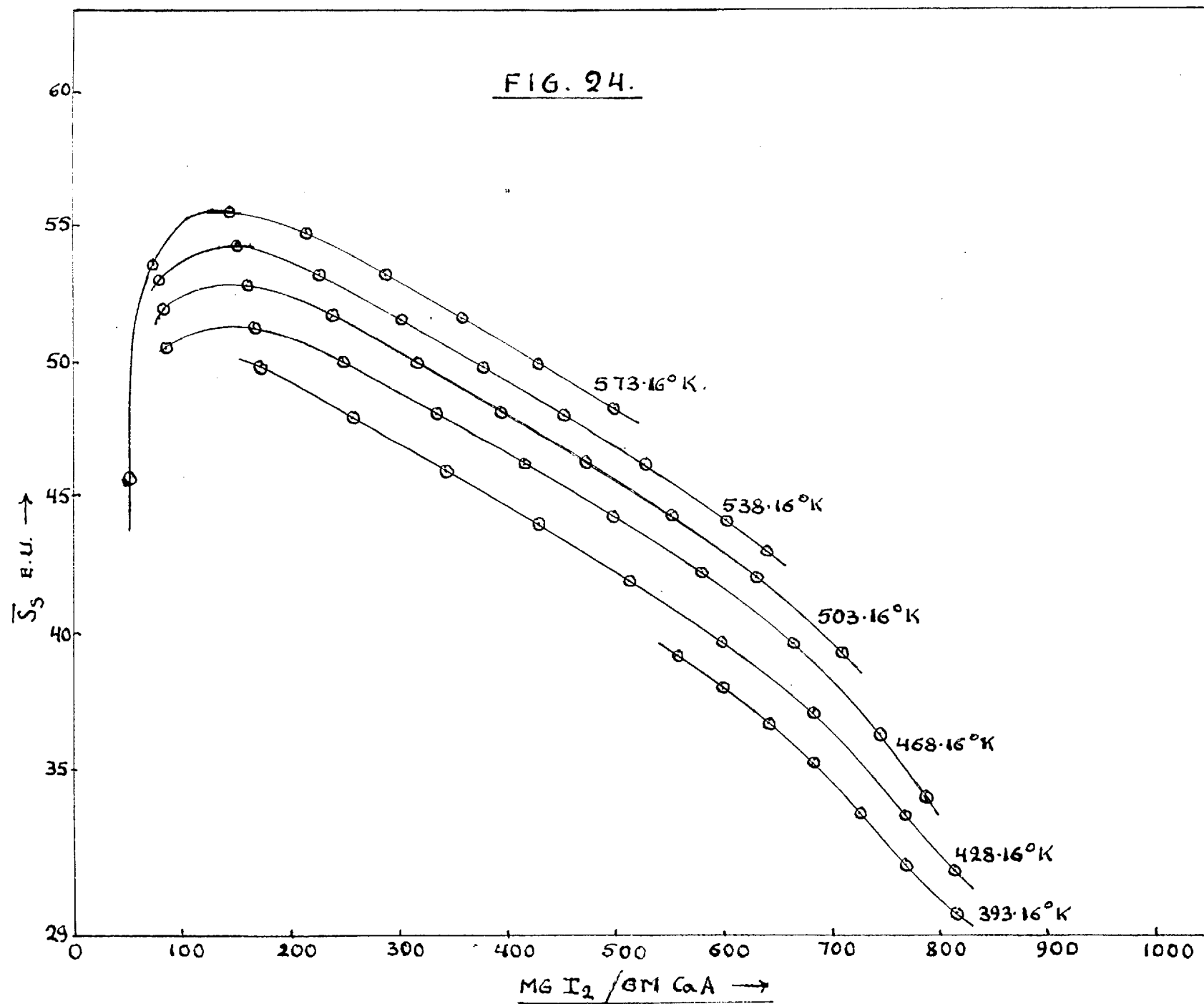
systems studied are shown in Fig. 23, 24 and 25. Due to the fact that thermal entropy is correlated with the isosteric heat ($\Delta\bar{H}$), the entropy curves tend to be mirror reflections of the isosteric heat curves. For very small values of θ the entropy has a low value suggesting, as shown by the isosteric heat curve, that the sorbate molecules are strongly bound to the sorption sites. As θ increases the entropy of the sorbate rises rapidly until it reaches a maximum at $\theta \sim 0.3$. The high value of the entropy at this point is reasonable since at this stage the sorbate molecule is less energetically bound than for any other value of θ , and so may have more vibrational and rotational freedom. At $\theta > \sim 0.3$, the partial molar entropy of sorbate falls steadily with θ , a behaviour attributed to the increase of sorbate-sorbate interaction coupled with increasing restriction to rotation and increasing frequency of vibration of the sorbed molecules (see Fig. 41).

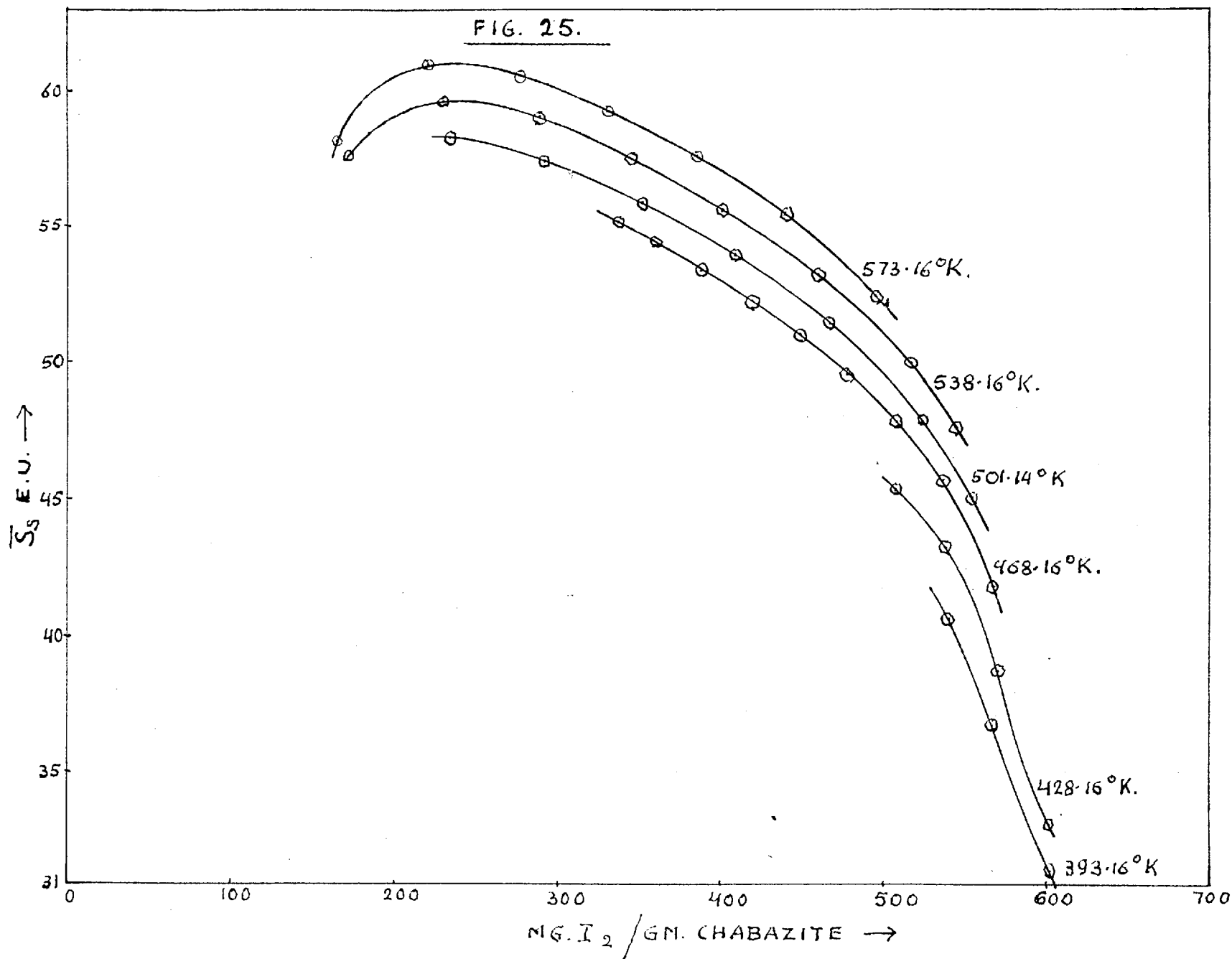
The partial molar entropy, $\bar{S}_s$, of the occluded molecules can be split into partial molar configurational entropy, $\bar{S}_c$, of the intracrystalline guest molecules which have undergone localized occlusion, and their differential thermal entropy, $\bar{S}_{Th}$.

$$\text{i.e. } \bar{S}_s = \bar{S}_c + \bar{S}_{Th} \quad 1.8.1. 2.$$

This assumption should be treated with caution however as Everett⁽¹⁵²⁾ has pointed out that the configurational entropy for energetically heterogeneous surfaces may not contain a separable term of the form $R \ln \frac{(1 - \theta)}{\theta}$ and hence the use of such an expression may be incorrect. Hill⁽¹⁵³⁾ also suggests that for a localized sorbed phase with interaction on a heterogeneous surface, the division of the entropy into configurational and non-configurational term is arbitrary.







In our case, however, it will be shown that the sorbed phase of iodine obeys the Langmuir ideal localized model over a wide range of θ and therefore it is reasonable that the partial molar configurational entropy, $\bar{S}_c$, of iodine be estimated in this range from the equation

$$\bar{S}_c = R \ln \frac{(1 - \theta)}{\theta} \quad 3.8.1. 3.$$

for which the isotherm constant is

$$K_1 = \frac{\theta}{p(1 - \theta)} \quad 3.8.1. 4.$$

The plot of the partial molar configurational entropy, thus calculated, against θ is shown in Fig. 26. Fig. 27 shows, for a typical example, the partial molar thermal entropy, obtained from equation 1.8.1. 2, plotted against amount sorbed. On the same Fig. is plotted $\bar{S}_s$ for comparison. According to the Langmuir model the thermal entropy should not vary with the amount sorbed. However, in the case of iodine occluded in zeolites it does vary with θ , as can be seen from Fig. 27.

3.8.2. Variation of thermal entropy with θ .

In Section 3.7, it has been established that the variation in isosteric heat is due to (a) initial surface heterogeneity for $\theta < 0.3$, and (b) sorbate-sorbate interaction, and this is, therefore, expected to give a deviation from the ideal isotherm equation of Langmuir. However, since in the derivation of the Langmuir isotherm equation a constant thermal entropy of the sorbed molecules is also assumed, it is clear that a variation of the thermal entropy of the sorbed species with θ will give rise to another deviation from the ideal Langmuir equation. Everett⁽¹⁵²⁾ proposed a

FIG. 26.

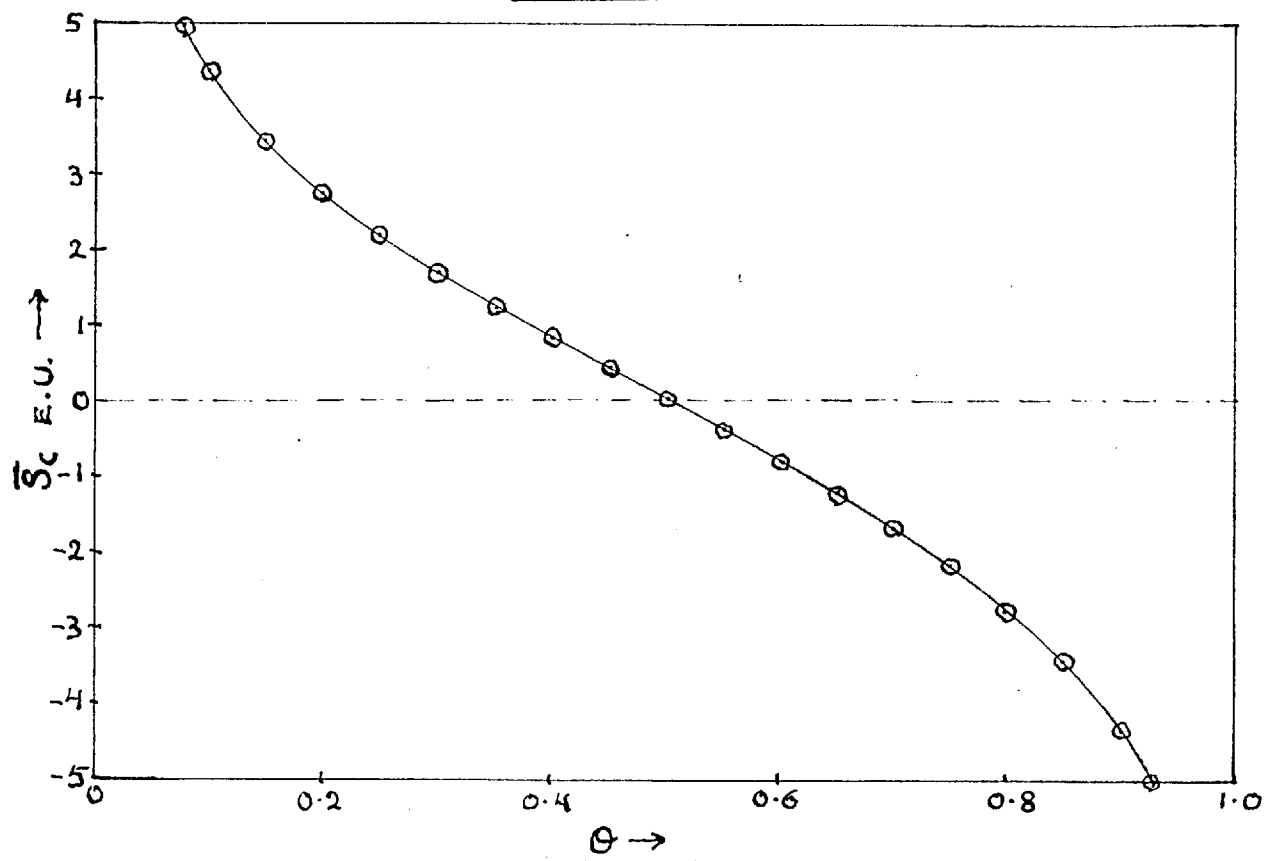
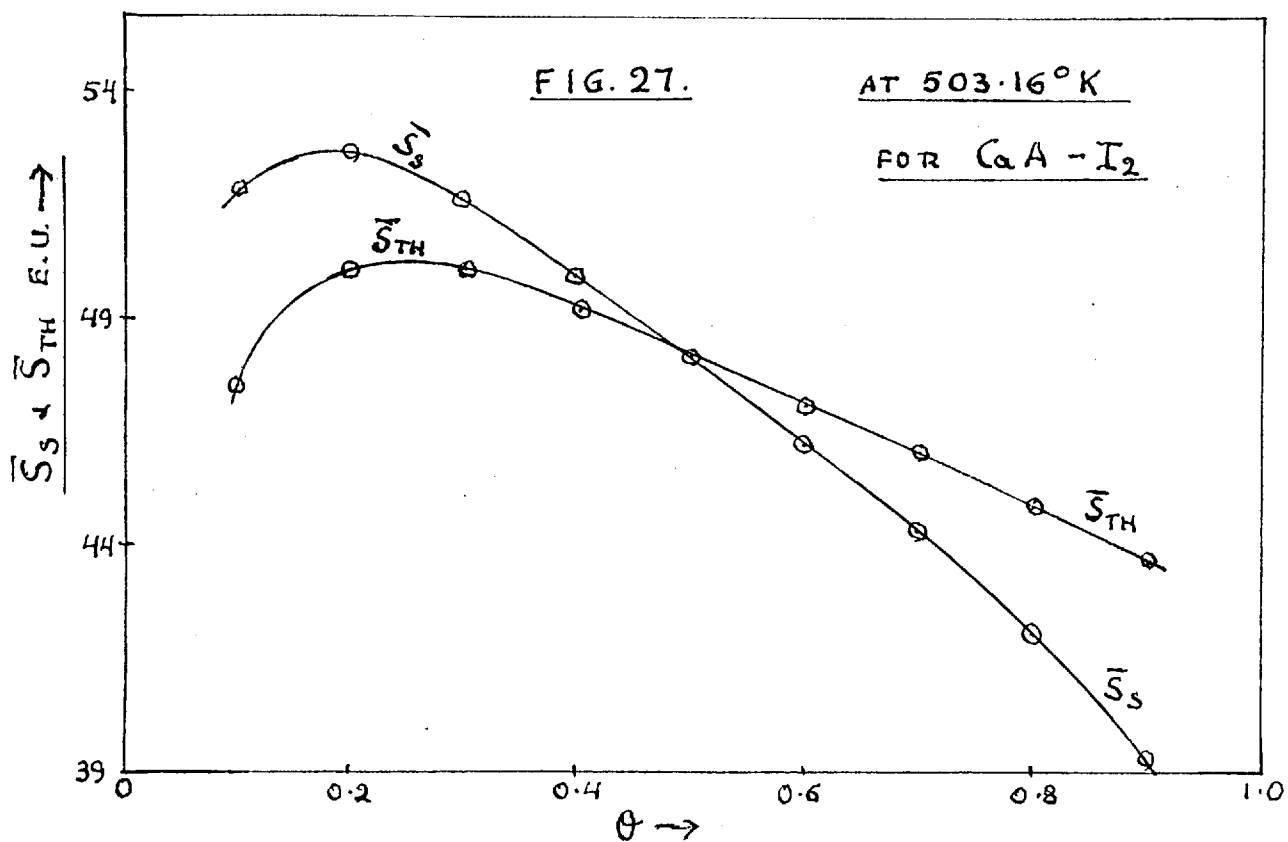


FIG. 27.

AT 503.16°K

FOR $C_6A - I_2$ 

more general isotherm equation, i.e.

$$P = \exp\left(\frac{-\Delta\bar{H}}{RT} + \frac{\Delta S^T}{R}\right) \frac{\theta}{(1 - \theta)} \quad 3.8.2. 1.$$

where $\Delta\bar{H} = \bar{H}_g - \bar{H}_s$
and $\Delta S^T = \bar{S}_g^0 - (\bar{S}_s - \bar{S}_c) = -(\Delta S^0 - \bar{S}_c)$.

ΔS^T is thus the entropy of adsorption leaving out the configurational entropy of sorbed molecules and assuming that the latter is given by

$$\bar{S}_c = R \ln \frac{(1 - \theta)}{\theta} \quad 3.8.2. 2.$$

From equation 3.8.2. 1. it follows that, if both $\Delta\bar{H}$ and ΔS^T are independent of θ , the equation becomes the ideal Langmuir equation, i.e.

$$K_1 = \frac{\theta}{p(1 - \theta)} \quad 3.8.2. 3.$$

If, however, only ΔS^T is independent of θ , the equation reduces to an equation similar to the Fowler⁽⁹⁸⁾ equation, allowing for the effect of mutual interaction between sorbed molecules, i.e.

$$P = K_6 \frac{\theta}{(1 - \theta)} \exp\left(\frac{2 w \theta}{kT}\right) \quad 3.8.2. 4.$$

provided the variation in isosteric heat is due only to the mutual attractions between sorbed molecules.

However, in this study it has been found that not only isosteric heat, but also the partial molar thermal entropy of occluded iodine varies with θ . Therefore Everett's equation (3.8.2. 1.) should give a better description of the actual behaviour of the sorbed molecules. Thus, as expected, if we consider the factor, $\exp\left[\frac{\Delta\bar{H} - T\Delta S^T}{RT}\right]$ from Everett's equation, and

substitute the values of $\Delta\bar{H} = f_1(\theta)$ and $\Delta S^T = f_2(\theta)$ into it and then multiply the quotient $K_1' = \frac{p(1-\theta)}{\theta}$ by this factor for different values of P we obtain a true constant. The factor $\exp\left[\frac{\Delta H - T\Delta S^T}{RT}\right]$ itself varies much less with θ than might be expected from individual θ -dependences of ΔH and of $T\Delta S^T$ because the two θ -dependences partially compensate. The variation with θ of the quotient K_1' is therefore reduced and in fact we shall see (Section 3.9) that it may be rather constant over certain considerable ranges in θ .

3.8.3. Variation of thermal entropy with $\Delta\bar{H}$, and vibrational frequency of occluded iodine.

A plot of the thermal entropy against $\Delta\bar{H}$ for iodine occluded in the synthetic zeolite, Linde Sieve 5A, at 503°K is almost linear as shown in Fig. 40.

Thus we may write

$$\bar{S}_{Th} = A + B\Delta\bar{H} \quad 3.8.3. 1.$$

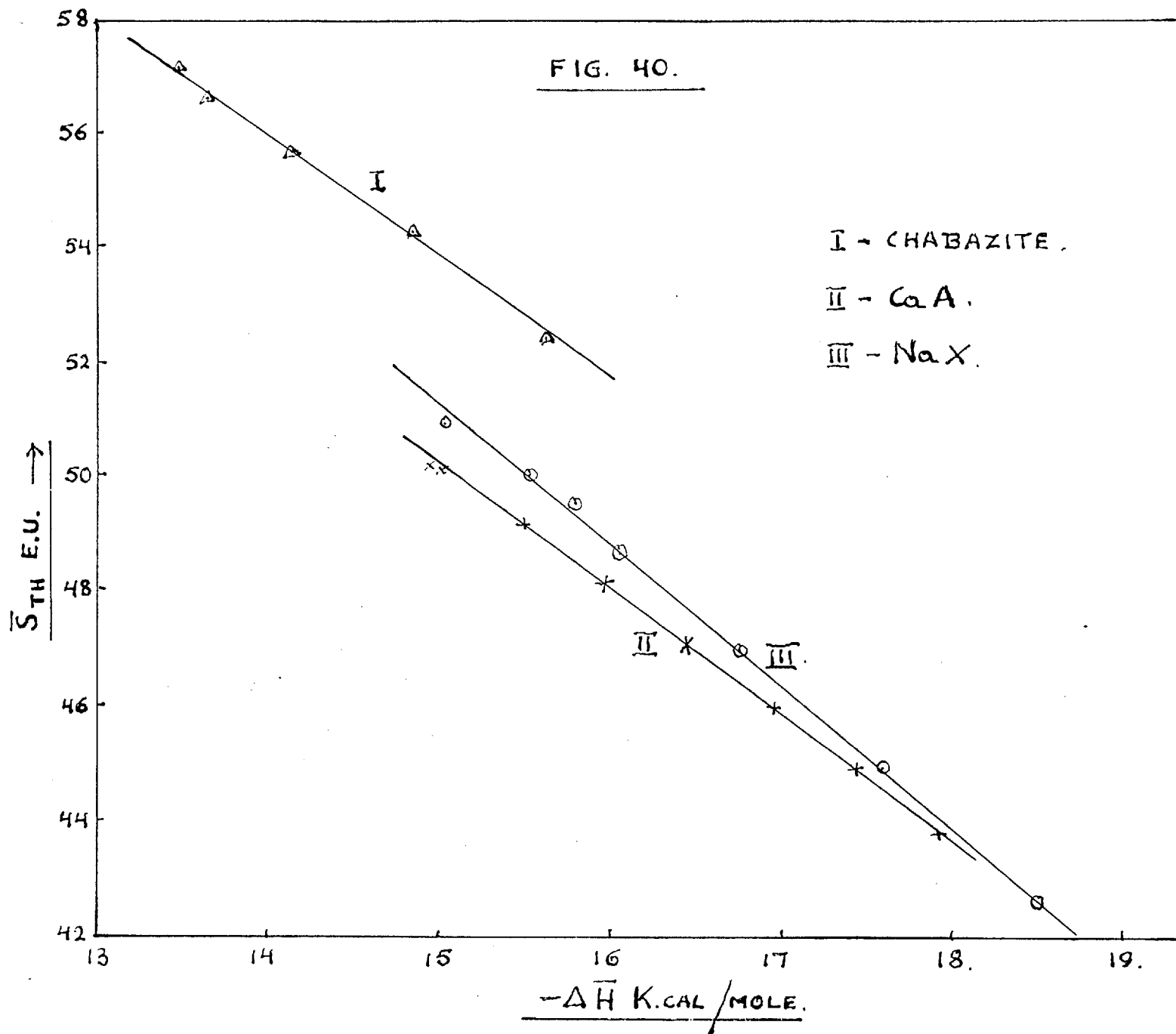
where A and B are constants which can be obtained from the graph (Fig. 40) for a given temperature of occlusion.

Also from Everett's isotherm equation

$$K(\theta) = \frac{P(1-\theta)}{\theta} = \exp\left(\frac{-\Delta\bar{H} + T\Delta\bar{S}}{RT}\right) \quad 3.8.3. 2.$$

$$= \exp\left[\frac{-(\bar{H}_s - \bar{H}_g) + T(\bar{S}_{Th} - \tilde{S}_g')}{RT}\right] \quad 3.8.3. 3.$$

where, $\tilde{S}_g'$ = integral entropy of sorbate in the gas phase at 1 atmosphere pressure and the given temperature.



Substituting 3.8.3. 1, in equation 3.8.3. 3, we get

$$K(\theta) = \frac{P(1 - \theta)}{\theta} = \exp \left[\frac{-\Delta \bar{H}}{RT} + \frac{A + B \Delta \bar{H}}{R} - \frac{\tilde{S}_g'}{R} \right] \quad 3.8.3. 4.$$

$$= \left[\frac{-F(\theta)(1 - BT)}{RT} + \frac{A - \tilde{S}_g'}{R} \right] \quad 3.8.3. 5.$$

$$= K_0 \exp \left[\frac{-F(\theta)(1 - BT)}{RT} \right] \quad 3.8.3. 6.$$

where $K_0 = \exp \left(\frac{A - \tilde{S}_g'}{R} \right)$

and $F(\theta)$ = function of $\theta = \Delta \bar{H}$.

Equation 3.8.3. 6. is a general isotherm equation for sorption of iodine in the three zeolites studied and should fit the experimental data.

We now consider the localised model (vi) of Table 3:

$$K(\theta) = \frac{1}{k'T} \left(\frac{kT}{2 \pi m} \right)^{\frac{3}{2}} \cdot \frac{1}{\bar{\nu}^5} \cdot \frac{kT}{8 \pi^3} \cdot \frac{1}{I} \exp \frac{\alpha}{RT} \quad 3.8.3. 7.$$

where I = principal moment of inertia of I_2 molecule,
 $\bar{\nu}$ = mean frequency of vibration of I_2 molecule,
 m = mass of I_2 molecule,
 k = Boltzman constant,
 k' = Boltzman constant expressed in cc.cm for isotherm pressure measured in cm.
 α = least energy required to remove sorbate molecule from infinite amount of zeolite to the gas phase.

$$\text{Also } \Delta \bar{H} = -\alpha + \frac{3}{2} RT \quad 3.8.3. 8.$$

$$\therefore K(\theta) = \frac{1}{k'T} \left(\frac{kT}{2 \pi m} \right)^{\frac{3}{2}} \cdot \frac{1}{\bar{\nu}^5} \cdot \frac{kT}{8 \pi^3} \cdot \frac{1}{I} \exp \left(\frac{-\Delta \bar{H} + \frac{3}{2} RT}{RT} \right) \quad 3.8.3. 9.$$

Equating 3.8.3. 4. with 3.8.3. 9. we get

$$\begin{aligned} \frac{1}{k'T} \left(\frac{kT}{2\pi m} \right)^{\frac{3}{2}} \cdot \frac{1}{\bar{\nu}^3} \cdot \frac{kT}{8\pi^3} \cdot \frac{1}{I} \cdot \exp\left(\frac{3}{2}\right) &= \exp\left[\frac{A + B\Delta\bar{H}}{R} - \frac{\tilde{S}_g'}{R} \right] \\ &= \exp\left(\frac{\bar{S}_{Th} - \tilde{S}_g'}{R} \right) \end{aligned}$$

3.8.3.10.

From equation 3.8.3.10, it follows that $\bar{\nu}$, the mean vibrational frequency of occluded iodine molecule, is a function of θ which can be calculated.

The mean vibrational frequency of iodine occluded in the zeolite Linde Sieve 5A at 503.16°K is shown in Fig. 41, as a function of θ . From this Fig. it is seen that at $\theta > 0.3$, the mean vibrational frequency, $\bar{\nu}$, increases with θ and as a result of this the entropy of occluded iodine, $\bar{S}_g$, decreases with θ at $\theta > 0.3$. See Figs. 23, 24, 25 and 27.

3.8.4. Comparison between sorbents.

Fig. 28 shows the plots against θ of the partial molar entropy of iodine occluded in the three zeolites at 538.16°K. The shapes of these curves suggest similarity in behaviour of occluded iodine in the three zeolites and the upward displacement of these curves suggest that iodine is more stable in faujasite (NaX) than in Linde Sieve 5A (CaA) than in chabazite, although the difference between faujasite and Linde Sieve A is negligible. The displacement of the entropy curves is the inverse of the displacement of the isosteric heat curves for the same sorbents (see Fig. 21, page 131), because entropy is correlated with $\Delta\bar{H}$, the isosteric heat.

FIG. 41.

I_2 IN $C_{\alpha A}$ -VARIATION OF MEAN VIBRATIONAL FREQUENCY AT 503.16° K.

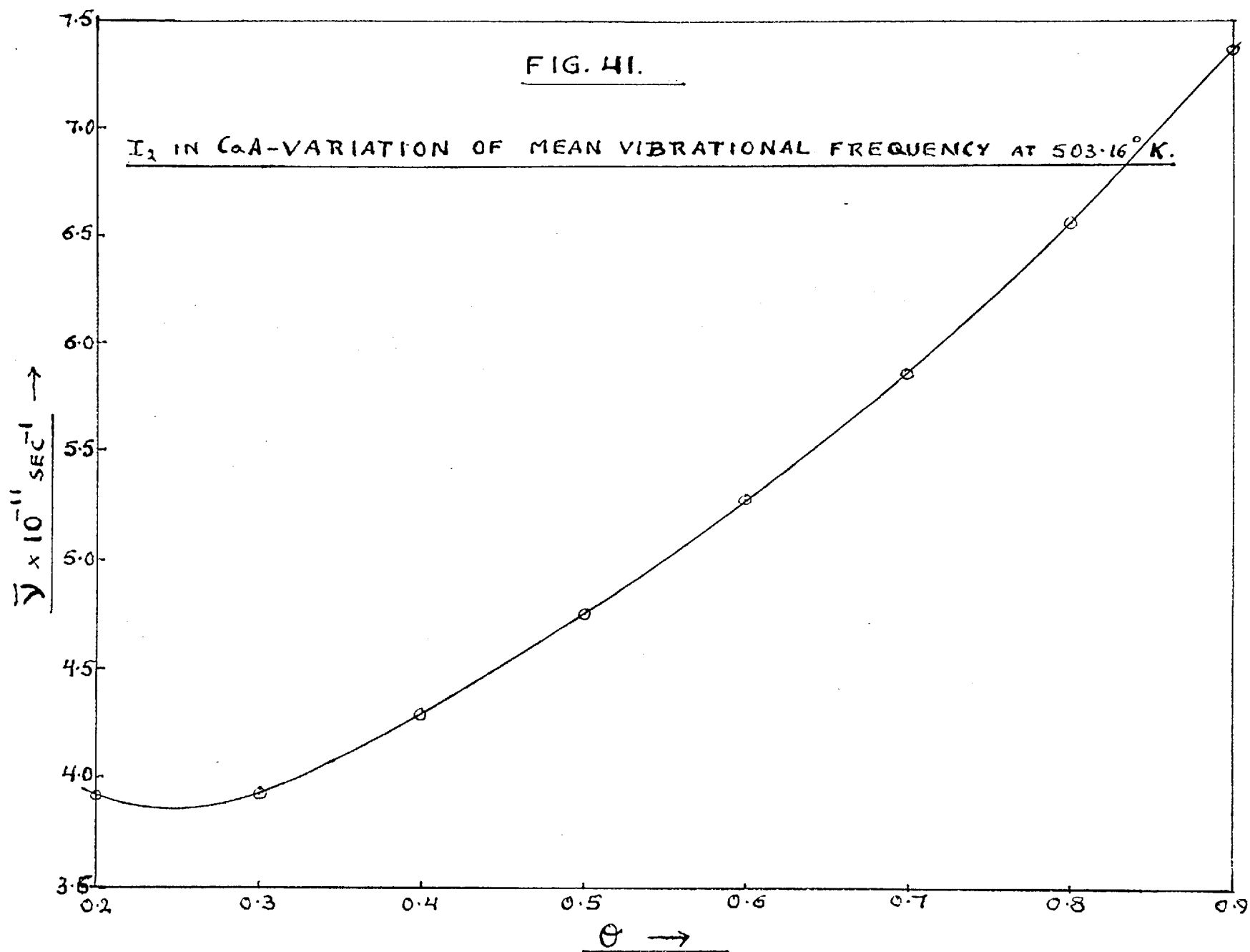
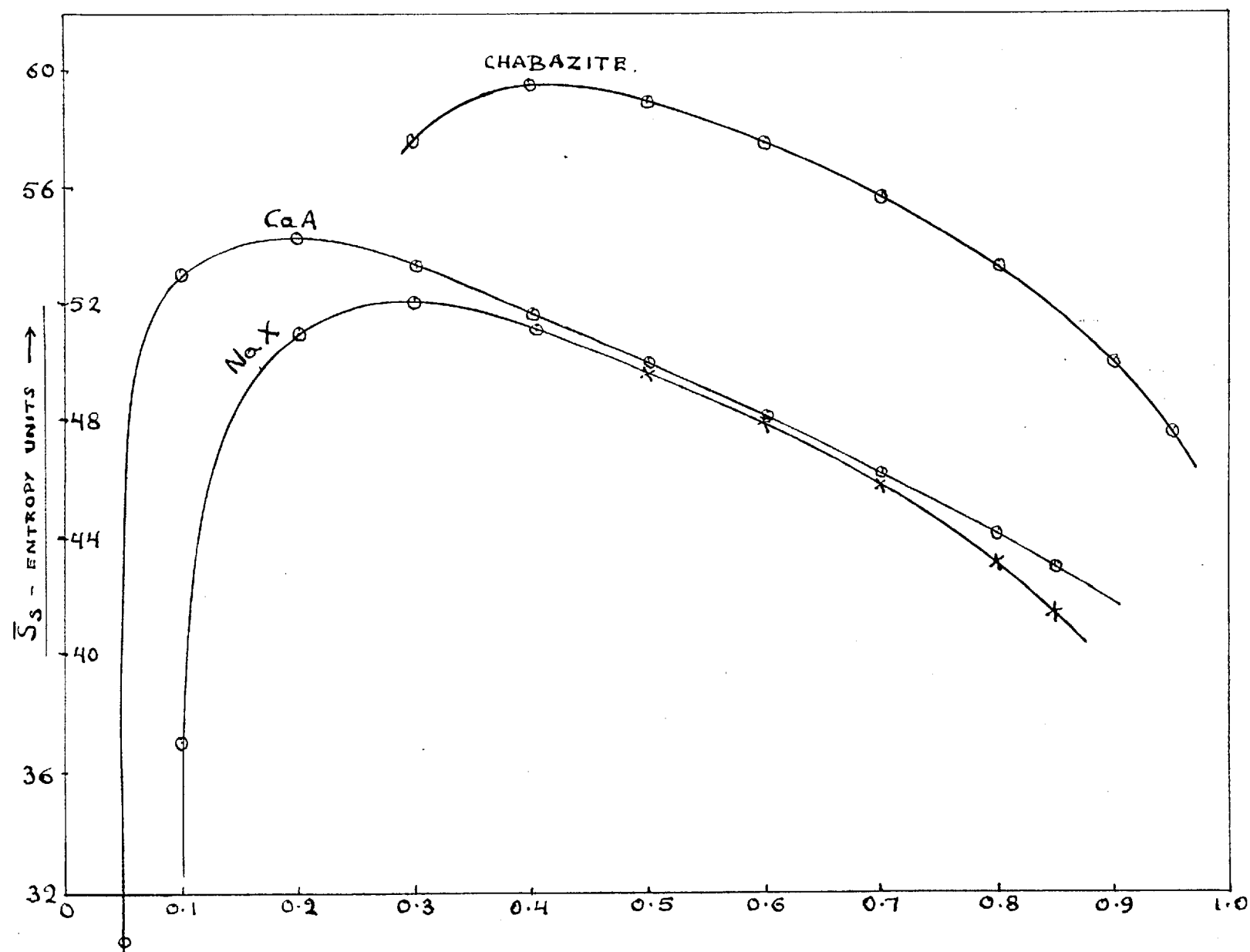


FIG. 28.

PARTIAL MOLAR ENTROPY OF IODINE OCCLUDED IN ZEOLITES AT 538.16°K.



3.9. Free Energy Consideration.

If we regard the crystal framework as inert, and consider the transfer of a mole of gaseous sorbate from the gas phase where its activity is a_g to an infinite amount of the zeolitic solution where its activity is a_z the free energy of transfer is⁽¹⁵⁴⁾:

$$\begin{aligned}\Delta A &= -RT \ln \frac{(a_e)_z}{(a_e)_g} + RT \ln \frac{a_z}{a_g} \\ &= -RT \ln K + RT \ln \frac{a_z}{a_g}\end{aligned}\quad 3.9. 1.$$

where $(a_e)_z$ and $(a_e)_g$ are respectively the activities of occluded and of gaseous sorbate and K is the equilibrium constant. If $a_z = a_g = 1$, then $\Delta A = \Delta A^\circ = -RT \ln K$

3.9. 2.

where ΔA° is the standard free energy of sorption, and $K = (a_e)_z / (a_e)_g$.

In an equilibrium system, $\Delta A = 0$, and so $\mu_g = \mu_z$, where μ denotes the chemical potential of sorbate molecules. For the gaseous sorbate

$$\frac{\mu_g}{kT} = \ln \frac{p}{kT} - \ln \frac{(2\pi m k T)^{3/2}}{h^3} - \ln j(T) \quad 3.9. 3.$$

for molecules of mass m at pressure p . $j(T)$ is the partition function for rotational, vibrational and electronic states of the molecule.

The chemical potential, μ_z , of the intracrystalline molecules can only be defined if a model for the sorbed state is available. For this purpose, the whole intracrystalline volume V_1 may for the simplest model be regarded as composed of N_s equal sites each able to accommodate one sorbate molecule, and that the situation

corresponds to localised sorption as in Langmuir's isotherm. Then

$$\frac{\mu_z}{kT} = \ln \left[\frac{\theta}{1 - \theta} \cdot \frac{1}{a(T)} \right] \quad 3.9. 4.$$

where θ is the fraction of sites occupied and $a(T)$ denotes the partition function for a sorbed molecule including its degrees of freedom relative to its intracrystalline environment. The equilibrium condition then gives:

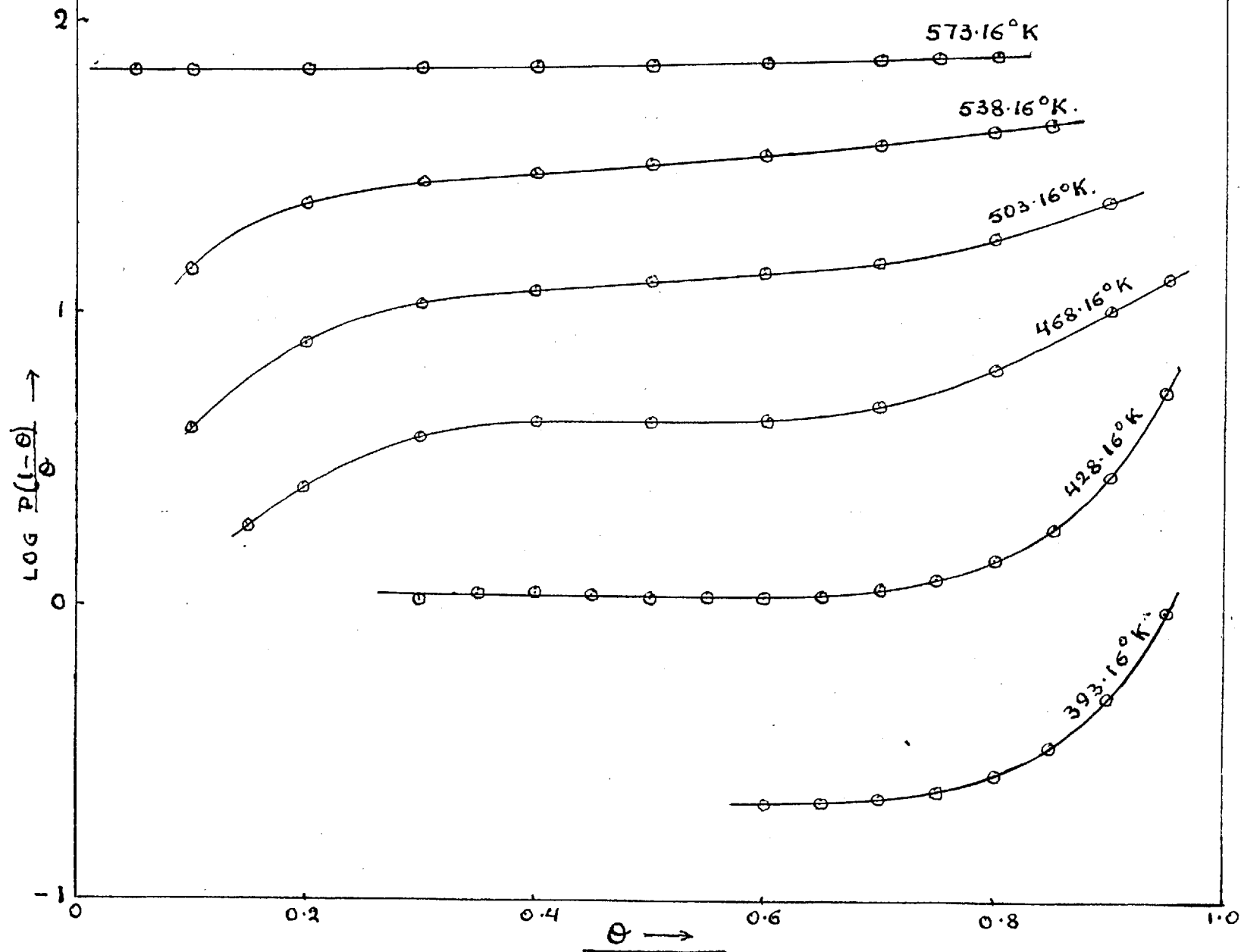
$$K_1 = \frac{\theta}{p(1 - \theta)} ; \quad \Delta A^\circ = RT \ln \frac{p(1 - \theta)}{\theta} \quad 3.9. 5.$$

$$\text{where } K_1 = \frac{kT(2\pi m kT)^{3/2}}{h^3} \cdot \frac{j(T)}{a(T)} \quad 3.9. 6.$$

To test the relationship between equation 3.9.5. and the Langmuir's ideal isotherm equation for localised sorption, the values of $\log \frac{p(1 - \theta)}{\theta}$ were evaluated from the experimental isotherms of occlusion of iodine in the three sorbents studied and were plotted against θ , the degree of coverage. The plots for iodine in faujasite, Linde Sieve 5A, and chabazite are shown in Figs. 29, 30 and 31. A comparative plot for the three sorbents at one temperature (538.16°K) are shown in Fig. 32.

It can be seen from Figs. 29, 30 and 31 that over a wide range of coverage, sometimes as much as $0.2 < \theta < 0.8$, the plots are reasonably straight lines and almost constant, supporting the idea of localised sorption. Better agreement is obtained at higher temperatures when the isotherms follow more closely the Langmuir equation. As the temperature decreases the experimental isotherms become more and more rectangular and the deviation from Langmuir's ideal model increases.

FIG. 29. — NaX.



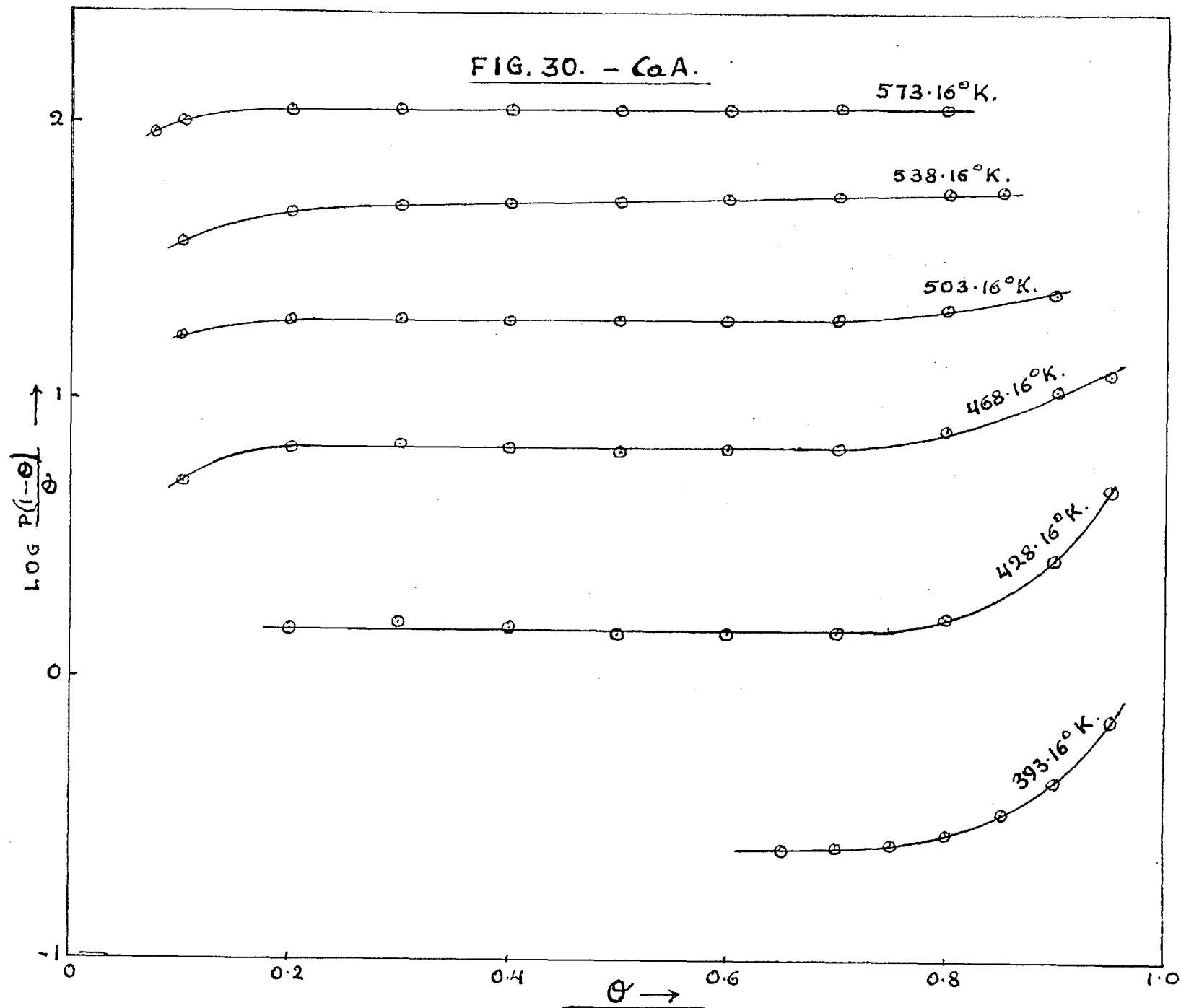


FIG. 31. — CHABAZITE.

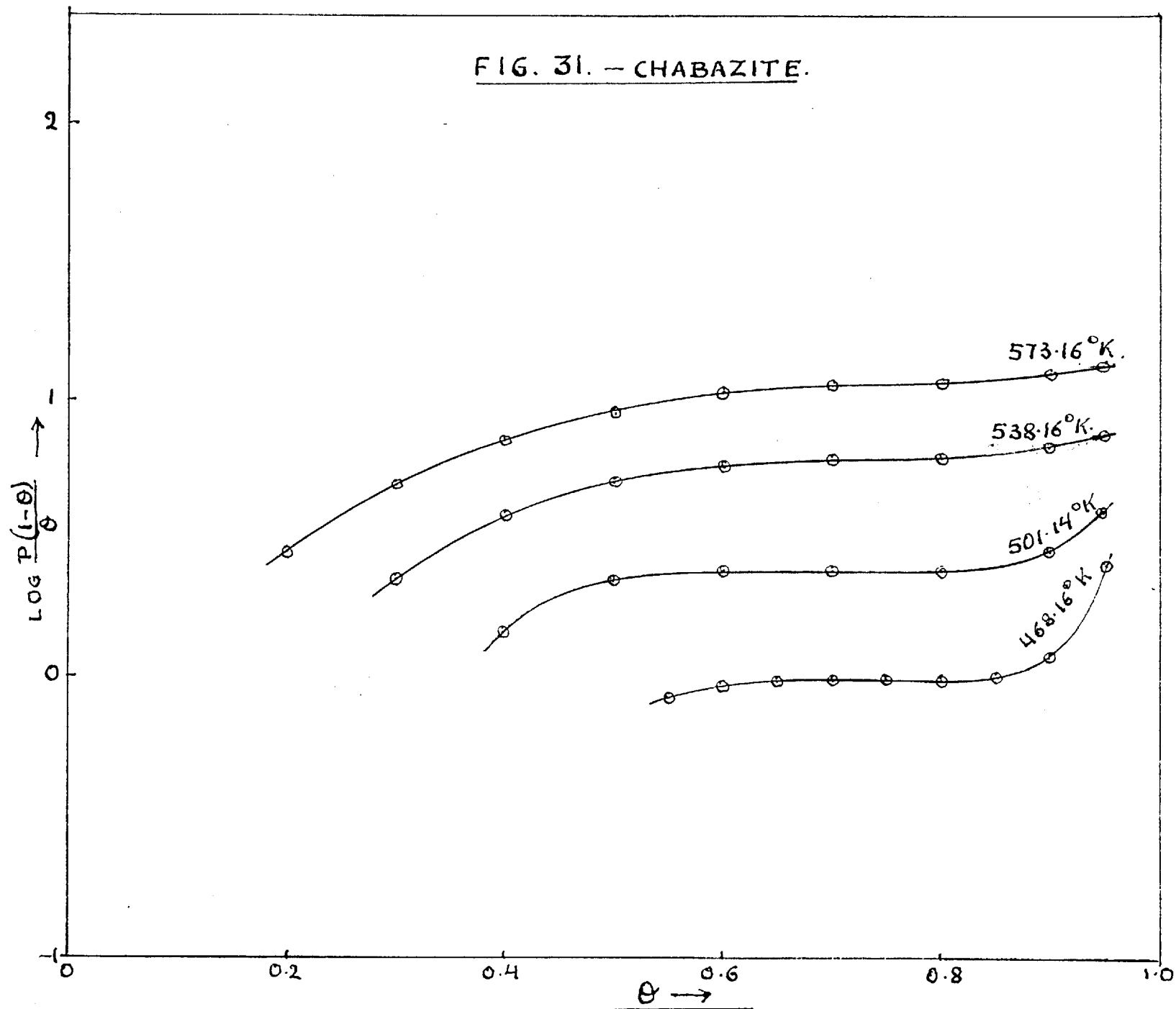
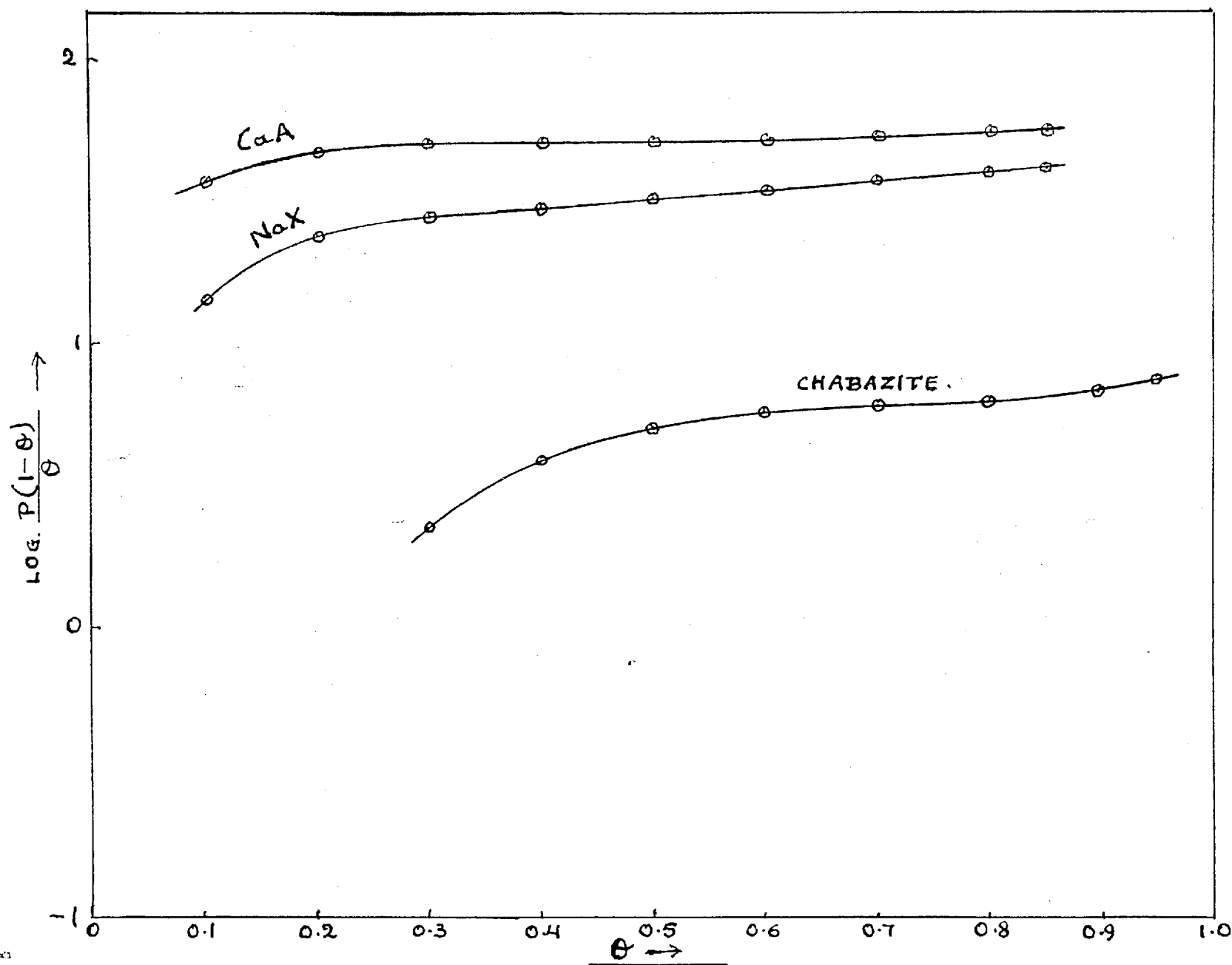


FIG. 32.
 $\log \frac{P(1-\theta)}{\theta}$ PLOTS FOR I_2 IN ZEOLITES AT 265°C .



For the $\log \frac{p(1 - \theta)}{\theta}$ plots it seems that the experimental isotherms give quite a good agreement with the Langmuir's ideal model for localised sorption, but if we look into the matter more deeply it is found that deviations occur.

The calculated values of the isotherm constant, K_1 , calculated using the experimental values of the pressure, p , vary slightly with coverage, the deviation increasing with decreasing isotherm temperature. The values of K_1 for one system are shown in Table 5 below.

Table 5.
Isotherm constant K_1 for iodine in CaA.

	120°C	155°C	195°C	230°C	265°C	300°C
θ	$K_1 \times$					
	$\times 1$	$\times 10$	$\times 10$	$\times 10^2$	$\times 10^2$	$\times 10^4$
0.1	-	-	1.963	5.910	2.697	9.833
0.2	-	6.685	1.412	4.980	2.101	8.865
0.3	-	5.921	1.365	5.164	1.975	8.766
0.4	-	6.473	1.502	5.333	1.955	8.949
0.5	-	6.944	1.595	5.263	1.934	9.091
0.6	-	7.008	1.565	5.048	1.915	8.978
0.7	3.891	6.854	1.504	4.907	1.821	8.730
0.8	3.472	5.855	1.231	4.469	1.717	-
0.9	2.288	3.632	0.892	4.058	-	-

The almost constant values obtained for $\log \frac{p(1 - \theta)}{\theta}$ against θ , over the range of coverage $0.2 < \theta < 0.8$ (Figs. 29, 30, 31), are due in part to the compensating contributions to ΔA , from the isosteric heat and the entropy of occluded molecules; both changing with θ in

the opposite direction.

Taking into account all the arguments in this section and bearing in mind the shortcomings of the Langmuir's ideal localised model, the fact that the experimental occlusion isotherms of iodine in the three zeolites studied give a reasonable agreement with the Langmuir's model over a large range of coverage, suggests that the sorption of iodine in these zeolites is localised, which is a reasonable assumption considering the large size of the iodine molecule relative to the intracrystalline cavities, and the large isosteric heats of sorption.

3.10. Thermodynamic Properties of the Sorbents.

This section will deal with the change in the thermodynamic properties of the sorbents studied. The theoretical aspects of this section were dealt with in section 1.3.5.

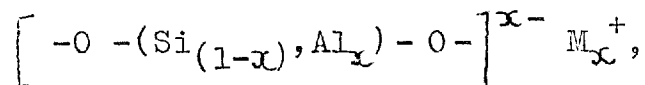
3.10.1. Change in chemical potential.

The change in chemical potential of the sorbent over which the equilibrium pressure of sorbate is P , relative to a reference state characterised by an equilibrium pressure P° is given by equation 1.3.5. 7.

$$\text{i.e. } \mu_A - \mu_A^\circ = V_M(P - P^\circ) - \frac{MRT}{m} \int_{P^\circ}^P \frac{\alpha}{P} dP \quad 3.10.1. 1.$$

where V_M = molecular volume of the lattice unit chosen,
 M = molecular weight of the unit,
 α = amount sorbed in gm/gm of outgassed sorbent,
 m = molecular weight of sorbate.

The unit chosen is one containing one silicon or aluminium atom and two oxygen atoms, i.e.



where M_x^+ (or $M_{\frac{1}{2}x}^{++}$) is the amount of monovalent (or divalent) cation required to neutralise the anionic charge, x^- .

The reasons for the choice of the above unit was explained in section 1.3.5. The pressure P° was chosen as zero pressure so that the reference state is one in which the zeolite is free of I_2 molecules.

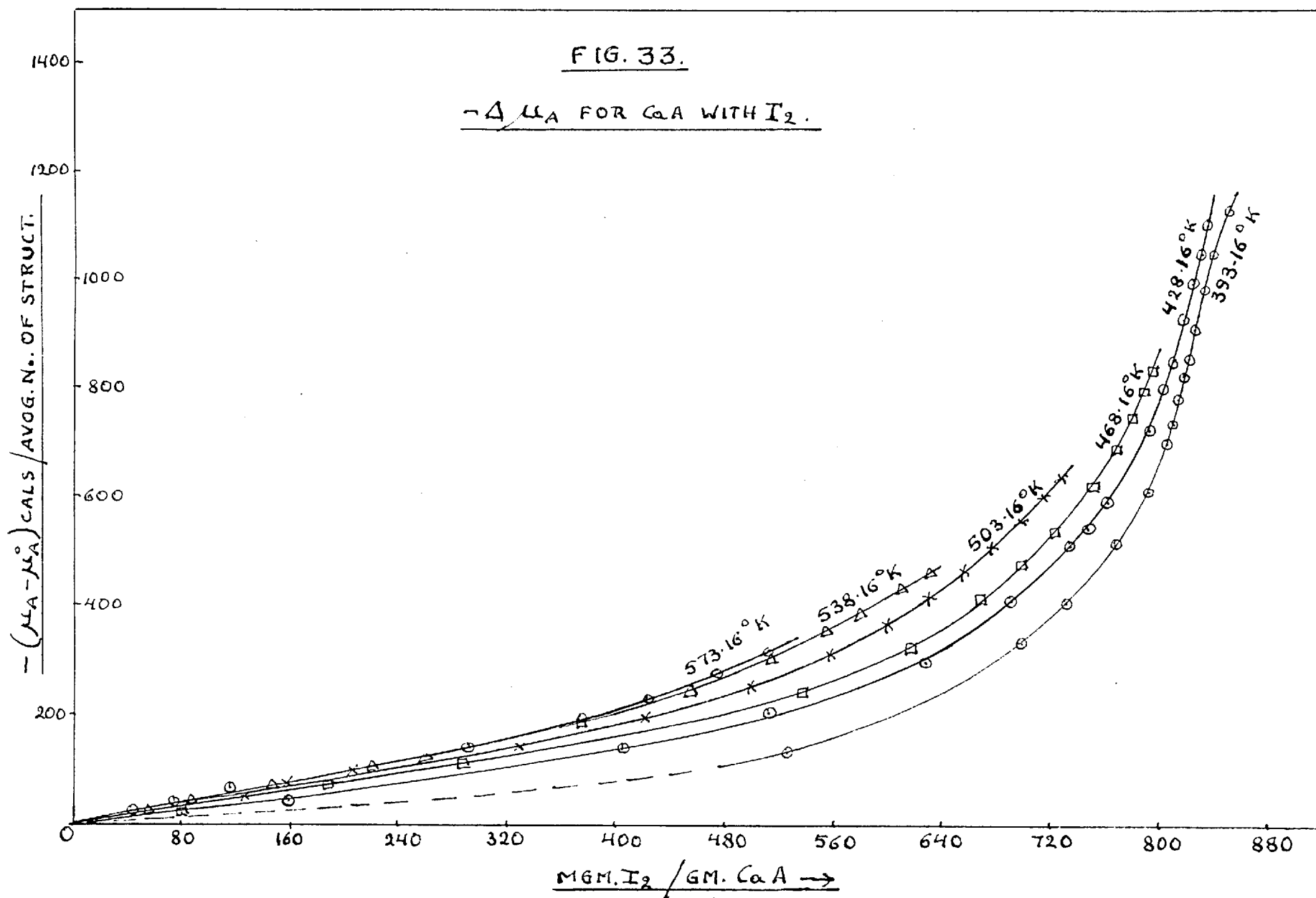
In order to evaluate $\Delta\mu_A = \mu_A - \mu_A^\circ$ from isotherm data two simplifying assumptions are made, which are implicit in equation 3.10.1. 1:

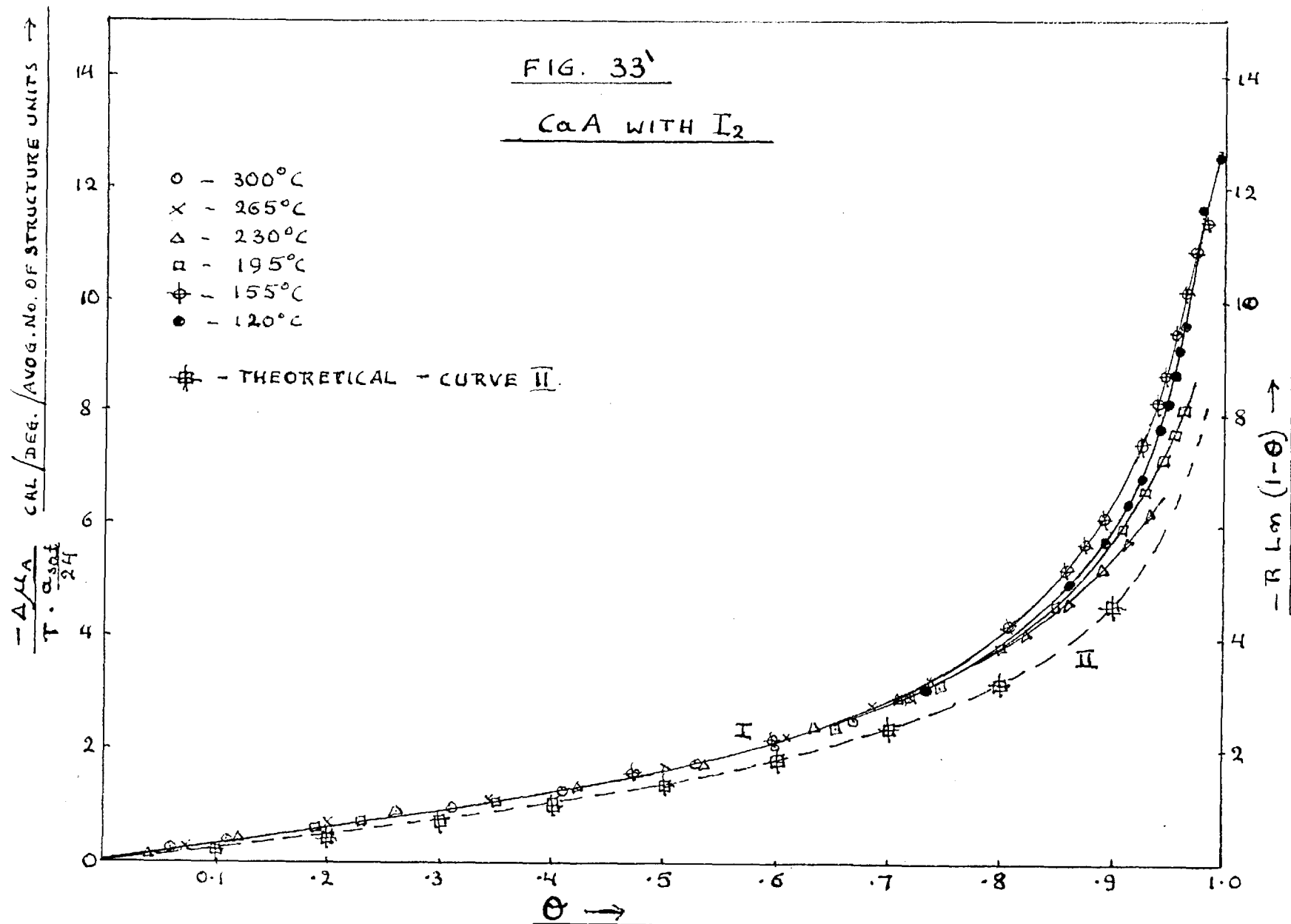
(i) the gas phase activity is assumed to be the same as the gas pressure;

(ii) it is assumed that there is no expansion of the lattice of zeolite on sorption, so that the volume of one mixed mole is equal to the external volume of the amount of zeolite lattice comprising one mixed mole of chosen lattice units and of sorbate molecules. This is a reasonable assumption for the robust three-dimensional zeolites studied.

$\Delta\mu_A$ was evaluated for the temperatures of the isotherms using equation 3.10.1. 1. and graphical integration of the integral $\int_{P_0}^P \frac{P}{P} dP$. Typical plots of

$-\Delta\mu_A$ against amount sorbed, for different temperatures, are shown in Fig. 33. The values of $-\Delta\mu_A$ at first increases steadily, as the amount sorbed increases, over wide range of θ and then much more rapidly as θ approaches one. The shapes of the $-\Delta\mu_A$ curves are of the form of the curve for Langmuir's ideal localised





model discussed later.

To obtain further information let us consider a statistical thermodynamic approach such as has been first given for clathrate phases of β -quinol^(159,160) and further developed for the more complex gas hydrates^(161,162).

In these phases either the intracrystalline cavities are empty, or they contain just one included guest molecule. In a system containing one kind of cavity, the lowering in chemical potential of the structural units of the host lattice is given by:

$$\Delta\mu_A = \mu_A - \mu_A^\circ = \frac{RT}{m} \ln (1 - \theta) \quad 3.10.1. 2.$$

where m denotes the ratio between the number of structural units and the number of cavities, and θ is the fraction of cavities occupied by guest molecules. At the same time this treatment requires that, as for Langmuir's isotherm

$$K_1' = \frac{P(1 - \theta)}{\theta} \quad 3.10.1. 3.$$

As far as the included molecules are concerned the postulates of Langmuir's isotherm are assumed, the cavities being identified with the sites. The host lattice is similarly regarded as an inert medium which provides the sites but is unaltered by inclusion.

The three zeolites studied contain more than one kind of cavity but only the largest cavity is accessible to guest molecules such as iodine. These cavities are very large and open, and can contain not one but a whole cluster of sorbed molecules. Thus each cavity provides not one, but a group of relatively uniform sites, the number of which depends on the size of the molecules included. Moreover, the molecules in

one cavity are in contact with those in neighbouring ones through wide windows, and the average number of sites per cavity is not necessarily a whole number and varies with temperature. It is the whole intracrystalline volume which provides the sites, and therefore its division into individual cavities is not warranted (see Section 3.7.3).

However, to extend the treatment of clathrates phases to three dimensional zeolites the terminology used for clathrates is conveniently retained. For the three zeolites studied $m = 24/n_{\text{sat}}$. Thus,

$$\Delta\mu_A = RT \frac{n_{\text{sat}}}{24} \ln (1 - \theta) \quad 3.10.1. 4.$$

with $\theta = \frac{n}{n_{\text{sat}}}$, where n denotes the actual number of included molecules per cavity. If the system obeys Langmuir's isotherm completely it follows from the above equation that $\Delta\mu_A/T$ should give a universal curve at all temperatures when plotted against θ . Moreover, for different sorbents this should still be true. How nearly this is the case helps in assessing the usefulness and validity of the isotherm model.

Fig. 33' (curve I) shows the plots of $\Delta\mu_A/T \frac{n_{\text{sat}}}{24}$ against θ , the degree of coverage for I_2 in CaA. It is seen that from 0 to $\theta > 0.8$ a nearly universal curve is obtained as suggested by equation 3.10.1. 4. Deviation begins to occur at $\theta > 0.8$. However, deviations from Langmuir's isotherm as θ tends to unity have already been noted. It is interesting that at small values of θ ($\theta < 0.3$) the $\Delta\mu_A$ curve (Fig. 33') does not show deviation from the universal curve, although deviations from Langmuir's isotherm exist for the sorbate (see sections 3.7, 3.8 and 3.9). Fig. 33' (curve II) shows,

for comparison, the theoretical plot of $-R \ln(1 - \theta)$ against θ . It is then seen that the universal curve of $\frac{\Delta\mu_A}{T \frac{n_{\text{sat}}}{24}}$ vs θ (curve I) lies near to but does not actually coincide with curve II. It is of course quite possible that isotherms other than that of Langmuir would lead to universal curves, but the closeness in position and shape of curves I and II is of particular interest in the examination of this isotherm.

3.10.2. Change in partial-molar entropy.

To evaluate the partial-molar entropy of the sorbent use was made of equation 1.3.5. 9, i.e.

$$\partial \left(\frac{\mu_A - \mu_A^\circ}{T} \right)_\infty = -(\bar{S}_A - \bar{S}_A^\circ) = -\Delta \bar{S}_A \quad 3.10.2. 1.$$

A graph of $-\Delta\mu_A$ against T , at constant amount sorbed, gave a straight line, the slope of which gave mean $\Delta\bar{S}_A$ over the temperature range 120 - 265°C. The temperature coefficient was too small in comparison with experimental error to be of any value.

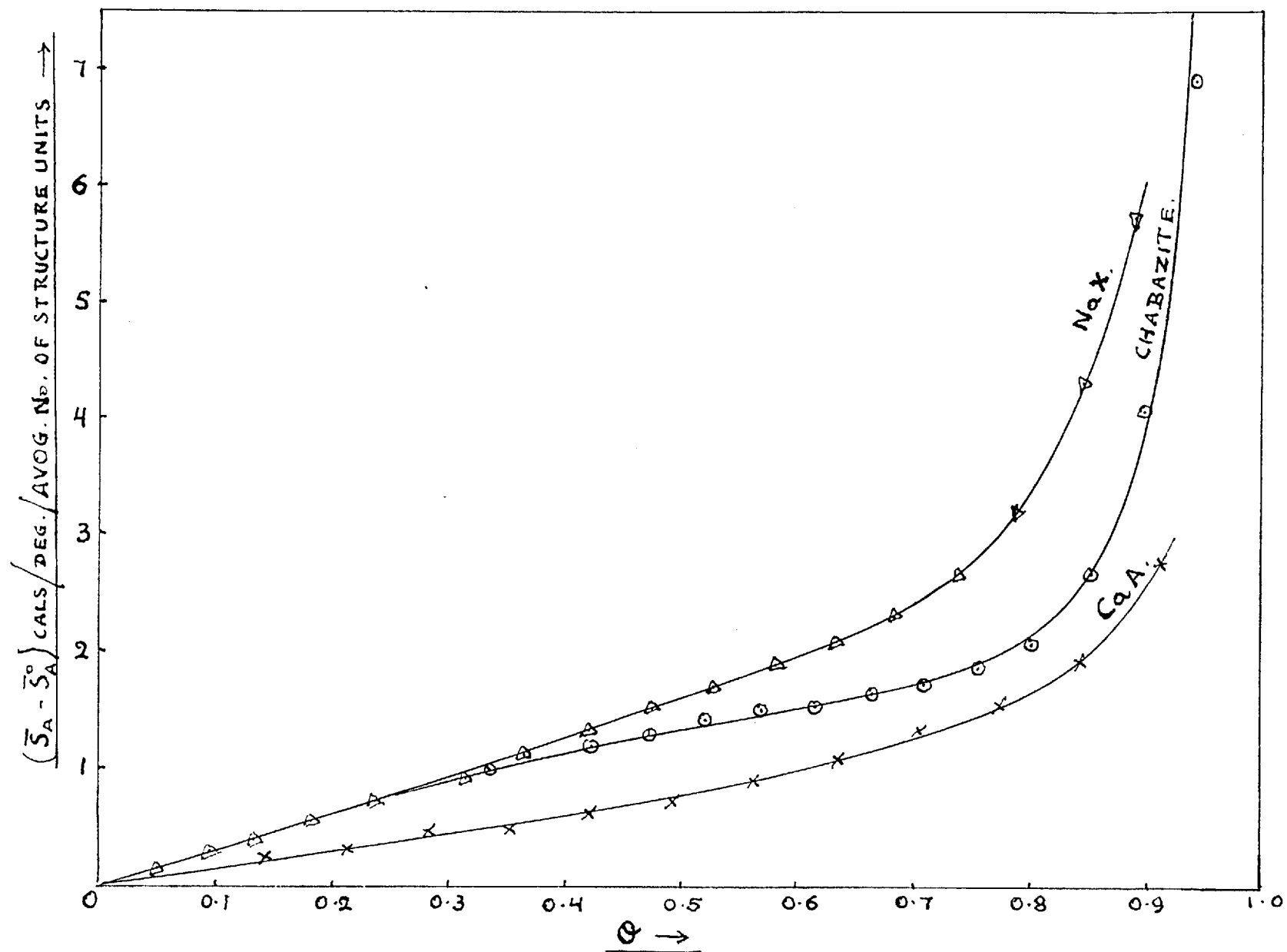
Fig. 34 shows the plots of the change in partial molar entropy, $\Delta\bar{S}_A$, against θ , for the three zeolites studied. It can be seen from the figure that the partial molar entropy of the sorbent increases as the number of I_2 molecules occluded in the sorbent increases.

Again for a Langmuir isotherm, in which nevertheless n_{sat} may vary with temperature

$$\begin{aligned} \Delta\bar{S}_A &= - \left(\frac{\partial \Delta\mu_A}{\partial T} \right)_\infty \\ &= \frac{-R}{24} \left[\frac{\partial n_{\text{sat}}}{\partial T} T \ln(1 - \theta) + n_{\text{sat}} \ln(1 - \theta) + \right. \\ &\quad \left. n_{\text{sat}} T \frac{\partial}{\partial T} \ln(1 - \theta) \right] \quad 3.10.2. 2. \end{aligned}$$

FIG. 34.

CHANGE IN PARTIAL MOLAR ENTROPIES OF ZEOLITES WITH ADDITION OF I_2 .



The main contribution to $\Delta \bar{S}_A$ will come from the middle term in the bracket (equation 3.10.2. 2.), as

$\frac{\partial n_{\text{sat}}}{\partial T}$ and $\frac{\partial}{\partial T} \ln (1 - \theta)$ are very small, i.e. -0.00576 and -0.0015 respectively for I_2 in CaA. Therefore the lateral displacement of the $\Delta \bar{S}_A$ curves (Fig. 34) is mainly due to the different value of n_{sat} for the three zeolites, although the temperature coefficients of n_{sat} and $\ln (1 - \theta)$ will also have an effect.

3.10.3. Change in partial molar enthalpy.

The change of partial molar heat content of the zeolites with addition of iodine can be derived from the chemical potential and the partial molar entropy change, by the application of the Gibbs-Helmholtz equation:

$$\text{i.e. } (\bar{H}_A - \bar{H}_A^\circ) = (\mu_A - \mu_A^\circ) + T(\bar{S}_A - \bar{S}_A^\circ) \quad 3.10.3. 1.$$

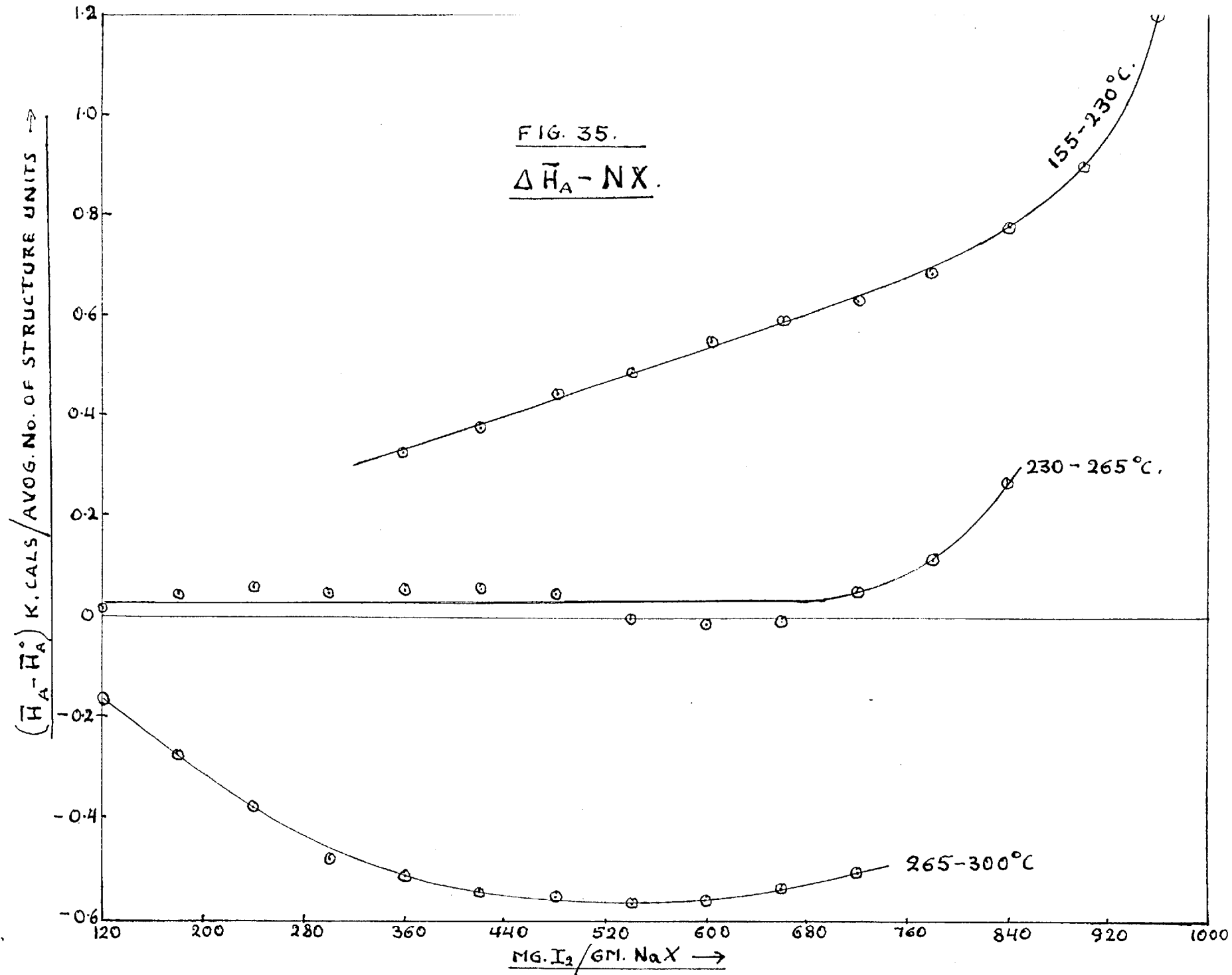
In this work use has been made of the following equivalent relationship:

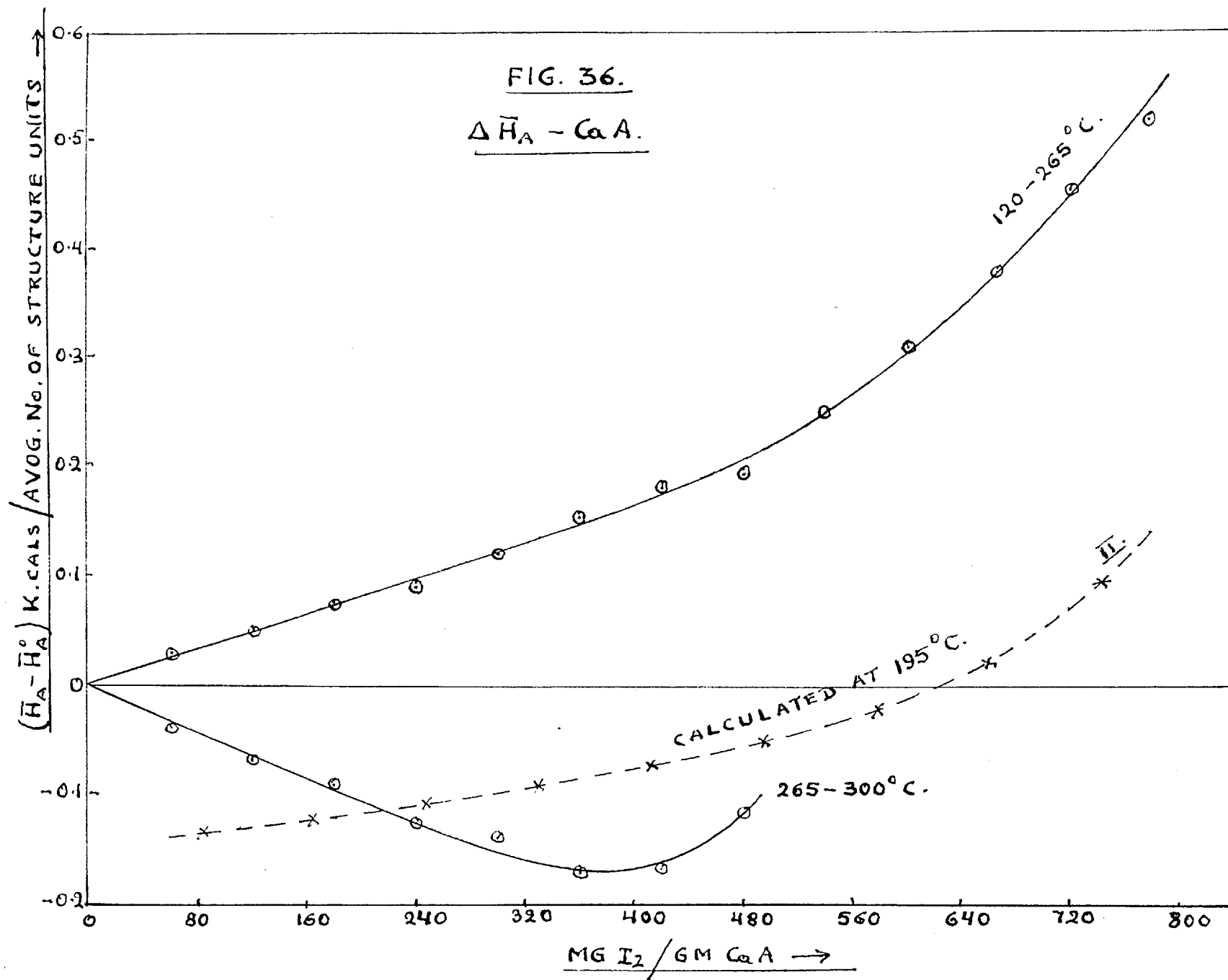
$$\left[\frac{\partial(\Delta \mu_A/T)}{\partial T} \right]_{\chi} = \frac{-\Delta \bar{H}_A}{T^2} = \frac{-(\bar{H}_A - \bar{H}_A^\circ)}{T^2} \quad 3.10.3. 2.$$

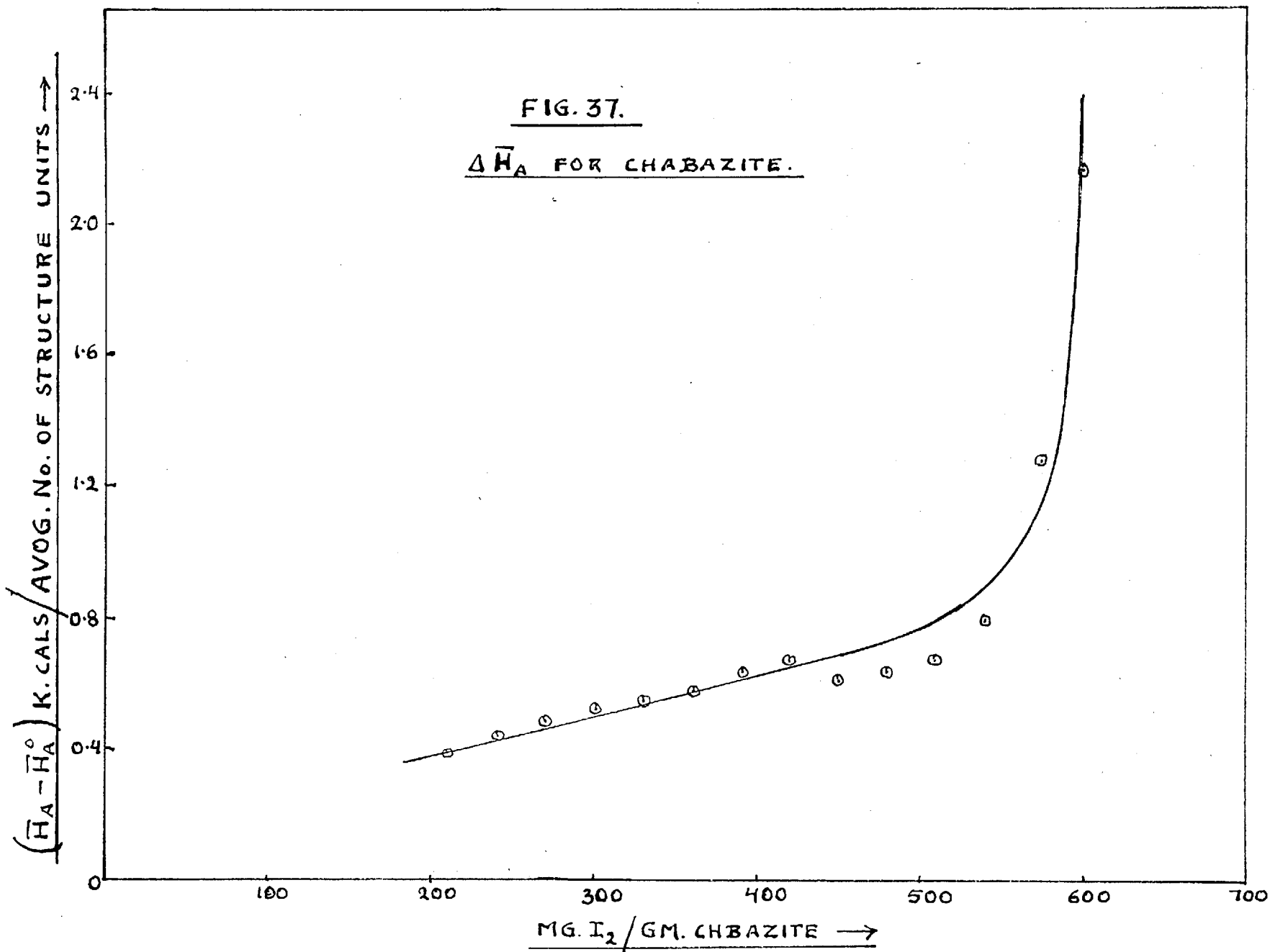
Assuming $\Delta \bar{H}_A$ to be independent of temperature and integrating, one gets:

$$\left[\frac{\Delta \mu_A/T}{1/T} \right]_{\chi} = \Delta \bar{H}_A \quad 3.10.3. 3.$$

Hence graphs of $-\Delta \mu_A/T$ against $1/T$ at constant amount sorbed were obtained and from their slopes $\Delta \bar{H}_A$ was calculated. The plots of $(\bar{H}_A - \bar{H}_A^\circ)$, the change in enthalpy of the sorbent, with increasing amounts of I_2 occluded in the crystals, are shown in Figs. 35, 36, 37, for the three zeolites studied. In general it can be said that at low coverage, the change in partial molar







enthalpy of the zeolites studied, is small but that $\Delta\bar{H}_A$ increases rather rapidly near saturation.

Again, for an ideal Langmuir isotherm (see equation 3.10.1. 4)

$$\begin{aligned}\frac{-\Delta\bar{H}_A}{T^2} &= \frac{\partial}{\partial T} \left(\frac{\Delta u_A}{T} \right)_{\alpha} \\ \therefore \Delta\bar{H}_A &= \frac{-RT^2}{24} \left[\frac{\partial(n_{\text{sat}})_{\alpha}}{\partial T} \ln(1 - \theta) \right. \\ &\quad \left. + n_{\text{sat}} \frac{\partial}{\partial T} \left\{ \ln(1 - \theta) \right\}_{\alpha} \right] \quad 3.10.3. 4.\end{aligned}$$

$\Delta\bar{H}_A = 0$ if θ for given sorption, α , and hence n_{sat} , do not change with temperature. In fact, however, θ corresponding to a fixed amount sorbed is a function of temperature, and in any case the Langmuir isotherm breaks down as a description of the system for small θ and as $\theta \rightarrow 1$.

To compare the experimentally obtained values of $\Delta\bar{H}_A$ with those obtained from equation 3.10.3. 4. experimentally obtained values of $\frac{\partial(n_{\text{sat}})_{\alpha}}{\partial T}$, and $n_{\text{sat}} \frac{\partial}{\partial T} \left[\ln(1 - \theta) \right]_{\alpha}$ were substituted in equation 3.10.3. 4. and the result plotted against amount sorbed (θ) in Fig. 36, curve II (for the sorption of I_2 in CaA at 195°C) as an example. It can be seen from Fig. 36 that the curve obtained from equation 3.10.3. 4. lies in part between those obtained from experimental values of $\left[\frac{\Delta u_A/T}{1/T} \right]_{\alpha}$ over two different temperature ranges.

However the calculated curve at 195°C refers to a temperature very near the mean of that for the upper curve of Fig. 36, to which it corresponds rather closely in shape. Nevertheless its vertical displacement may

represent a deviation from the Langmuir's ideal model.

3.10.4. Comparison of partial-molar thermodynamic properties of the sorbents.

A comparative plot of the variation in chemical potential of the three sorbents studied with the degree of filling θ , is shown in Fig. 38. The lateral displacement of these curves is mainly due to different values of n_{sat} for the three sorbents as can be seen from equation 3.10.1. 4.. These are in the sequence n_{sat} for NaX > CaA > Chabazite. From Fig. 34 it follows that at any given degree of occupancy, θ , of the intracrystalline volume, the change in the partial molar entropy of the sorbent is greater for NaX than for chabazite than for CaA. The sequence is determined by the values of n_{sat} and the temperature coefficients of n_{sat} and θ (see equation 3.10.2. 2.) all being different for the three sorbents. The same argument applies to Fig. 39 which shows plots of $(\bar{H}_A - \bar{H}_A^\circ)$ against θ for the three sorbents. The values of $\Delta\bar{S}_A$ and $\Delta\bar{H}_A$ shown in the two last mentioned figures are mean values for the temperature range 120 - 230°C.

Summarising section 3.10, it can be seen that on considering the thermodynamic properties of the sorbents together, that $\Delta\mu_A$, $\Delta\bar{S}_A$, and $\Delta\bar{H}_A$ are negligibly small at low amounts sorbed but increase rather rapidly at larger amounts sorbed. Similar behaviour has been observed by Bratt (1958) in the sorption of water and ammonia in faujasite, and by Reucroft (1959) in the case of sorption of fluorocarbons in faujasite. In our case (sorption of I_2 in NaX, CaA and chabazite) it has been shown that $\Delta\mu_A$ curves give rather close agreement with the Langmuir's ideal localised model up to $\theta = 0.8$,

FIG. 38.

COMPARISON OF CHEMICAL POTENTIAL AT 468.16°K.

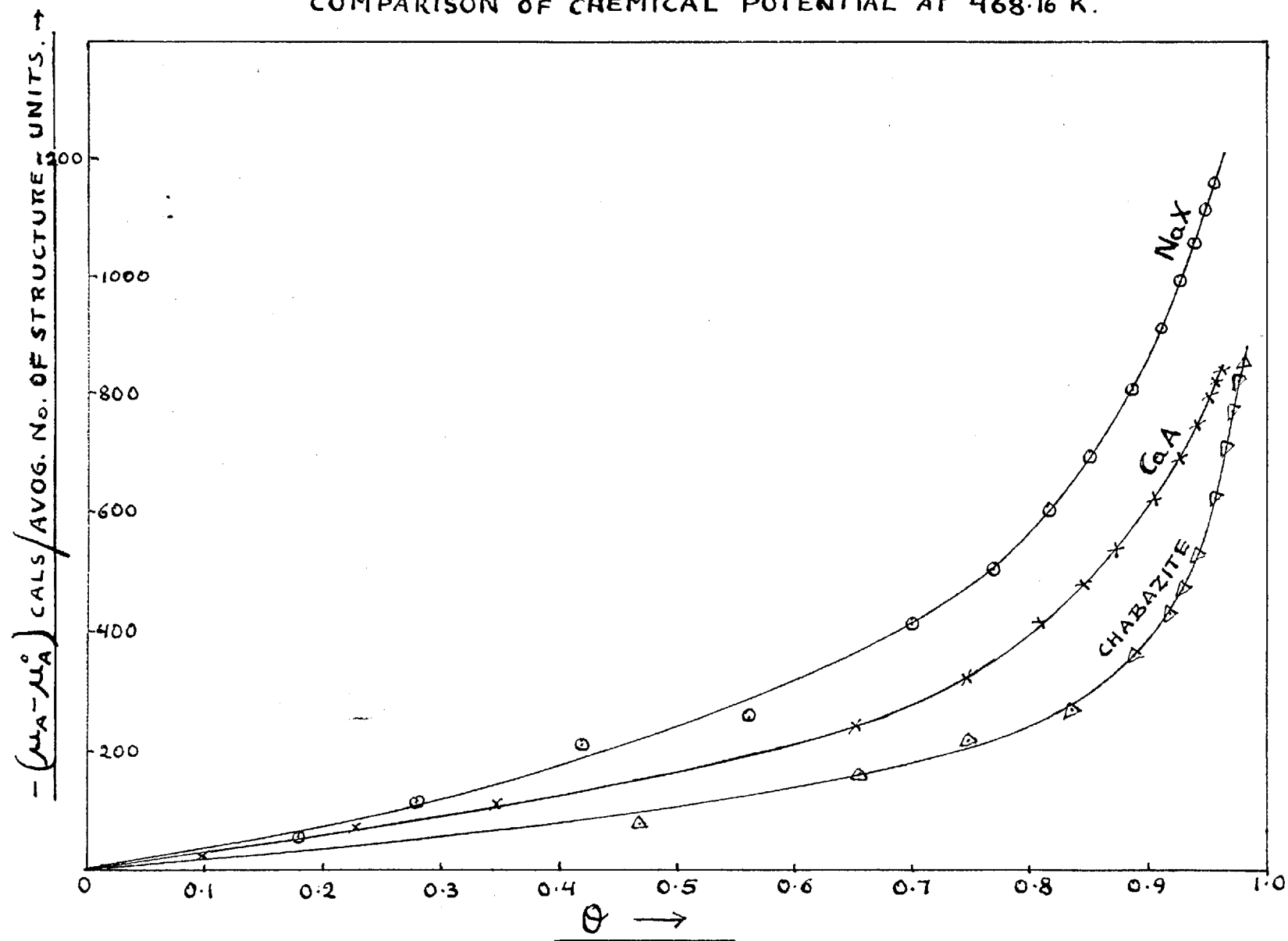
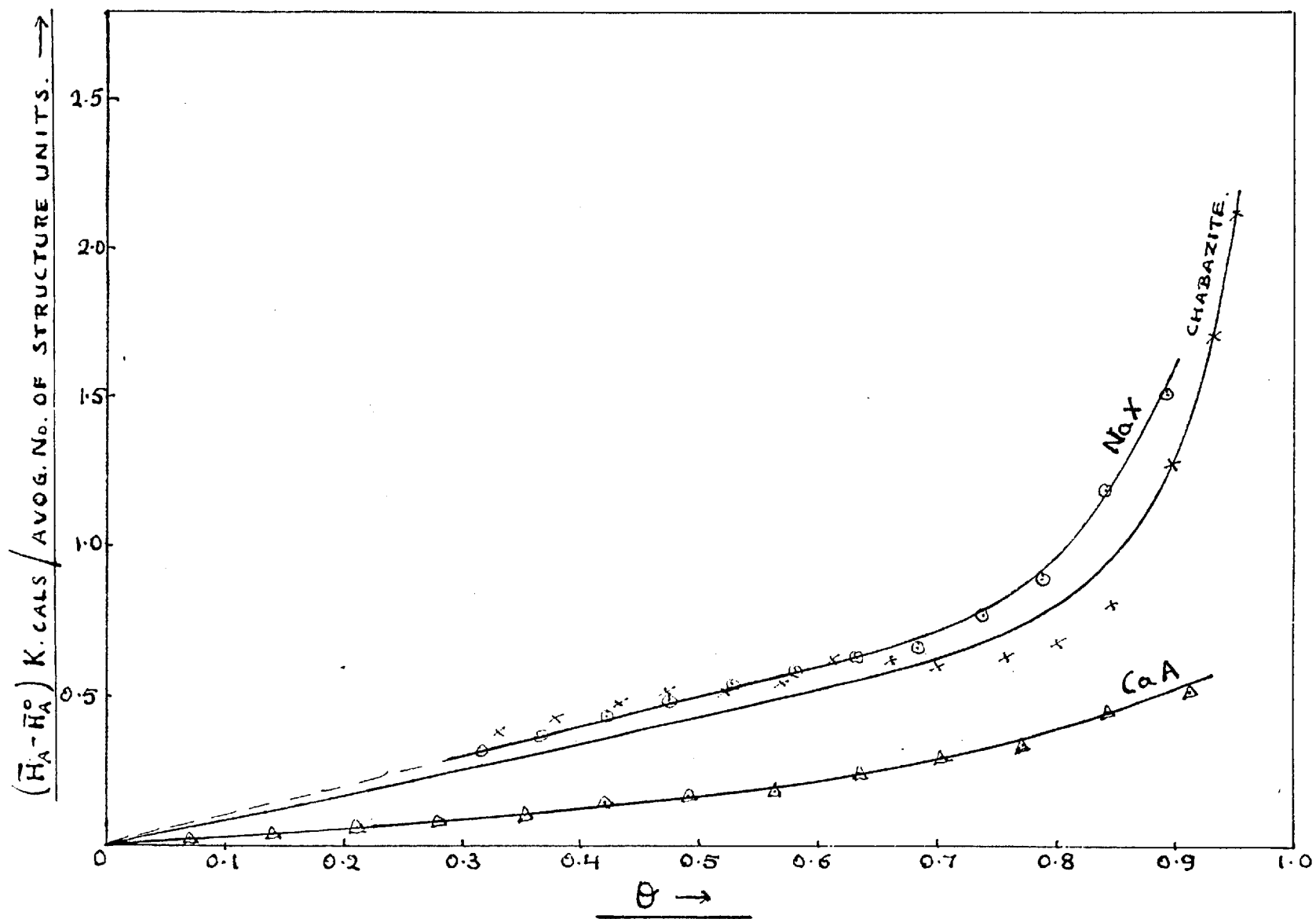


FIG. 39.

PARTIAL MOLAR ENTHALPY OF THE SORBENTS - SORBED WITH I_2



at $\theta > 0.8$ deviation occurs. However, in the case of $\Delta\bar{S}_A$ and $\Delta\bar{H}_A$ larger deviation from Langmuir's model occur.

The main usefulness in obtaining from experimental data the thermodynamic functions of the solid sorbent is thus in providing additional means of assessing the degree of applicability and limitations of isotherm models, of which of course Langmuir's isotherm is only one. It would be of interest to obtain expressions for $\Delta\mu_A$, $\Delta\bar{S}_A$ and $\Delta\bar{H}_A$ for other models, e.g. localised sorption with interaction. However, since we have established that thermal entropy is a function of θ , and since $\Delta\bar{H} = -q_{st}$ is a rather complex function of θ , no simple isotherm model could be expected to apply for all θ . It would be expected, if a model could give a perfect fit for all of a family of isotherms, that every partial molar property of both sorbent and sorbate could be calculated correctly from the model. The change in thermal entropy with θ opposes the effect of change in $\Delta\bar{H} = -q_{st}$ with θ , so that the free energy function as represented by Langmuir's isotherm is reasonable over large part of the range. This is often true of free energy functions. An example is the solution of benzene in rubber, where the lattice model gives a good description of the free energy function, but gives a less satisfactory account of the entropy component.

3.10.5. Comparison of changes in thermodynamic properties of sorbent with those of sorbate.

For this purpose sorption of iodine in Linde Sieve 5A (CaA) has been chosen at the medium range of temperature covered in this study.

The change in chemical potential, $\Delta\mu_A$, of the sorbent can be compared with the change in free energy when a mole of sorbate is transferred from the gas phase at a standard pressure P_0 to the sorbed phase having an equilibrium pressure P :

$$\text{i.e.} \quad \Delta A = RT \ln \frac{P}{P_0} = \mu_s - \mu_g$$

where P = equilibrium pressure of the sorbate,

P_0 = standard pressure = 1 atmosphere,

μ_s = chemical potential of the sorbate in the sorbed phase,

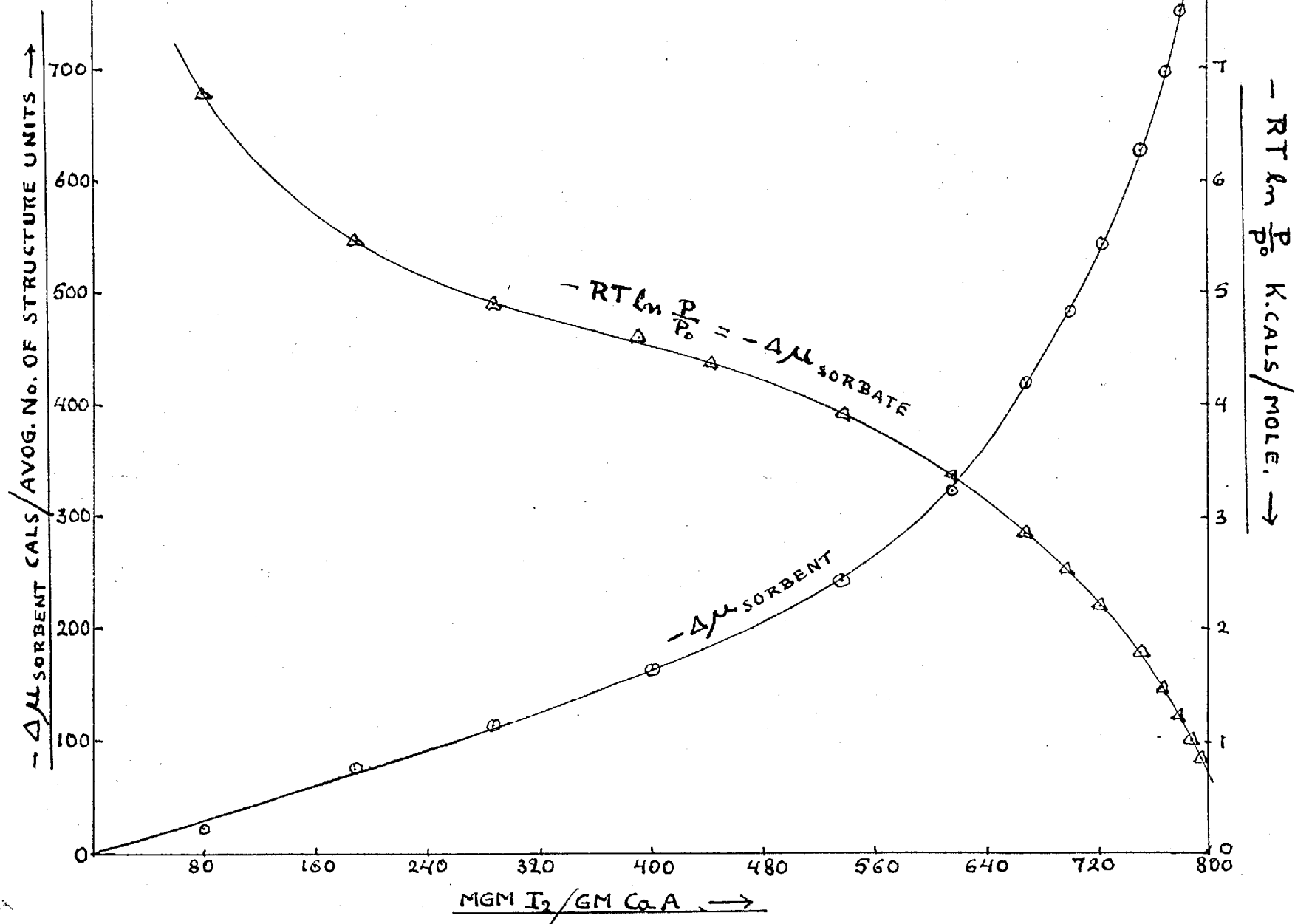
μ_g = chemical potential of sorbate in the gas phase.

Fig. 42 shows plots of $-\Delta u_A$ and $-RT \ln \frac{P}{P_0}$ versus amount sorbed at 468.16°K. The plots of isosteric heats of sorption, ΔH , and $\Delta \bar{H}_A$ of sorbent, and entropy of sorbate in the sorbed state, $\bar{S}_s$, and $\Delta \bar{S}_A$ - sorbent versus amount sorbed at 503.16°K, are shown in Figs. 43 and 44 respectively. From these graphs it can be seen that the magnitudes of the change of the thermodynamic properties of sorbent are very small in comparison with the magnitudes of corresponding thermodynamic properties of sorbate and they change in the opposite direction to that of the sorbate.

3.11. Discussion of X-ray Data.

X-ray diffraction patterns of the outgassed and sorbed, with iodine or bromine, crystals have shown a gradual weakening of the original diffraction pattern of the outgassed crystal as the degree of intracrystalline filling increased, and the appearance of new diffraction lines. However, no superstructure due to specific

FIG. 42.



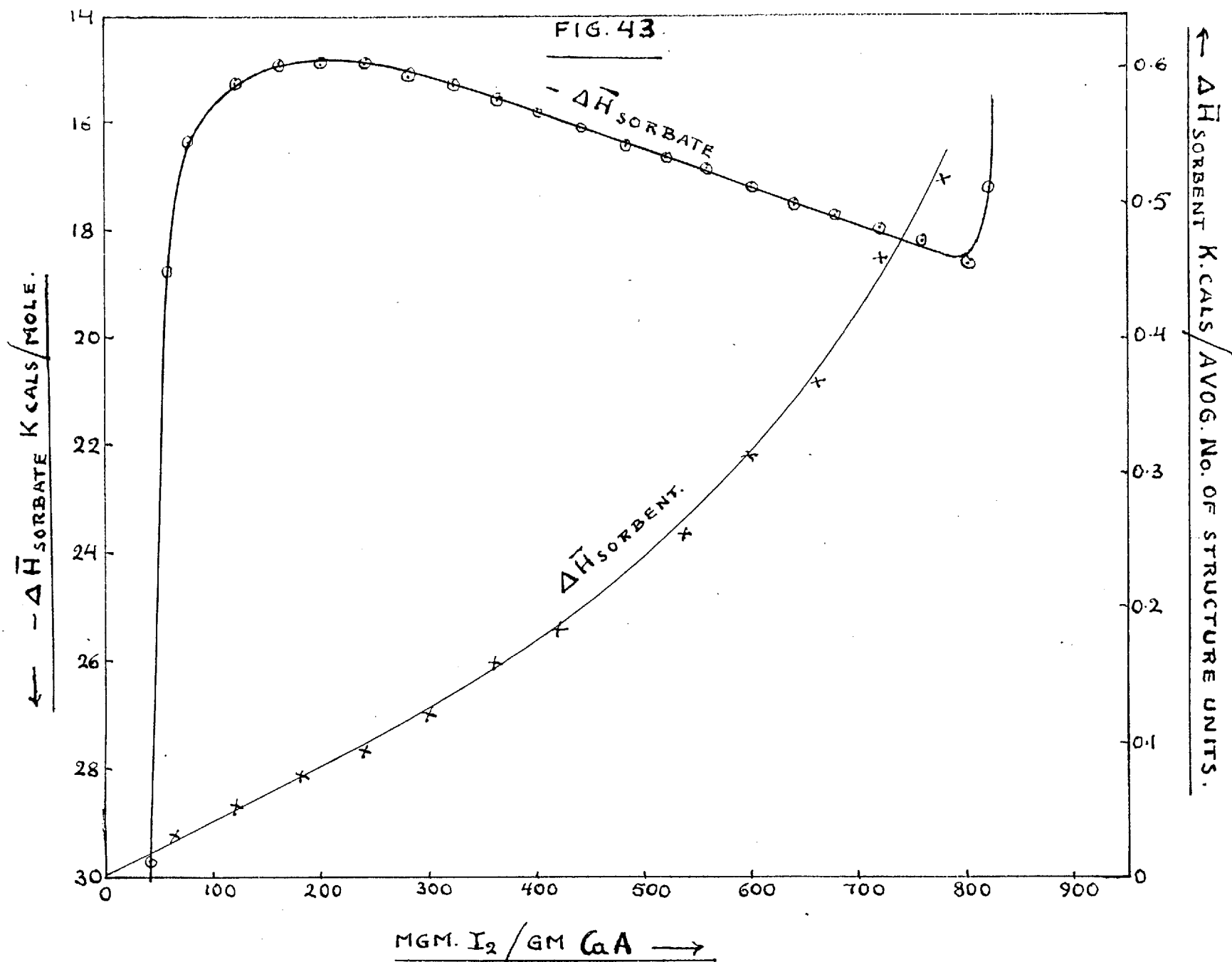
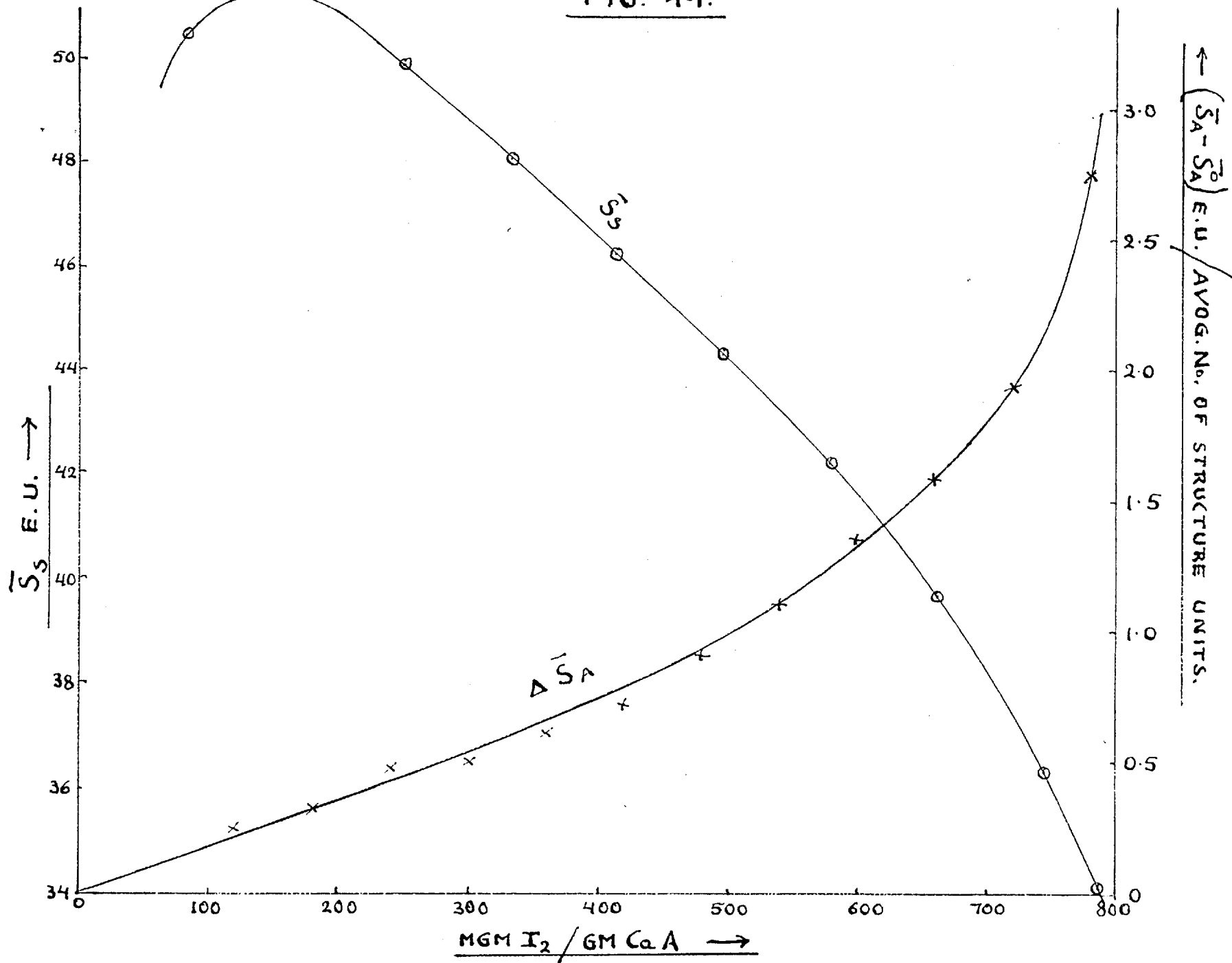


FIG. 44.



arrangement of iodine or bromine molecules inside the cages was observed. The positions of the diffraction cones of fully, as was possible, sorbed crystals with iodine and bromine, were exactly the same. This and the above observation suggest that the final pattern is given by diffraction from the clusters of heavy molecules (iodine or bromine) located in the large cavities (cages) of the crystals.

The spacings between lines on the diffraction photographs were measured with a Vernier ruler, the "d" spacings were calculated and the diffraction lines were indexed by the use of Björstrom's Chart. The measurement was repeated 2 - 3 times to eliminate error in reading the scale; all measurements gave a good agreement. Positions of theoretical lines were calculated from the assumed positions of diffracting groups and the following intensity equation:

$$\text{Intensity} = I = f(\theta)s^2$$

$$s^2 = A^2 + B^2$$

$$A = \sum_r \psi_r \cos 2\pi (hX_r + kY_r + lZ_r)$$

$$B = \sum_r \psi_r \sin 2\pi (hX_r + kY_r + lZ_r).$$

where, s = intensity factor, and h, k, l , are the indices. The indices and intensity of the theoretically obtained lines corresponded to those obtained from the diffraction photographs.

In all cases it was found that the group symmetry of the fully sorbed crystals remained unchanged, that is it was the same as that of outgassed crystals, but the unit cell dimensions decreased in all cases on

sorption. This can be explained by the strong sorbent-sorbate and sorbate-sorbate interaction resulting in the shrinkage of the lattice. The previous can be inferred from the high isosteric heat of sorption and high interaction energy, in the case of iodine in the zeolites studied which has been discussed in the previous section. By analogy bromine should behave similarly on sorption. Table 6 gives the unit cell dimensions of the outgassed and 'fully' sorbed (with I_2 or Br_2) zeolites.

Table 6.

Zeolite	Unit cell	Unit cell dimensions Å	
		Outgassed	'fully' sorbed
Faujasite	cubic	a=25.127	a=25.098
Linde Sieve 5A	cubic	a=12.352	a=12.124
Chabazite	hexagonal	a=13.335 c=15.668 $\frac{c}{a} = 1.175$	a=13.660 c=15.30 $\frac{c}{a} = 1.12$

The relevant X-ray diffraction data are given in Appendix VII.

In the calculation of the "d" spacings, in each case an appropriate correction was applied for the film shrinkage with time and expansion during processing.

4. Summary of Results and Discussion.

An apparatus has been designed and built for the study of sorption of vapours and gases in general, and in particular for the study of sorption of vapours of solids reactive and corrosive towards mercury and tap-grease, up to the temperature of 350°C, and in the pressure range up to 1 atmosphere.

Using this apparatus, occlusion isotherms of iodine in the zeolites: faujasite (NaX), Linde Sieve 5A (CaA), and chabazite, were obtained for the temperature range 120-300°C. All the isotherms were completely reversible and reproducible, and hence were used for the evaluation of thermodynamic properties associated with the sorption process. The sorption of aluminium chloride in faujasite, on the other hand, was found to be irreversible.

The dependence of saturation values on temperature and the similarity of the thermal expansion coefficient of the sorbed material to that of the solid sorbate suggests that, at saturation, sorbed iodine behaves like a condensed phase filling a limited container, the variation of the volume of the container with temperature being small in comparison to that of the sorbed solid.

The isotherm data and the thermodynamic quantities associated with the sorbate were compared with isotherm equations predicted by simple ideal models and it was found that over the range of coverage, $0.3 < \theta < 0.8$, the Langmuir ideal localised model gives a reasonable description of the sorbed state. At $\theta < 0.3$, and at near saturation deviations arise due to the

variation of the isosteric heat of sorption and thermal entropy with amount sorbed. The Everett isotherm equation therefore gives a better description of the sorbed state than the Langmuir equation.

The isosteric heat curves for iodine occluded in the three sorbents were of similar shape. The high values of, $\Delta\bar{H} = -q_{st}$, at $\theta < 0.3$, were considered to be due to the contribution to $\Delta\bar{H}$ from the induced dipole-field interaction. The steady increase in $\Delta\bar{H} = -q_{st}$, after $\theta = 0.3$ was shown to be compatible with increasing contributions to $\Delta\bar{H}$ from sorbate-sorbate energy of interaction as θ approaches 1. The main energy contribution to $\Delta\bar{H} = -q_{st}$, comes from what seems to be a relatively constant energy of sorbate-lattice oxygens interaction.

It has been shown that the thermal entropy of occluded iodine varies linearly with $\Delta\bar{H}$, the isosteric heat of occlusion, and that the decrease in partial molar entropy of the sorbed phase with θ , after $\theta = 0.3$, is due to the increasing restriction to rotation and increasing mean frequency of vibration of the sorbed molecules.

The energy of interaction of iodine molecule with the framework oxygens was calculated, by summation of individual interactions, for the iodine molecule placed in different positions in the cavity and in the plane of the 12-membered ring (window) in faujasite; and on approaching the 8-membered ring in Linde Sieve 5A, and in chabazite. It was concluded that:

- (i) all iodine is located in the large cavities and the interconnecting windows;
- (ii) the iodine molecule takes up, preferentially,

positions near the wall of the cavity and with its longer diameter parallel to the plane of the wall;

(iii) the iodine molecule must pass through the 8-membered window, in Linde Sieve 5A and in chabazite, so oriented that its longer diameter is perpendicular to the plane of the window;

(iv) thus oriented it diffuses easily into the cavities in Linde Sieve A, but a small activation energy may be required for iodine to diffuse into chabazite;

(v) in faujasite the iodine molecule diffuses into the crystal by preferentially taking up positions near the frame of the 12-membered ring with its shorter diameter perpendicular to the frame, and then diffuses into the crystal by moving from one sorption site to a neighbouring one or by rolling along the ribs of the framework.

To obtain additional information, changes in thermodynamic properties of the sorbents were evaluated and compared with those expected on the basis of Langmuir's localised model. Similar conclusions were arrived at as in the case of the consideration of thermodynamic properties of the sorbate.

The analysis of X-ray diffraction photographs of outgassed and sorbed with iodine and bromine sorbents has shown a small contraction of the unit cell on sorption. This was explained by strong sorbate-lattice and sorbate-sorbate interaction.

Appendix I.

Isotherm Data.

P = equilibrium pressure in mm Hg.

x = amount sorbed in mg/gm of outgassed sorbent.

Iodine in Faujasite (NaX).

<u>at 393.16°K</u>		<u>at 428.16°K</u>	
<u>Sorption</u>		<u>Sorption</u>	
<u>P</u>	<u>x</u>	<u>P</u>	<u>x</u>
0.36	715.286	0.52	368.352
0.84	900.103	1.13	579.184
1.33	934.775	2.52	776.431
2.22	984.895	4.63	866.462
3.34	1008.867	7.04	930.404
7.00	1049.593	10.76	961.950
14.69	1075.282	15.89	989.728
25.99	1091.752	27.32	1019.370
40.59	1102.148	52.02	1048.167
60.43	1111.712	82.84	1065.223
81.48	1119.726	119.50	1076.858
102.54	1133.255	178.16	1090.508
<u>Desorption</u>		240.95	1100.444
11.13	1067.012	300.22	1111.101
3.94	1020.000	<u>Desorption</u>	
0.62	829.50	24.26	1014.091
		15.37	986.081
		1.26	615.246
		0.72	477.850

Iodine in Faujasite (NaX).at 468.16°KSorption

<u>P</u>	<u>x</u>
0.48	192.681
1.42	305.474
3.42	458.790
5.19	613.373
12.08	770.112
19.04	834.250
30.74	887.672
46.13	924.800
72.47	960.378
110.17	987.584
151.73	1005.965
200.53	1021.299
249.47	1030.123
300.50	1039.461

Desorption

175.75	1014.340
57.47	943.112
7.16	670.749
2.30	385.20
0.78	238.30

at 503.16°KSorption

<u>P</u>	<u>x</u>
0.62	122.889
1.20	167.843
3.57	266.058
6.18	366.030
10.16	468.735
20.99	632.436
31.52	710.229
44.69	765.912
67.05	820.474
92.67	857.401
129.52	891.807
180.93	920.241
247.39	946.856
301.29	963.379

Desorption

216.00	938.201
110.98	877.790
55.44	797.808
20.22	626.367
8.20	420.40
2.00	210.00

Iodine in Faujasite (NaX).

<u>at 538.16°K</u>		<u>at 573.16°K</u>	
<u>Sorption</u>		<u>Sorption</u>	
<u>P</u>	<u>x</u>	<u>P</u>	<u>x</u>
0.80	73.385	0.79	21.656
1.80	106.011	1.45	27.757
3.75	151.759	3.94	51.362
11.61	293.513	8.26	112.830
22.13	404.296	18.98	201.648
32.89	493.662	35.23	318.122
52.85	597.400	60.57	425.432
71.82	656.843	90.65	514.695
102.05	716.783	131.06	594.009
150.18	774.764	171.88	644.471
201.41	812.654	221.24	687.363
251.88	839.181	259.95	716.150
302.82	861.241	303.19	739.232
<u>Desorption</u>		<u>Desorption</u>	
180.20	801.292	200.86	680.490
89.86	696.769	113.35	571.623
41.26	555.657	53.22	402.718
6.87	223.902	12.95	168.211
2.80	130.550	6.00	74.211
1.16	87.000	2.20	33.878

Sorption after going down the temperature cycle
at 538.16°K

P	0.60;	25.0;	51.30;	132.50;	230.5;
x	21.03;	248.475;	390.012;	596.310;	695.63.

Iodine in Linde Sieve A (CaA).

<u>at 393.16°K</u>		<u>at 428.16°K</u>	
<u>Sorption</u>		<u>Sorption</u>	
<u>P</u>	<u>x</u>	<u>P</u>	<u>x</u>
0.40	526.664	0.29	158.979
1.39	700.954	1.28	404.684
2.15	733.328	2.19	510.821
4.16	768.192	3.84	628.531
6.91	794.295	7.56	689.845
11.50	807.956	13.12	734.673
22.23	819.262	16.74	749.188
34.68	826.213	21.94	762.903
50.64	831.858	31.47	
13.95	810.880	46.57	792.642
17.55	814.376	67.21	803.181
26.22	822.353	86.69	809.571
74.08	837.917	124.00	818.193
106.03	850.991	177.94	826.137
		233.25	831.627
		282.45	836.186
		303.07	839.430
<u>Desorption</u>		<u>Desorption</u>	
96.77	845.745	72.23	805.745
3.03	754.597	28.68	776.094
0.70	648.153	3.50	598.520
0.55	570.132		

Iodine in Linde Sieve A (CaA).

<u>at 468.16°K</u>		<u>at 503.16°K</u>	
<u>Sorption</u>		<u>Sorption</u>	
<u>P</u>	<u>x</u>	<u>P</u>	<u>x</u>
0.52	79.909	0.52	52.437
2.18	188.450	2.51	91.997
3.95	286.211	5.02	156.946
5.34	390.601	7.29	205.525
7.08	442.052	13.60	328.508
12.51	537.658	22.25	419.901
20.81	618.380	35.62	499.989
35.80	668.242	51.03	558.607
50.54	698.332	70.57	600.642
70.02	722.276	92.45	630.504
109.81	749.579	119.55	656.004
155.86	767.027	153.21	677.994
200.07	778.502	199.22	699.748
251.58	787.880	253.52	716.071
300.52	794.176	297.10	726.835
<u>Desorption</u>		<u>Desorption</u>	
74.75	727.326	56.01	576.291
32.37	660.309	20.02	402.153
12.60	542.913	7.96	232.305
		4.50	143.682
		1.01	61.191

Iodine in Linde Sieve A (CaA).

<u>at 538.16°K</u>		<u>at 573.16°K</u>	
<u>Sorption</u>		<u>Sorption</u>	
<u>P</u>	<u>x</u>	<u>P</u>	<u>x</u>
0.70	38.824	0.64	20.240
2.41	54.568	2.52	28.078
5.10	86.184	5.58	44.442
12.44	148.609	12.41	75.226
26.71	258.707	27.30	137.227
51.81	377.439	51.08	219.714
81.42	455.610	78.31	291.641
120.13	514.149	166.24	423.645
159.38	554.890	124.78	375.813
195.80	580.845	231.75	476.528
251.18	610.954	296.78	513.079
299.01	629.830	<u>Desorption</u>	
<u>Desorption</u>		198.46	455.590
141.15	541.147	20.26	119.520
14.44	168.947	4.00	36.170
7.21	107.602	1.41	22.691
1.20	42.613		

Check after going down the temperature cycle
at 538.16°K.

P 0.78; 5.04; 22.75; 68.14; 130.27; 223.00
x 39.52; 85.61; 233.04; 422.11; 531.98; 595.10.

Iodine in Chabazite.at 393.16°KSorption

<u>P</u>	<u>x</u>
0.57	496.235
1.31	550.785
2.32	566.623
4.30	574.627
5.72	578.439
13.56	588.611
25.18	599.617
47.91	615.083
76.83	631.022
103.52	644.446

Desorption

36.02	607.106
19.10	593.761
8.76	583.056
1.71	559.740
0.82	525.903

at 428.16°KSorption

<u>P</u>	<u>x</u>
0.56	393.030
1.55	495.391
2.39	528.750
3.86	550.037
7.34	561.501
11.09	567.585
20.05	572.812
30.64	577.270
64.04	585.414
110.80	594.241
156.79	599.776
210.71	608.426
261.74	614.940

Desorption

41.20	578.840
15.15	570.192
3.01	540.803
0.98	452.002

Iodine in Chabazite.at 468.16°KSorption

<u>P</u>	<u>x</u>
0.64	280.611
1.82	390.861
2.98	446.124
4.40	498.752
9.42	530.190
15.64	548.455
22.02	554.985
34.95	562.510
73.15	570.837
123.20	574.941
180.70	579.522
289.09	584.787

Desorption

239.49	582.270
50.02	567.261
12.11	541.203
3.92	474.739
1.50	367.682
0.92	315.501

at 501.14°KSorption

<u>P</u>	<u>x</u>
0.66	211.788
2.31	290.909
3.79	346.482
6.24	426.007
10.23	472.610
31.07	532.481
21.60	518.495
42.49	542.518
84.05	556.300
125.71	563.469
187.39	567.402
245.68	570.507
293.24	573.503

Desorption

55.86	547.679
12.51	488.021
5.20	396.304
2.62	304.826
1.30	250.713

Iodine in Chabazite.

<u>at 538.16°K</u>		<u>at 573.16°K.</u>	
<u>Sorption</u>		<u>Sorption</u>	
<u>P</u>	<u>x</u>	<u>P</u>	<u>x</u>
0.74	168.940	0.53	101.500
2.81	229.738	5.21	225.402
4.00	266.773	7.51	259.036
11.17	369.156	14.34	318.869
24.00	452.483	30.04	396.961
35.90	487.496	56.21	453.956
56.28	512.770	94.34	486.208
122.50	540.998	159.59	508.761
150.60	547.368	304.68	527.051
183.24	551.782	<u>Desorption</u>	
236.18	556.537	233.53	517.657
299.34	559.788	72.02	471.233
<u>Desorption</u>		22.20	364.205
86.88	529.249	9.01	275.186
28.02	470.012	2.42	172.702
13.20	389.752	0.78	114.113
5.01	286.425		
2.10	215.031		

Check after going down the temperature cycle
at 573.16°K

P	3.60;	17.97;	41.55;	85.07;	153.75.
x	182.0;	343.0;	428.02;	480.3;	507.5.

Appendix II.

Isosteric Heat Data.

$$-q_{st} = \Delta \bar{H} = \widetilde{H}_g - \bar{H}_s \text{ kcals per mole.}$$

x = mass sorbed in mg/gm of outgassed sorbent.

I₂ in Faujasite (NaX)

<u>x</u>	<u>-ΔH</u>
60	38.644
100	28.707
150	21.527
200	18.241
250	17.038
300	16.418
350	16.201
400	16.152
450	16.212
500	16.222
550	16.263
600	16.566
650	16.895
700	17.042
750	16.998
800	17.363
850	17.734
900	18.007
950	18.401
1000	18.907
1050	19.452
1075	19.733
1100	17.484

I₂ in CaA

<u>x</u>	<u>-ΔH</u>
40	29.699
60	18.810
80	16.449
120	15.290
160	14.913
200	15.089
240	15.020
280	15.178
320	15.459
360	15.725
400	15.932
440	16.167
480	16.552
520	16.675
560	16.734
600	17.135
640	17.548
680	17.685
720	17.922
760	18.020
800	18.645
820	17.256

Iodine in Chabazite.

<u>x</u>	<u>-ΔH</u>
140	18.338
170	16.424
200	14.535
230	13.746
260	13.036
290	13.473
320	13.551
350	13.650
380	13.826
410	14.165
440	14.503
470	15.058
500	15.177
530	15.669
560	16.123
605	16.466
620	15.189

Appendix III.

Entropy Data.

- $\bar{S}_s$ = Partial molar entropy in sorbed state (E.U.).
 $\bar{S}_c$ = Partial molar configurational entropy (E.U.).
 $\bar{S}_{Th}$ = Partial molar thermal entropy = $\bar{S}_s - \bar{S}_c$ (E.U.).
 x = Mass sorbed mg/gm of outgassed sorbent.
 θ = x/x_{sat} = fractional coverage.

Iodine in Faujasite (NaX).

<u>at 393.16°K</u>			<u>at 428.16°K</u>		
<u>θ</u>	<u>x</u>	<u>$\bar{S}_s$</u>	<u>θ</u>	<u>x</u>	<u>$\bar{S}_s$</u>
0.70	798.0	38.200	0.55	621.5	44.603
0.75	855.0	36.374	0.60	678.0	43.281
0.80	912.0	34.363	0.65	734.5	41.873
0.85	969.0	31.969	0.70	791.0	40.310
0.90	1026.0	29.045	0.75	847.5	38.504
0.95	1083.0	25.370	0.80	904.0	36.530
			0.85	960.5	34.325
			0.90	1017.0	31.364
			0.95	1073.5	27.339
			0.50	565.0	45.790
<u>at 468.16°K</u>			<u>at 503.16°K</u>		
<u>θ</u>	<u>x</u>	<u>$\bar{S}_s$</u>	<u>θ</u>	<u>x</u>	<u>$\bar{S}_s$</u>
0.20	217.4	45.979	0.15	156.6	42.700
0.25	271.75	48.658	0.20	208.8	47.219
0.30	326.1	49.968	0.30	313.2	51.278
0.40	434.8	50.059	0.40	417.6	51.726
0.50	543.5	48.244	0.50	522.0	50.043
0.60	652.2	47.324	0.60	626.4	47.851
0.70	760.9	43.176	0.70	730.8	45.314
0.80	869.6	39.606	0.80	835.2	42.188
0.90	978.3	35.088	0.90	939.6	38.228
0.95	1032.65	32.092			

Iodine in Faujasite (NaX).

<u>at 538.16°K</u>			<u>at 573.16°K</u>		
θ	x	$\bar{S}_s$	θ	x	$\bar{S}_s$
0.10	99.0	33.998	0.10	93.0	33.255
0.20	198.0	47.909	0.20	186.0	48.207
0.30	297.0	52.334	0.30	279.0	52.982
0.40	396.0	53.143	0.40	372.0	54.408
0.50	495.0	51.781	0.50	465.0	53.510
0.60	594.0	49.804	0.60	558.0	51.847
0.70	693.0	47.535	0.70	651.0	49.815
0.80	792.0	44.874	0.75	697.5	48.733
0.85	841.5	43.298			

Iodine in Linde Sieve A (CaA).

<u>at 393.16°K</u>			<u>at 428.16°K</u>		
θ	x	$\bar{S}_s$	θ	x	$\bar{S}_s$
0.65	555.6	39.190	0.20	170.7	49.844
0.70	598.3	37.973	0.30	256.0	47.892
0.75	641.0	36.764	0.40	341.3	45.860
0.80	683.8	35.352	0.50	426.6	43.980
0.85	726.5	33.630	0.60	511.9	41.955
0.90	769.2	31.582	0.70	597.3	39.797
0.95	812.0	29.756	0.80	682.6	37.197
			0.90	767.9	33.396
			0.95	810.6	31.419

Iodine in Linde Sieve A (CaA).

<u>at 468.16°K</u>			<u>at 538.16°K</u>		
<u>θ</u>	<u>x</u>	<u>$\bar{S}_s$</u>	<u>θ</u>	<u>x</u>	<u>$\bar{S}_s$</u>
0.10	82.7	50.479	0.05	37.6	30.248
0.20	165.4	51.311	0.10	75.1	53.041
0.30	248.1	49.830	0.20	150.2	54.335
0.40	330.9	48.031	0.30	225.3	53.197
0.50	413.6	46.256	0.40	300.4	51.481
0.60	496.3	44.324	0.50	375.6	49.780
0.70	579.0	42.257	0.60	450.7	48.101
0.80	661.7	39.697	0.70	525.8	46.250
0.90	744.4	36.354	0.80	600.9	44.169
0.95	785.8	34.101	0.85	638.4	43.111

<u>at 503.16°K</u>				
<u>θ</u>	<u>x</u>	<u>$\bar{S}_s$</u>	<u>$\bar{S}_c$</u>	<u>$\bar{S}_{Th}$</u>
0.10	78.6	51.898	4.366	47.532
0.20	157.2	52.828	2.755	50.073
0.30	235.9	51.729	1.684	50.045
0.40	314.5	49.943	0.806	49.137
0.50	393.1	48.137	0.000	48.137
0.60	471.7	46.275	-0.805	47.080
0.70	550.3	44.368	-1.683	46.051
0.80	628.9	42.155	-2.754	44.909
0.90	707.5	39.396	-4.366	43.762

Iodine in Linde Sieve Aat 573.16°K

<u>θ</u>	<u>x</u>	<u>$\bar{S}_s$</u>
0.075	53.4	45.668
0.10	71.2	53.577
0.20	142.4	55.511
0.30	213.5	54.661
0.40	284.7	53.145
0.50	355.9	51.603
0.60	427.0	49.988
0.70	498.2	48.288

Iodine in Chabaziteat 393.16°K

<u>θ</u>	<u>x</u>	<u>$\bar{S}_s$</u>
0.85	539.7	40.556
0.90	571.4	36.899
0.95	603.2	31.515

at 428.16°K

<u>θ</u>	<u>x</u>	<u>$\bar{S}_s$</u>
0.80	507.9	45.404
0.85	539.7	43.439
0.90	571.4	38.842
0.95	603.2	33.192

Iodine in Chabazite.at 468.16°K

θ	x	$\bar{S}_s$
0.55	328.5	55.283
0.60	358.3	54.411
0.65	388.2	53.382
0.70	418.0	52.172
0.75	447.9	50.890
0.80	477.8	49.484
0.85	507.6	47.921
0.90	537.5	45.816
0.95	567.3	41.866

at 501.14°K

θ	x	$\bar{S}_s$
0.40	233.5	58.300
0.50	291.9	57.138
0.60	350.3	55.773
0.70	408.7	53.991
0.80	467.1	51.542
0.90	525.4	48.035
0.95	554.6	45.078

at 538.16°K

θ	x	$\bar{S}_s$
0.30	172.4	57.487
0.40	229.9	59.625
0.50	287.4	58.866
0.60	344.8	57.490
0.70	402.3	55.607
0.80	459.8	53.307
0.90	517.2	50.136
0.95	546.0	47.649

at 573.16°K

θ	x	$\bar{S}_s$
0.30	164.9	58.114
0.40	219.8	60.957
0.50	274.8	60.533
0.60	329.7	59.254
0.70	384.7	57.626
0.80	439.6	55.447
0.90	494.6	52.501
0.95	522.0	50.250

Vibrational frequency of I₂ in CaA at 503.16°K.

<u>θ</u>	<u>$\bar{\nu}$ sec⁻¹</u>
0.2	3.9071 x 10 ¹¹
0.3	3.9190 x 10 ¹¹
0.4	4.2943 x 10 ¹¹
0.5	4.7485 x 10 ¹¹
0.6	5.2818 x 10 ¹¹
0.7	5.8593 x 10 ¹¹
0.8	6.5722 x 10 ¹¹
0.9	7.3727 x 10 ¹¹

Appendix IV.

Thermodynamic Properties of the Sorbents.

- $\mu_A - \mu_A^\circ$ = Change in chemical potential of sorbent
in cals.
 $\bar{S}_A - \bar{S}_A^\circ$ = Change in partial molar entropy of sorbent
in E.U.
 $\bar{H}_A - \bar{H}_A^\circ$ = Change in partial molar enthalpy of sorbent
in kcals.

The standard state is taken as that at which the equilibrium pressure of sorbate vapour = 0, i.e. outgassed sorbent.

- x = Mass sorbed in gm/gm of outgassed sorbent.
 θ = x/x_{sat} = fractional coverage.

Faujasite with I₂.(A) $\mu_A - \mu_A^\circ$

<u>at 573.16°K</u>		<u>at 538.16°K</u>	
<u>x</u>	<u>$-(\mu_A - \mu_A^\circ)$</u>	<u>x</u>	<u>$-(\mu_A - \mu_A^\circ)$</u>
0.021656	7.257	0.073385	23.011
0.027757	11.659	0.106011	43.132
0.112830	43.495	0.151759	72.807
0.201648	83.034	0.293513	142.979
0.318122	132.847	0.404296	206.569
0.425432	194.951	0.493662	260.289
0.514695	253.933	0.597400	336.052
0.594009	316.955	0.656843	392.931
0.644471	369.386	0.716783	462.713
0.687363	422.275	0.774764	545.754
0.716150	457.424	0.812654	613.014
0.739232	492.567	0.839181	665.592
		0.861241	709.764

<u>at 503.16°K</u>		<u>at 468.16°K</u>	
<u>x</u>	<u>$-(\mu_A - \mu_A^\circ)$</u>	<u>x</u>	<u>$-(\mu_A - \mu_A^\circ)$</u>
0.122889	37.698	0.192601	51.054
0.167843	63.954	0.305474	117.419
0.266058	139.727	0.458790	225.410
0.366030	184.835	0.613373	257.206
0.468735	241.334	0.770112	416.189
0.632436	344.759	0.834250	506.487
0.710229	425.401	0.887672	606.956
0.765912	489.635	0.924800	696.518
0.820474	575.049	0.960378	809.145
0.857401	654.990	0.987584	913.400
0.891807	724.667	1.005965	993.485
0.920241	805.262	1.021299	1055.754
0.946856	888.575	1.030123	1114.209
0.963379	939.093	1.039461	1159.939

Faujasite with I₂.

<u>at 428.16°K</u>		<u>at 393.16°K</u>	
<u>x</u>	<u>$-(\mu_A - \mu_A^\circ)$</u>	<u>x</u>	<u>$-(\mu_A - \mu_A^\circ)$</u>
0.368352	92.449	0.715286	168.693
0.579184	175.160	0.900103	311.486
0.776431	330.659	0.934775	395.313
0.866462	447.843	0.984895	500.526
0.930404	536.247	1.008867	589.182
0.961950	633.956	1.049593	749.402
0.989728	713.051	1.075282	927.776
1.019370	834.016	1.091752	1053.807
1.048167	984.047	1.102148	1152.061
1.065223	1089.868	1.111712	1246.037
1.076858	1196.846	1.119726	1314.375
1.090508	1292.166	1.133255	1367.759
1.100444	1361.890		
1.111101	1417.659		

<u>at 488.16°K</u>		<u>at 448.16°K</u>	
<u>x</u>	<u>$-(\mu_A - \mu_A^\circ)$</u>	<u>x</u>	<u>$-(\mu_A - \mu_A^\circ)$</u>
0.176	50.397	0.330	95.361
0.195	59.681	0.374	114.513
0.264	102.651	0.5295	202.422
0.369	167.900	0.6975	312.733
0.461	209.012	0.7825	390.048
0.577	281.953	0.863	492.322
0.718	398.652	0.932	639.638
0.826	545.846	0.981	800.338
0.873	634.682	1.004	896.504
0.9195	757.980	1.031	1020.654
0.9705	930.282	1.0605	1199.526
0.997	1036.270	1.0755	1313.867

Faujasite with I₂.(B) $\bar{S}_A - \bar{S}_A^\circ$.428.16 - 503.16°K.

θ	x	$(\bar{S}_A - \bar{S}_A^\circ)$
0.895	1.020	5.750
0.842	0.960	4.333
0.789	0.900	3.243
0.737	0.840	2.657
0.684	0.780	2.343
0.631	0.720	2.114
0.579	0.660	1.914
0.526	0.600	1.729
0.474	0.540	1.507
0.421	0.480	1.329
0.368	0.420	1.114
0.316	0.360	0.929

503.16-- 538.16°K

x	$(\bar{H}_A - \bar{H}_A^\circ)$
0.120	0.010
0.180	0.047
0.240	0.060
0.300	0.050
0.360	0.053
0.420	0.057
0.480	0.043
0.540	-0.010
0.600	-0.023
0.660	-0.010
0.720	+0.050
0.780	+0.113
0.840	+0.267

(C) $\bar{H}_A - \bar{H}_A^\circ$.538.16 - 573.16°K.

x	$-(\bar{H}_A - \bar{H}_A^\circ)$
0.120	0.165
0.180	0.275
0.240	0.375
0.300	0.485
0.360	0.515
0.420	0.545
0.480	0.550
0.540	0.570
0.600	0.565
0.660	0.535
0.720	0.505

428.16 - 503.16°K

θ	x	$(\bar{H}_A - \bar{H}_A^\circ)$
0.316	0.360	0.317
0.368	0.420	0.370
0.421	0.480	0.447
0.474	0.540	0.487
0.526	0.600	0.547
0.579	0.660	0.593
0.631	0.720	0.627
0.684	0.780	0.673
0.737	0.840	0.777
0.789	0.900	0.897
0.842	0.960	1.197
0.895	1.020	1.523

Linde Sieve A (CaA) with I₂.

$\mu_A - \mu_A^\circ$

<u>at 573.16°K</u>	
<u>$\underline{x}$</u>	<u>$-(\mu_A - \mu_A^\circ)$</u>
0.0202	7.186
0.0281	19.848
0.0444	29.473
0.0752	45.172
0.1372	71.004
0.2197	106.969
0.2916	142.111
0.4237	193.198
0.3758	229.915
0.4765	278.847
0.5131	318.515

<u>at 503.16°K</u>	
<u>$\underline{x}$</u>	<u>$-(\mu_A - \mu_A^\circ)$</u>
0.0524	16.318
0.0920	55.622
0.1570	80.183
0.2055	101.009
0.3285	145.173
0.4199	197.961
0.5000	260.780
0.5586	313.190
0.6006	367.749
0.6305	414.763
0.6560	462.487
0.6780	508.047
0.6998	557.178
0.7161	603.785
0.7268	637.479

<u>at 538.16°K</u>	
<u>$\underline{x}$</u>	<u>$-(\mu_A - \mu_A^\circ)$</u>
0.0388	12.632
0.0546	32.079
0.0862	48.186
0.1486	78.904
0.2587	125.283
0.3774	189.162
0.4556	247.811
0.5142	304.909
0.5549	351.558
0.5809	387.150
0.6110	432.854
0.6298	465.970

<u>at 468.16°K</u>	
<u>$\underline{x}$</u>	<u>$-(\mu_A - \mu_A^\circ)$</u>
0.0799	22.669
0.1885	75.448
0.2862	114.620
0.5377	242.921
0.6184	324.441
0.6682	419.985
0.6983	482.783
0.7223	544.238
0.7496	627.048
0.7670	697.151
0.7785	749.880
0.7879	798.590
0.7942	837.947

Linde Sieve A (CaA) with I₂.

$$\underline{\mu_A - \mu_A^\circ.}$$

<u>at 428.16°K</u>		<u>at 393.16°K</u>	
<u>x</u>	<u>-($\mu_A - \mu_A^\circ$)</u>	<u>x</u>	<u>-($\mu_A - \mu_A^\circ$)</u>
0.1590	41.768	0.5267	132.976
0.4047	148.040	0.7010	335.344
0.5108	214.159	0.7333	409.224
0.6285	299.741	0.7682	519.229
0.6899	413.849	0.7943	612.769
0.7347	513.689	0.8080	701.815
0.7492	546.288	0.8109	736.984
0.7629	595.185	0.8144	784.125
0.7926	731.677	0.8193	821.535
0.8032	802.967	0.8224	858.947
0.8096	851.844	0.8262	912.067
0.8182	931.260	0.8319	984.634
0.8261	996.388	0.8379	1050.454
0.8316	1051.324	0.8510	1129.732
0.8362	1102.195		
0.8394	1116.428		

Linde Sieve A (CaA) with I₂.

$$\bar{S}_A - \bar{S}_A^\circ$$

$$393.16 - 538.16^\circ\text{K}$$

θ	x	$\bar{S}_A - \bar{S}_A^\circ$
0.913	0.780	2.750
0.842	0.720	1.917
0.772	0.660	1.575
0.702	0.600	1.360
0.632	0.540	1.100
0.562	0.480	0.910
0.491	0.420	0.710
0.421	0.360	0.610
0.351	0.300	0.490
0.281	0.240	0.480
0.211	0.180	0.325
0.140	0.120	0.263

$$\bar{H}_A - \bar{H}_A^\circ$$

$$538.16 - 573.16^\circ\text{K}$$

$$393.16 - 538.16^\circ\text{K}$$

x	$-(\bar{H}_A - \bar{H}_A^\circ)$	θ	x	$\bar{H}_A - \bar{H}_A^\circ$
0.480	0.115	0.070	0.060	0.0325
0.420	0.165	0.140	0.120	0.0525
0.360	0.170	0.211	0.180	0.0750
0.300	0.135	0.281	0.240	0.0875
0.240	0.125	0.351	0.300	0.120
0.180	0.090	0.421	0.360	0.160
0.120	0.070	0.491	0.420	0.1825
0.060	0.040	0.562	0.480	0.190
		0.632	0.540	0.250
		0.702	0.600	0.3125
		0.772	0.660	0.320
		0.842	0.720	0.458
		0.913	0.780	0.515

Chabazite with I_2 .

$\mu_A - \mu_A^\circ$.

at 573.16°K

<u>x</u>	<u>$-(\mu_A - \mu_A^\circ)$</u>
0.1015	31.802
0.2254	197.761
0.2590	222.406
0.3189	280.163
0.3970	361.188
0.4540	436.251
0.4862	506.838
0.5088	584.826
0.5177	641.984
0.5271	683.531

at 501.14°K

<u>x</u>	<u>$-(\mu_A - \mu_A^\circ)$</u>
0.2218	62.028
0.2909	159.463
0.3465	200.831
0.4260	261.938
0.4726	321.742
0.5325	463.438
0.5185	414.042
0.5425	507.631
0.5563	599.893
0.5635	663.550
0.5674	719.380
0.5705	760.913
0.5735	788.158

at 538.16°K

<u>x</u>	<u>$-(\mu_A - \mu_A^\circ)$</u>
0.1689	51.484
0.2297	138.007
0.2668	170.706
0.3692	261.033
0.4525	350.421
0.4875	403.490
0.5128	463.999
0.5410	575.671
0.5474	608.231
0.5518	637.992
0.5565	676.107
0.5598	713.279

at 468.16°K

<u>x</u>	<u>$-(\mu_A - \mu_A^\circ)$</u>
0.2806	73.729
0.3909	160.216
0.4461	223.774
0.4988	267.499
0.5302	362.235
0.5485	431.461
0.5550	478.824
0.5625	533.466
0.5708	629.982
0.5749	715.550
0.5795	771.958
0.5850	855.630
0.5823	824.719

Chabazite with I₂.at 428.16°K

<u>x</u>	<u>-(μ_A-μ_A[°])</u>
0.3930	100.770
0.4954	213.103
0.5288	276.334
0.5500	336.318
0.5615	418.518
0.5676	480.721
0.5728	549.582
0.5773	602.891
0.5854	693.938
0.5942	764.974
0.5998	807.128
0.6084	851.494
0.6149	889.199

at 393.16°K

<u>x</u>	<u>-(μ_A-μ_A[°])</u>
0.4962	121.338
0.5508	219.286
0.5666	280.328
0.5746	355.299
0.5784	389.469
0.5886	490.955
0.5996	565.914
0.6151	645.449
0.6310	705.595
0.6445	747.384

S_A - S_A[°].

<u>θ</u>	<u>x</u>	<u>S_A-S_A[°]</u>
0.945	0.600	6.925
0.898	0.570	4.073
0.851	0.540	2.700
0.803	0.510	2.059
0.756	0.480	1.882
0.709	0.450	1.725
0.662	0.420	1.661
0.614	0.390	1.546
0.567	0.360	1.543
0.520	0.330	1.457
0.473	0.300	1.386
0.425	0.270	1.243
0.378	0.240	1.121
0.331	0.210	1.007

H_A - H_A[°].

<u>θ</u>	<u>x</u>	<u>H_A-H_A[°]</u>
0.331	0.210	0.390
0.378	0.240	0.437
0.425	0.270	0.487
0.473	0.300	0.525
0.520	0.330	0.547
0.567	0.360	0.577
0.614	0.390	0.640
0.662	0.420	0.673
0.709	0.450	0.603
0.756	0.480	0.627
0.803	0.510	0.860
0.851	0.540	0.794
0.898	0.570	1.298
0.945	0.600	2.165

CaA with I₂.at 573.16°K

θ	x	$\frac{-\Delta\mu_A}{T_x \frac{a_{sat}}{24}} \text{ cal/s}$
0.03	0.020	0.066
0.04	0.028	0.182
0.06	0.044	0.270
0.11	0.075	0.413
0.19	0.137	0.649
0.31	0.220	0.978
0.41	0.292	1.300
0.60	0.424	2.102
0.53	0.376	1.767
0.67	0.477	2.550
0.72	0.513	2.913

at 503.16°K

0.07	0.052	0.154
0.12	0.092	0.524
0.20	0.157	0.756
0.26	0.206	0.952
0.42	0.329	1.369
0.53	0.420	1.772
0.64	0.500	2.459
0.71	0.559	2.953
0.76	0.601	3.467
0.80	0.631	3.910
0.83	0.656	4.360
0.86	0.678	4.790
0.89	0.700	5.253
0.91	0.716	5.692
0.93	0.727	6.010

at 538.16°K.

θ	x	$\frac{-\Delta\mu_A}{T_x \frac{a_{sat}}{24}} \text{ cal/s}$
0.05	0.039	0.117
0.07	0.055	0.296
0.12	0.086	0.445
0.20	0.149	0.728
0.34	0.259	1.157
0.50	0.377	1.746
0.61	0.456	2.288
0.69	0.514	2.815
0.74	0.555	3.245
0.77	0.581	3.574
0.81	0.611	3.996
0.84	0.630	4.301

at 468.16°K

0.10	0.080	0.218
0.23	0.189	0.727
0.35	0.286	1.104
0.65	0.538	2.341
0.75	0.618	3.126
0.81	0.668	4.047
0.85	0.698	4.652
0.87	0.722	5.244
0.91	0.750	6.042
0.93	0.767	6.717
0.94	0.779	7.225
0.95	0.788	7.694
0.96	0.794	8.074

CaA with I₂.

<u>at 428.16°K.</u>			<u>at 393.16°K.</u>		
<u>θ</u>	<u>x</u>	$\frac{-\Delta\mu_A}{T x^{a_{sat}}_{24}}$ cal/s	<u>θ</u>	<u>x</u>	$\frac{-\Delta\mu_A}{T x^{a_{sat}}_{24}}$ cal/s.
0.19	0.159	0.426	0.62	0.527	1.476
0.47	0.405	1.511	0.82	0.701	3.722
0.60	0.511	2.186	0.86	0.733	4.541
0.74	0.629	3.060	0.90	0.768	5.762
0.81	0.690	4.225	0.93	0.794	6.800
0.86	0.735	5.244	0.945	0.808	7.788
0.88	0.749	5.577	0.949	0.811	8.179
0.89	0.763	6.076	0.953	0.814	8.702
0.93	0.793	7.469	0.959	0.819	9.117
0.94	0.803	8.197	0.962	0.822	9.532
0.95	0.810	8.696	0.967	0.826	10.122
0.96	0.818	9.506	0.973	0.832	10.927
0.97	0.826	10.171	0.980	0.838	11.658
0.975	0.832	10.732	0.996	0.851	12.537
0.980	0.836	11.251			
0.984	0.839	11.396			

<u>θ</u>	<u>-R ln(1 - θ) cal/s</u>
0.1	0.209
0.2	0.443
0.3	0.709
0.4	0.015
0.5	1.377
0.6	1.821
0.7	2.392
0.8	3.198
0.9	4.575

CaA with I₂.

$$\begin{aligned}
 \frac{\partial}{\partial T} \left(\frac{\Delta \mu_A}{T} \right)_x &= \frac{-\Delta \bar{H}_A}{T^2} \\
 &= \frac{\partial}{\partial T} \left[\left(\frac{n_{\text{sat}}}{24} \right) R \ln(1 - \theta) \right]_x \\
 &= \underbrace{\frac{\partial (n_{\text{sat}})_x}{\partial T} \cdot \frac{R}{24} \ln(1 - \theta)}_{\text{I}} + \underbrace{\frac{R n_{\text{sat}}}{24} \cdot \frac{\partial}{\partial T} [\ln(1 - \theta)]_x}_{\text{II}}
 \end{aligned}$$

At 195°C = 468.16°K.

$$\frac{\partial (n_{\text{sat}})_x}{\partial T} = -0.00576 \text{ molecules/deg.}$$

$$\frac{\partial}{\partial T} [\ln(1 - \theta)]_x = -0.00152.$$

θ	I	II	I+II	$\frac{\Delta \bar{H}_A}{T^2} \text{ kcal/s}$ $= (I+II) T^2 \text{ kcal/s}$
0.1	0.000050	-0.000669	-0.000619	-0.136
0.2	0.000106	"	-0.000563	-0.123
0.3	0.000170	"	-0.000499	-0.109
0.4	0.000244	"	-0.000425	-0.093
0.5	0.000331	"	-0.000338	-0.074
0.6	0.000437	"	-0.000232	-0.051
0.7	0.000574	"	-0.000095	-0.021
0.8	0.000768	"	+0.000099	+0.022
0.9	0.001098	"	+0.000429	+0.094

Appendix V.Free Energy Data.

x = mass sorbed in mg/gm outgassed sorbent,
 p = pressure of sorbate vapour in mm. Hg
 θ = fraction of surface covered,
 K_1 = equilibrium constant.

I₂ in Faujasite (NaX).

<u>at 393.16°K</u>		
<u>x</u>	<u>θ</u>	<u>$\frac{p(1-\theta)}{\theta}$</u>
684.0	0.60	0.21200
798.0	0.70	0.22286
912.0	0.80	0.26250
1026.0	0.90	0.48666
741.0	0.65	0.21538
855.0	0.75	0.23500
969.0	0.85	0.33000
1083.0	0.95	0.97366

<u>at 428.16°K</u>		
<u>x</u>	<u>θ</u>	<u>$\frac{p(1-\theta)}{\theta}$</u>
339.0	0.30	1.0337
452.0	0.40	1.1250
565.0	0.50	1.0800
678.0	0.60	1.0667
791.0	0.70	1.1657
904.0	0.80	1.4750
1017.0	0.90	2.8889
395.5	0.35	1.1106
508.5	0.45	1.1171
621.5	0.55	1.0636
734.5	0.65	1.0877
847.5	0.75	1.2833
960.5	0.85	1.8706
1073.5	0.95	5.6314

<u>at 468.16°K</u>		
217.4	0.20	2.5120
326.1	0.30	3.8500
434.8	0.40	4.3350
543.5	0.50	4.3000
652.2	0.60	4.2867
760.9	0.70	4.8643
869.6	0.80	6.5000
978.3	0.90	10.533
1032.7	0.95	13.579
163.1	0.15	1.8700

<u>at 503.16°K</u>		
104.4	0.1	4.0500
208.8	0.2	7.9200
313.2	0.3	10.920
417.6	0.4	12.045
522.0	0.5	13.000
626.4	0.6	13.733
730.8	0.7	15.300
835.2	0.8	18.750
939.6	0.9	25.222

I₂ in Faujasite (NaX).

<u>at 538.16°K</u>			<u>at 573.16°K</u>		
<u>x</u>	<u>θ</u>	<u>$\frac{p(1-\theta)}{\theta}$</u>	<u>x</u>	<u>θ</u>	<u>$\frac{p(1-\theta)}{\theta}$</u>
99.0	0.90	14.130	46.5	0.05	68.400
198.0	0.80	23.960	93.0	0.10	68.400
297.0	0.70	27.300	186.0	0.20	68.800
396.0	0.60	30.000	279.0	0.30	68.132
495.0	0.50	33.100	372.0	0.40	70.050
594.0	0.40	35.200	465.0	0.50	72.800
693.0	0.30	38.057	558.0	0.60	73.334
792.0	0.20	43.000	651.0	0.70	76.500
841.5	0.15	45.529	744.0	0.80	78.250
			697.5	0.75	77.999

I₂ in Linde Sieve A (CaA).

<u>at 393.16°K</u>			
<u>x</u>	<u>θ</u>	<u>$\frac{p(1-\theta)}{\theta}$</u>	<u>K₁</u>
555.56	0.65	0.247	4.049
598.29	0.70	0.257	3.891
641.03	0.75	0.262	3.817
683.76	0.80	0.288	3.472
726.50	0.85	0.347	2.882
769.23	0.90	0.437	2.288
811.97	0.95	0.763	1.359

I₂ in Linde Sieve A (CaA).at 428.16°K.

<u>x</u>	<u>θ</u>	$\frac{p(1-\theta)}{\theta}$	<u>K₁</u>
170.7	0.20	1.496	0.6685
256.0	0.30	1.689	0.5921
341.3	0.40	1.545	0.6473
426.6	0.50	1.440	0.6944
511.9	0.60	1.427	0.7008
597.3	0.70	1.459	0.6854
682.6	0.80	1.708	0.5855
767.9	0.90	2.753	0.3632
810.6	0.95	4.734	0.2112

at 468.16°K

<u>x</u>	<u>θ</u>	$\frac{p(1-\theta)}{\theta}$	<u>K₁x10²</u>
82.7	0.1	5.094	19.631
165.4	0.2	7.080	14.124
248.1	0.3	7.326	13.650
330.9	0.4	6.660	15.015
413.6	0.5	6.270	15.949
496.3	0.6	6.390	15.650
579.0	0.7	6.650	15.038
661.7	0.8	8.125	12.308
744.4	0.9	11.211	8.920
785.8	0.95	12.624	7.921

I₂ in Linde Sieve A (CaA).at 503.16°K

<u>x</u>	<u>θ</u>	$\frac{p(1-\theta)}{\theta}$	<u>K₁x10²</u>
78.6	0.1	16.920	5.910
157.2	0.2	20.080	4.980
235.9	0.3	19.364	5.164
314.5	0.4	18.750	5.333
393.1	0.5	19.000	5.263
471.7	0.6	19.810	5.048
550.3	0.7	20.378	4.907
628.9	0.8	22.375	4.469
707.5	0.9	24.642	4.058

at 538.16°K

<u>x</u>	<u>θ</u>	$\frac{p(1-\theta)}{\theta}$	<u>K₁x10²</u>
75.1	0.1	37.080	2.697
150.2	0.2	47.600	2.101
225.3	0.3	50.626	1.975
300.4	0.4	51.150	1.955
375.6	0.5	51.700	1.934
450.7	0.6	52.226	1.915
525.8	0.7	54.912	1.821
600.9	0.8	58.250	1.717
638.4	0.85	57.171	1.749

I₂ in Linde Sieve A (CaA).At 573.16°K

<u>x</u>	<u>θ</u>	$\frac{p(1-\theta)}{\theta}$	<u>K₁x10³</u>
35.6	0.05	74.100	13.495
53.4	0.075	92.498	10.811
71.2	0.1	101.700	9.833
142.4	0.2	112.800	8.865
213.5	0.3	114.084	8.766
284.7	0.4	111.750	8.949
355.9	0.5	110.000	9.091
427.0	0.6	111.389	8.978
498.2	0.7	114.543	8.730

I₂ in Chabazite.at 393.16°K

<u>x</u>	<u>θ</u>	$\frac{p(1-\theta)}{\theta}$
539.67	0.85	0.182
571.42	0.90	0.400
603.17	0.95	1.599

at 428.16°K

<u>x</u>	<u>θ</u>	$\frac{p(1-\theta)}{\theta}$
507.92	0.80	0.450
539.67	0.85	0.517
571.42	0.90	1.909
603.17	0.95	9.152

at 468.16°K

<u>x</u>	<u>θ</u>	$\frac{p(1-\theta)}{\theta}$
328.46	0.55	0.851
358.32	0.60	0.921
388.18	0.65	0.965
418.04	0.70	0.995
447.90	0.75	1.009
477.76	0.80	1.013
507.62	0.85	1.036
537.48	0.90	1.199
567.34	0.95	2.641

I₂ in Chabazite.

<u>at 501.14°K</u>			<u>at 538.16°K</u>		
<u>x</u>	<u>θ</u>	$\frac{p(1-\theta)}{\theta}$	<u>x</u>	<u>θ</u>	$\frac{p(1-\theta)}{\theta}$
233.52	0.4	1.482	172.41	0.3	2.263
291.90	0.5	2.280	229.88	0.4	3.900
350.28	0.6	2.548	287.35	0.5	5.040
408.66	0.7	2.420	344.82	0.6	5.870
467.05	0.8	2.395	402.29	0.7	6.306
525.42	0.9	2.853	459.76	0.8	6.250
554.61	0.95	3.945	517.23	0.9	6.882
			545.97	0.95	7.627

<u>at 573.16°K</u>		
<u>x</u>	<u>θ</u>	$\frac{p(1-\theta)}{\theta}$
109.90	0.2	2.860
164.85	0.3	4.969
219.80	0.4	7.170
274.75	0.5	8.980
329.70	0.6	10.672
384.65	0.7	11.454
439.60	0.8	11.750
494.55	0.9	12.321
522.03	0.95	13.150

Appendix VI.

Inter-Molecular Forces Data.

(Sorbate-Lattice Interaction)

- A = dispersion constant in cal $\cdot$ cm⁶,
a = distance between the centre of molecule and the
centre of cavity (or centre of ring) in Å,
Q_D = dispersion energy in cal $\cdot$ gm mole,
Q_R = repulsion energy in cal $\cdot$ gm mole,
Q = total interaction energy in cal $\cdot$ gm mole.
r = distance between centres of molecules.
a_c = length of unit cell edge.

Intermolecular Interaction in Faujasite.Tables of r^2/a_c^2 .

Positions measured along a line joining the centres of two cavities and passing through the centre of 12-membered ring. Zero at the centre of left hand cavity; +ve to the right; -ve to the left; distance between each position = 0.544 Å.

Frame- work Oxygen Atoms	No. of atoms	Position of I_2						
		-1	-2	-3	-4	-5	-6	-7
ia	3	.1109	.10118	.09244	.08463	.07776	.07181	.06682
ib	3	.1160	.1115	.1079	.1052	.1035	.10265	.1028
ic	6	.1305	.1404	.1513	.1631	.1758	.1895	.2041
iib	3	.1003	.1065	.1137	.1218	.1309	.1409	.1518
iic	6	.08795	.08188	.07673	.07256	.06931	.06698	.06561
iiia	6	.07859	.06966	.06167	.05462	.04851	.04332	.03909
iiib	6	.08580	.08408	.08330	.08346	.08456	.08658	.08956
iiic	6	.09831	.10909	.12081	.1333	.14705	.16158	.17705
iiid	6	.09302	.09850	.10494	.11230	.12060	.12984	.14002
iva	3	.07195	.06143	.05187	.04323	.03553	.02877	.02295
ivb	3	.08427	.08608	.08883	.09251	.09713	.10268	.10919
ivc	6	.08963	.09679	.10489	.11393	.12391	.13481	.14667
va	3	.06964	.05995	.05121	.04340	.03653	.03059	.02560
vb	3	.08937	.09941	.11040	.12232	.13518	.14897	.16371
vc	6	.08196	.08458	.08816	.09266	.09810	.10448	.11180
vi	6	.12425	.11088	.09845	.08696	.07641	.06679	.05811

Tables of r^2/a_c^2 , continued.

Frame- work Oxygen atoms	No. of atoms	Position of I_2						
		-8	-9	0	1	2	3	4
ia	3	.06276	.05964	.1215	.1331	.1456	.1590	.1734
ib	3	.1039	.1059	.1215	.1279	.1353	.1436	.1528
ic	6	-	-	.1215	.1134	.10632	.10015	.09491
iib	3	.1637	.1765	.09496	.09059	.08715	.08446	.08310
iic	6	.06516	.06565	.09496	.10291	.11178	.12161	.13236
iiia	6	.03578	.03341	.08846	.09927	.1110	.12369	.13730
iiib	6	.09346	.09830	.08846	.09206	.09658	.10206	.10846
iiic	6	.19346	-	.08846	.07955	.07158	.06455	.05846
iiid	6	.15114	.16318	.08846	.08484	.08216	.08042	.07962
iva	3	.01806	.01410	.08340	.09579	.10911	.12337	.13857
ivb	3	.11662	.12498	.08340	.08347	.08446	.08641	.08929
ivc	6	.15946	.17318	.08340	.07811	.07375	.07035	.06787
va	3	.02154	.01841	.08026	.09182	.10431	.11775	.13212
vb	3	.17938	.19598	.08026	.07202	.06485	.05856	.05320
vc	6	.12006	.12924	.08026	.07950	.07968	.08080	.08286
vi	6	.05037	.02879	.13855	-	-	-	-

Tables of R^2/a_c^2 , continued.

Frame- work oxygen atoms	No. of atoms	Position of I_2						
		5	6	7	8	9	10	11
ia	3	.1887	.2049	-	-	-	-	-
ib	3	.1630	.1741	.18614	.19912	-	-	-
ic	6	.09061	.08724	.08481	.08332	.08277	.08315	.08447
iib	3	.08248	.08279	.08405	.08624	.08936	.09343	.09843
iic	6	.14405	.15668	.17025	.18476	.20019	-	-
iiia	6	.15185	.16734	.18377	.20114	-	-	-
iiib	6	.11580	.12408	.13330	.14346	.15454	.16658	.1795
iiic	6	.05331	.04908	.04581	.04346	.04205	.04158	-
iiid	6	.07976	.08082	.08284	.08578	.08966	.09448	.10024
iva	3	.15471	.17177	.18979	.20874	-	-	-
ivb	3	.09311	.09786	.10355	.11018	.11774	.12625	.1357
ivc	6	.06633	.06573	.06607	.06734	.06965	.07270	.07678
va	3	.14743	.16367	.18086	.19898	-	-	-
vb	3	.04878	.04529	.04275	.04114	.04046	.04073	.04193
vc	6	.08586	.08978	.09466	.10046	.10720	.11488	.1235

Tables of r^2/a_c^2 , continued.

Atom	Position of I_2								
	12	13	14	15	16	17	18	19	20
ia	-	-	-	-	-	-	-	-	-
ib	-	-	-	-	-	-	-	-	-
ic	.08673	.08993	.09406	.09913	.1051	.1121	.1200	.1288	.1385
iib	.1044	.1113	.1191	.1278	.1375	.1481	.1597	.1722	.1856
iic	-	-	-	-	-	-	-	-	-
iiia	-	-	-	-	-	-	-	-	-
iiib	.1935	-	-	-	-	-	-	-	-
iiic	-	-	-	-	-	-	-	-	-
iiid	.1069	.1146	.1231	.1327	.1431	.1545	.1668	.1801	.1942
iva	-	-	-	-	-	-	-	-	-
ivb	.1461	.1574	.1696	.1828	.1970	-	-	-	-
ivc	.08180	.08776	.09467	.1025	.1113	.1210	.1316	.1432	.1557
va	-	-	-	-	-	-	-	-	-
vb	.04407	.04715	.05117	.05612	.06201	.06883	.07660	.08530	.09494
vc	.1331	.1436	.1550	.1674	.1807	.1949	-	-	-

Tables of r^2/a_c^2 .

Lateral Displacement in the 12-membered ring.

Oxygen atom	No. of atoms	Distance from centre of the ring in Å ^o				
		0.5	1.0	1.5	2.0	1.75
iiic ₂	1	.05011	.05940	.06950	.08038	.07484
iiic ₁	1	.03387	.02694	.02080	.01546	.01804
iiic ₃	2	.04605	.05129	.05732	.06415	.06064
iiic ₄	2	.03793	.03505	.03298	.03169	.03224
vb ₂	2	.04113	.04231	.04429	.04706	.04558
vb ₃	2	.04806	.05617	.06508	.07478	.06983
vb ₁	2	.03420	.02845	.02350	.01934	.02133
ic ₅	2	.09459	.1068	.1198	.1336	.1266
ic ₃	2	.07251	.06265	.05359	.04532	.04936
ic ₁	2	.09170	.1010	.1112	.1221	.1165
ic ₄	2	.07540	.06844	.06227	.05689	.05948
ic ₂	2	.08644	.09052	.09539	.1011	.09812
ic ₆	2	.08066	.07894	.07803	.07791	.07788

Energy of Interaction of I_2 with framework oxygens
in Faujasite.

Position	Distance from centre of L.H. cage A	-Q kcal/s/ mole	Position	Distance from centre of L.H. cage A	-Q kcal/s/ mole
-9	-4.896	4.529	6	3.264	5.104
-8	-4.352	14.771	7	3.808	5.672
-7	-3.808	12.936	8	4.352	6.220
-6	-3.264	9.269	9	4.896	6.562
-5	-2.720	6.546	10	5.440	6.682
-4	-2.176	4.721	11	5.984	6.562
-3	-1.632	3.692	12	6.528	6.220
-2	-1.088	3.073	13	7.072	5.672
-1	-0.544	2.756	14	7.616	5.104
0	0	2.626	15	8.160	4.495
1	0.544	2.800	16	8.704	3.941
2	1.088	3.140	17	9.248	3.477
3	1.632	3.477	18	9.792	3.140
4	2.176	3.941	19	10.336	2.800
5	2.720	4.495	20	10.880	2.626

Energy of Interaction of I₂ with framework oxygens in Faujasite on approaching 12-membered ring, from outside crystal, along axis through the centre of the cage and centre of the window, and perpendicular to the plane of the window.

Position	Distance from centre of window Å	-Q kcal/mole
20	5.440	1.588
19	2.896	2.013
18	4.352	2.528
17	3.808	3.004
16	3.264	3.580
15	2.720	4.210
14	2.176	4.883
13	1.632	5.508
12	1.088	6.090
11	0.544	6.497
10	0	6.612

Energy of Interaction of I_2 with framework oxygens in Faujasite; I_2 in the plane of the 12-membered ring.

Distance from centre of ring A	0	0.5	1.0	1.5	1.75	2.0
-Q, kcals/mole	6.682	7.237	8.608	10.742	10.859	7.211

Energy of Interaction of I_2 with 8-membered ring 4.2 Å free diameter in Linde Sieve A; I_2 approaching along axis perpendicular to the plane of the ring and with its longer diameter parallel to the axis of approach.

Distance from centre of ring A	0	1	2	3	4	5
-Q, kcals/mole	12.072	12.444	9.462	5.128	2.296	1.030

Energy of Interaction of I_2 with 8-membered ring 4.2 Å free diameter in Linde Sieve A; rotating I_2 approaching along axis perpendicular to the plane of the ring.

Distance from centre of ring A	0	1	2	3	4	5
Q, kcals/mole	+22.941	+9.422	-3.036	-3.783	-2.064	-0.986

Energy of Interaction of I_2 with 8-membered ring 3.9 Å free diameter in Chabazite; I_2 approaching along an axis passing through the centre of the ring and perpendicular to the plane of the ring; I_2 has its longer diameter parallel to the line of approach.

Distance from centre of ring Å	0	1	2	3	4	5
-Q, kcals/mole	8.854	12.035	10.663	5.712	2.551	1.118

Energy of Interaction of I_2 with 6-membered ring 2.2 Å free diameter; I_2 oriented and approaching in similar manner as for 8-membered ring in chabazite.

Distance from centre of ring Å	0	1	2	3	4	5
Q, kcals/mole	+577.8	+199.7	+0.399	-7.974	-3.338	-1.298

Iodine-Iodine Interaction; $r_e = 4.3\text{Å}$.

I_2-I_2 distance Å	Q kcals Avog. No. of pairs
3.5	+9.140
4.0	-1.302
4.5	-1.742
5.0	-1.192
5.5	-0.747
6.0	-0.467
6.5	-0.297
7.0	-0.193
7.5	-0.129
8.0	-0.088

Appendix VII.X-ray Diffraction Data.

Intensity of the lines were estimated visually
and

s	=	strong,	w	=	weak,
m	=	medium,	v	=	very.

Faujasite (NaX).

<u>Outgassed.</u>			<u>Fully sorbed with I₂ or Br₂.</u>		
d Å	hkl indices	Intensity	d Å	hkl indices	Intensity
8.93	220	v.s.	9.03	220	w.
7.64	311	v.s.	7.665	311	s.
5.79	331	v.s.	6.30	004	v.w.
4.864	551	v.w.	5.135	224	w.
4.45	440	w.	4.835	115	w.
4.21	531	v.w.	4.436	404	m.s.
3.835	335	v.s.	4.188	531	m.s.
3.358		v.s.	3.964	620	v.w.
3.059		w.	3.832	533	v.s.

Linde Sieve (CaA).

<u>Outgassed</u>			<u>Fully sorbed with I₂ or Br₂.</u>		
d Å	hkl indices	Intensity	d Å	hkl indices	Intensity
13.865	100	v.v.s.	4.912	211	v.w.
8.84	101	w.	4.047	300	s.
7.198	111	s.	3.666	311	w.
5.54	102	s.	3.239	321	w.
5.072	112	w.	2.950	410;322	m.s.
4.362	202	w.	2.859	411	m.s.
4.121	003	v.s.	2.663	421	v.w.
3.726	113	s.	2.342	511	v.w.
3.30	213	v.s.	2.134	404	w.
			2.030	424;6000	w.
			1.895	540;621	m.s.
			1.730	632;700	s.

Chabazite.

Outgassed.			Fully sorbed with I ₂ or Br ₂ .		
d Å	hkl indices	Intensity	d Å	hkl indices	Intensity
9.45	10 $\bar{1}$	v.s.	9.47	10 $\bar{1}$	m.
6.67	102;110	s.	6.90	110	w.
5.485	201	w.	5.57	201	s.
5.23	003	v.w.	4.70	20 $\bar{2}$	v.v.w.
4.24	21 $\bar{1}$	v.s.	4.33	21 $\bar{1}$	v.s.
3.875	212	m.	4.095	113	m.
3.725	104	m.	3.87	212	m.
3.356	214;220	w.	3.64	10 $\bar{4}$	v.s.
3.25	204	w.	3.436	220	m.
3.15	303	m.	3.218	204;311	s.
3.034	105;31 $\bar{2}$	m.	3.112	30 $\bar{3}$	w.
2.93	21 $\bar{4}$	m.	2.916	21 $\bar{4}$;40 $\bar{1}$	v.s.
2.85	223	v.s.	2.708	32 $\bar{1}$;10 $\bar{5}$	v.w.
			2.548	410;322	w.
			2.522	D215;314	m.
			2.298	330	m.
			2.143	405	m.

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A Short Account of Work done under
Dr. D. C. Bradley at Birkbeck College.

"The Mechanism of Meerwein-Pondorf-Verley
Reduction and Oppenauer Oxidation".

by

S. Wasilewski.

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1.1. General Information about the Reaction.

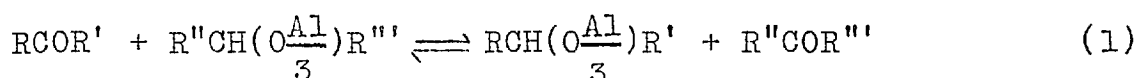
The Meerwein-Pondorf-Verley Reduction and the Oppenauer Oxidation, are complementary reactions which together constitute a reversible transformation between carbonyl and carbinol compounds in the presence of metallic alkoxides.

The reduction of carbonyl compounds by the use of metallic alkoxides was discovered in 1925 by Verley, Meerwein and Schmidt, and independently by Pondorf in 1926. Later Oppenauer pointed out that alcohols can be oxidised by a similar method, using acetone as hydrogen acceptor. At first, sodium and magnesium alkoxides were used for the Meerwein-Pondorf-Verley reduction, but later it was found that aluminium alkoxides are weaker condensing agents than sodium and magnesium alkoxides and are soluble in both alcohols and hydrocarbons, and therefore they are better for that purpose. Also, using aluminium alkoxides reduction does not stop at an intermediate stage; no pinacol formation has been observed, and pinacols are not reduced further by this reagent^(1,2,3). The possibility that the nitroso group may be reduced by aluminium alkoxides has been suggested by the same authors but no details of such a reduction have been published.

Alkoxides of other metals have been used, in the M.P.V. reduction, including magnesium ethoxide⁽⁴⁾; iodo- and bromo-magnesium ethoxides^(5,6,7); sodium ethoxide⁽⁸⁾; stannic and zirconium alkoxides⁽⁹⁾. Meerwein found that from all these aluminium alkoxides were the best, the next in order being zirconium alkoxides. Today it has become customary to refer to a reduction of carbonyl compound as the M.P.V. reduction, when aluminium alkoxides are used for the purpose.

The importance of the M.P.V. reduction and Oppenaur oxidation arises because aluminium alkoxides are very mild reducing agents. Multiple bonds are not reduced, and because of the very small energy required to shift the equilibrium of the reaction it is of biological importance.

The M.P.V.-Oppenauer reaction may be represented by the following equation:



This equation represents equilibrium between two oxidation-reduction systems:



If the system (2) has a higher potential than (3), equilibrium will be displaced to the right in (1) and vice versa. Thus by suitably varying the conditions a carbonyl compound can be reduced in a good yield to a hydroxyl (carbinol) compound, or the reverse change can be brought about.

Relative strengths of some carbonyl compounds as oxidising agents expressed in terms of the calculated oxidation-reduction potential is given below⁽¹⁰⁾:-

<u>Carbonyl compound</u>	<u>E_o (mV)</u>
Chloral	277
Formaldehyde	257
Acetaldehyde	226
iso-Butyraldehyde	220
Benzaldehyde	197
Cyclohexanone	162
Benzophenone	129
Acetone	129
Acetophenone	118
Diethyl ketone	110
Camphor	82
Δ ¹¹ -Cholestenone	63

Generally any carbonyl compound high in this list will oxidise more or less completely an alcohol corresponding to a carbonyl low in the series. In quantitative terms, if two carbonyl compounds differ in oxidation potential by 100 mV then at equilibrium the reaction mixture will contain 2% of the higher potential compound and 98% of the lower one. For a difference of 50 mV, the figures are: 12.5% and 87.5%; for difference of 10 mV, 40% and 60% respectively. However, the reaction may be brought to completion by continuous removal of one component, so that it is not essential to have a difference in potential of 100 mV to ensure a maximum yield.

In choosing an oxidant or reductant for a compound whose potential has not been calculated, it is useful to keep in view certain generalizations on the effect of structure on the oxidation potential of carbonyl compounds⁽¹¹⁾.

(a) Replacement of H on a carbonyl compound carbon by alkyl or aryl group lowers the oxidation potential,

e.g.	HCHO	260 mV
	CH ₃ CHO	226 mV
	(CH ₃) ₂ CO	129 mV.

(b) Replacement of H on a carbon adjacent to a C=O group has a similar but less marked effect,

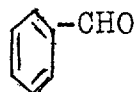
e.g.	CH ₃ .CHO	226 mV
	(CH ₃) ₂ CH.CHO	220 mV
	(CH ₃) ₃ C.CHO	211 mV.

(c) Many alkyl or aryl groups have much the same effect on the potential as methyl groups. There are, however, a few with exceptionally high potentials,

e.g.	Cyclohexanone	162 mV
	ter. Butyl phenyl ketone	169 mV
	Benzhydrol methyl ketone	182 mV
	Dibenzyl ketone	216 mV.

(d) The presence of an α β double bond brings about a distinct lowering of the oxidation potential as shown by the comparison of crotonaldehyde, benzaldehyde and cinnamaldehyde with acetaldehyde and isobutyraldehyde, e.g.

CH₃CH = CH - CHO 194 mV; CH₃CHO 226 mV.



197 mV; isobutyraldehyde 220 mV.



-CHO = CH - CHO

187 mV; isobutyraldehyde 220 mV.

On the other hand a carbon attached to a double bond in the β γ position has little effect, e.g. Δ^3 -cyclohexanone has the same potential as cyclohexanone.

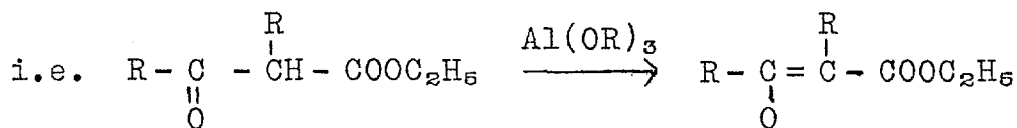
(e) Replacement of H by oxygen in the α -position of a ketone produces a marked increase in potential as shown by the following series:

Acetone	129 mV
Methoxyacetone	189 mV
Dimethoxyacetone	350 mV.

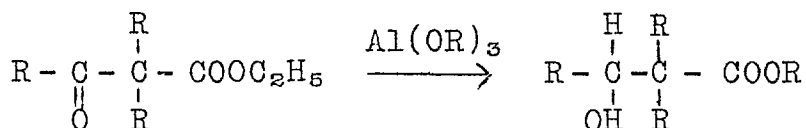
(f) Substitution of H by chlorine also results in an increase of oxidation potential.

e.g. Acetaldehyde	226 mV
Chloral	277 mV.

The M.P.V. reduction may also be applied to esters. In general, β -keto esters and β -di-ketones which are capable of enolisation, form the aluminium salt of the enolic form and are not reduced, but if there are no enolisable hydrogens then reaction proceeds smoothly⁽¹²⁾.



but,



If a phenolic ketone or a keto-acid forms a salt which is insoluble in the reaction medium, reduction may proceed slowly or not at all. If the salt is moderately soluble, or if the phenolic or acidic group is converted to the ether or ester, reduction will occur.

In the case of compounds containing nitrogen the reaction is hindered or may not take place at all, due to the fact that aluminium alkoxide may form a complex with the nitrogen compound of the type $\text{R}_3\text{N}^+:\text{AlR}_3^-$, which

may remove the alkoxide from the sphere of action. The complex formation is explained by the fact that the aluminium atom, in the alkoxide, with an open sextet of electrons, exhibits acidic properties^(13,14).

Since aluminium alkoxide functions effectively as a catalyst for alcohol exchange in esters, reduction of keto-esters by aluminium isoprop-oxide frequently yields the isopropyl ester of the hydroxy acid⁽¹⁵⁾.

γ -ketoesters, upon reduction, usually give rise to lactones of the hydroxy acids. A similar reaction was found to occur when the carbon atoms between the keto and ester groups were included as a part of a ring.

With trans isomers, lactone formation is prevented by steric factors.

The formation of a lactone occurs in the reduction mixture in the presence of excess of isopropyl alcohol, and not during the subsequent isolation and purification⁽¹⁶⁾.

Reduction of esters of hydroxy ketones usually is accompanied by cleavage of the ester group and the product is a glycol. Ether and acetal linkages are not affected.

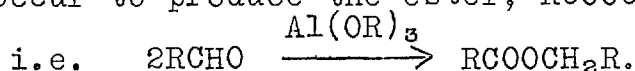
In the case of α -bromo and chloroketones the reaction proceeds sometimes with the elimination of the halide atom⁽¹⁶⁾.

The more important side reactions which may occur in the M.P.V. reduction are:

(a) Condensation - more pronounced with aldehydes than ketones.

Dilute solutions minimise this effect⁽¹⁷⁾. High temperature increases the amount of polymers formed and condensation. In addition the Tischchenko reaction

may occur to produce the ester, RCOOCH_2R ^(18,19).



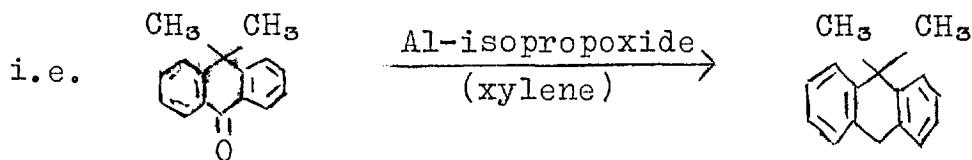
This reaction occurs to a greater extent in benzene solution than in isopropyl alcohol. It appears that an excess of Al-isopropoxide has the desired effect of speeding up the reduction reaction and thus minimises the side reactions in the case of aliphatic aldehydes, but is disadvantageous in the case of aromatic aldehydes⁽²⁰⁾.

(b) Dehydration of the alcohol to the corresponding hydrocarbon.

(c) Migration of double bond from the α , β to the β , γ position with respect to the carbonyl group.

(d) Ether formation sometimes occurs even by recrystallisation of the ketone from alcohol, but this is not a common side reaction.

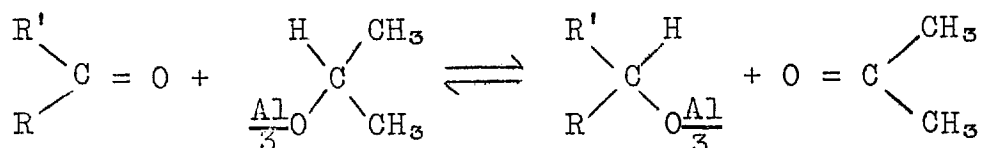
(e) Reduction of a ketone to a hydrocarbon. This reaction is not usually found but sometimes may occur as in the case of 9, 9 dimethyl-anthrone-10 reduction in xylene solution,



In the case of Oppenauer oxidation the aluminium alkoxide must be a tertiary alcohol, as otherwise it will be dehydrated during the reaction⁽²¹⁾.

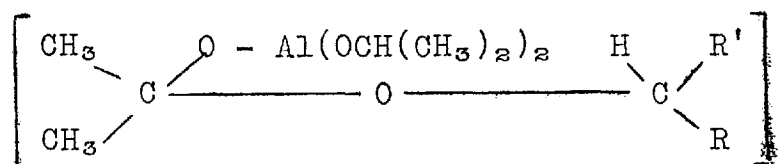
1.2. The Mechanism - Historical.

In 1925, Meerwein, Pondorf and Verley represented the reaction by the following equilibrium:



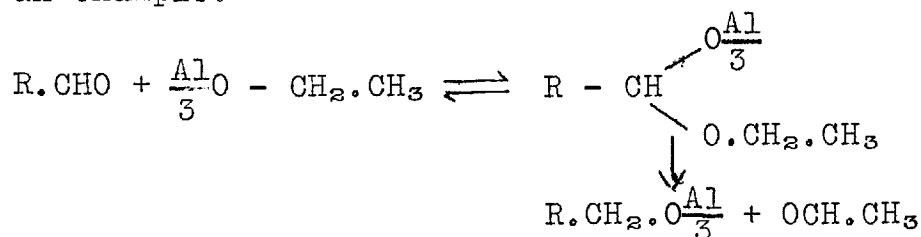
and postulated the formation of a hemiacetal as an intermediate step,

i.e. considering the above equation the hemiacetal will be



This consequently breaks up into acetone and aluminium alkoxide^(22,23,24).

First substantiation of this mechanism was given by Meerwein⁽²⁵⁾, who considered the following equation as an example:

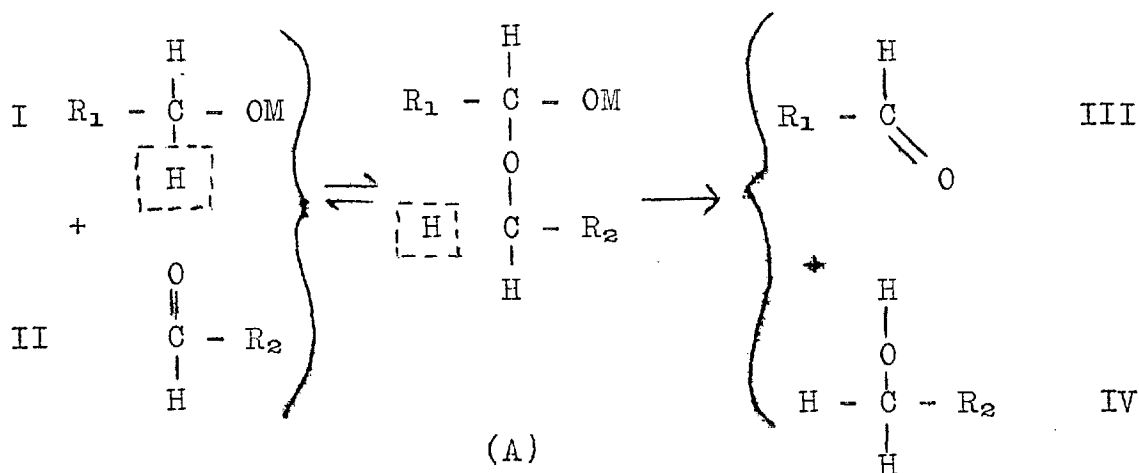


He postulated that first aldehyde combines with the alcohol or alkoxide forming aldehyde-alkoholate (hemiacetal), which later disproportionates in the other direction.

The formation of the intermediate hemiacetal is shown, he argued, by the fact that solution of alcoholate in ethanol gives slight alkaline reaction towards phenolphthalein, but on addition of aldehyde, which itself is neutral, the solution gives red colour with methyl red.

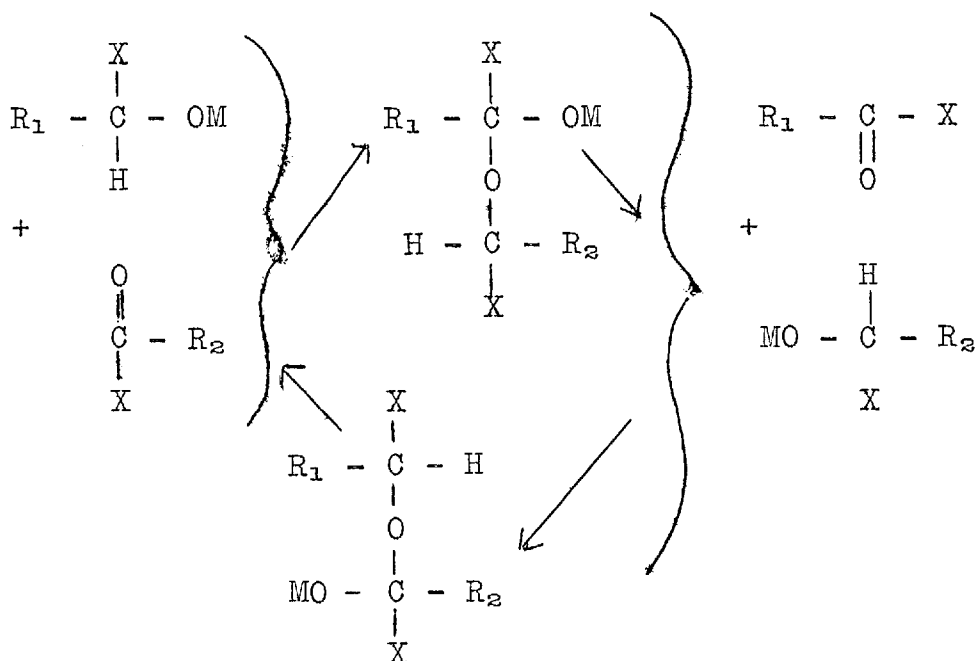
This, he said, is due to the high dissociation constant of the transition product. The second stage, i.e. the decomposition of the hemiacetal into acetaldehyde and a new alcoholate, corresponds to the known decomposition by heat of ether into aldehyde and hydrocarbons.

In 1926, Pondorf⁽²⁶⁾ proposed the following mechanism:



During the reaction a hydrogen atom $\boxed{\text{H}}$, attached initially to carbon, becomes loose and is accepted by the carbon atom of the carbonyl compound while oxygen forms a link with the alcoholate, thus forming an intermediate complex (A). The complex then splits into a carbonyl compound and alcoholate or an alcohol.

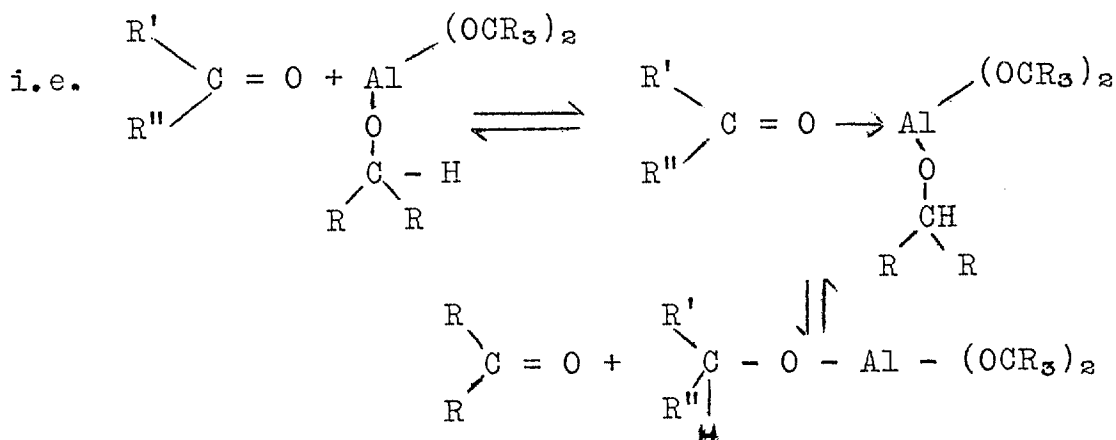
In the case of secondary alcohols the reaction can be represented as follows:



where X is R or H.

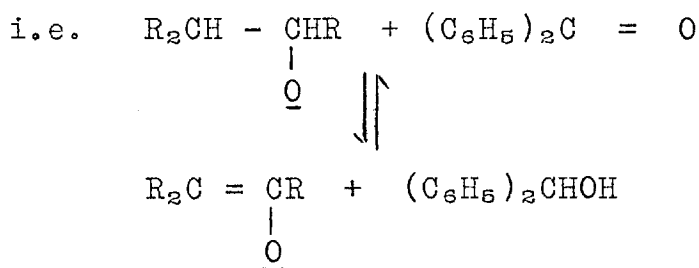
Pondorf substantiated this theory by the known fact that alcohol at high temperature has the tendency to liberate hydrogen and to change itself into an oxo-compound. It has been observed that the function of alcoholate is to lower the required temperature for that change.

Wagner-Jauregg in 1933⁽²⁷⁾ approached the mechanism by the study of racemisation of alcoholates. He observed that racemisation of alcoholates always takes place on heating, when the asymmetric carbon atom is bound directly to a -ONa group or is separated from this group by only one carbon atom. For this to take place a carbonyl compound must be present. He, therefore, postulated the following mechanism:



In 1943, Davies and Hodgson⁽³⁰⁾, postulated hydrogen bonding in the transition complex. In their opinion the function of aluminium alkoxide is to activate one of the alcoholic hydrogen atoms for the purpose of hydrogen bonding and not to facilitate the replacement of one alkoxy group, in the aluminium alkoxide, by another. They supported this view by the fact that n-butanol and cinnam-aldehyde give 72% of PrCHO, whereas with benzaldehyde the yield is only 48%. They assumed that this improved reactivity is readily explained by the enhanced negativity of the aldehyde oxygen in the cinnamaldehyde due to the double bond in the side chain.

In 1945, Woodward, Wendler and Brutschy⁽³¹⁾, suggested an ionic mechanism involving proton transfer,



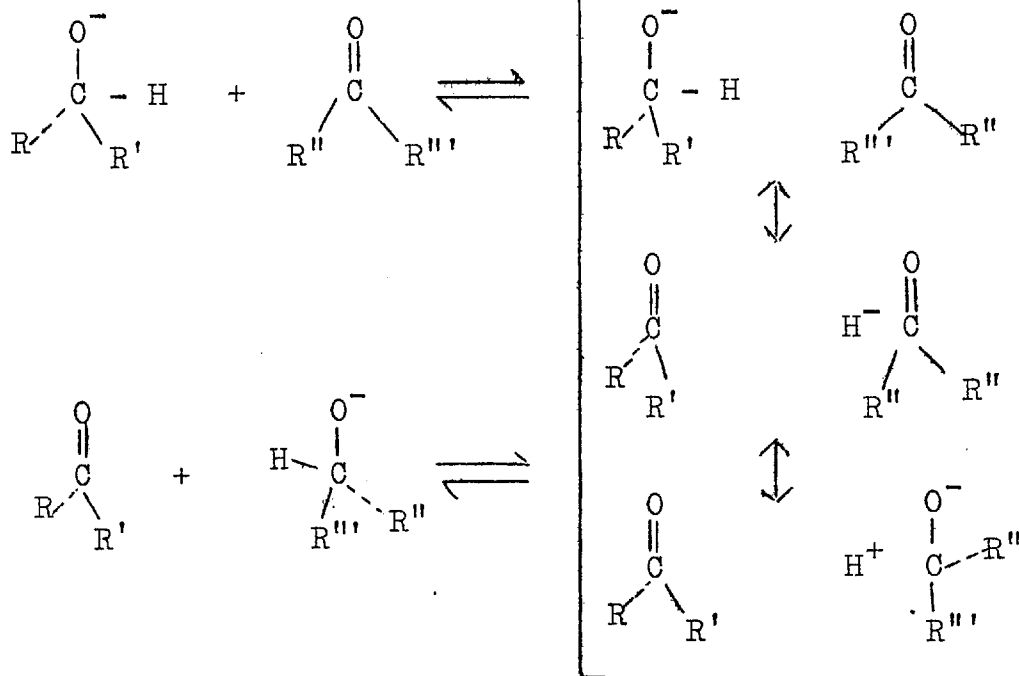
On the other hand, Michaelis in 1946⁽³²⁾ postulated free radical mechanism involving single electron steps and proton transfer,

dissociates into acetone and an aluminium derivative of the carbinol formed in the reduction.

They conclude that aluminium-isopropoxide is shown in this reaction to be a true reductant and not merely a catalyst, because reduction may be carried out in the absence of free isopropyl alcohol, using aluminium-isopropoxide either alone, in the fused state, or dissolved in hydrocarbons. Further, they maintained that in the M.P.V. reduction the aluminium-alkoxide functions as a reductant and not by virtue of any alkoxide ion which it may provide, because nitro groups are unaffected; halogens atoms are only removed when highly reactive, and there is retention of optical activity during the reduction of ketones such as pipertone, which readily undergo racemisation in the presence of alkoxide ion. The marked superiority of aluminium-alkoxides over alkoxides of other metals points to some unique property of the aluminium atom, such as covalent radius or bond length.

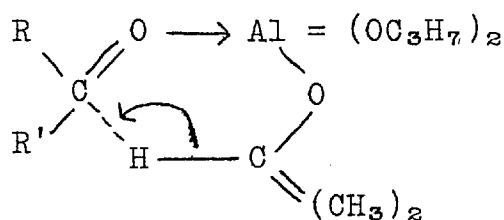
They also investigated the reduction, by aluminium-alkoxides, of some substituted cyclohexanones which may give rise to cis-trans-substituted cyclohexanols. They have found that as the apparent steric hindrance is increased either in the ketone or the reducing alcohol, there is an increase in the proportion of the cis-isomer in the mixture of alcohols produced, (e.g. 2-methyl-cyclohexanone gives 50% of cis form, whereas menthene gives 70% of the cis form). They have constructed models of the postulated transition state and concluded that these models clearly showed that the above mentioned trend should be observed in such reductions.

e.g.



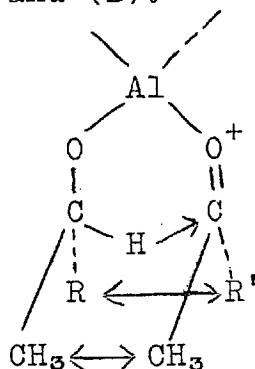
(A) Resonance hybrid

Thus postulating an ionic mechanism, or a six-membered quasi-ring phase (B).

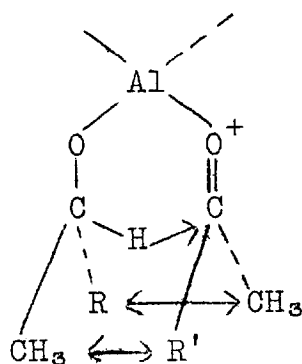


Doering and Richard, 1950,⁽³⁶⁾ investigated the possibility of a six-membered-ring transition compound in the M.P.V./Oppenauer reaction from steric point of view. They have observed, using aluminium alkoxide, partial assymmetric reduction in two systems: (+)-2-butanol(I) with 6-methyl-2-heptanone(II), and (+)-3-methyl-2-butanol(III) with methyl-cyclohexyl ketone (IV), pairs in which the configurational relationship of the alcohols involved seems to be established. As a

result they postulated the following transition states (A) and (B).



(A)



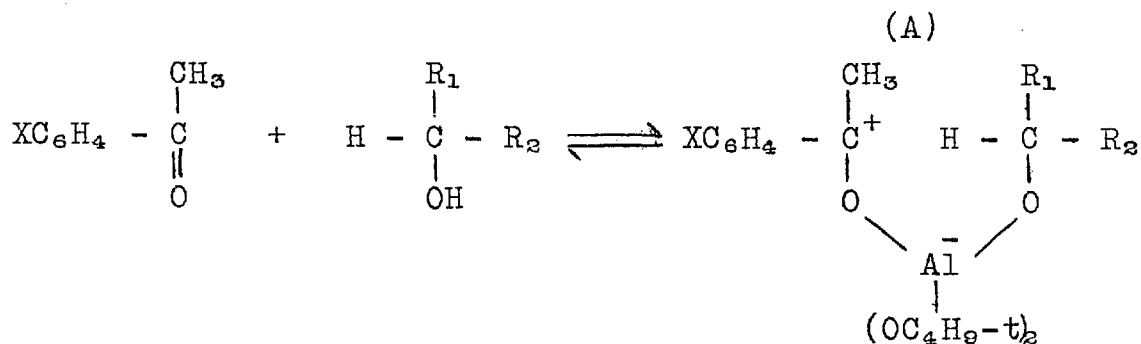
(B)

They argued that this mechanism satisfies, among others, the condition that solvent deuterium does not participate and, in consequence of the close approach of the components in the transition state, implies the stereochemical conditions that partial asymmetry should be observed in the reduction of unsymmetrical ketones with optically active carbinols. They consider that their experiments support both the gross stereochemical consequence and the experimentally less accessible pseudo-six-membered ring character of the mechanism. The reasonable hypothesis that steric interference between R - R' and CH₃ - CH₃ in (A) will exceed that between R - CH₃ and R' - CH₃ in (B) must be coupled with the pseudocyclic hypothesis, (A and B), in order to allow for the fact that the configurations of the reducing alcohol and the predominating enantiomer (B) of the reduced alcohol are the same.

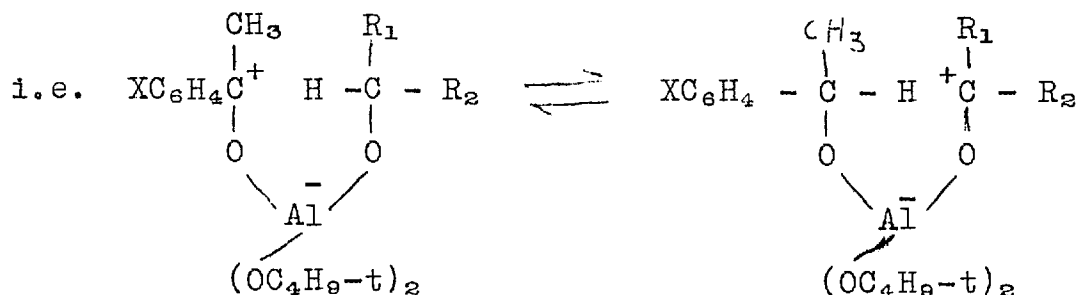
Rekasheva and Miklykhin, 1951,⁽³⁷⁾ carried out the M.P.V. reduction in a deuterium solvent (EtOD) and have shown beyond doubt that the source of hydrogen in the C - H links, which arise upon the reduction of

aldehydes by solutions of aluminium alkoxides in EtOD, are the hydrogen atoms connected to the carbon atoms in the reducing agent, and the transfer of hydrogen from a carbon atom of one compound to those of another proceeds intramolecularly, i.e. without participation of the solvent.

McGowan, 1951,⁽³⁸⁾ adopted Jackman's mechanism (Nature, 1949) and postulated that equilibrium is established by a proton moving from one carbon atom to another in the complex, i.e. for equilibrium between substituted acetophenone, $\text{CH}_3\text{COC}_6\text{H}_4\text{X}$, and an alcohol, $\text{R}_1\text{R}_2\text{CHOH}$, in the presence of aluminium-tert-butoxide. First the alcohol and ketone combine with the aluminium-tert-butoxide to form a complex (A).



Secondly, the equilibrium is then set up by the proton on the one carbon atom moving to the positive carbon in the complex to an extent determined by the relative basicity of these two carbon atoms. When the complex decomposes, the positive carbon will become a carbonyl, and the $>\text{CHO} - (\text{Al})$ group a $>\text{CHOH}$ group.

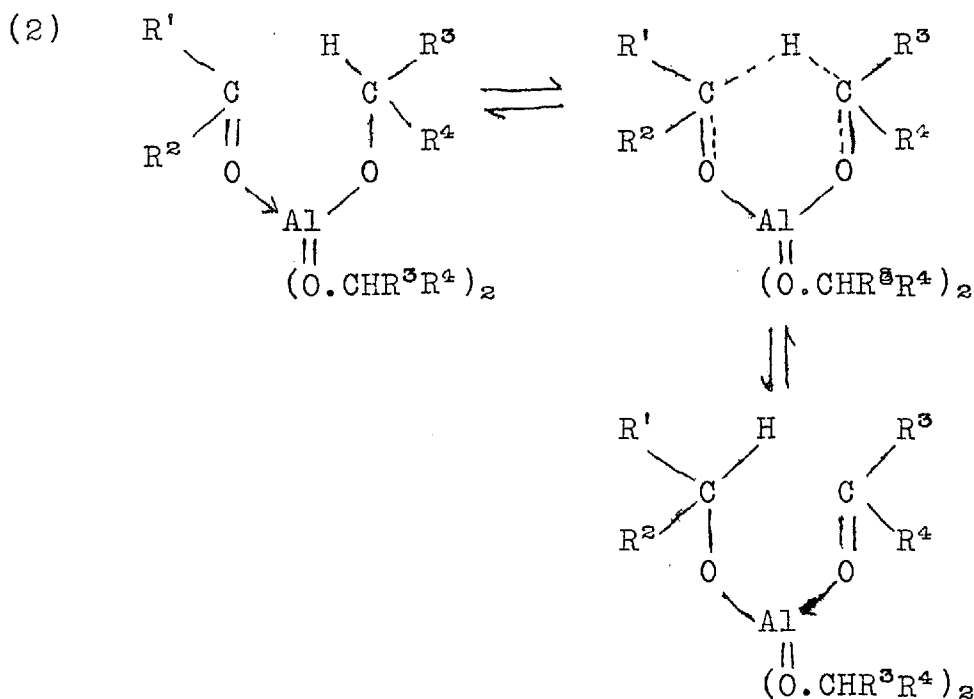
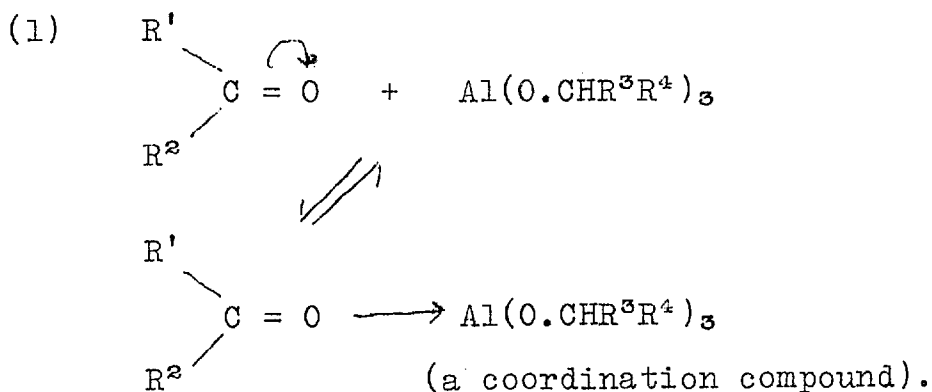


He adopted the hypothesis that the equilibrium is determined by some stage which involves the movement of an electric charge, and studied the influence of meta- and para-phenyl derivatives. Allocating an "effective charge" Q to each phenyl group and assuming that the reaction rate or equilibrium is determined by a change of the charge on the atom next to the phenyl group, $RT \ln K + 14Q$ should be a constant when the atom becomes more positive; while $RT \ln K - 14Q$ will be a constant when the atom becomes more negative; K being the velocity or equilibrium constant. The effect of the phenyl group is reduced when it is situated farther from the site where the change of charge occurs, and it was shown that $RT \ln K \pm 14Q/2^n$ is then a constant, where n is the number of saturated carbon atoms between the site of change of charge and the phenyl group.

It is assumed that the aluminium atom remains negative throughout, but $14Q/2^4$ will have to be subtracted to account for the appearance of positive charge on the carbon atom five atoms away from the phenyl group. The mechanism therefore suggests that the difference between $-\Delta G^\circ$ and $14Q - 0.825Q$ should be a constant as is seen from the table below:

X in $\text{CH}_3\text{COC}_6\text{H}_4\text{X}$	$-\Delta G^\circ$ kcal (39)	$13.175Q$
p-OCH ₃	4.6	4.4
p-CH ₃	5.3	4.8
H	5.4	5.2
m-OCH ₃	5.5	5.7
p-Br	6.0	5.9
m-NO ₂	7.0	7.4
p-NO ₂	7.9	7.9

In 1952, Jackman and Macbeth⁽⁴⁰⁾ proposed the following mechanism consisting of two main steps:



The first step, i.e. the formation of coordination compound between carbonyl oxygen and the aluminium atom, they explained by the fact that an aluminium atom possesses p-orbitals available for coordination.

The superiority of Al-alkoxides over other alkoxides, they argued, is due to their ability to

coordinate with carbonyl compounds to a degree sufficient to permit the reaction to proceed at a measurable speed. Thus the amphoteric aluminium alkoxides may be regarded as functioning as acids.

The second step (2) in the mechanism, i.e. cyclic transition state, is favoured because of the possibility of resonance in such a system with an equivalent lowering of the activation energy. It is possible that the fact that the $\alpha\beta$ double bond is not reduced may be a consequence of the cyclic transition state, as 1:4 addition would require a sterically less favourable eight-membered ring⁽⁴¹⁾. The achievement of asymmetric syntheses in this reaction supports the cyclic mechanism of Doering and Young⁽⁴²⁾.

To get more evidence about the mechanism, Jackman and Macbeth studied polarimetrically the kinetics of the reaction. They measured the rate of racemisation of an aluminium derivative of an optically active alcohol, by the corresponding ketone. This method was favoured, as the possibility of the formation of mixed alkoxides no longer exists, and the rate process under consideration goes to completion unaffected by an opposing reaction. They studied the racemisation of two systems: (a) that of (+)-aluminium-1-methyl propoxide (but-2-oxide), and (b) (+)-aluminium-1-methyl-heptyl oxide, with the corresponding ketone. They found that in both cases, the rate of racemisation was dependent on the ratio of the concentrations of the alkoxide and ketone. As a result the following equation for the reaction rate has been obtained:

$$k = \frac{[A]}{[B]_t} \ln \frac{a_o}{a_t}$$

where, k = rate constant

$[A]$ = concentration of alkoxide,

$[B]$ = concentration of ketone.

This equation is consistent with the postulated mechanism, provided the associated nature of aluminium alkoxide is borne in mind. Assuming that the rate of hydrogen transfer (2) is slow compared with the rate at which the initial equilibrium is attained, the rate of racemisation is given by the equation:

$$R = k_1 [(+)\text{complex}] \quad (1)$$

Whereas for each experiment the racemisation process was found to obey, within certain limits, the general first order equation

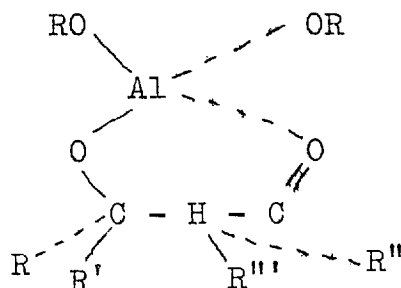
$$k = \left(\frac{1}{2t} \right) \ln \left(\frac{a_0}{a_t} \right) \quad (2)$$

where, a_0 and a_t are optical rotations at zero time and time t seconds, respectively. The coefficient ($\frac{1}{2}$) takes into account the fact that the racemisation is complete when $\frac{1}{2}$ of the alkoxide molecules have undergone inversion.

Williams et al, 1953,⁽⁴³⁾ used deuterium as tracer in the reduction of cyclohexanol. They support the cyclic mechanism involving transfer of hydrogen atom from the carbinol carbon atom of the alkoxide to the carbonyl carbon atom of the ketone.

Doering and Aschner, 1953,⁽⁴⁴⁾ supported the idea of the cyclic transition state in which hydrogen is transferred directly.

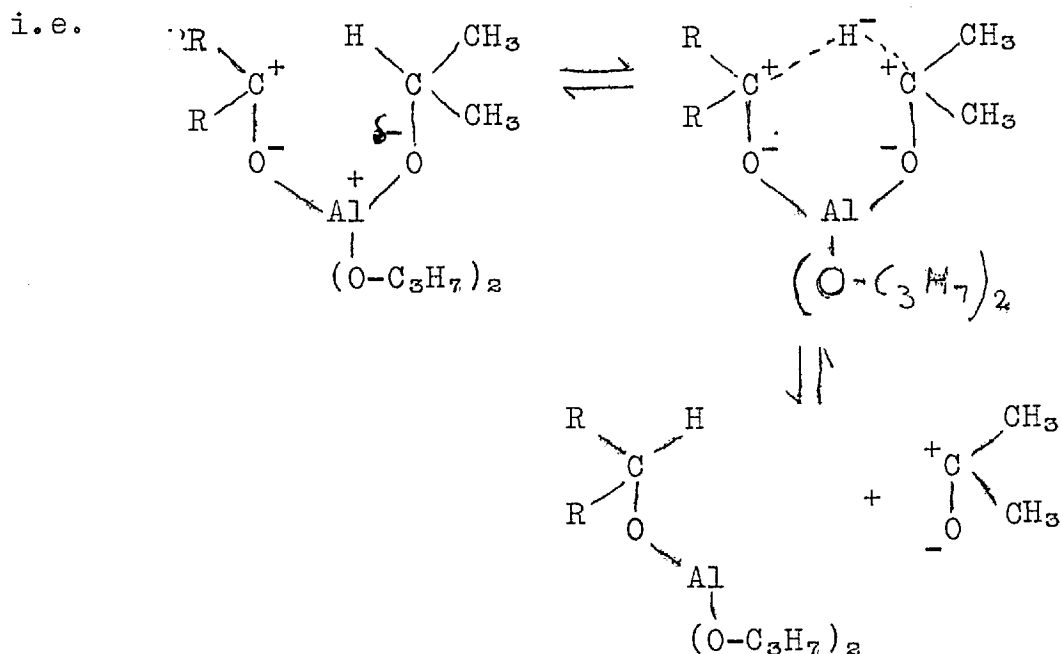
i.e.



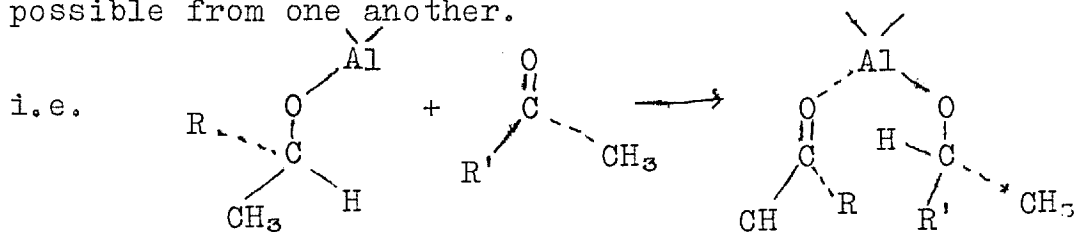
They investigated the reaction using racemisation as tracer, and have found that the racemisation of (-)2-methyl-butanol-1, is unaffected by substances which often inhibit free-radical chain mechanism.

The origin of the hydrogen atom, which becomes attached to the carbinol carbon in the reduction of carbonyl group, has been established by using racemisation as a measure of the oxidation-reduction, and solvent deuterium as a tracer for hydrogen. They have found that the reaction does not incorporate solvent deuterium and hence the mechanism is intramolecular, involving direct, carbon to carbon, transfer of hydrogen with its electrons.

Francen and Krauch, 1955,⁽⁴⁵⁾ are also in favour of the already proposed cyclic mechanism:



From one molecule of alkoxide and one molecule of ketone, a coordination compound is formed. Inside the cyclic complex, hydride ion (H^-) goes from carbinol carbon atom of the alkoxide to the positively polarized carbonyl carbon atom. The complex has two functions: first the complex arranges itself in the most favourable way. This clarifies the fact that from optically active alcohols partly asymmetric products are formed. Inside the complex the parts arrange themselves so that the steric transfer is least difficult: if R and R' are longer parts, they will place themselves in the complex in such a way that they are situated as far as possible from one another.



Secondly, the coordination of aluminium with the oxygen of the carbonyl group increases the positive charge on the carbonyl carbon atom and thus facilitates the acceptance of hydride ion (H^-). The complex formation has made it possible for the carbinol-carbonyl equilibrium to take place without difficulty. The side of the equilibrium is determined by the Redox potential of alkoxide-Ketone or alkoxide-aldehyde system. The aluminium alkoxide provides the hydrogen in this redox reaction, and therefore cannot be considered as a catalyst only. When the reaction takes place in isopropanol as solvent, then during dissociation of aluminium alkoxide new aluminium-isopropoxide is formed so that with less than theoretical amount of aluminium isopropoxide the reaction can be completed and, therefore, in this case aluminium-alkoxide seems to be a catalyst.

2. Experimental Work and Discussion.

2.1. Introduction.

The main object of this research was to study the mechanism of the M.P.V./Oppenauer reaction using a different method of kinetic study and then to make a comparative study using different alkoxides of metals of group 3A and 5A of the periodic table. To check on the origin of the hydrogen used in the M.P.V. reduction, deuterium solvent was to be used.

For the purpose of this study secondary butanol was selected as the alcohol and methyl ethyl ketone (M.E.K.) as the ketone. An inert solvent, methylcyclohexane, was to be used.

Secondary butanol was chosen because of its comparatively simple three-dimensional structure. It has four different groups attached to the alcoholic carbon, each one could be easily labelled and hence is suitable for study of the kinetics of this reaction by the radioactive tracer method. Secondly, it has only one replaceable hydrogen suitable for labelling with D. Thirdly by using the mixture of s-butanol alkoxide and methyl ethyl ketone in an inert solvent such as methylcyclohexane, there could be no side reactions present. And, fourthly, s-butanol can be resolved into optically active isomers.

2.2. Resolution of s-butanol.

At the time of this work no optically active s-butanol was available on the market due to the difficulty of optical resolution of the dl-form and the very poor yields so far obtained. The resolution was therefore

carried out and by modification of the method of resolution a good yield of the d- and l-form was obtained (65% yield on theoretical value).

First the secondary butanol was converted to s-butyl hydrogen phthalate and this in turn into a brucine salt. The brucine salt was then fractionally crystallised and the product hydrolysed.

2.2a. Preparation of s-butyl hydrogen phthalate.

s-butyl hydrogen phthalate was prepared by heating phthalic anhydride and dry s-butanol in molar proportions. Several experiments have been performed, varying the time and temperature of reaction. The best result has been obtained by heating the components together for about 20 hours at 105°C, with constant stirring. This gave almost quantitative yield.

Experimental.

s-butyl alcohol b.p. 99.5°C was dried by the ternary azeotrope method using benzene and isopropanol (b.p. 82.45°C).

Ternary azeotrope - water, benzene and isopropanol has boiling point 66.51°C, and the following composition: water - 7.5%, isopropanol 18.7%, benzene 73.8% by weight.

Binary azeotropes formed:

- (a) Water - isopropanol - b.p. 80.3°C; 12.6% water;
- (b) isopropanol-benzene - b.p. 71.92°C; 33.3% isopropanol;
- (c) water-benzene - b.p. 69.2°C; 8.83% water;
- (d) s-butanol-benzene - b.p. 78.5°C; 15.4% alcohol;
- (e) water-s-butanol - b.p. 87.5°C; 27.3% water.

Benzene b.p. 80.15°C.

The azeotropic resolution was carried out on a 100 cm long

column packed with single turn Fenske's helices, corresponding to about 120 theoretical distillation plates. Phthalic anhydride - $C_6H_4(CO)_2O$ (148.11 gm) - 1 mole and s-butyl alcohol - $C_4H_{10}O$ (74.12 gm) - 1 mole were placed in 1 $\frac{1}{2}$ three necked flask, fitted with a stirrer, reflux condenser and a thermometer, and were heated using a heating mantle for 20 hours with constant stirring, keeping the temperature at about 105°C. The mixture was poured, when cold, into concentrated sodium carbonate solution (5 molar) containing 1.5 mol of sodium carbonate. This was extracted 3 - 4 times with ether in a separating funnel.

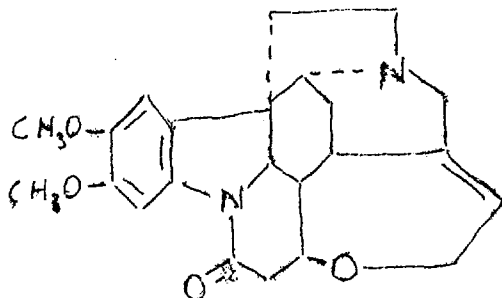
Until now the product, s-butyl hydrogen phthalate, obtained by other workers by almost similar method, was in the form of a viscous oil. This was considered to be due to occlusion of traces of ether and therefore the traces of ether were removed from the aqueous portion by bubbling air through it overnight. The s-butanol hydrogen phthalate was precipitated from the carbonate solution with 50% hydrochloric acid, with stirring. The acid mixture was allowed to settle down; the main portion of the aqueous layer was poured off and the rest removed in a separating funnel. The white solid so obtained was washed several times with cold water and dried. It was then dissolved in dry chloroform (about 1 litre), to remove phthalic acid and neutral esters, filtered and evaporated to dryness under reduced pressure - first using water pump, then a rotary oil motor pump.

The solid was ground into a fine powder in a mortar and was used for the preparation of brucine salt.

2.2b. Preparation of brucine salt and resolution.

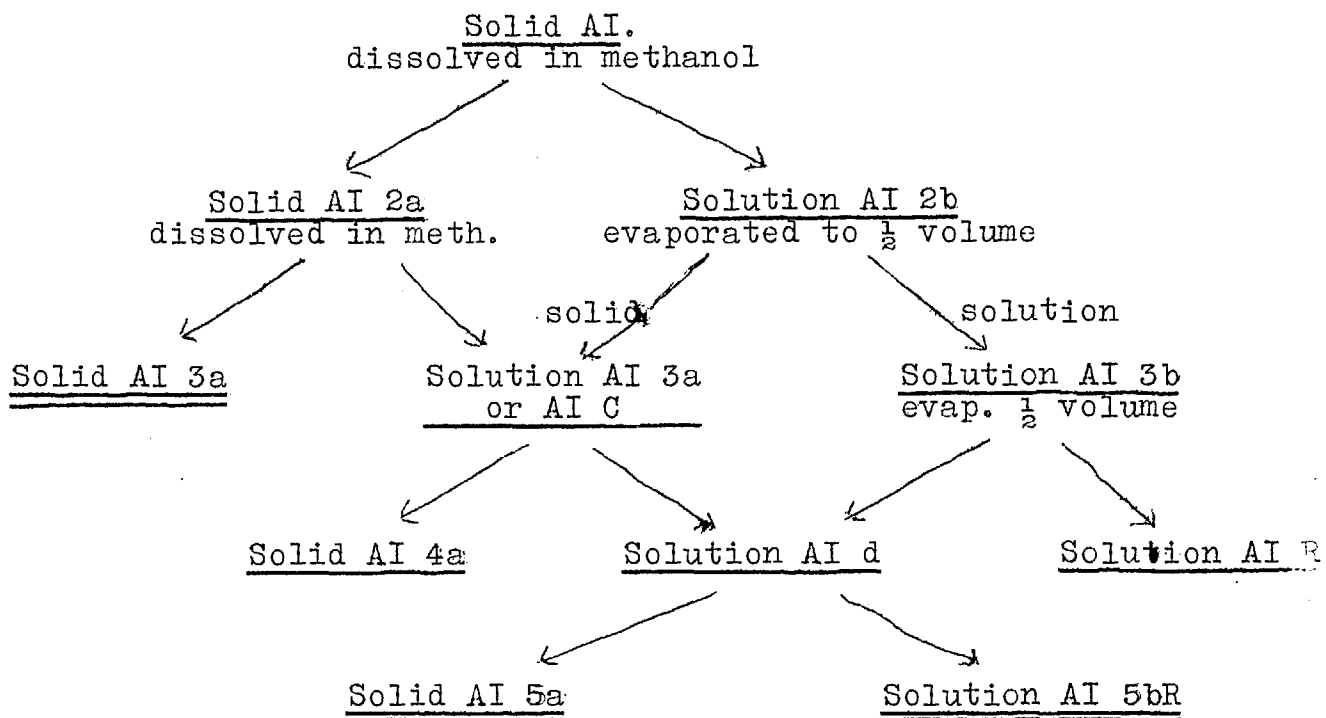
500 gm of brucine, $C_{23}H_{25}N_2O_4$ (dimethoxy strichrine) m.p. 178°C , $[\alpha]_D = -80.1^\circ$.

i.e.



was mixed with 283 gm of s-butyl hydrogen phthalate in a mortar; transferred to a 5 litre three necked flask fitted with a stirrer and a reflux condenser. 1.5 l. of acetone was added and this was refluxed with constant stirring for 24 hours. The mixture was filtered hot giving solid AI. The remaining solution was left for a day at room temperature, when more solid was deposited. This was filtered off giving solid AII. The filtrate was kept in a refrigerator for 3 days depositing more solid, which was filtered off giving solid AIII and solution AIII.

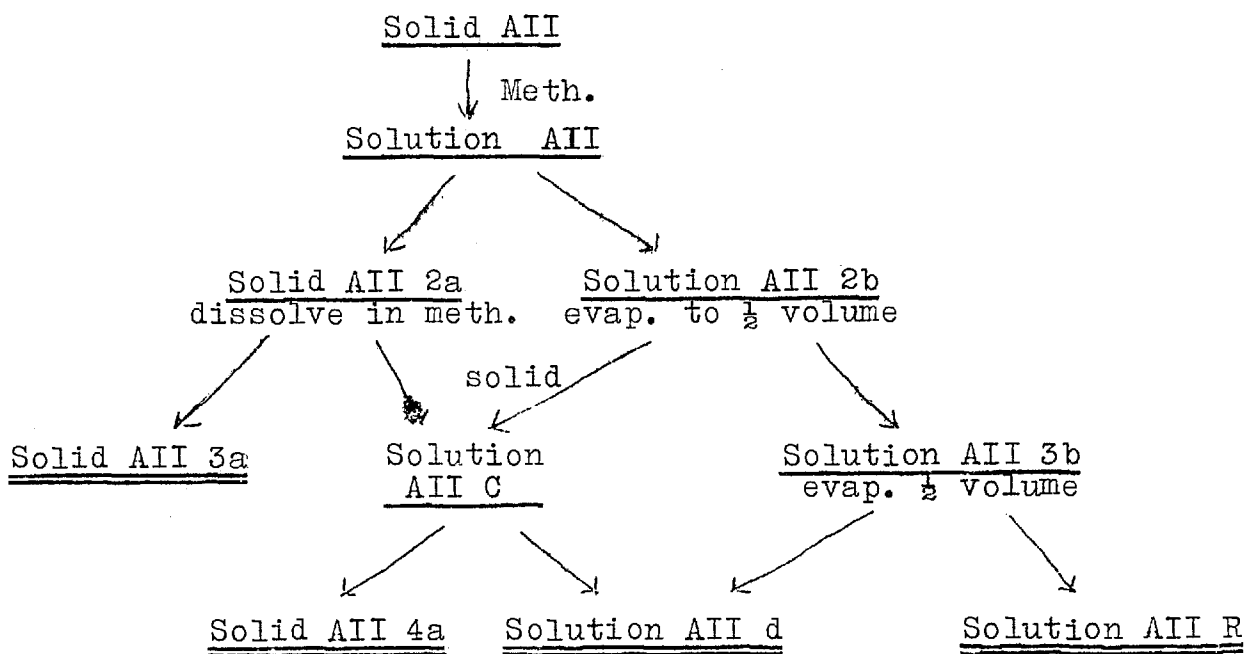
Solid AI was recrystallised from minimum amounts of methanol in the following manner:



28 gm of Solid AI 3a were obtained, m.p. 160°C;

$[\alpha]_D^{20} = -14^\circ$ in chloroform, and 9 gm of solid AI 4a, m.p. 160°C; $[\alpha]_D^{20} = -14.4^\circ$ in chloroform.

Solid AII was recrystallised from minimum amounts of methanol in a similar manner:



127 gm of solid AII 3a were obtained, m.p. 160°;

$[\alpha]_D^{20} = -13.31^\circ$ in chloroform,

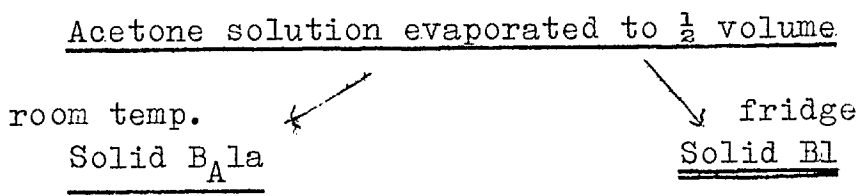
$= -3.72^\circ$ in c.4 ethanol,

and 36 gm of solid AII4a, m.p. 160°C;

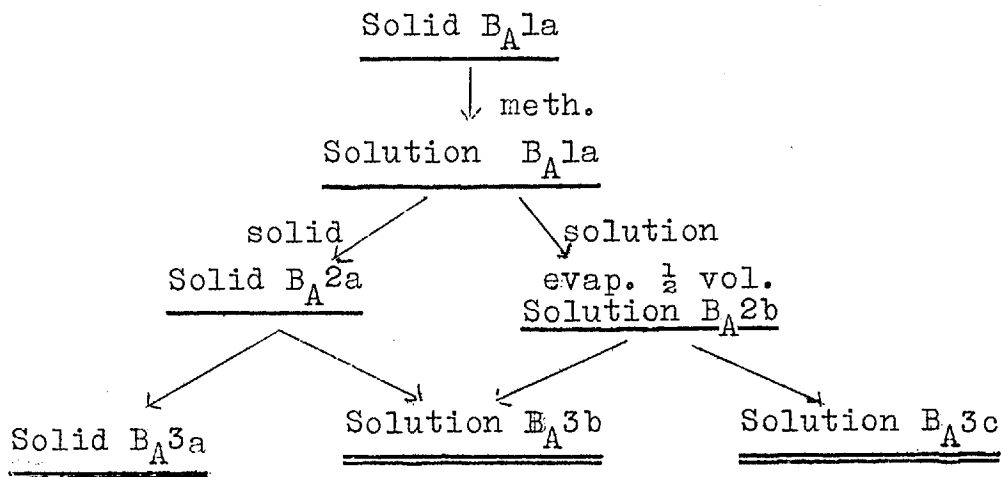
$[\alpha]_D^{20} = -13.9^\circ$ in chloroform.

Solid AIII, was dissolved in methanol but did not crystallise out, therefore it was combined, after evaporation to dryness, with solid B 3a and solid D, and fractionated from acetone in the refrigerator.

Solution AIII, was evaporated to $\frac{1}{2}$ volume, left standing at room temperature for 24 hours and then, after filtering off the deposited solid B_A1a, was placed in a refrigerator for a few days where more solid, B_A1, was deposited, i.e.



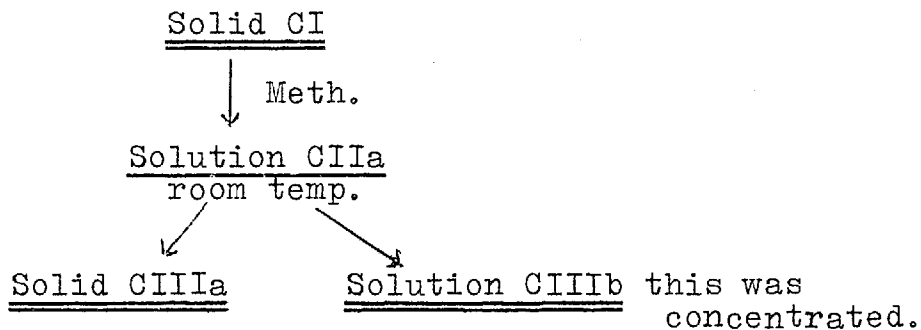
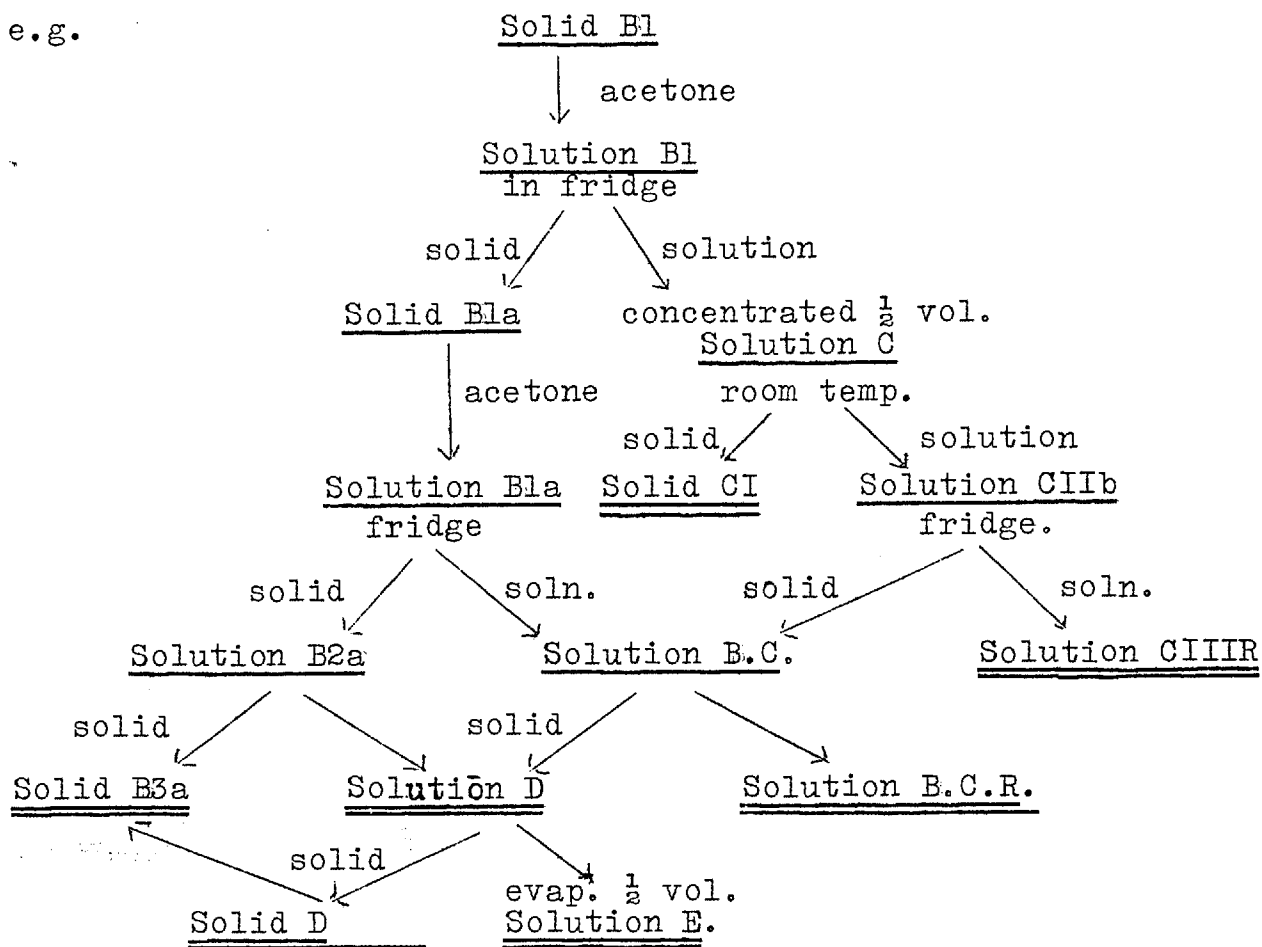
Solid B_A1a was recrystallised from methanol in the following manner:



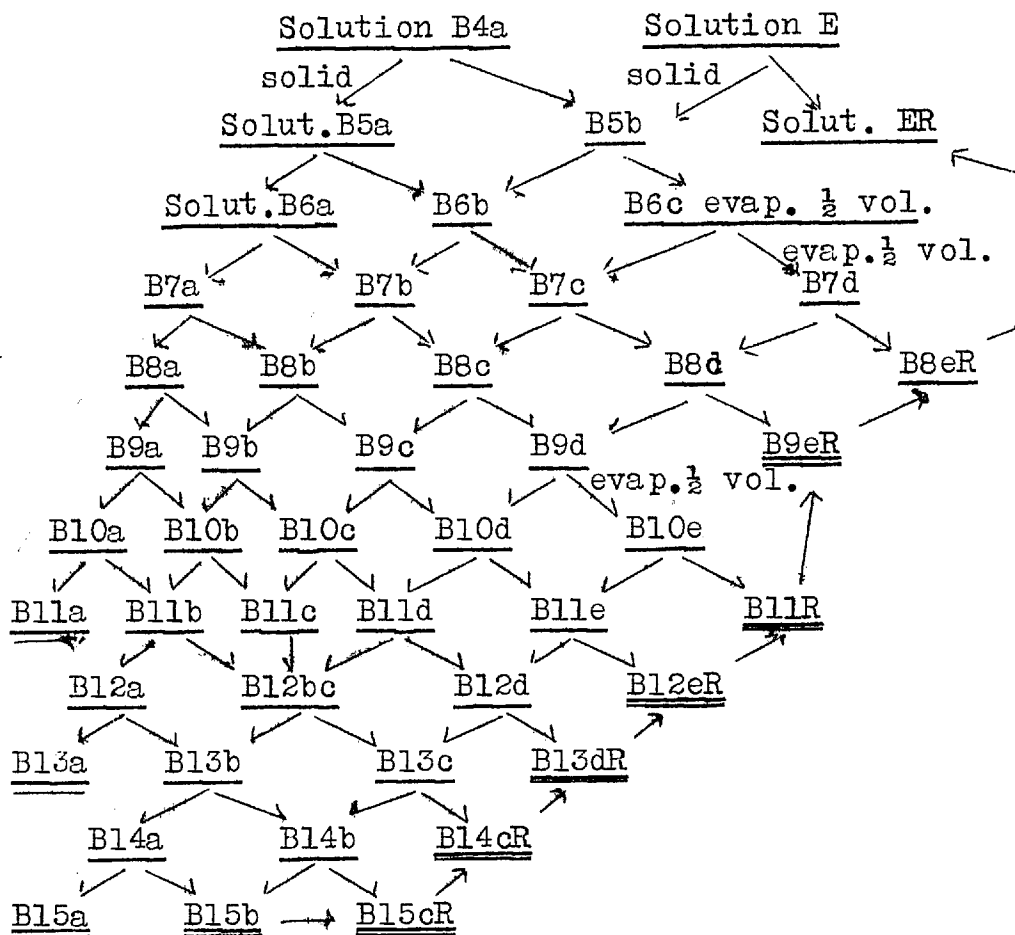
Solid B_A3a was deposited in the form of triangular prisms m.p. 215°C, and after analysis was found to be the brucine hydrogen phthalate.

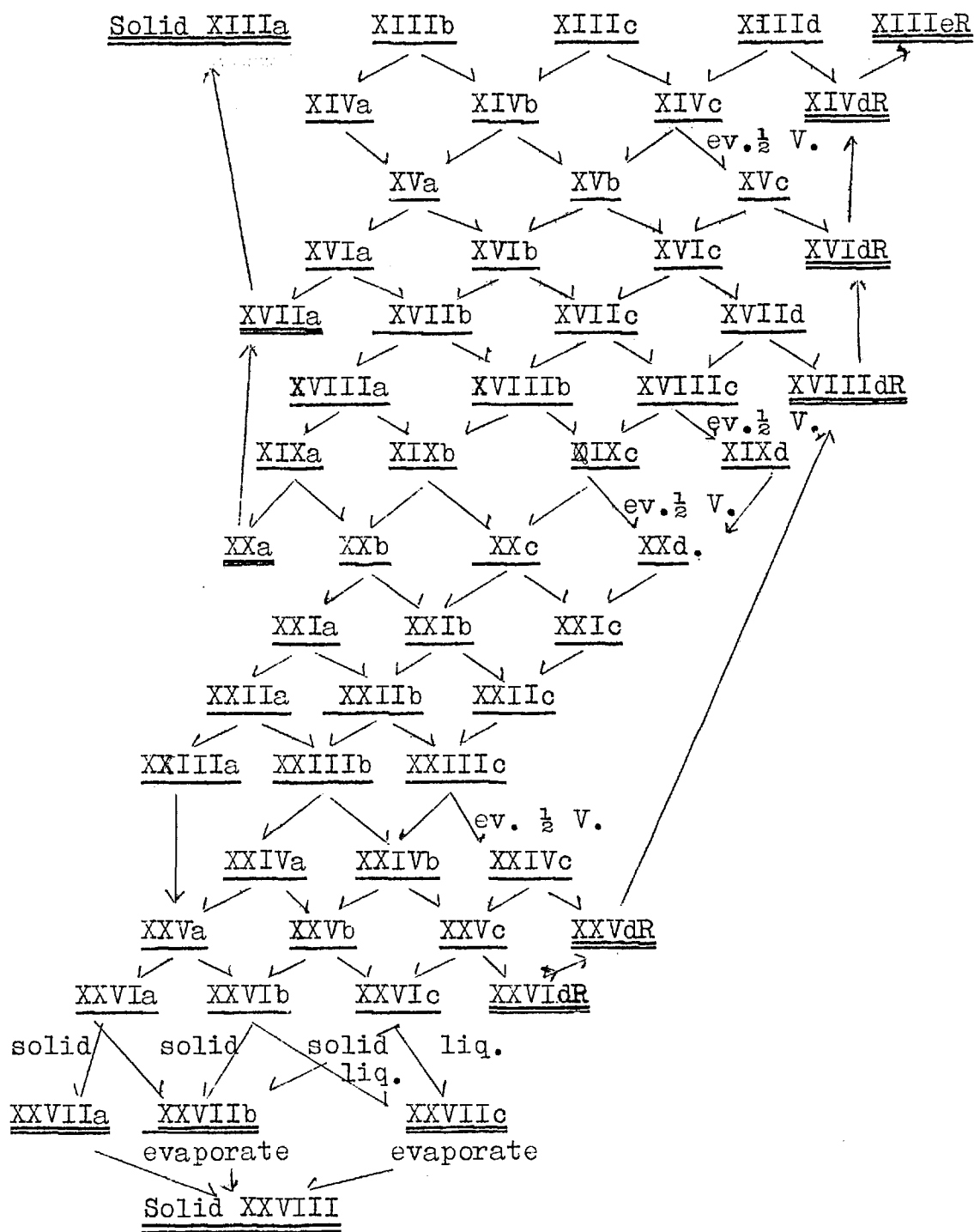
Solid B1 was recrystallised from acetone in the refrigerator giving solid B1a and solution B1b, which was evaporated to $\frac{1}{2}$ volume giving solution C. Solution C was left in room temperature for a day and the deposited Solid, C1, was filtered off. The remaining solution was placed in the refrigerator where more solid was deposited, i.e. solid C1Ib.

e.g.



Solids AIII, B3a and D were combined together and dissolved in 1.5 l of acetone giving solution B4a which was treated as follows, all the time using acetone as solvent and carrying out the fractional crystallisation in the refrigerator:





2.2c. Hydrolysis of Brucine Salt. (All sp. rot. in c.4. ethanol).

By carrying out a series of preliminary experiments the best way for the hydrolysis of s-butyl-H-phthalate was found to be the following:

(1) Acetone residues, that is fractions: ER, B8eR, B9eR, B10eR, B11R, B12eR, B13dR, B14cR and B15cR, were combined, evaporated under reduced pressure first with a filter pump using a steam bath then using an oil rotary motor pump.

The solid weighed 169 gm.

The solid was ground in a mortar, placed in 1 litre quick fit flask; 500 ml of 15% NaOH solution was added and some bumping stones. The mixture was refluxed in an atmosphere of nitrogen the fractions being collected at the top of a distillation column (80 cm) packed with Fenske's helices.

The following fractions were obtained using reflux ratio 1:15.

- (a) b.p. 55-72°C, which was found to be mainly acetone,
- (b) b.p. 72-85°C.,
- (c) b.p. 85-87°C, this was the binary azeotrope of water and s-butanol. The distillation was continued until the temperature of the distillate reached 100°C.

The s-butanol was salted out from the distillate by saturating it with anhydrous potassium carbonate; the aqueous layer was separated in a separating funnel.

The water-s-butanol azeotrope was decomposed with calcium hydride which reacted rapidly with water leaving behind the dry s-butanol: 9 gm, $[\alpha]_D^{20} = -5.54^\circ$. This was redistilled using a small distillation apparatus

consisting of an approximately 2 cm long distillation column packed with Fenske's helices, and a stilt-head. The s-butanol so obtained has b.p. 99. -99.5°C, $[\alpha]_D^{20} = -5.5^\circ$, $n_D^{20} = 1.39695$; yield 6 gm.

(2) Hydrolysis of the fraction B11a, was carried out in a similar manner.

Solid B11a had m.p. 98-100°C then partial decomposition occurred; $[\alpha]_D^{20} = -17.4^\circ$.

The s-butanol obtained after hydrolysis and drying had b.p. 98-99.5°C; $[\alpha]_D^{20} = -10.4^\circ$, $n_D^{20} = 1.39695$; yield 9.5 gm.

(3) Hydrolysis of fraction B15a. This fraction had m.p. 130-140°C, $[\alpha]_D^{20} = -12.1^\circ$; weight 40 gm. The dry s-butanol obtained has b.p. 99.5°C; $[\alpha]_D^{20} = -5.54^\circ$.

(4) Hydrolysis of solid from methanol residues.

Solutions: IVR, XIIeR, XIIIeR, XIVdR, XVIdR, XVIIIdR, XXVdR, and XXVIdR were combined and evaporated to dryness under reduced pressure. 147 gm was obtained of solid which had $[\alpha]_D^{20} = -7.27^\circ$.

This brucine salt of s-butyl-H-phthalate was first hydrolysed with 20% HCl. The impure s-butyl-H-phthalate was separated in a separating funnel then dissolved in 500 ml of 20% sodium carbonate solution and the precipitated brucine was filtered off at the pump and washed with dilute sodium carbonate solution. The filtrate was acidified with 20% HCl, left standing for a day and then the pure s-butyl-H-phthalate was filtered off. This was refluxed with 15% sodium hydroxide solution, using an 80 cm column as for the acetone residue. The water-s-butanol azeotrope was salted out with potassium carbonate, dried with calcium hydride and redistilled.

This gave 6 gm of pure s-butanol b.p. 99.5°C,
 $[\alpha]_D^{20} = +1.1^\circ$.

2.2d. Recovery of Brucine.

Brucine was recovered from the HCl solution by neutralising the solution with 20% sodium carbonate solution, filtering off the precipitated brucine, and washing it with dilute sodium carbonate solution. The precipitate was then dissolved in chloroform. The chloroform layer was separated in a separating funnel. Chloroform was evaporated, first using a filter pump then a rotary oil pump. The brucine so obtained was recrystallised from 25% ethanol (1 l.). This was left in a refrigerator overnight, then filtered at the pump, washed with 25% ethanol, dried in an oven at 90-100°C, then at 120°C.

The brucine so obtained was in the form of long needles, m.p. 170-172°C; $[\alpha]_D^{20} = -82^\circ$.

(5) Hydrolysis of brucine salt from XXVIII, that is fractions XXVII a, m.p. 164°C, $[\alpha]_D^{20} = -3.1^\circ$
 XXVII b, m.p. 164°C, $[\alpha]_D^{20} = -4.1^\circ$
 XXVII c, m.p. 164°C, $[\alpha]_D^{20} = -4.4^\circ$

This was refluxed with 15% NaOH solution in an atmosphere of nitrogen. The water-s-butanol azeotrope was salted out with K_2CO_3 , filtered, dried with CaH_2 , filtered and redistilled using a small distillation column of about 2 cm length packed with single turn Fenske's helices.

The d-s-butanol has b.p. 99.5°C; $[\alpha]_D^{20} = +13.5^\circ$.

(6) Hydrolysis of the main fraction, that is:

VIIIIa,	m.p. 159°C;	$[\alpha]_D^{20} = -2.2^\circ,$
XIIIIa,	m.p. 164°C;	$[\alpha]_D^{20} = -2.94^\circ,$
XVIIa,	m.p. 164°C;	$[\alpha]_D^{20} = -2.7^\circ,$
XXa,	m.p. 164°C;	$[\alpha]_D^{20} = -2.54^\circ.$

Total 63 gm.

This was dissolved in 20% HCl, the s-butyl-H-phthalate separated in a separating funnel, dissolved in 20% sodium carbonate solution, and the precipitated brucine filtered off. The solution was acidified with 50% HCl, left for a day, and the pure s-butyl-H-phthalate filtered off. This was refluxed with 15% NaOH in an atmosphere of nitrogen, collecting the ætrotrope, b.p. 87°C, and the aqueous mixture up to 100°C. The ætrotrope was salted out with solid K_2CO_3 , decomposed with CaH_2 , filtered and redistilled using small distillation column.

The alcohol boiled at 98.5°C/752.5 mm.

It was the pure dextro-rotary enantiomorph of the s-butanol, i.e. d-s-butanol.

$$[\alpha]_D^{20} = +14^\circ, \text{ (literature value } [\alpha]_D^{20} = +13.8^\circ.$$

$$[\mu]_D^{20} = 1.39745.$$

2.2e. Brucine was recovered from the HCl solution by neutralising it with 20% Na_2CO_3 solution, filtering, dissolving it in chloroform. From chloroform it was extracted with 20% sulphuric acid (500 ml), using small portions 3 times. The brucine sulphate was decomposed with 20% ammonia, the brucine was filtered off at a pump, washed with dilute ammonia, then with water, recrystallised

from 25% ethanol (leaving overnight in a refrigerator). The crystals were filtered out, washed with 25% ethanol and dried in an oven first at 90°C, then at 120°C.

2.3. From the experiments on resolution of d-l-s-butanol described in the previous paragraphs it became obvious that the brucine salt of the dextro-rotary-s-butanol-hydrogen-phthalate crystallises easily from methanol, while the laevo-rotary form was completely soluble in all proportions. Secondly, the dextro-form of the brucine salt was deposited at room temperature from fairly concentrated acetone solution, while mainly the laevo-form was deposited at zero degree centigrade in the refrigerator. Thirdly, the d- and l-forms of the brucine salt had slightly different melting point. Fourthly, the d-s-butanol and l-s-butanol have refractive indices differing by about 5 units in the fourth decimal place.

These observations were utilised for new methods in study of the M.P.V./Oppenauer reaction kinetics, and a new method of resolution of s-butanol into its optically active forms. These will be described later.

Utilising the first and the second observation mentioned above a quick method of resolution of s-butanol was obtained giving good yield of comparatively pure d-s-butanol, and l-s-butanol of purity good enough for the study of kinetics by polarimeter.

This resolution was in principle similar to the one previously described, but only 8 recrystallisations of the brucine salt deposited at room temperature from the mother liquor of acetone, were carried out from minimum amounts of methanol.

1.5 Mole of brucine salt gave, on hydrolysis of the product after 8 recrystallisations from methanol, 22 gm of d-s-butanol, $[\alpha]_D^{20} = +12^\circ$ (literature, $[\alpha]_D^{20} = +13.8^\circ$). This yield is 40% on the theoretical basis. Also 40 gm of l-s-butanol was obtained, $[\alpha]_D^{20} = -7^\circ$ (no literature value is available). This is 7% yield on the theoretical value.

It is worth while mentioning that no method for obtaining the l-s-butanol form is given in the literature. During this work almost pure l-s-butanol was obtained by the accurate (long) method described previously. On hydrolysis of fraction B.11.a, the l-s-butanol so obtained had specific rotation $[\alpha]_D^{20} = -10.4^\circ$.

2.4. Resolution by zone melting technique.

During the experiments described above it was observed that the fractions of the brucine salt of s-butyl hydrogen phthalate containing the d- and l-forms of s-butanol had different melting points. Therefore in principle it should be possible to resolve the alcohol by the zone melting technique. Hence an apparatus for this purpose was designed and built. It consisted in principle of (1) a 1 m long pyrex tube 6 mm diameter (thick walled) terminated with ground glass joints and stoppers; (2) a small circular heater made of brass, 5 cm external diameter, 1 cm internal diameter and 1 cm thick. The heating coil was fixed inside the cylinder and secured in position by Pyruma cement; (3) a slow electric motor with reduction gears and reduction wheels.

The melted salt was placed inside the tube. The tube was placed inside the central opening in the small furnace and the furnace, after the melting started, travelled down the tube at the rate of 1.5 mm per hour.

After 12 runs the tube was cut into 3 sections, and the contents were dissolved in methanol and recrystallised.

For the experiment fraction Vd, was used which had specific rotation $[\alpha]_D^{20} = -6.02^\circ$.

The top segment of the tube after zone melting gave $[\alpha]_D^{20} = -26.58^\circ$ in chloroform.

The middle section $[\alpha]_D^{20} = +8.58^\circ$.

The specific rotation of the bottom section was impossible to measure due to a dark colour imparted to the salt due to partial decomposition of brucine just above the melting point of the brucine salt.

Thus it can be seen from the above data that the s-butanol can be resolved by the zone melting technique. Unfortunately the salt used for this experiment decomposes just above its melting point and therefore it is necessary to choose a different salt of s-butanol.

However, the purpose of this study was the mechanism of the M.P.V./Oppenauer reaction, and enough optically active s-butanol had already been obtained, and so the zone melting technique was left waiting for a more opportune time.

2.5. Purification of Methyl Ethyl Ketone. (M.E.K.).

Commercial M.E.K. was converted into its bisulphite compound using excess of a saturated solution of sodium meta bisulphite. After about 3 hours of shaking, the white solid was filtered off at the pump, washed with alcohol and then with ether. The solid was dried in a desiccator connected to a water pump, and then decomposed with 20% sodium hydroxide solution.

The aqueous layer was separated in a separating funnel; the water-M.E.K. azeotrope was distilled using 80 cm long column packed with single turn Fenske's helices. The azeotrope (11.3% water), b.p. 73°C , was decomposed by calcium hydride and was fractionated using the same column previously dried in an oven at 120°C after washing the column with absolute alcohol. It was cooled in a stream of dry nitrogen for over an hour.

The pure M.E.K., b.p. 79.6°C , was stored over dehydrated copper sulphate (AnalaR) in a glass flask fitted with a ground glass stopper.

The AnalaR copper sulphate was dehydrated by heating it for 4 days in an oven at 140°C , and then under reduced pressure (1 mm Hg) at 180°C for another 4 days.

2.6. Purification of Methyl-cyclohexane.

Commercial methyl-cyclohexane was shaken for 3 hours with 10% of its volume of oleum. This was repeated until the oleum remained colourless. The oleum layer was separated in a separating funnel. The main fraction was washed with 5% sodium hydroxide solution and then with water until neutral to litmus. It was then stored over $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ for over a fortnight. The dry methyl-cyclohexane was filtered and then fractionated over sodium wire, to remove last traces of water, using an 80 cm long fractionating column packed with Fenske's helices. The main fraction boiling point 101°C , was stored over sodium wire.

It was subjected to U-V-spectroscopic analysis in search of aromatic impurities and proved to be spectroscopically pure.

2.7. Preparation of Aluminium Isopropoxide.

Aluminium foil (80 gm) was cut into small pieces, dried in an oven at 120°C, and then placed in a desiccator overnight. The foil was then placed in a 2 l. flask fitted with a nitrogen delivery tube and a reflux condenser. 1 l. of azeotropically dried isopropanol was added and a few mgs. of mercuric chloride. The mixture was warmed slightly to initiate the reaction and nitrogen was passed. After a few minutes the reaction proceeded on its own without heating and with copious evolution of hydrogen. To prevent loss of solvent with the stream of gas, nitrogen was cut off when the pressure of hydrogen was high enough to prevent access of air. Nitrogen was passed again towards the end of the reaction and the mixture was heated to keep it at its boiling point.

The crude product was redistilled at reduced pressure; boiling occurred at 120°C at about 1 mm pressure. It was then recrystallised from dry isopropanol. The yield was quantitative.

2.8. Preparation of Al-s-butoxide by alcoholic exchange.

The Al-s-butoxide was prepared by Doering and Young, and by Jackman by alcoholic exchange. However, during this study the purity of the Al-s-butoxide so prepared was suspected on the basis of the steric factor of the incoming s-butanol groups and the theoretical mechanism of the alcoholic exchange. These suppositions were proved to be right.

Experimental: About 5 gm of twice redistilled Al-isopropoxide was placed in a 500 ml flask. Dry binary azeotrope of benzene and s-butanol was added (8.5 ml of s-butanol), then dry benzene up to about two thirds the

volume of the flask. The mixture was warmed slowly after connecting the flask to an 80 cm distillation column packed with single turn Fenske's helices, and then fractionated collecting first the isopropanol-benzene azeotrope, b.p. 71.92°C (33.3% of isopropanol), then a few drops of s-butanol-benzene azeotrope, b.p. 78.5°C (15.4% of s-butanol), and afterwards pure benzene b.p. 80.15°C . After two thirds of the benzene was removed the flask was disconnected and the rest of benzene was removed under reduced pressure. The above alcoholic exchange was carried out in an atmosphere of nitrogen to prevent oxidation of the alkoxide.

A viscous transparent substance was obtained. This was analysed for Al and other components and was proved to be aluminium di-butoxide-mono-isopropoxide, proving that the theoretical consideration outlined at the beginning of the paragraph were right.

2.9. New method for preparation of Al-s-butoxide.
(S.W. method).

The preparation of Al-s-butoxide by alcoholic exchange, method used by other workers, suffers from the following shortcomings:

- (a) large excess of s-butanol have to be used;
- (b) s-butanol is lost during exchange as binary azeotrope of s-butanol and benzene.

These are serious losses considering the scarcity of optically active s-butanol.

(c) the alkoxide obtained by this method is not a pure Al-s-butoxide. It contains one isopropanol group. This is most serious point in consequent study of the reaction mechanism.

Therefore a method has been devised which gets rid of all the above shortcomings.

The method: s-butanol (30 ml, i.e. 24 gm) was added to a large excess of dry benzene followed by 6 ml of dry isopropanol. The mixture was refluxed slowly under a 120 cm long fractionating column packed with single turn Fenske's helices. Fractions were collected at the head of the column using a high reflux ratio (1:16 - 1:20).

First fraction, b.p. 66.5°C, a ternary, water-isopropanol and benzene azeotrope - discarded.

Second fraction, b.p. 71.92°C, a binary azeotrope of isopropanol and benzene - discarded.

Third fraction, b.p. 78.5°C, a binary azeotrope of s-butanol and benzene - collected.

The fractionation was continued until the temperature reached 80°C and some benzene was also collected. The composition of the binary azeotrope of s-butanol-benzene is 15.4% of s-butanol by weight.

The third fraction, that is the binary azeotrope of s-butanol and benzene, was refluxed with 2.4 gm of dry, clean aluminium foil in the collecting flask (round bottomed), fitted with a reflux condenser in a slow stream of nitrogen. A few mgs of mercuric chloride was added to initiate the reaction. The heating was continued for 24 hours. At the end of that period the flask was connected to a 80 cm long fractionating column packed with single-turn Fenske's helices. The slight excess of s-butanol was collected at the top of the column as its binary azeotrope with benzene and stored for future use. The heating was then continued until most of the benzene was removed.

The experiment, throughout, was carried out in an atmosphere of dry nitrogen.

Last traces of benzene were removed by an oil rotary vacuum pump.

The product was redistilled under reduced pressure (0.02 mm Hg), and a transparent viscous substance was obtained, b.p. 120°C/0.02 mm, yield = 16 gm.

Analysis of the product shown it to be 100% Al-s-butoxide, i.e. $\text{Al}(\text{OC}_4\text{H}_9)_3$.

The optically active form of Al-s-butoxide was prepared by the same method. Analysis for Al- and s-butoxy groups again showed that the product was pure $\text{Al}(\text{OC}_4\text{H}_9)_3$.

3. Kinetic Study of M.P.V./Oppenauer Reaction.

For this purpose a thermostat capable of maintaining temperature constant to 0.01°C, was designed and constructed.

Alkoxides are extremely hygroscopic, are hydrolised by the smallest traces of moisture, and easily oxidisable. Therefore all experiments had to be carried out in atmosphere of dry nitrogen.

For the purpose of measuring and transferring the reaction mixture to the reaction vessel a vacuum multi-burette was designed and made, operated by a vacuum pump and dry nitrogen. The burette was permanently connected to storage bulbs by means of ground glass joints. The liquids were sucked into the burette from storage bulbs through sintered glass filters. With this arrangement the reacting liquids once introduced to the storage bulbs were excluded from moisture and from

contact with the atmosphere for a whole series of experiments.

3.1. Polarimetric study. For this purpose a 2 dm. long cell with a thermostating jacket was specially adapted. The inlet of the tube was fitted with a glass delivery tube which was fixed permanently to the cell by means of polythene tube (about 5 cm long) and terminated with a tap and a ground glass joint which could be attached to the vacuum burette. Once the liquids have been introduced the tap was closed, the polarimeter tube detached from the burette and was placed inside the polarimeter ready for study.

Two preliminary experiments were conducted using 50/50 mixture of:

(a) 8 gm of d-Al-s-butoxide in 36.35 gm of methyl-cyclohexane, and

(b) 2.8682 gm of methyl ethyl ketone in 89.525 gm of Me-cyclohexane.

Both experiments were carried out at room temperature (21.5 - 22.0°C).

It required 36 hours for complete racemisation of the d-Al-s-butoxide.

The plot of specific rotation, $[\alpha]_t$, against time gave the common asymptotic curve for 1st order reactions, and the plot of $\log \frac{\alpha_0}{\alpha_t}$ against time gave in both cases straight line, showing that the reaction is of first order as suggested by Jackman. From the slope the reaction velocity constants, K, were evaluated. These were: (1) $K = 3.7 \times 10^{-5} \text{ sec}^{-1}$, (2) $K = 3.64 \times 10^{-5} \text{ sec}^{-1}$. These are in agreement with values obtained by Jackman for a similar reaction.

3.2. Study by means of Interference Refractometer.

During this study it has been observed that the d- and l-form of s-butanol have different refractive indices, the difference being about 5 units in the fourth decimal place. The difference between pure d-s-butanol $[\mu]_D^{20} = 1.39745$, and dl-s-butanol $[\mu]_D^{20} = 1.39710$ being 3.5 units in fourth decimal place.

It was concluded that the difference is small enough for interference fringes to be observed and therefore the kinetics can be studied by means of Interferometer. As there was a good Rayleigh Interference Refractometer in the department it was decided to use it for this purpose. The same solutions as described for the polarimetric study were introduced in 50/50 proportions into a one cm long quartz cell, fitted with a ground glass stopper terminated with a vacuum tight collapsable membrane. The solutions were injected into the cell by means of a hypodermic syringe from a micro-pipette in a dry box in an atmosphere of nitrogen. A second similar cell was filled with similar solutions but of the inactive alcohol. This served as a standard of reference. The distance through which one fringe moved was measured with time.

The distance through which the fringe moved is proportional to the refractive index of the solution, n , and also to the number, m , of fringes passing, as follows from the equation:

$$(n - 1)l = m\lambda \quad (1)$$

where, λ = wavelength of monochromatic light used, and l = length of the cell (1 cm).

The relation between refractive index and optical rotation as given by Fresnel (1825) is:

$$\alpha = \frac{\pi}{\lambda} (n - n_r) \quad (2)$$

where, λ = wavelength of monochromatic light used,
 α = angle of rotation per cm of medium,
 n = refractive index of left polarized light,
 n_r = refractive index of right polarized light.

Monochromatic helium light was used throughout the experiment and as a source for the reference line.

From equations (1) and (2) it follows that there is a linear relation between the refractive index and the distance one particular fringe moves with time and also a linear relation between refractive index and specific rotation, .

Therefore to study the kinetics of this reaction the distance through which the fringe moved was plotted against time.

This gave a straight line which came to a stop after the reaction has terminated. It is of interest to mention that the fringe stopped moving after exactly the same time as was taken to complete the racemisation in the polarimetric study, that is after 36 hours.

From the straight line relation of the graph it appears that the reaction is of the zero order in accord with equation (1), section 1.2.

$$\text{i.e.} \quad R = k_1 \left[(+) \text{ complex} \right]$$

However, this is not a conclusive result as the observations were conducted at room temperature and more rigorous experiments are required to draw any valid conclusions.

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