

~~THE~~ PREPARATION AND SORBENT PROPERTIES
OF ALKYL AND ARYL AMMONIUM POLYPHOSPHATES

by

Timothy John LOCKE, B.Sc., A.R.I.C.

A Thesis submitted for
The Degree of Doctor of Philosophy
of the University of London

December, 1962.

Chemistry Department,
Imperial College of Science and Technology,
London, S. W. 7.

ABSTRACT

A number of different methods have been used in the preparation of substituted ammonium polyphosphates. Products produced in different ways always had the same unit cells, but the degree of crystallinity and texture of the products varied with the method of preparation. The most crystalline products were obtained by ion exchange of inorganic polyphosphates. Sorption was studied with amyl-, heptyl-, nonyl-, dodecyl- and cetyl-trimethyl-ammonium and anilinium polyphosphates. A number of different sorbates were used. Ethanol and amyl alcohol were found to react with primary alkyl ammonium polyphosphates, the effect becoming considerable in the case of the system amyl alcohol/amyl ammonium polyphosphate. Anilinium polyphosphate was also found to react with ethanol. Such reaction tended to alter the sorptive capacity of the polyphosphates.

In addition, the sorption of water, nitromethane and a number of hydrocarbons was studied. Normally, reaction did not occur with these sorbates. Thermodynamic evidence was obtained for some of these systems and it was attempted to interpret such evidence qualitatively in terms of models.

Cetyl trimethylammonium polyphosphate differed from the other sorbents, both in structure and its tendency to dissolve in the sorbates. Equilibrium was attained very slowly with this sorbent.

Information has been obtained by X-ray measurements about changes in the unit cells of certain polyphosphates in equilibrium with varying pressures of sorbates. This has been discussed in terms of the extent of uptake of such vapours, as determined by sorption measurements.

ACKNOWLEDGEMENTS

I wish to express my gratitude to Professor R. M. Barrer, F.R.S., for his guidance, encouragement and many helpful discussions in the course of this work.

I also wish to thank the technical staff of the College, particularly Mr. A. Maddell of the glass-blowing workshop, for their invaluable assistance.

I am indebted to Dr. I. S. Kerr for help in carrying out X-ray studies, and to other members of staff and colleagues for valuable discussions.

I am grateful to Scottish Agricultural Industries Limited for a grant to enable me to carry out this work.

TABLE OF CONTENTS

1.	INTRODUCTION	1
2.	THE POLYPHOSPHATES	
2.1	General structures.	1
2.2	The preparation of sodium and ^{potassium} poly- metaphosphates.	2
2.3	The preparation of substituted ammonium polyphosphates.	3
3.	SURVEY OF SWELLING PHENOMENA	
3.1	Swelling of some layer compounds in one dimension.	6
3.2	Swelling of mono n-alkyl ammonium polyphosphates.	12
3.3	Two-dimensional swelling.	13
3.4	Swelling of polymers.	21
4.	SORPTION	
4.1	General.	22
4.2	Thermodynamics of sorption.	22
4.3	Sorption isotherm equations.	25
4.4	Hysteresis in sorption.	32
5.	POLYMER SOLUTION THEORY	33
6.	EXPERIMENTAL, APPARATUS AND TECHNIQUES	
6.1	High vacuum system.	36
	A. Pumping system.	36
	B. Distillation train.	39
	C. Subsidiary thermostat units.	39
	D. Sorption unit.	40
	E. Measurements.	42
	F. Springs.	42

9.3	Comparison of alkyl ammonium polyphosphates as sorbents for hydrocarbons.	126
9.4	Other sorption studies on primary ammonium polyphosphates.	135
10.	SORPTION OF CETYL TRIMETHYL AMMONIUM POLYPHOSPHATE.	164
	SUMMARY.	171
	APPENDIX.	173
	REFERENCES.	199

LIST OF ABBREVIATIONS

μ	chemical potential
R	gas constant
T	temperature
p or P	pressure
H	enthalpy
S	entropy
G	Gibbs' free energy
n	number of moles
X	an extensive quantity
V	volume
A.P.P.	ammonium polyphosphate
R.V.P.	relative vapour pressure
K.S.	potassium Kurrol's salt
M.S.	high temperature form of sodium Maddrell's salt

1. INTRODUCTION

During the past decade considerable interest has been shown in the properties of inorganic polymers. Due to this a great deal of work has been carried out on polyphosphates, concerning their properties in biological systems, as water softening agents, in promoting the activity of detergents, as fertilisers, film forming agents and so on. In view of the possibility of providing new chromatographic materials and sorbents, and also of investigating one or two-dimensional swelling within crystals, it was thought interesting to examine the sorptive behaviour of a number of substituted ammonium polyphosphates with a wide range of sorbates.

2. THE POLYPHOSPHATES

2.1. General structures

A very large number of polyphosphates are known, differing from one another in chain length, crystal structure, and chain arrangement, as well as in the nature of their cations.

All of these materials are, however, based on phosphorus atoms tetrahedrally surrounded by oxygen atoms. Neighbouring tetrahedra are joined through P-O-P linkages. By this means three different types of chain may be formed - straight, branched or cyclic. The first type are very numerous. The tri- and tetra-metaphosphates are the only important examples of the cyclic type, but a number of larger rings have been demonstrated to exist in solutions of Graham's salt (which is a vitreous sodium polyphosphate) (1). Branched chains must exist in at least two crystalline compounds, of empirical formulae $\text{CaO} \cdot 2\text{P}_2\text{O}_5$ and $2\text{CaO} \cdot 3\text{P}_2\text{O}_5$,

which have been prepared by Hill, Faust and Reynolds (2), but X-ray studies on P_2O_5 and other phosphates indicate that branching points in polyphosphate chains are rather unstable as they have much localised π bond character on their free oxygen atom, and thus little resonance energy. They are believed to exist only in polyphosphates in which the ratio of M^+ to P is less than one, where M^+ represents one equivalent of any cation, and P one gram atom of phosphorus. Such branching points are also believed to hydrolyse rapidly in aqueous solution (3).

Straight chain polyphosphates are relatively stable in neutral solution, though they have been shown to degrade slowly, mainly from the ends of the chains, to give primarily ring compounds. This type of hydrolysis occurs at a greater rate in alkaline solution, but is accompanied by significant random chain scission in acid solution (4).

The polyphosphates investigated in this work were straight chain polymers of effectively infinite length. Their monomer units were therefore $(X^+PO_3^-)$ and the contribution from end groups would be negligible.

2.2. The preparation of sodium and potassium poly-metaphosphates

Several polymetaphosphates of sodium and potassium are known. The first two were reported by Graham (5) in 1833-34. These were vitreous sodium metaphosphate and a material also prepared later by R. Maddrell (6), now known as Maddrell's salt or $(NaPO_3)_n$ II. Another form was reported in 1941 by Partridge, Hicks and Smith (7). This is a low temperature form of Maddrell's salt and is known as $(NaPO_3)_n$ III.

In 1892 Tamman (8) reported that his collaborator,

Kurrol, had prepared yet another form, now called $(\text{NaPO}_3)_n^{\text{IV}}$. This is best produced by seeding a melt of $(\text{NaPO}_3)_n$ in the temperature range 550°C - 600°C and quenching the product. This form is called sodium Kurrol's salt, after the discoverer.

The potassium metaphosphates are as follows. Potassium Kurrol's salt is easily prepared, as will be described later in the experimental section. (See also Osterhead and Audrieth (9)). Pascal (10) showed by differential thermal analysis studies that three forms of potassium Kurrol's salt occur, but that all of them revert to the same form at room temperature. There is also a potassium polymetaphosphate glass. Generally, the Maddrell's salts are relatively insoluble in water or saline solutions, whereas the Kurrol's salts are insoluble in water but soluble in saline solutions.

The organic polyphosphates used in this work were all obtained either from potassium Kurrol's salt which is $(\text{KPO}_3)_n$ or from form II of sodium Maddrell's salt, of formula $(\text{NaPO}_3)_n$. Their structures are discussed subsequently in section 8.

2.3. The preparation of substituted ammonium polyphosphates

Preparations of a number of different quaternary ammonium polyphosphates were reported by Iler in 1952 (11). His work was concerned mainly with the production of films, and an investigation of some properties of polyphosphates bearing on this is described. The methods of preparation used were as follows. Soluble materials were produced by suspending Kurrol's salt (K.S.) in water and adding the appropriate form of cation exchange resin, with stirring, over a period of about an hour. The solution was then

filtered, and the product obtained by evaporation.

Another method used was to suspend the sodium form of an anion exchange resin with K.S. and stir until a viscous solution of the soluble sodium/potassium polyphosphate was formed. Long chain quaternary ammonium bromides or chlorides were added to this solution, and the corresponding polyphosphates collected as waxy, rubbery or gummy precipitates.

By use of the hydrogen form of an ion exchange resin a solution of polymetaphosphoric acid was prepared at 0°C. By neutralising this solution with the quaternary base tetramethyl ammonium polyphosphate was prepared. The same product was also made by exposing solid lead polymetaphosphate to the action of tetramethyl ammonium sulphide. This gave a viscous solution of the polyphosphate, from which lead sulphide was removed by centrifuging.

The methods used by Iler gave high molecular weight products, since his starting materials were also of high molecular weight, and products with a degree of polymerisation of 1000 or more were readily obtained. However, by viscosity studies, he showed that degradation of the polyphosphate chains occurred in the liquid state. Van Wazer (12) draws attention also to the effects of acidity and temperature in increasing the rate of degradation of the chains.

Cetyl pyridium polyphosphate of low average molecular weight had been made previously by Downey (13) and also by Steigmann (14) by the addition of the bromide to a solution of glassy sodium metaphosphate.

Ebel and Colas (15) studied the combination of poly and meta phosphates with organic bases. They found that various monamines, diamines, and hydrazines would

precipitate their metaphosphates from an acid solution of Graham's salt, and also that short chain polyphosphates and cyclic metaphosphates were precipitated from less acid solutions, some quantitatively. Various biologically occurring organic bases caused precipitation of up to 95% of the polyphosphate present at pH 2-4, and they suggested such precipitations as a means of isolating biological bases, the free base being subsequently liberated with HCl.

Quaternary ammonium polyphosphates with linear polyphosphate chains have been prepared by Tayler (16) by the following method. $\text{NH}_4\text{H}_2\text{PO}_4$ was heated at 350-400°C for 2-3 hours, thus forming polymeric $(\text{NH}_4\text{PO}_3)_n$. This was dissolved in water, and the pH adjusted to between 7 and 8 with NaOH. Cetyl trimethyl ammonium bromide was added, and the corresponding polyphosphate precipitated. He found that, in general, those quaternary polyphosphates with one of their alkyl chains longer than 6 C atoms were greasy solids. Quaternary ions with smaller chains gave water soluble polyphosphates.

In 1958, Weiss and Michel (17) reported the preparation of a number of polyphosphate materials by ion exchange of potassium Kurrol's salt. The method appears to be a quite general one, and was extensively used in the present research. It was shown by these workers that the exchange of two primary ammonium polyphosphates reached equilibrium in about 8 hours, and graphs for the equilibrium percentage of exchange against the normality of the exchange solution are given for three primary ammonium polyphosphates and cetyl trimethyl ammonium polyphosphate.

A discussion of the merits of the various preparative methods is given in section 7.

3. SURVEY OF SWELLING PHENOMENA

3.1. Swelling of some layer compounds in one dimension

Most of the present work is concerned with the sorptive behaviour of lamellar polyphosphates. These materials have organic material "sandwiched" between plates made of cross-linked polyphosphate chains. It is therefore of interest to consider the sorptive behaviour of some similar compounds.

Considerable work has been completed by Barrer and co-workers on various substituted ammonium montmorillonites, which are clays having rigid aluminosilicate plates. Barrer and MacLeod (18 and 19) found that non-polar molecules were sorbed only on the external surfaces of the particles of the natural clay, and that certain polar molecules were sorbed only after a certain threshold pressure had been reached. On the other hand, with the tetra ethyl and tetra methyl clays non-polar sorbates were intercalated without any threshold pressure. It was discovered also that benzene molecules were apparently sorbed perpendicularly to the sheets. Molecular sieve properties were noted in the organic derivatives.

Barrer and Reay (20) then studied sorption on tetra-, tri-, di- and monomethyl ammonium montmorillonites, and discovered that the d_{001} spacing of the clays increased on sorption of certain large molecules. The tetramethyl ammonium clay displayed the greatest affinity for the sorbate in such cases, since the lamellae were already moved a greater distance apart than in the other clays. In addition to molecular shape, other factors were involved, as was shown by the sorption of benzene in a perpendicular orientation to the sheets, despite the fact that this

required an expansion of the lattice which would not have been necessary with a flat arrangement of the benzene rings. Nearly all of the isotherms measured in this work were of type II in Brunauer's classification. From calculations of the surface area for both polar and non-polar molecules, it was inferred that different sorption centres were involved, the polar molecules forming clusters round the cations, and the non-polar molecules being sorbed on the aluminosilicate sheets.

Barrer and Kelsey (21) continued the work on monomethyl and tetramethyl ammonium montmorillonites and also extended that carried out by Barrer and Reay previously with dimethyl dioctadecyl ammonium montmorillonite (Bentone 34). In general, the earlier work with methyl- and tetramethylammonium montmorillonites was extended, and thermodynamic values were derived for various systems involving them. It was shown that sorption was exothermic, and the partial molar entropy change of the sorbate was negative in every case, and over the whole range of sorption.

The interlamellar space of bentone 34 was, however, effectively filled with its large cations. It was demonstrated that sorption into this material represented a mixing process of sorbate molecules with the chains of the cations. The sorbate/sorbent affinity depended in part on the cohesive energy density of the sorbate, and the large positive partial molar entropies of sorption which were found experimentally were correlated with statistical calculations of such entropies based on a "mixing" model. In general, sorption on Bentone 34 was endothermic. The isotherms tended to be linear up to high relative vapour pressures of the sorbate, and showed some hysteresis.

It will be shown that the lamellar polyphosphates

investigated in the present work exhibit similarities with both Bentone 34 and the bentonites with small organic cations. As shown in section 8.2 their interlamellar volume is completely filled with alkyl chains, and their isotherms are nearly linear, as was the case for Bentone 34. However, the thermodynamics of sorption indicated a very different mechanism of sorption, involving interactions with a polar environment, somewhat similar to that occurring with the other organic montmorillonites which have been mentioned.

The structural differences between the montmorillonites and the lamellar polyphosphates stem partly from the rigidity of the montmorillonite sheets, as compared with the easily rearranged polyphosphate sheets (see section 9.2.2) and partly from the intermediate size of the primary ammonium ions of the polyphosphates between those of the methyl ammonium and dimethyldioctadecyl ammonium ions used with the bentonites. Apart from these differences, the charge density on the plates was about 2-3 times as great in the polyphosphates as in the montmorillonites, and it is almost certainly more regular. This would lead to a much closer and more regular packing of cations in the former case, presumably rendering their alkyl chains more rigid, and making participation in a mixing process by such chains more difficult.

Much of the work on the subject of one-dimensional swelling has been carried out by Weiss and co-workers. They have measured the swelling of a number of lamellar aluminosilicates with varying charge densities on their plates in the stearylammmonium form (22). Although these compounds have sheet separations varying from 18\AA to 31\AA in the outgassed state, they all had a constant sheet

separation of a little less than 50\AA under n dodecyl alcohol. It follows from this that the amount of alcohol taken up became greater as the charge density became lower. The fact that all the swollen materials had the same sheet separation suggests that the alkyl chains of the cations may lie at the same angle to the plates in each case, the space between the cations being occupied by dodecyl alcohol. Weiss suggested that the alcohol molecules might lie parallel to the alkyl chains of the cations, which he suggested might be at an angle of 56° to the sheets in batavite. He supported this contention by evidence from a Fourier projection in hexylammonium batavite and evidence about the most energetically stable arrangement for hydrogen bonding between the amine heads and the oxygen atoms in the sheets. The likelihood of an angle of 56° being energetically favourable was also supported by X-ray data obtained for a number of primary ammonium and straight chain diammonium batavites.

It also appeared that an angle of 56° was favoured in the case of some organic vermiculites (23), but the angles adopted by the chains seem to be more variable with these materials.

It was noted in the cases of all of the lamellar aluminosilicates that certain alcohols were very effective swelling agents.

Investigations were carried out with a series of alcohols in order to find how their ability to cause swelling varied with chain length. It was found that with n-butyl-, n-hexyl-, n-octyl-, and n-dodecyl ammonium vermiculites and octadecyl ammonium muscovite (24), the longer the alkyl chain of the swelling alcohol, the greater was the swelling produced, throughout the range of alcohols investigated, which varied in chain length

from C_1 to C_{18} . The alcohols with chain lengths of less than 8 carbon atoms were not so effective as aromatic hydrocarbons in causing swelling, while those of greater chain length were in general more effective.

It appears from the foregoing work, therefore, that the following factors are of great importance in deciding the swelling ability of substituted ammonium layer type compounds.

1. The charge density of the plates. In general a low charge density favours the intercalation of swelling liquids.

2. The most energetically favourable angle of the cation chains. Where the sheets in the compounds are rigid this may be determined by a consideration of the possibilities of hydrogen bonding between the amine beads and the sheets. If the sheets are flexible the most favourable angle of the cation chains will vary according to the sheet orientation.

3. The possibilities of interaction between the sheets and the swelling agent. Aromatic compounds and alcohols (which would be capable of hydrogen bonding) appear to be good swelling agents.

4. The shape, size and polarity of the molecules to be taken up.

5. The sizes of any cavities in the sorbent.

Polyphosphates have quite highly charged sheets (about 31.2\AA^2 per unit charge) and seem to have no cavities. Since their sheets are not very rigid, the angles adopted by the cation chains will presumably be subject to reasonably free variation. The structural consequences of sorption into lamellar polyphosphates are discussed in sections 9.2 and 9.3

but from a consideration of the points mentioned above, copious sorption into lamellar polyphosphates could not be expected, and was not normally found to occur.

One-dimensional swelling has been found to occur with primary alkyl ammonium dititanates (25), and a number of primary alkyl ammonium forms of several organophilic autunites (26), under a wide variety of organic liquids, and in calcium monoalkylphosphates (27) with organic materials which were capable of hydrogen bonding. However, the most interesting case of swelling from the view point of this work is that of the substituted ammonium polyvanadates of the formula $\{X^+(VO_3^-)\}_n$. The behaviour of these polyvanadates appears to be completely analogous to that of polyphosphates.

Primary ammonium polyphosphates and polyvanadates were both assigned a sheet structure, on very similar evidence to that discussed for polyphosphates in section 8.2. It was found with both series of compounds that unidimensional swelling would occur with certain alcohols, aldehydes and carboxylic acids (28,29). The most effective alcohols for swelling were those which had alkyl chains of the same length as those of the cations of the polyphosphate or polyvanadate. It was found that the anilinium and benzidinium polyvanadates were unstable, due to the anion oxidising the cation in the crystalline state. Anions with $(V_3O_8^-)_n$ repeating units showed very different sorptive behaviour, and swelled in water, hydrocarbons, alcohols, esters, ketones and nitro-compounds.

The polyvanadate sheets consist of chain anions which are held together by hydrogen bonding to common amine heads, as discussed with polyphosphates in section 8.2. It follows that polyvanadates with quaternary ammonium ions

will have no binding between their anions since there is no possibility of hydrogen bonding with such cations. Thus the anion chains will not necessarily lie in plates in such compounds, and the compound would be expected to swell in two dimensions on sorption. It has been shown that cetyl trimethyl ammonium polyvanadate will swell in two dimensions, as will the corresponding polyphosphate (28, 29).

3.2. Swelling of mono n-alkyl ammonium polyphosphates

Extensive studies of the swelling properties of the mono n-alkyl ammonium polyphosphates with alcohols, were published in 1960 by Weiss and Michel (29). The paper also gives some information about the unit cells of dodecyl ammonium polyphosphate when swollen with aldehydes and carboxylic acids.

Five homologues of the polyphosphate series were treated with a number of straight chain alcohols. It was found that the greatest swelling was caused by alcohols of approximately the same chain length as the cations of the polyphosphate (see Table 1).

A number of polyphosphates were also exposed to the alcohol which had the same alkyl chain length as their cations, and their unit cell dimensions were as shown in Table 2. The last column shows the change in d_{100} spacing (= sheet separation) per CH_2 unit. From the fact that the average value of this was $2.5\overset{\circ}{\text{A}}$, it was deduced that, in the swollen state, the alkyl chains were probably vertical to the sheets. If this were the case, an increment of about $2.52\overset{\circ}{\text{A}}$ would be expected. It was discovered that the d_{001} spacing in the swollen state was a little greater than in the unswollen state. Since, as discussed

TABLE 1

Layer separation in various primary alkyl ammonium polyphosphates under alcohols of increasing chain length.

Swelling agent	$d(100)$ in Å				
	Hexyl-ammonium-polyphosphate	Nonyl-ammonium-polyphosphate	Dodecyl-ammonium-polyphosphate	Myristyl-ammonium-polyphosphate	Stearyl-ammonium-polyphosphate
Dry	19.2 ₅	25.0	30.3	34.1	41.6
Under					
Ethanol	20.0	26.8			
Propanol	20.2	26.7			
Butanol	20.3	27.0			
Pentanol	20.3	27.4			
Hexanol	20.1	28.4	30.3	34.1	41.6
Heptanol	20.0	28.7	30.4	34.1	41.6
Octanol	19.6	28.9	34.1	34.1	41.6
Nonanol	19.5	29.6	34.9	34.1	41.9
Decanol	19.5	28.4	35.5	39.6	41.9
Undecanol	19.3	27.7	35.5	39.6	47.6
Dodecanol	19.3 ₅	28.0	36.3	40.3	48.7
Tetradecanol	19.3 ₅	27.7	36.9	41.1	48.7
Hexadecanol	19.3 ₅	28.0	35.1	44.3	49.3
Octadecanol	19.3 ₅	26.7	34.1	45.2	50.3

TABLE 2

Unit cells of various primary ammonium polyphosphates under their corresponding alcohol.

Alkyl chain	Unit cell dimensions in Å			
	b-axis (Fibre axis)	d(001)	d(100)	$\Delta d(100)$
Ethyl	4.5 ₉		11.1	
Propyl	4.5 ₆	14.0 ₅	14.7	3.6
Butyl	4.5 ₉	14.2	14.8	0.1
Amyl	4.5 ₉	14.1	18.9 ₅	4.1 ₅
Hexyl	4.5 ₅	14.1 ₅	20.1	1.1 ₅
Heptyl	4.5 ₉	14.1	23.3	3.2
Octyl	4.5 ₉	14.2	25.2	1.9
Nonyl	4.5 ₇	14.0	29.6	4.4
Decyl	4.4 ₅	14.0 ₅	31.2	1.6
Undecyl	4.5 ₉	14.1	34.1	2.9
Dodecyl	4.5 ₈	14.2	36.3	2.2
			Average	<u>2.5₂ Å/C.Atom</u>

TABLE 3

x=	Sheet separation in n-dodecylammonium-polyphosphate in Å under			
	n-alcohols $n-C_xH_{2x+1}OH$	n-alkyl- aldehydes $n-C_{x-1}H_{2x-1}CHO$	n-alkyl- carboxylic acids $n-C_{x-1}H_{2x-1}COOH$	n-alkyl- nitriles $n-C_{x-1}H_{2x-1}CN$
2	30.3		31.0	30.3
3	30.3	30.3	35.0	30.3
4	30.3	30.3	35.3	30.4
5	30.3	30.6	35.3	30.4
6	30.3	35.1	35.2	30.6
7	30.4	-	35.2	-
8	34.1	35.2	35.2	30.5
9	34.9	35.3	35.5	-
10	35.5	35.5	35.5	30.4
11	35.5	-	-	
12	36.3	37.0	37.6	
14	36.9	-		
16	35.1	-		
18	34.1	-		
Dried at 60°C and 1mm pressure		30.3		

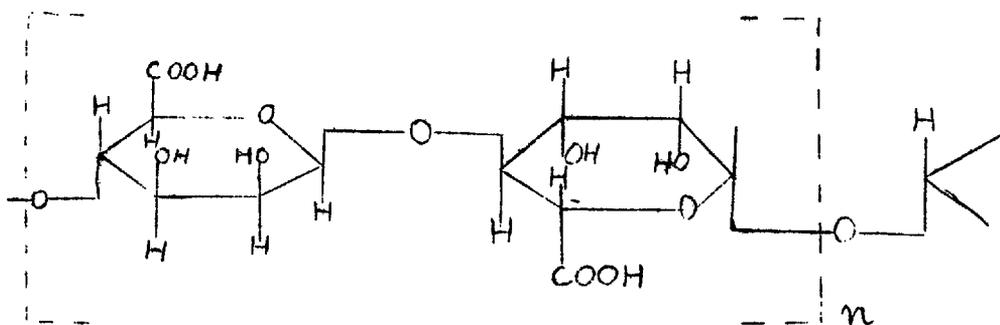
in section 9.2.2 a vertical orientation of the alkyl chains must involve the disturbance of hydrogen and other bonds unless the d_{001} spacing is reduced, these findings imply that such disturbance is not very unfavourable energetically.

The values for the sheet separations in dodecyl ammonium polyphosphates under various liquids are shown in Table 3.

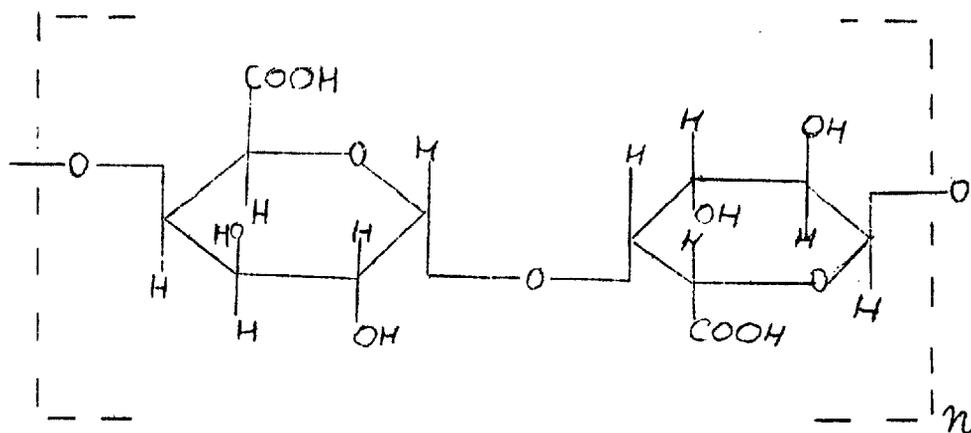
3.3. Two-dimensional swelling

A number of compounds have been shown to exhibit two-dimensional ordered swelling. The swelling of quaternary ammonium polyphosphates (29) and polyvanadates (28), and of salts of poly-d-galacturonic (30) and poly-d-mannuronic (30 and 31) and mercury amido sulphonic (32) acids has been studied by means of X-rays.

The studies with galacturonates and mannuronates gave very similar results. This was to be expected since their structures are very similar, as shown below.



Poly-d-mannuronic acid (Alginic acid)



Poly-d-galacturonic acid (Pectic acid)

The unit cell dimensions of the substituted ammonium salts of these compounds varied in the outgassed state according to their previous history, but the evidence for the ordered two-dimensional swelling of such compounds with the dodecyl ammonium and cetyl trimethyl ammonium salts using water and long chain alcohols as swelling agents was conclusive. The dodecyl ammonium alginate was also swollen by toluene, butyl acetate, xylene and decane; the cetyl trimethyl ammonium alginate by toluene, butyl acetate and benzene. The dimethyl dioctadecyl ammonium alginate was swollen by toluene, xylene, butyl acetate, decane and decanol, but apparently not by water, though it seems possible that swelling under water may have been masked by difficulties with the X-ray techniques. Dodecyl ammonium alginate apparently took up small polar molecules without swelling, by sorption into pre-existing holes, and a structure to explain this has been proposed (31).

Similar investigations of the swelling of cetyl trimethyl ammonium polyphosphate (17) and polyvanadate (28) and of octadecyl pyridium polyphosphate (17) showed that swelling occurred with water, aromatic compounds and

alcohols, as well as with other materials, as shown in the tables below. However, considerable variations occurred in the unit cell dimensions in the outgassed state, according to the previous history of the sample in the case of the polyvanadate. The unit cell for cetyl trimethyl ammonium polyphosphate is shown as being tetragonal with dimensions of 4.8, 22.2 and 22.2^oÅ in Table 5, the same workers (in Table 4) assign to the same compound a similar unit cell with repeat distances of about 32.1 or 31.5^oÅ. The ratio between the differing repeat distances is $\sqrt{2}$. The ratios between the repeat distances for the polyphosphates in the swollen state which occur in both tables are $\sqrt{2}$ for butyl acetate and toluene, but only 1.0 for n-decanol and 1.63 for water. The ratios of $\sqrt{2}$ may be due to errors in the values in Table 5 associated with the nature of the X-ray equipment used and the faintness of certain lines (17). An explanation of certain discrepancies in the cell dimensions of some outgassed materials has been promised by the authors in a future paper (28).

The results of the X-ray work on the three compounds are shown in Tables 4-6.

Doubt is cast on the reliability of the results in Table 6 by Weiss and Michel, who state (17) that in the case of the swollen quaternary ammonium polyphosphates, they found relatively broad diffractions for the b axis, and diffuse and often intense diffraction lines for the swelling liquids. They further explained the X-ray patterns which they obtained in terms of two separate series of d spacings, which they indexed as arising out of tetragonal unit cells. Also, in some cases, the diffraction pattern obtained could not be explained on the basis of two such series, as there were additional lines present.

TABLE 4

Two-dimensional swelling of cetyl trimethyl ammonium polyvanadate and polyphosphate (28)

Swelling Agent	Polyvanadate Fibre Separation	Polyphosphate
Dried at 0.1 mm and 20°C	30.3, 26.4, or 24.9	32.1 or 31.5
Swollen under:		
water		45.2
butyl acetate	34.6	37.2
nitrobenzene	30.8	39.6
toluene	42.6	43.7
n-octanol	38.5	40.3
n-decanol	41.8	42.5
n-dodecanol	45.3	45.2
n-tetradecanol	46.7	49.3
n-hexadecanol	49.3	50.3

TABLE 5

Two-dimensional swelling of cetyl trimethyl ammonium polyphosphate (17)

Swelling Agent	Fibre Separation in Å	Fibre Repeat Distance
Dried at 0.1 mm and pressure 60°C	22.2	4.8 ₄
Under:		
water	27.7	
ethanol	29.8	5.0 diffuse
nonanol-(1)	40.3	4.0 "
decanol-(1)	42.5	4.0 "
toluene	30.9	5.0 "
xylene	31.4	5.0 "
nitrobenzene	27.4	
acetonitrile	32.6	4.0 "
di-n-butylether	29.4	4.0 "
butyl acetate	26.2	4.0 "
diethylketone	30.0	4.0

TABLE 6

Two-dimensional swelling of octadecyl pyridinium polyphosphate

Swelling Agent	Fibre Separation in A	Fibre Repeat Distance
Dried at 65°C and 0.1 mm	24.2	4.5
Under: water	28.2	4.5
ethanol	105(†)	4.5
decanol-(1)	43.5	4.5
benzene	28.5	4.6 diffuse
toluene	33.9	4.6
nitrobenzene	26.0	4.5

It would, therefore, seem that some of the work which is the basis of this discussion on two-dimensional swelling should be accepted with reservations.

3.4. Swelling of polymers

Since the materials used in the present work contain a large proportion of organic groups, it is instructive to compare their swelling properties with those of polymers which are completely organic.

An X-ray investigation of the swelling of a natural rubber which was partly crystalline and partly amorphous has been carried out by Volkova and Vol'kenshtein (33). It was found that, although the relative proportions of amorphous and crystalline material varied with uptake of kerosine, the X-ray diffraction pattern from the crystalline regions remained unchanged. With small amounts of sorption the proportion of crystalline material was found to increase, presumably because the solvent gives the polymer chains a greater mobility, which allows them to orient themselves, but with large amounts of sorption, the rubber became completely amorphous. These results indicate that uptake of paraffins into rubber occurs into its amorphous regions, and crystalline regions become amorphous as more solvent is imbibed. This "melting" of crystalline regions in the presence of a low molecular weight solvent is in accordance with the theory of Flory (34).

Parker and Michaels (35) have concluded from sorption data using small molecules as sorbates that the crystalline regions in polyethylene acted only by taking up space. They found that the amount sorbed was directly proportional to the amount of amorphous material present.

It is apparent, therefore, that if sorption in the systems referred to in sects. 9 & 10 follows the pattern of sorption into rubber and polyethylene, the organic regions of their structure will be randomised. Their

gross structure will, however, be at least partly maintained by their inorganic framework. There is a possibility, however, that where the alkyl chains of the sorbents are short, they are prevented from randomising by their attachment to a rigid structure.

4. SORPTION

4.1. General

When an outgassed solid is allowed to make contact with a gas or vapour, there is a tendency for molecules of the latter to be removed to an energetically favourable environment within or on the surface of the solid. This process is termed "sorption", the gas or vapour is called the sorbate, and the solid the sorbent. Sorbate molecules may be held at the surface of the solid by attractive physical forces only (physical sorption) or by chemical reaction with the sorbent (chemisorption). They may also in some cases (e.g. zeolites) enter the interior of the solid, so that the whole of the sorbent is involved rather than only the external surface. The polyphosphates studied in the present work sorbed internally as well as externally.

4.2. Thermodynamics of sorption

Reviews of the various approaches to thermodynamic treatments of sorption have been made in the recent past by Hill (37,38,39), Everett (40,41), and Drain (42).

There are two chief approaches to this problem. That of solution thermodynamics treats the sorbed phase as a solution and derives partial molar quantities of the

components of the solution; the other regards the sorbate in the sorbed phase as being in the potential field of the unperturbed solid. This latter approach leads to integral molar quantities of the sorbate. Assuming that the sorbent is unperturbed, the results of both treatments are equivalent. Only one will be given here. In solution thermodynamics, one has for one component of a solution

$$\mu_1^{\hat{}} + RT \ln P/p_0 = \mu_1 = \bar{H}_1 - T\bar{S}_1 \quad (1)$$

assuming that the vapour obeys the ideal gas laws. For a pure liquid

$$\mu_L^{\hat{}} = H_L - TS_L \quad (2)$$

$$\left. \begin{aligned} \mu_1 - \mu_L^{\hat{}} &= \bar{H}_1 - H_L - T(\bar{S}_1 - S_L) \\ \text{i.e. } \Delta\mu_1 &= \Delta\bar{H}_1 - T\Delta\bar{S}_1 \end{aligned} \right\} \quad (3)$$

It may also be shown that, since

$$\begin{aligned} G &= H + T\left(\frac{\partial G}{\partial T}\right)_{n,P} \\ \frac{H}{T^2} &= \frac{G}{T^2} - \frac{1}{T}\left(\frac{\partial G}{\partial T}\right) = -\frac{\partial\left(\frac{G}{T}\right)}{\partial T} \end{aligned} \quad (4)$$

and

$$\frac{\partial\left(\frac{\Delta\mu_1}{T}\right)}{\partial T} = -\frac{\Delta\bar{H}_1}{T^2} = \frac{\partial(R \ln P/p_0)}{\partial T} \quad (5)$$

This may be re-expressed as

$$-\frac{\Delta\bar{H}_1}{R} = \frac{\partial(\ln P/p_0)}{\partial\left(\frac{1}{T}\right)} \quad (6)$$

Where $\Delta\bar{H}_1$ is the enthalpy change in transferring one mole of sorbate to an infinite quantity of sorbent from the pure liquid. From equation (3)

$$\Delta\bar{S}_1 = \bar{S}_1 - S_L = R \ln P/p_0 + \frac{\Delta\bar{H}_1}{T} \quad (7)$$

Thus both heats and entropies of sorption may be found from isotherm data. If it is required to find the enthalpy of sorption from the gas phase it is necessary to add the latent heat of evaporation of the liquid to the above heat change, and to make a corresponding alteration in the entropy change. All values given in this thesis refer to the liquid as the standard state.

Integral values

In order to obtain integral values from the partial molar thermodynamic quantities obtained by the above methods, it is necessary to perform the integration

$$\tilde{X} = \frac{1}{N_1} \int_0^{N_1} \bar{X}_1 dn_1 \quad (8)$$

graphically (N_1 being the amount sorbed). This method will prove unreliable where the calculations of values at low coverage are inaccurate.

Thermodynamic properties of the sorbent

From the Gibbs Duhem relationship at constant temperature

$$\sum n_i d\mu_i = VdP \quad (9)$$

Now for two components let $N_1 = \frac{n_1}{n_1+n_2}$ and $N_2 = \frac{n_2}{n_1+n_2}$.

Also let V_m be the volume per mixed molecule.

$$\begin{aligned} \therefore N_1 d\mu_1 + N_2 d\mu_2 &= V_m(N_1+N_2)dP \\ &= V_m dP \end{aligned} \quad (10)$$

$$\therefore d\mu_2 = \frac{V_m dP - N_1 d\mu_1}{1 - N_1} \quad (11)$$

But $d\mu_1 = d\mu_{\text{gas}}$ at equilibrium,

$$\therefore \mu_2 - \mu_2^0 = \int_0^P \frac{V_m}{1-N_1} dP - \int_0^P \frac{N_1}{1-N_1} RT d \ln P \quad (12)$$

The first of these terms is negligible for ordinary pressures, and $N_1=0$ when $p=0$,

$$\therefore \Delta\mu_2 = \mu_2 - \mu_2^0 \simeq -RT \int_0^P \frac{N_1}{1-N_1} d \ln P \quad (13)$$

$$= - \frac{MRT}{m} \int_0^P \frac{x}{P} dP \quad (14)$$

where x is the weight sorbed per sorbent unit of molecular weight M , and m is the molecular weight of the sorbate.

The corresponding changes in entropy and enthalpy may be calculated from the relationships,

$$\Delta\bar{S}_2 = \bar{S}_2 - \bar{S}_2^0 = - \frac{\partial}{\partial T} (\mu_2 - \mu_2^0) \quad (15)$$

$$\Delta\bar{H}_2 = \bar{H}_2 - \bar{H}_2^0 = - \frac{\partial}{\partial \left(\frac{1}{T}\right)} \left(\frac{\mu_2 - \mu_2^0}{T} \right) \quad (16)$$

or if the entropy change is known, the enthalpy change is given by

$$\bar{H}_2 - \bar{H}_2^0 = \mu_2 - \mu_2^0 + T(\bar{S}_2 - \bar{S}_2^0) \quad (17)$$

4.3. Sorption isotherm equations

Many attempts have been made to describe mathematically the variations of sorption with sorbate pressure. Many of these contain several adjustable parameters which allow curves of almost any shape to be plotted by selecting appropriate values for these parameters. In order to be meaningful, such isotherm equations should correctly describe the variations in the isotherms with temperature, and be based on physical models which are themselves reasonable and from which the parameters involved in the isotherm can be independently deduced. Several typical isotherms may now be described.

(a) Freundlich suggested a purely empirical equation in 1906 (43) to describe the sorption of vapours at low pressures. This was

$$x = kp^n \quad (1)$$

where x was the amount sorbed, p the pressure, and k and n arbitrary constants, n being greater than one.

(b) The Langmuir isotherm: Langmuir (44) derived an isotherm for a model based on the following assumptions:

1. A surface with a finite number of sorption sites of equal energy.
2. Sorption confined to a monolayer, each site accommodating only one molecule.
3. No interactions between sorbed molecules.
4. Sorbed molecules are localised.

By equating the rates of sorption and desorption the equation

$$kp(1 - \theta) = \theta \quad (2)$$

may be obtained, where θ is the proportion of sites filled. The constant k will depend only on the temperature. The same equation has been derived thermodynamically (45) and statistically (46).

The equation may also be written

$$v = \frac{v_m bp}{1+bp} \quad (3)$$

where v is the volume sorbed, b is a function of the temperature, and v_m is the volume contained in a monolayer.

In fact, however, surfaces are rarely homogeneous, and interactions between sorbed molecules are almost certain to occur (47). Hill (48) also shows that the

transition from localised to mobile adsorption in the first adsorbed layer takes place at low temperatures when the potential barriers against movement of adsorbed molecules are 1 kcal or less. He therefore concludes that localised physical adsorption is rare at the temperatures normally used for sorption measurements. Tompkins (49) concludes that even in chemisorption, localised sorption is more rare than is generally thought. Despite these drawbacks, the Langmuir model has been widely used.

Attempts have been made to modify it to take account of surface heterogeneity (49, 57), but unless the energy distribution of the sites is known, it is not possible to employ such treatments.

(c) Polanyi's potential theory: Polanyi (50) considered that a solid surface had a field of force which attracted and thus compressed a gas which was in contact with it. By assuming that the adsorption potential was invariant with temperature, and that sorbed molecules obeyed the same equation of state as they did in the gas phase, it was possible, if an isotherm had been determined at one temperature, to calculate the heats and temperature dependence of sorption. The theory, as originally proposed, assumed that long range forces were involved, but was later modified (51) so that this assumption is no longer necessary. It has been shown that such long range forces are most unlikely to exist (52,53,54). However, evidence from the vapour pressures of toluene and isopropyl alcohol in capillaries of from 0.8 to 3.0 μ in radius is considered by Folman and Shereshovsky (56) to indicate long range forces, and they quote the results of other workers in support of this view. There is, however, no accepted theory which would allow for the existence of such forces.

(d) The Brunauer, Emmett and Teller isotherm: The most important theoretical isotherm for multimolecular sorption is that proposed by Brunauer, Emmett and Teller (58). It is usually referred to as the B.E.T. isotherm. The physical model behind it does not require long range forces. It is assumed that the first layer of sorbate is formed on localised sites, which are all of equal energy, and that the occupation of any site is unaffected by the occupation of any neighbouring site.

The second and subsequent layers are supposed to form mainly by the operation of dispersion forces. Such layers are regarded as liquid like, and their energy of sorption is regarded as being due to the heat of liquefaction of the sorbate.

The isotherm equation was derived by equating the rates of sorption and desorption at equilibrium in each successive layer, and was presented for two cases. The first case, where the number of layers which may be formed is infinite is as shown below,

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m C} + \frac{C-1}{v_m C} \frac{p}{p_0} \quad (4)$$

where p_0 is the saturated vapour pressure, v_m the volume sorbed in a complete monolayer, and v the equilibrium volume sorbed at p pressure. The constant C is connected with the rates of sorption and desorption in the first and higher layers. It is given by

$$C = \frac{a_1 b_1}{b_1 a_1} e^{\frac{E_1 - E_L}{RT}} \quad (5)$$

where a is the constant connected with the condensation process, b is that connected with the evaporation process,

E_1 is the energy of sorption in the first layer, and E_L the energy of liquefaction.

When the maximum number of condensed layers is n , the equation becomes

$$v = \frac{v_m C x}{(1-x)} \left\{ \frac{1 - (n+1)x^n + nx^{n+1}}{1 + (C-1)x - Cx^{n+1}} \right\} \quad (6)$$

where $x = \frac{p}{p_c}$. Derivations based on a statistical treatment have been given by Hill (59).

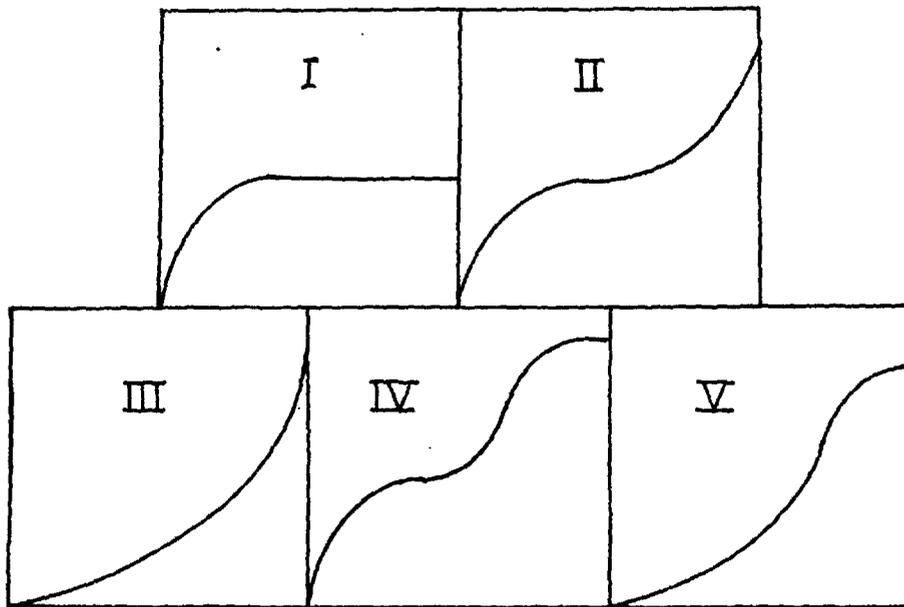
The usefulness of this isotherm stems from its universality. It can produce isotherms of all of the five types shown in figure 1 with appropriate values of C , v_m and n . The numbering adopted follows Brunauer's classification (60).

If $n=1$, the equation reduces to a Langmuir isotherm, (type I). If n is infinite, a type III isotherm is obtained when $E_1 < E_L$, and a type II isotherm when $E_1 > E_L$. Where n is restricted by channel size, type IV or V isotherms are produced, the former when $E_1 > E_L$, the latter when $E_1 < E_L$.

(e) Refinements of the B.E.T. isotherm: Hill has modified the B.E.T. equation to account for lateral interactions of the sorbate molecules (59) and for mobile first layer sorption (48). When lateral interactions were taken into account capillary condensation was shown to be predicted in certain cases (59, 61). The first layer of sorbate may well be in a partly mobile state, in which case a more correct model would be between the B.E.T. picture and Hill's mobile layer modification.

It has been pointed out (62) that a molecule with a coordination number of twelve in the liquid state would

FIG.1



ISOTHERM TYPES IN PHYSICAL ADSORPTION.

only have six nearest neighbours in a two-dimensional film. It is therefore obvious that the energy of sorption of molecules in layers beyond the first would not in general occur with the heat of liquefaction in the absence of interactions other than dispersion forces. The higher layers will be increasingly volatile due to this lower heat of sorption, and also because successive layers will be increasingly uncovered.

Barrer, Mackenzie and MacLeod (63, 64) have derived a series of isotherms of the B.E.T. type to account for such increasing volatility. Their isotherms have been shown to fit some experimental data excellently, and apparently give exceedingly accurate values of surface areas. However, an additional arbitrary constant is required and the same isotherm does not fit every system.

Halsey (62) has pointed out that the derivation of the B.E.T. equation requires that sorption may occur on top of any existing sorbed molecule, even if it is isolated. He has pointed out that if only three molecules have to be grouped together in order to form a site for sorption above them, it is unlikely that there is any significant multilayer formation until the first layer is at least half filled.

It is evident that no rigorous theory of sorption can be used at present. In order to account for the behaviour of any experimental system it is therefore necessary to adopt some approximate treatment which is appropriate to its case.

4.4. Hysteresis in sorption

The existence of stable and reproducible hysteresis was demonstrated in sorption isotherms obtained by Rao (66). Such sorption hysteresis in various systems has been explained in terms of thermodynamically irreversible changes in the sorbate (67, 68, 69, 70, 71) or in the sorbent (72, 73, 74, 75, 76).

A general theory of hysteresis has been developed by Everett et al based on thermodynamic considerations (77, 78, 79, 80). He suggested that a system could be considered as being made of microscopic independent domains each of which could exist in one of two states. The state of the system may be described by the normal variables with an additional one involving the proportion of domains in each state. The system may thus be considered as being in thermodynamic equilibrium. It is not likely that the domains are independent in real systems, however, and it is difficult to determine the proportion of domains in each state. The theory gives rise to seven theorems about hysteresis. Enderby (81, 82) has extended Everett's treatments and considered the interactions of domains. With a one-dimensional array of domains, when the transformation of a domain aids that of its neighbours, all but two of Everett's theorems are shown to hold. When, however, the transformation hinders that of neighbouring domains nearly all of his theorems no longer hold (82).

5. POLYMER SOLUTION THEORY

As one of the sorbents studied in this work had sorption properties with some resemblance to those shown by rubber, it is of interest briefly to examine the theory of the solution of non-crosslinked polymers.

A method for calculating the entropy of athermal mixing of polymer and solvent molecules has been proposed by Flory (83, 84) using a quasi crystalline lattice as a model. Each cell of the lattice may be occupied either by a segment of a polymer chain (of volume equal to one sorbate molecule) or by one sorbate molecule. The entropy of mixing may thus be calculated from the number of ways of arranging n_1 sorbate molecules and n_2 polymer chains of x segments each on the lattice. The entropy change is found to be

$$\Delta S = -k[n_1 \ln v_1 + n_2 \ln v_2] \quad (1)$$

where v_1 and v_2 are the volume fractions of sorbate and sorbent respectively, and k is the Boltzmann constant.

$$v_1 = \frac{n_1}{n_1 + xn_2}, \quad v_2 = \frac{xn_2}{n_1 + xn_2}$$

By differentiation of (1) w.r.t., n

$$\Delta \bar{S}_1 = -R \left\{ \ln v_1 + \left(1 - \frac{1}{x}\right) v_2 \right\} \quad (2)$$

where $\Delta \bar{S}_1$ is the partial molar configurational entropy of the sorbate, and R is the gas constant. Various more refined treatments based on the same model are available, but these do not usually fit experimental data better than the simple theory above (83). Flory (85) has pointed out that, due to the spatial requirements of real species, the lattice should be altered as the composition of the mixture changes.

Hildebrand and Scott (86) give a derivation based partly on work by Scatchard (87) for the integral and partial molar heats of mixing which assumes that:

1. The mutual energy of two molecules depends only on the distance between them and their relative orientation, and is not affected by the presence of other molecules between or around them or by the temperature. That is, that the energies of molecular pairs are additive. This is not exactly true for dispersion forces.

2. The distribution and orientation of the molecules is random. This neglects the ordering effects of intermolecular potentials and of molecular shapes.

3. No volume change occurs on mixing.

On this basis the energy of mixing (ΔU_M) was given by

$$\Delta U_M = (x_1 V_1 + x_2 V_2) A_{12} v_1 v_2 \quad (3)$$

where x_1 and x_2 are mole fractions, V_1 and V_2 the molar volumes, and $A_{12} = C_{11} + C_{22} - 2C_{12}$, where $C_{11} = \frac{U_1}{V_1}$ and $C_{22} = \frac{U_2}{V_2}$, U_1 and U_2 being the energies of vaporisation of the pure liquids.

It is then assumed that $C_{12} = \sqrt{C_{11} C_{22}}$.

$$\therefore A_{12} = (C_{11}^{\frac{1}{2}} - C_{22}^{\frac{1}{2}})^2 \quad (4)$$

C_{11} and C_{22} are termed the cohesive energy densities of the liquids.

The partial molar energy for component 1 is thus,

$$\Delta \bar{U}_1 = v_2^2 V_1 (C_{11}^{\frac{1}{2}} - C_{22}^{\frac{1}{2}})^2 \quad (5)$$

but $\Delta \bar{U}_1 = \Delta \bar{H}_1$ (since the volume change is neglected),

$$\therefore \Delta \bar{H}_1 = v_2^2 V_1 (C_{11}^{\frac{1}{2}} - C_{22}^{\frac{1}{2}})^2 \quad (6)$$

Thus, using also $\Delta H_M = (x_1V_1 + x_2V_2)(C_{11}^{\frac{1}{2}} - C_{22}^{\frac{1}{2}})^2 v_1v_2$
 (the simple entropy calculation given earlier),

$$\Delta \bar{G}_1 = RT \left\{ \ln v_1 + \left(1 - \frac{1}{m}\right)v_2 + V_1(C_{11}^{\frac{1}{2}} - C_{22}^{\frac{1}{2}})^2 v_2^2 \right\} \quad (7)$$

Experimental confirmation of the theory

Treatments along such lines as those mentioned above have provided good agreement with experimental results in the case of the rubber/benzene system (88,89) but other systems have not shown such agreement, especially when polar molecules have been used.

The above results indicate, however, that the maximum sorption should occur when the cohesive energy densities of sorbate and sorbent are equal. Gee (90, 91) and Scott and Magat (92) have carried out investigations to test this conclusion and have found it to be fairly realistic in the case of systems involving rubbers.

6. EXPERIMENTAL APPARATUS AND TECHNIQUES

6.1. High vacuum system

A. Pumping system: The pumping system is shown in Fig. 2. It consisted of an Edwards "Speedivac" rotary pump, which could pump down to a pressure of 10^{-9} mm of mercury. This was connected as shown by a ground glass socket joint (which was made airtight with picein wax) to a rubber pressure tube secured with jubilee clips, leading to an oil buffer volume. This was arranged as shown, so that, if the pump failed for any reason, the oil which had flowed into the buffer volume could be almost completely removed by simply restarting the pump.

An inlet tap was provided above the oil trap, in order to allow the apparatus to be filled with air at any time, if necessary. The low vacuum line was fed through a tap from this point.

The low vacuum side of a single stage mercury diffusion pump was fed through another tap, and a 5-litre buffer volume was provided at this point so that evacuation of the high vacuum line could continue while the rotary pump was being used for other purposes. The high vacuum side of the diffusion pump led through another tap to a cold trap. At this point a low vacuum lead was provided for rough evacuation of the high vacuum line.

The arrangement of taps allows the cold trap to be isolated for emptying, without letting air into the other parts of the apparatus, and also allows air to be let into the high vacuum line through the cold trap, thus drying it.

A McLeod gauge was provided to read the pressure

FIG.2

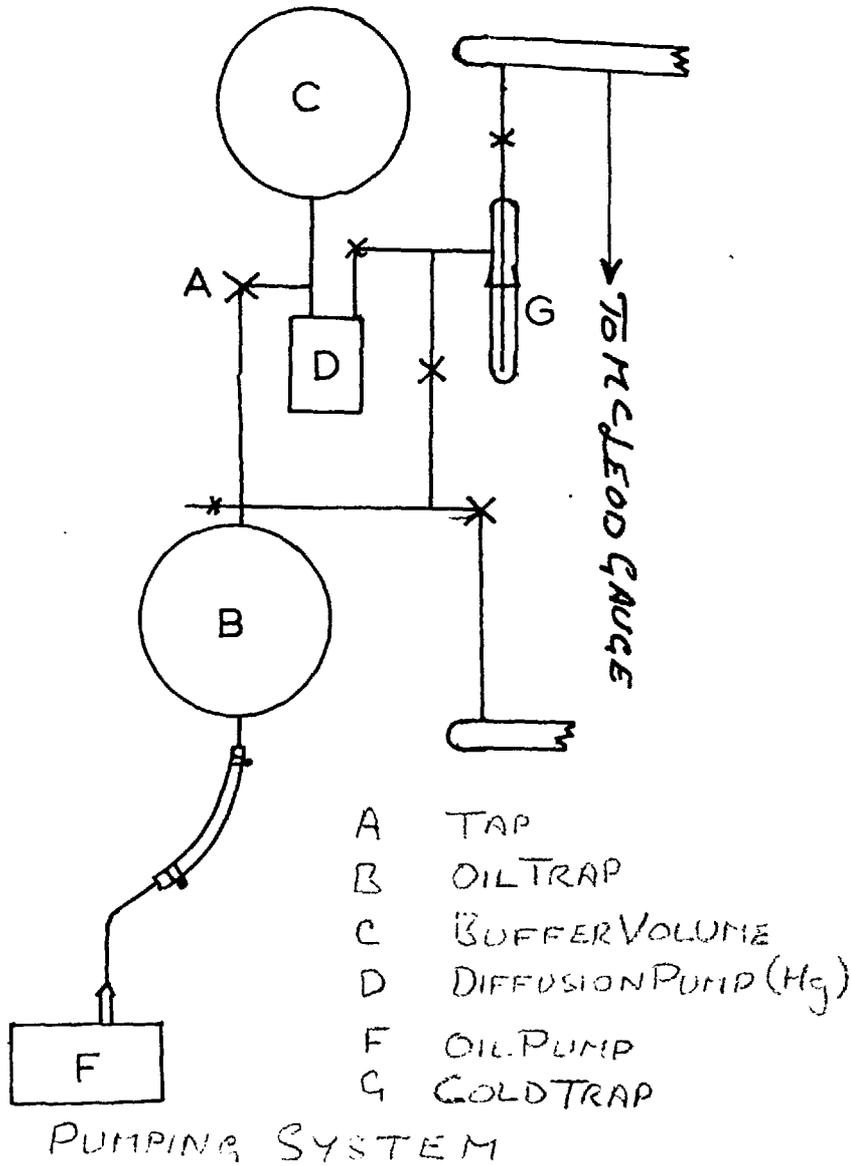
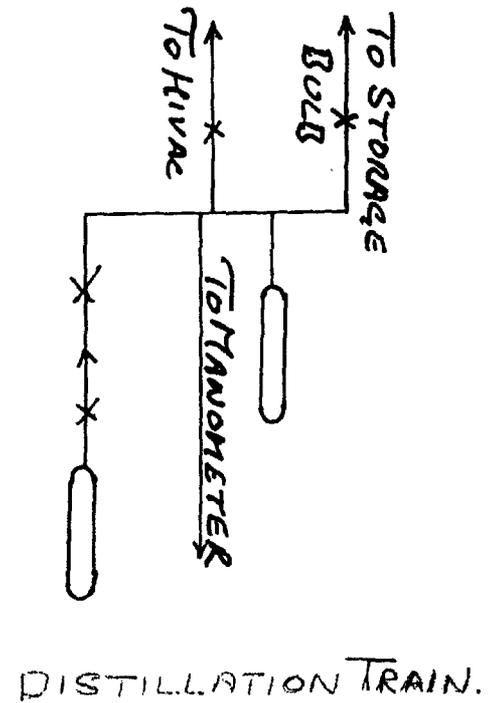


FIG.3



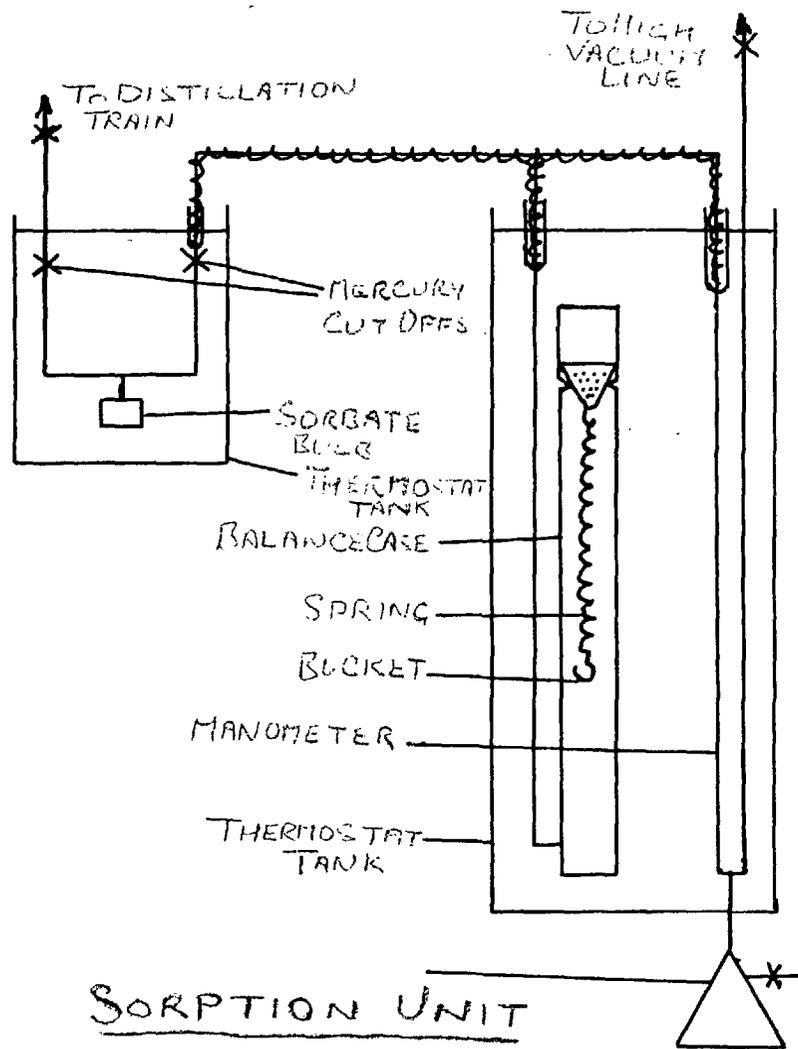


FIG. 4

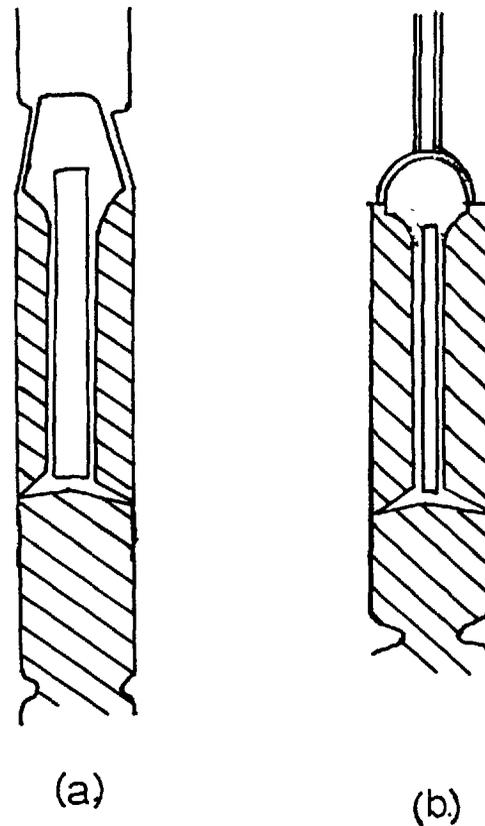


FIG. 5

in the high vacuum line. Pressures of 10^{-6} to 10^{-7} cm of mercury were usually obtained. The gauge provided a useful means of testing parts of the apparatus for leaks.

The high vacuum side was isolated by closing tap A when pumping the low vacuum line down, since otherwise the pressure in the high vacuum line increased.

The low vacuum line was used for evacuating the McLeod gauge, cut-offs, manometers and a preparative vacuum system. The high vacuum line evacuated the remainder of the system.

B. Distillation train: This was altered from time to time, but consisted of a socket joint to which the flask of sorbate was attached, at least one manometer, and at least one bulb into which sorbate could be distilled. In its simplest form it is shown in Fig. 3.

C. Subsidiary thermostat units: These were arranged as shown in Fig. 4. They consisted essentially of a storage bulb isolated by mercury cut offs from the distillation train on the one side, and on the other from the sorption vessel. The whole unit could be surrounded by a 5-litre beaker containing a heating bulb, stirrer and temperature regulator. This could be used as a water thermostat. By lowering the outlet cut offs and adjusting the temperature, the sorbate pressure in the sorption vessel could be set. The outlet tube was surrounded, as shown, by heating wire until it reached the main thermostat. This was protected from the action of water by in seals. The heating wire prevented vapour condensing between the sorption vessel and the subsidiary thermostat unit when the temperature of the thermostat was greater than that of the room.

Cut-offs of two kinds were used, and an unsuccessful attempt was made to use a P.T.F.E. tap instead of an inlet cut-off. The first type of cut-off to be used was the "traditional" type shown in Fig. 5a. As mercury is admitted the float rises to meet ground surfaces on the inside of the cut off wall, and fits tightly there, allowing no mercury to pass.

To overcome the difficulties of the floats sticking or letting mercury past, a new type of cut-off was made (see Fig. 5b). This was based on the idea of raising a ball joint on the float against a socket fused into the glass. Such cut-offs gave, in almost every case, freedom from the faults mentioned above, but it was found that the joint between the socket and the cut off wall was a source of weakness, and tended either to leak or to develop leaks on being used, since the floats tended to come to rest rather heavily unless great care was taken. This strained the glass at its weakest point. The glass was therefore carefully sealed on the outside with "Araldite", which was then coated with picein wax. The picein wax was painted on in a benzene solution, and the benzene was then evaporated by warming. The wax thus protected the Araldite from attack by the water in the thermostat tank, which had previously been found to cause certain samples of Araldite to decay and flake off in similar circumstances.

D. Sorption unit: Sorption was measured gravimetrically using a McBain Bakr silica spring balance (95). The springs were suspended from floats inside pyrex tubes (see Fig. 4). The samples to be investigated were placed in pyrex buckets weighing about 0.2 gm and each was hung on to the end of a spring. The lengths of the springs were determined with the aid of cathetometers.

Some of the balance cases had cone and socket joints at the tops, and others were opened and closed by glass blowing. Apiezon "T" grease was used in these joints, whereas in parts of the apparatus which were not affected by temperature Apiezon "N" grease was used.

The balance cases were fed with vapour from a point near to their bottoms. Thus, if mercury entered by accident it did not get into the bucket and damage the spring.

The pressure was read from a manometer which was filled with mercury from a reservoir under the tank. One limb was connected to the high vacuum system and the other to the balance case. The manometer could be used for out-gassing if the mercury was lowered.

There was a tap at the high vacuum side of the manometer and also one on the distillation train side of the subsidiary thermostat unit. The whole of the experimental unit could therefore be isolated from the remainder of the apparatus, during a run, except for the use of the low vacuum line to operate one cut off. Two thermostat tanks were used. Both were of similar design, but one contained three balance cases, and the other two. The tanks were approximately 12" x 19" x 29" in size, having glass backs and fronts. Measurements were made from the front. Illumination was provided from the back by means of four long 60 watt bulbs, with white screens behind them to reflect their light. The sides of the tanks were of metal, and heat-insulated with asbestos. Two stirrers operated through the whole depth of the tank, one driving water down and the other propelling it up. The stirrers were sited so as to cause minimum interference with illumination.

Steady heating was provided from the bottom of the tank by means of a 1 kw heater supplied with current from a Variac transformer. This was used to adjust the temperature of each tank to a little below the required temperature, additional heating being supplied by carbon filament heating bulbs or electrothermal hot rod heaters which were suspended from the top of the tank, and switched on and off through a relay actuated by a Sunvic bimetallic temperature control device.

A water cooling coil was provided in one tank only, due to lack of space in the other. On all thermostat tanks, constant level devices of standard design were used.

E. Measurements: It was found that if the balance cases were evacuated and illuminated for a prolonged time the springs became appreciably shorter. This was due to the heating effect on the spring. In a vacuum the heat could not be conducted away. Lights were therefore switched on for the minimum possible time when readings were to be taken. If an error of this sort occurs, it affects the reading obtained for the extension of the spring when outgassed more than subsequent ones, and thus gives an isotherm which is rather too high throughout.

Measurements were taken from the top and bottom of the spring at each isotherm point, as it was found that the top supports moved slightly between one equilibrium point and the next.

F. Springs: These were calculated by hanging known weights on them in the thermostatted balance

cases at various temperatures and measuring the extensions produced. The calibrations were made at least twice, and the springs were found to be reproducible to within 0.004 cm in length. The makers state that the quality of the silica is sufficient to give reproducibility of .002 cm in length, but there is about a .002 cm error in cathetometer readings, and the total error is therefore about .004 cm. The separation of the tips of the springs was measured in each case, the spring hooks being given kinks to make weights on them always sit in the same place.

The extension/weight graphs obtained for springs were usually slightly curved, but, as done in the present work, no appreciable error was involved by taking the best straight line for the region of the graph actually being used in an experiment.

The springs, which were supplied by the Thermal Syndicate Limited, had 40 turns and sensitivities of about 20 cm per gram. The maximum loads were 1 gram or a little more.

6.2. Determination of sorption isotherms

A. Outgassing: Before sorption measurements were commenced samples were outgassed to constant weight. With some sorbates the temperatures used were a little over 100°C, but a temperature of 77°C was used in the majority of cases. The temperatures of degradation of samples were determined previously by heating the materials at various temperatures in ovens, subsequent X-ray patterns being taken. In addition, visual examination showed obvious degradation at high temperatures. Thermogravimetric and differential thermal analysis of samples of

anilinium polyphosphate, the material which exhibited the most marked changes, indicated that these changes did not occur until substantially above the outgassing temperatures. However, by heating this material at about 160°C for 24 hours a green liquid was produced. This contained solid particles with a different powder pattern from the starting material, which it was not possible to index. Cetyl pyridinium polyphosphate decomposed to produce brownish, tarry material below 100°C but above 60°C on prolonged heating, but no sorption experiments were made using this sorbent.

Slight continuous losses in weight by amyl ammonium polyphosphate were shown to occur by heating at 120°C or above. The loss amounted to about 0.04% of its weight per hour at 120°C, but rose to about 0.1% per hour at 135°C. These figures were obtained by heating the polyphosphate in a vacuum for up to 60 hours at the appropriate temperature, after the material had already been outgassed.

The highest temperature normally used for outgassing was 77°C, but this did not suffice for the complete removal of ethanol, amyl alcohol or butyric acid. Some form of chemical combination probably occurs in these cases.

B. Determination of isotherms: Isotherms were obtained by gently increasing the pressure to the required value for each point, and measuring the spring extensions at equilibrium. When the saturation vapour pressure was reached desorption was commenced, continuously reducing pressure from one point to the next. This procedure allowed reversibility or hysteresis to be investigated.

Equilibrium was normally attained with the primary alkyl ammonium polyphosphates within about two hours, but for the cetyl trimethyl ammonium polyphosphate the time taken was about 24 hours for moderate sorptions and up to a week for large sorptions.

Buoyancy corrections were seldom necessary, as the errors involved were rarely greater than the errors in determining spring lengths. Details of calculations for such corrections are given by Kelsey (21) and will not be given here.

6.3. X-ray diffraction powder photographs

X-ray diffraction patterns were taken with CuK α radiation using appropriate cameras, the design of which will not be discussed here. For lines of high d spacings a flat-plate camera was used, the plate being usually at a distance of 12 cm from the specimen. This allowed lines up to 30 \AA to be measured. A nickel filter was used in taking these photographs. A Guinier camera was used with a quartz monochromator for powder photographs, wherever suitable, while other powder photographs were taken with a 9 cm diameter Debye-Scherrer camera.

6.4. Sorbates

The sorbates were obtained as follows. Distilled water was redistilled before use. Ethyl alcohol was obtained free from impurity other than water from Sir Robert Burnett and Co., and dried by distilling from sodium wire in a vacuum. Nitromethane was a standard product supplied by the General Chemical and Pharmaceutical Co. Ltd. AnalaR grade benzene was used. The iso-octane

was "Spectrosol" grade, supplied by Hopkin and Williams, The cyclohexane was spectroscopic grade material supplied by British Drug Houses Ltd. n-Heptane of I.T.P. specification was used. The amyl alcohol and butyric acid used were ordinary organic reagent standards.

All of the sorbates were distilled in the apparatus, the middle fraction being selected. All were freed from air by freezing them and then allowing them to melt under a high vacuum at least twice, except in cases where the evaporation of the sample was so rapid under these conditions that the sample remained frozen. In the latter case, the sample bulb was isolated to allow the sorbate to melt, and then the bulb was evacuated for a time.

7. THE PREPARATION OF POLYPHOSPHATES

7.1. Kurrol's and Maddrell's salts

The parent materials were obtained as follows. The high temperature form of sodium Maddrell's salt was obtained containing between 2 and 4% soluble matter but free from other polyphosphates, from the Monsanto Chemical Co., U.S.A. This will be referred to as Maddrell's salt (M.S.) subsequently in this account.

The potassium Kurrol's salt (subsequently referred to here as Kurrol's salt, K.S.), was made by heating KH_2PO_4 for several weeks. When first heating it was found necessary to raise the temperature slowly up to 300°C , because vigorous evolution of water vapour caused frothing, and overflow of phosphate. As a precautionary measure, therefore, the furnace was lined with asbestos paper.

The K.S. had previously been prepared by Weiss and Michel (17) in alumina crucibles or in porcelain crucibles with resistant glazing. The latter were not available in this country, and in any case were attacked by the polyphosphate, resulting in contamination of the solid contiguous with the walls. Alumina crucibles broke when the concrete-like polyphosphate mass had to be chipped out, and due to their high cost it was decided to prepare further quantities of K.S. in a battered platinum crucible which was due to be remade. Due to the flexibility of the platinum no detectable damage was caused on chipping the product out, and this appeared to be the cheapest and most satisfactory method of preparation.

Samples of K.S. were prepared under a wide variety of heating conditions (from 300°C-700°C) for periods between a few days and four weeks, and using both fast and slow cooling methods. Only one form was found to be stable at room temperatures as shown by X-ray diffraction powder patterns, thus confirming the work of Pascal (10). Phase transitions were shown to occur at 248°C, 445°C and 640°C by differential thermal analysis.

A polyphosphate glass can be prepared by prolonged heating above the MP (807°C) but this was not prepared.

The K.S. prepared by heating for short times became gummy and sticky overnight in the presence of water, and in the presence of NaCl solution this effect was rapid. This makes such material unsuitable for exchange. This trouble was cured by heating at 400°C for four weeks. The phenomenon is probably due to the presence of traces of arsenic, which, when included in the phosphate chains, causes the chains to hydrolyse rapidly in the presence of water at the points where arsenic atoms replace phosphorus.

However, the chains would also become longer with prolonged heating, which may have a subsidiary effect.

The concrete-like mass had strata of slightly coloured material, particularly at the bottom of the crucible, which is probably due to the small quantity of heavy metals in the AnalaR KH_2PO_4 used settling to the bottom. Only the white areas were selected for this work.

7.2. The preparation of substituted ammonium polyphosphates

1. General principles: Three principal methods were used for the preparation of organic polyphosphates, each of which has various modifications.

The first, as used by Weiss and Michel (17, 93) was simple exchange, by which the K.S. or M.S. was brought into equilibrium with solutions of the organic material, either in aqueous alcohol or water. The second was precipitation, from the soluble sodium/potassium salt, (prepared from K.S.). The third was preparation by neutralisation of a solution of polyphosphoric acid (also prepared from K.S.) as described by Iler (11).

The main advantages of the first method are that it avoids the degradation of the polyphosphate chain which occurs particularly when using ^{the} polyphosphoric acid preparation method. Also, since the X-ray diffraction pattern of the starting material is known, its disappearance can be noted by taking powder photographs after each exchange stage, thus indicating when exchange is complete. The most highly crystalline products may be made by this method.

The disadvantages of the method are that the kinetics of exchange are sometimes slow (2-3 months for aniline⁴⁴⁴⁴ polyphosphate), and, if the product is gummy or waxy, conglomerates consisting of K.S. or M.S. surrounded by waxy material are formed which prevent the included non-exchanged polyphosphate from coming into contact with the exchange solution. This can be overcome, in the two cases where it was experienced, by vacuum drying at 65°C for about 12-16 hours followed by pulverising and re-exchanging. This effectively breaks up the conglomerates, but as they reform in contact with water, the process has to be repeated several times. The method is also unsuitable where the products are soluble.

The precipitation method is as follows. A solution of sodium-potassium polyphosphate is prepared either by heating K.S. with a .2N NaCl solution, or with the sodium form of an ion exchange resin. Solution appears to occur by an ion exchange mechanism, which "peels off" chains from the surface of the K.S. particles.

As the solution formed is very viscous, it is not practicable to make a very strong solution with the ion exchange resin, as dissolution is slow when the solution is treacly. The advantage of the ion exchange dissolution method is that it results in the absence of chloride ions in the product, and a reduction in total Na and K concentration. The clear, viscous solution is then added to an amine hydrochloride solution, usually in a Waring blender and washed and kneaded, to remove by-products.

The neutralisation method was performed as follows. Potassium-sodium polyphosphate solution was prepared by the ion exchange method. This was then chilled in freezing mixture to 0°C approximately. A cation exchange column

15 cm long, which had been carefully regenerated with hydrochloric acid so that no sodium or potassium was detectable in its effluent by a flame test, and subsequently washed until no chloride ions were revealed by the AgNO_3 test, was then chilled by mixing with ice and pouring cold water through. To improve the effectiveness of chilling, the column was lagged with cotton wool.

The polyphosphate solution was passed through the column until it was 1/10th exhausted. It was found necessary to drain this effluent into an evacuated receptacle in order to increase the rate of flow of the liquid (which is quite viscous). Otherwise the temperature of the effluent rose, and caused degradation of the polyphosphate chains. The resulting polyphosphoric acid was collected in a flask containing ice made from distilled water. The product was sodium and potassium free, as checked by the flame test. The organic product was then prepared by adding the free amine to the solution.

In cases where the product was soluble in water, it was produced by neutralising the polyphosphoric acid to about pH 8 with free amine and then freeze drying the solutions formed.

The concentrations of polyphosphoric acid produced were low, due to the difficulty of passing polyphosphate solutions more concentrated than 1% through the column due to their viscosity. As viscous solutions took a long time to pass through the column, their temperature rose, thus increasing the rate of chain degradation. The low concentrations resulted in preparations by this method being on a rather small scale.

Products obtained by this method were exceedingly

pure, but not very crystalline. The method is unsuitable for the preparation of alkylammonium polyphosphates when the amine salts are insoluble at low temperatures, because if the temperature is raised in order to dissolve the amine and thus allow neutralisation of the acid, the polyphosphate chain tends to degrade.

2. Individual preparations:

(a) Cetyl trimethyl ammonium polyphosphate: This substance was one of two which imbibed water, becoming waxy. The material was produced by an ion exchange method, using the amine chloride solution. The bromide is sparingly soluble at room temperatures (101). The material was prepared by shaking K.S. and M.S. with a 50% excess of amine chloride. The resulting waxy conglomerate, containing unchanged parent material surrounded by product, would not continue to exchange, as the diffusion of ions through the waxy mass of product was slow. The conglomerate was therefore dried at 60°C under vacuum, pulverised and re-exchanged. This process had to be repeated a number of times before the parent material had all reacted. The complete preparation took 2-3 months. Both K.S. and M.S. gave the same products.

The product from this treatment was crystalline and gave an X-ray powder pattern containing a large number of lines when the product was in equilibrium with atmospheric water vapour. This pattern could not be indexed. However, a sample of the material was dried at 60°C under vacuum and packed into a capillary in a dry box. It was then found that its unit cell was tetragonal with repeat distances of 4.7 and 25.8 Å. This result may indicate that the sample was not completely dry, as it disagreed with that of Weiss and Michel (17). The unit cell edges

were given as 4.8 Å and 22.2 Å, but they now consider that values of 4.8 Å and between 31.5 and 32.1 Å are correct (28). However, the cetyl trimethyl ammonium chloride used for our preparation, which was supplied as being 95% pure by the manufacturers, was later admitted by them to be of unknown purity. In view of the tendency for such materials to be contaminated by other quaternary amines in the products of other manufacturers, it was decided to produce another sample of polyphosphate from a pure parent material. Only the bromide was available in a sufficient state of purity (95%) and, as this is insoluble at room temperatures, it was inconvenient to make the corresponding polyphosphate by a lengthy exchange process. For this reason, it was made by mixing a solution of chloride free sodium/potassium polyphosphate with a solution of cetyl trimethyl ammonium bromide at 45°C in a Waring blender. An excess of the sodium/potassium polyphosphate solution was used, in order to ensure that the product was not contaminated by cetyl trimethyl ammonium bromide.

The polyphosphate was kneaded in distilled water in order to remove as much of the unchanged parent materials as possible. The product from this was then warmed with a large volume of ethanol, when it became a viscous fluid forming a separate layer. The surplus ethanol was then decanted off, and the polyphosphate equilibrated with fresh ethanol several times. The polyphosphate fluid was then dried by exposing it to a pressure of about 10^{-4} cm of mercury at a temperature of 60°C. This formed a froth of bubbles, which was later pulverised and re-dried.

It was found that the product from this treat-

ment was free from sodium, potassium and bromine, and its particles were very fine. The latter property is invaluable in a sample of this product which is to be used for sorption experiments, as the time required before equilibrium is reached with this sorbent is considerable and the rate of uptake of sorbate appears to be diffusion-controlled (sect. 10). The material prepared by this method was amorphous, and it was not possible to crystallise it despite many attempts. It was thus not possible to follow sorption in this material by X-ray investigations.

(b) Cetyl pyridium polyphosphate: This material was first prepared by the same method as that used for cetyl trimethyl ammonium polyphosphate, but, as noted earlier, when the material was heated under vacuum in order to dry it a tarry degradation product was produced, so the products produced in this manner were usually impure.

A new product was then made by precipitation from a sodium/potassium polyphosphate solution in a Waring blender, by adding insufficient cetyl pyridinium chloride for quantitative precipitation. The product contained sodium and potassium, as indicated by a flame test, and also contained chloride. This material was therefore washed and kneaded with distilled water, and also some of it was dissolved in distilled water by warming and the product recovered by drying. A sample which was free from chloride, sodium and potassium was eventually produced.

(c) Dimethyldioctadecyl ammonium polyphosphate: This material was prepared by adding insufficient hot ammonium salt for complete precipitation to a sodium/potassium polyphosphate solution (prepared by ion exchange), in a

Waring blender. The product was carefully washed and was found to be sodium, potassium and halide free without further treatment. It is a waxy, yellowish material which cannot be powdered when dried. It seems to be practically insoluble in organic solvents, but it forms gels with some.

The unit cell of this material was determined, and was found to be orthorhombic with repeat distances of 33, 36 and about 4.5 \AA , although the latter value was very uncertain. The density of the compound was calculated using these values for the cell dimensions and assuming that there were four monomer units per unit cell, and was found to be about 0.8 gm/cc . The density of the material was then estimated by suspending it in liquids of varying density, and was found to be over 1.0 gm/cc , though it was difficult to be sure that the samples used were free of included air. It is difficult to see how five monomer units could be contained in a unit cell, or how the doubtful axis could be in error by 20%. The two other long chain quaternary ammonium polyphosphates produced for this work were waxy if they contained water, and when dried became brittle. It seems possible, therefore, that the waxy texture of the dimethyl dioctadecyl ammonium polyphosphate, coupled with its large unit cell, indicates the presence of water in the sample which was X-rayed. Weiss and Michel (17) have shown that the unit cells of both cetyl trimethyl ammonium and octadecyl pyridinium polyphosphates expand on exposure to water.

The great stability of any such water included in the structure, as indicated by our failure to remove it by vacuum drying, suggests an analogy with the sorption of ethanol into cetyl trimethyl ammonium polyphosphate

where a 1:1 mole ratio of ethanol to sorbent was found to give a very stable product (section 10). If such a 1:1 mole ratio of water to sorbent applied in the case of dimethyl dioctadecyl ammonium polyphosphate, the density as calculated previously would, however, be increased only slightly.

The most likely explanation seems to be that there are six monomer units per unit cell, that the 4.5 (b) axis is too small by about 10%, and that the dimethyl dioctadecyl ammonium salt which was used contained about 40% of shorter chain length material, which the manufacturers informed us was frequently the case. It is also possible that the unit cell is not of orthorhombic symmetry, and the apparent fit obtained was fortuitous, but this is considered to be unlikely.

(e) Tetramethyl ammonium polyphosphate: This material was produced by neutralising a polyphosphoric acid solution to pH 8.5 with the amine hydroxide, taking the general precautions mentioned before. As the material is soluble in water, in order to recover the product (which depolymerises in hot water, as judged by reduction in solution viscosity), the material was freeze dried (i.e. the solution was spread round the sides of a vessel which was then evacuated by a vacuum pump through a large cold trap. The water vapour given off by the ice was thus removed, and the ice was prevented from melting by the cooling effect of the evaporation of this water).

The product was a hard, plastic-like substance which rapidly absorbed water from the atmosphere to give a rubbery or tacky material.

(f) Tetra-n-butyl ammonium polyphosphate: This was very similar to the tetramethyl compound, and was prepared in the same manner.

(g) Mono-n-propyl ammonium polyphosphate: This material was also prepared as above, and was likewise found to be water soluble. On freeze drying "cobwebs" of product were produced, but these collapsed to give a tiny quantity of sticky material.

(h) Amyl ammonium polyphosphate: This was prepared in the same manner, and though it was at first produced in solution, it was obtained as a rather papery product on freeze drying. This material was prepared on a larger scale than the previous three, as it was desired to make reasonably extensive investigations of its properties.

The unit cell had one axis of 17.2 \AA but the other two were less certain, as various slightly different arrangements of indexing fitted the d-spacings. With all the arrangements tried, however, approximate agreement with Weiss and Michel's results was obtained. These were 17.5, 13.6 and 4.7, the cell being orthorhombic. The slight difference in the $17.2 (17.5) \text{ \AA}$ axis may possibly be due to free amine being included in their material, since this would, almost without doubt, cause the cell to swell.

In order to compare amyl ammonium polyphosphate as a sorbent with materials prepared by ion exchange, a further sample was prepared by that method. This sample was identical in X-ray pattern, except that the lines were sharper, indicating that the product was more crystalline.

The exchange solution was made up with an approximately fivefold excess of amine salt and renewed four times before exchange was judged to be complete.

(i) n-Heptyl ammonium polyphosphate: This was prepared by neutralising polyphosphoric acid, when the product precipitated, and also by ion exchanging Kurrol's salt. Both products showed the same X-ray diffraction pattern, but the lines were sharper in the case of the ion-exchanged material.

The a axis at 22.0 \AA was greater than Weiss and Michel's result by 0.6 \AA , but our material contained free amine, as judged from the strong smell. On heating at 110°C there seemed to be a small (0.2 \AA) contraction in the a axis associated with loss of smell, which may confirm the above suggestion.

(j) Nonyl ammonium polyphosphate: This material was prepared by ion exchange of Kurrol's salt with nonyl ammonium chloride. A fivefold excess of a 40% solution of the ammonium salt in water was used, the solution being renewed three times.

The unit cell of this compound was orthorhombic with two axes of 24.9 and 4.5 \AA , the other being uncertain. Weiss and Michel report values of 25.0 \AA and 4.5 \AA , their other repeat distance being uncertain also.

(k) Dodecylamine polyphosphate: This was also prepared by an exchange method. Dodecylammonium hydrochloride was first prepared from the free amine, and the hydrochloride was used for exchange.

As the exchange was to be at room temperature a difficulty was encountered with this and similar molecules. This was that long chain "surface active" type molecules are characterised by solubilities which are low below a critical temperature, increase sharply around this temperature, and are fairly high above it. (See, for example, Murray and Hartley (95)). This means that, although the amine may dissolve quite well on heating the solution to, say, 35°C, and may remain supersaturated on cooling, when the K.S. or M.S. is put in it may cause precipitation of amine.

The solubility of dodecylamine hydrochloride is 0.3 gm per 100 gm H₂O at 20°C and 60.1 gm per 100 gm at 40°C. In order to improve solubility at 20°C the solution was made up in 20% ethanol/80% water mixture. The solubility of dodecylamine hydrochloride in this is 11.5 gm/100 gm at 20°C (94).

Exchange proceeded quite quickly and after renewal of the exchange solution and shaking for a few weeks the material was carefully washed with alcohol/water mixture and dried.

From X-ray powder patterns the unit cell was determined to be orthorhombic with repeat distances of 4.45, 14.4 and 30.3 Å. Weiss and Michel obtained 4.50, 13.8 and 30.3 Å. Both K.S. and M.S. were used, and the products were identical.

(1) Octadecyl ammonium polyphosphate: This material had to be prepared at elevated temperature due to the insolubility of octadecyl ammonium chloride in water or water/alcohol mixture at room temperature. A 30% alcohol

solution was made of a 50% excess of octadecyl ammonium chloride at boiling point, and K.S. was then introduced. Satisfactory exchange was achieved within one hour. There is a possibility that a proportion of the octadecyl-ammonium chloride might be converted to the ethyl octadecyl-ammonium salt, using this method of preparation, but it has been shown (17) that primary amines are unaffected by the presence of free secondary amine which presumably implies that the primary ammonium polyphosphates are more stable, and would therefore be formed preferentially.

The unit cell of this material has been determined. It is orthorhombic, the repeat distances being 4.43, 13.6 and 41.7 Å, compared with Weiss and Michel's results of 4.5, 13.7, and 41.7 Å.

(m) Anilinium polyphosphate: This was prepared by an "exchange" method. Ten gram samples of Kurrol's salt and Maddrell's salt were each shaken with 250 ml of 8% aniline hydrochloride solution for a week, when the solution was renewed. The solution provided an 80% excess of anilinium ions over the amount necessary for complete exchange in the case of potassium Kurrol's salt, and a 5% excess in the case of Maddrell's salt. After ^{each} exchange step the solids were X-rayed.

This process was repeated for 2 - 3 months, the solution being renewed at less frequent intervals after the first few times, as it was thought that any Na⁺ or K⁺ ions would then be present in insufficient concentration to cause any significant back reaction.

Both starting materials gave the same product, but at the end of the exchange period it was found that the X-ray pattern of the parent material was undetectable in

the case of the Kurrol's salt, but not in the case of the Maddrell's salt. The product from Kurrol's salt was therefore used.

The powder pattern has been investigated, and two axes were found to be in agreement with Weiss and Michel (5.1 Å and 15.0 Å). The other appeared to be twice as big (about 28 Å instead of 13.9 Å). This corresponds to a repeat distance in the sheets of about double the normal length. This might be due to an arrangement of two similar polyphosphate chains adjacent to two enantiomorphous chains instead of the normal arrangement as considered in section 8.

Analytical results indicated full exchange of the K.S. product, as did X-ray evidence.

(n) Phenylene diamine polyphosphate: The kinetics of the production of this material are very slow, but 70-80% exchange was obtained on prolonged exposure to a 50% excess of phenylene diamine hydrochloride solution. These exchange percentages are based on analytical results for carbon, hydrogen and nitrogen and are not very reliable.

Because of the slowness of exchange for this material it has also been prepared by a polyphosphoric acid precipitation with phenylene diamine hydrochloride. The material obtained was sludge-like instead of powdery, suggesting that the product was rather amorphous, possibly because depolymerisation had occurred. The mother liquor contained HCl after this precipitation, and this would have caused some hydrolysis of the polyphosphate chains as the preparation was allowed to stand. The X-ray pattern was diffuse, but the unit cell was orthorhombic with

repeat distances of approximately 4.9, 9.7 and 13.2 Å as against values of 5.0, 9.7 and 13.1 reported by Weiss and Michel.

TABLE 7

The unit cells of polyphosphates produced in this work, compared with those of Weiss and Michel (17) (in brackets).

Organic Polyphosphates		in Å		
		b axis	a	c
<u>Quaternary ammonium ions</u>				
Cetyltrimethylammonium polyphosphate	Tetragonal	4.7 (4.8 ₄)	25.8 (22.2)	
Dimethyldioctadecylammonium polyphosphate	Orthorhombic	4.5 diff	33	36
Amylammonium polyphosphate	Orthorhombic	4.7 (4.7)	17.5 (17.5)	13.6 (13.6)
n-Heptylammonium polyphosphate	Orthorhombic	(4.5 ₃)	22.0 (21.4)	uncertain
Anilinium polyphosphate	Orthorhombic	5.1 (5.1)	15.0 (15.0)	28 (13.9)
Dodecylamine polyphosphate	Orthorhombic	4.45 (4.50)	30.3 (30.3)	14.4 (13.8)
Octadecylammonium polyphosphate	Orthorhombic	4.43 (4.5)	41.7 (41.7)	13.6 (13.7)
Phenyl diamine polyphosphate	Orthorhombic	4.9 (5.0)	9.7 (9.7)	13.2 (13.1)
Nonyl ammonium polyphosphate	Orthorhombic	4.5 (4.5 ₃)	24.9 (25.0)	uncertain

(3) Analytical tests

For all of the preparations the best check on purity of products is the absence of parent materials.

In the case of materials produced by direct ion exchange one good check is the X-ray evidence, but in general, absence of sodium, potassium and halide ions is necessary before one can be certain of purity. The tests used were as follows. For a sodium and potassium test, the material was dissolved in AnalaR hydrochloric acid, and a flame test carried out on the product. This provides a very rigorous test for sodium in particular, and all materials used in sorption experiments were sodium and potassium free.

The halide test used was as follows. The polyphosphate ion precipitates as silver polyphosphate when silver nitrate is added to the acid solution, and in order to destroy this and organic matter the materials to be tested were fused in a sodium peroxide/sodium hydroxide mixture in a nickel crucible. The products were dissolved in nitric acid and silver nitrate solution added. All materials used were free from halide.

Phosphorus could be reliably estimated by a prolonged heating of the material in concentrated nitric acid, which broke down the polyphosphate ions to orthophosphate ions, and oxidised organic matter. This was followed by an ordinary phosphate determination.

Hydrogen, nitrogen and carbon analyses were generally unreliable and non-reproducible, probably because the combustion methods of analysis used gave phosphate glasses containing organic matter. If the other information is available, however, one can be reasonably sure

of the purity of products without knowing these analyses. A nitrogen analysis could probably be carried out by the Kjeldahl method. Analyses have to be done on micro quantities of materials, and this method was then found to be very sensitive to laboratory atmosphere impurities. The method is also unsuccessful when the nitrogen is bound in certain ways, e.g. in the pyridine ring.

Materials produced by neutralising sodium and potassium free polyphosphoric acid produced from the pure Kurrol's salt were assumed to be in a pure state except for possible free amine. This was removed by warming until any odour vanished. In the course of production or experiment the polyphosphate chains may degrade slightly, producing some uncombined phosphate units, but this can hardly be cured by analytical control.

8. THE STRUCTURE OF POLYPHOSPHATE MATERIALS

8.1. Potassium Kurrol's Salt

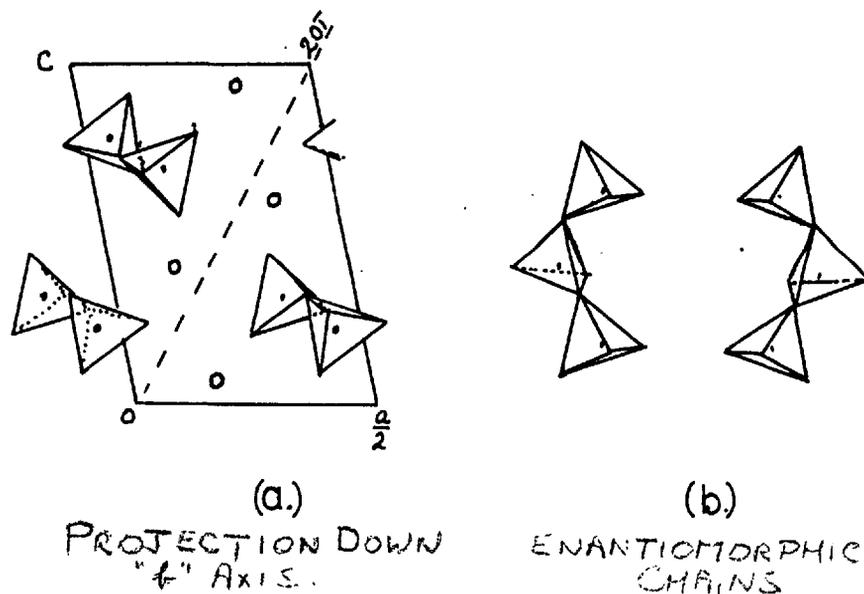
A recent (May 1962) letter from K. H. Jost to Die Naturwissenschaften concerning the structure of potassium Kurrol's salt (96) has cast considerable light on the crystalline arrangement of this material. As yet a paper embodying the full structure determination has not appeared, but the general picture is clear.

The unit cell of Kurrol's salt was determined by Jost to be monoclinic, with cell parameters $a=14.02 \text{ \AA}$, $b=4.54 \text{ \AA}$, $c=10.28 \text{ \AA}$, $\beta=111.5^\circ$. This confirms the results of Andress and Fischer (110), Corbridge (111) and Weiss and Michel (17). The d spacings given by this unit cell were calculated, and compared with the d spacings of material prepared in this work, as obtained from a powder pattern. Very close agreement was obtained.

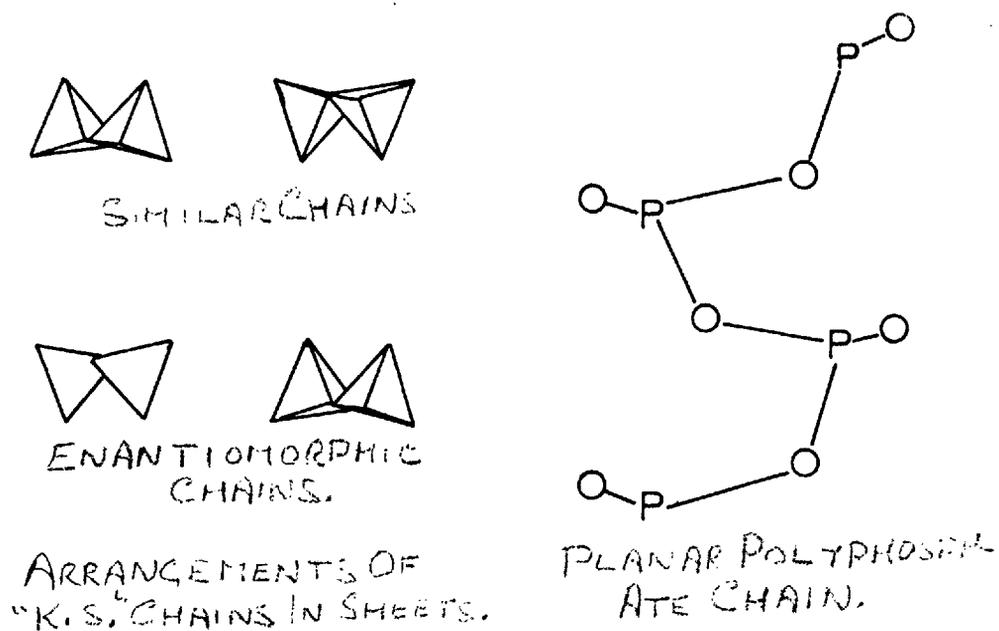
The structure of potassium Kurrol's salt is shown in Fig. 5a. It will be observed that two types of polyphosphate chain are present. These are enantiomorphs of one another, and are shown in Fig. 5b. The repeat distance along these chains corresponds to the b edge of the unit cell, and is approximately equal to the repeat distance along the b axis of all the primary alkyl ammonium and α,ω -diammonium polyphosphates prepared by Weiss and Michel and those prepared in this work.

8.2. The structure of primary alkyl ammonium polyphosphates

A. General structure: These organic polyphosphates also have another repeat distance of approximately 13.8 \AA which remains almost unchanged throughout

FIG.5

STRUCTURE OF POTASSIUM KURROL'S SALT.

FIG.6

the homologous series. The unit cells are orthorhombic. This led to the suggestion by Weiss and Michel (17) that the polyphosphate chains lie parallel to one another in sheets, with the substituted ammonium ions lying between the sheets. Parallel polyphosphate chains would be held together by hydrogen bonding to common amine heads. The repeat distance along the chains would correspond to one edge of the unit cell and the repeat distance across the chains would correspond to the other. Since an increase in the length of the alkyl ammonium ion would simply push the polyphosphate sheets apart, these repeat distances would remain constant. The other repeat distance of the unit cells would increase in order to accommodate the larger ion. This hypothesis would account for all of the observed unit cells. Weiss and Michel's data for the unit cells of primary alkyl ammonium polyphosphates are given in Table 8, and for diammonium polyphosphates in Table 9.

The close agreement of the b axis values between that for Kurrol's salt (K.S.) and that for the organic polyphosphate suggests that the arrangement of atoms in the polyphosphate chains is identical. A shorter polyphosphate chain repeat unit has been found by Corbridge (97) in rubidium Kurrol's salt, where the chain is arranged as shown in fig. 9. A repeat distance equal to or longer than that in potassium K.S. could be obtained by making the chains planar. This will be discussed later.

A wire model was constructed of some polyphosphate chains like those proposed in Jost's letter. Bond lengths for the PO_4 tetrahedra were taken from the data for rubidium Kurrol's salt given by Corbridge (97), and shown in Table 10, which were in close agreement with those in

TABLE 8

Unit cell dimensions of mono-n-alkyl ammonium polyphosphates $(RNH_3PO_3)_n$

Carbon atoms in alkyl chain	Cell dimensions (in Å) Materials dried at 60°C and .1 mm pressure			Change in sheet separation (d_{100} spacing) in Å per carbon atom added to the alkyl chains
	Fibre (b) axis d_{010}	d_{001}	Sheet Separation d_{100}	
2	4.6	13.8	11.4	
3	4.5	13.5	13.4	2.0
4	4.6	13.6	15.1	1.7
5	4.7	13.6	17.5	2.4
6	4.5	13.8	19.3	1.8
7	4.5	uncertain	21.4	2.1
8	4.5	uncertain	23.5	2.1
9	4.5	13.8	25.0	1.5
10	4.5	13.9	26.5	1.5
12	4.5	13.8	30.3	1.9
14	4.4	13.8	34.1	1.9
16	4.4	13.8	36.7	1.4
18	4.5	13.7	41.7	2.4
$(KPO_3)_n$	4.5	13.8	10.0	
				Average 1.9

TABLE 9

Cell dimensions of alkyl α, ω -diammoniumpolyphosphates

Carbon atoms in the alkyl α, ω -diammonium ion $[\text{H}_3\text{N}-(\text{CH}_2)_x\text{NH}_3]^{2+}$	Cell dimensions of the polyphosphates after drying at 60°C and 0.1 mm Sheet separation		
	Fibre axis b axis	d_{001}	d_{100}
6	4.4	13.6	12.1
7	4.4	13.4	11.4
8	4.5	13.7	14.3
10	4.5	13.7	15.9
12	4.5	13.6	17.8

$(\text{NH}_4\text{PO}_3)_4$ (98) and P_4O_{10} (99). The (O)-P-O-P-(O) and (P)-O-P-O-(P) angles in the chains of the model had to be distorted somewhat from those adopted in rubidium K.S. in order to give the correct repeat distance along the chain. That distortion of these angles readily occurs may be seen from the data for ammonium tetrametaphosphate (98).

TABLE 10

Bond Lengths for the PO_4 Tetrahedron (97)

P-O ₁	1.621 Å	}	oxygen atoms linked to two phosphorus atoms
P-O _{1'}	1.624 Å		
P-O ₂	1.474 Å	}	"free" oxygen atoms (i.e. linked to one phosphorus atom)
P-O ₃	1.438 Å		

TABLE 11

N-O distances in Ammonium Tetrameta Phosphate (98)

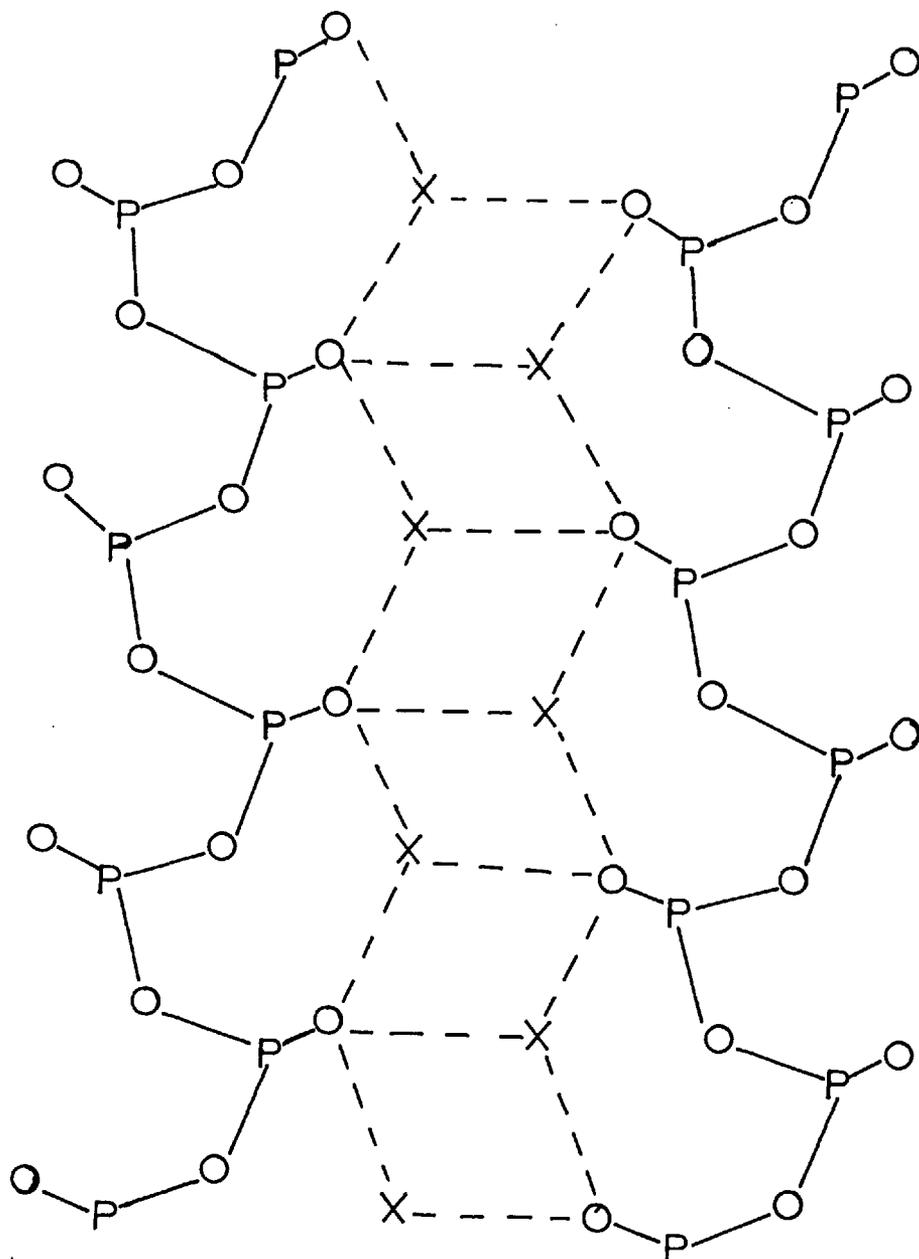
NH_4 (1)	NH_4 (11)
2.79	2.80
3.03	2.85
3.14	2.82
3.38	3.25

A model substituted ammonium ion was constructed for use with the polyphosphate chains. Tetrahedral angles and bond lengths of about 2.9 Å were assumed for this. The lengths assumed for the hydrogen bonds are approximately those reported by Romers et al in ammonium tetrametaphosphate. Relevant data are listed in Table 11.

Hydrogen bonding was assumed to take place only on to "free" oxygen atoms (i.e. those linked only to *one* phosphorus) since, if one considers the covalent bond systems theoretically possible, it may be found that these atoms possess most of the negative charge of the polyphosphate chain.

It was found that, with a tetrahedral arrangement of hydrogen bonds round the nitrogen atom, three such bonds could be made to "free" oxygen atoms of the polyphosphate chains, and that there were more of such favourable positions for amine heads than amine heads available for them. Each head was bonded to two oxygen atoms of one chain and one of another. The repeat distance across the pairs of chains (a axis) was estimated from the model constructed according to the preceding data to be about 13-14 Å. It is difficult to make such a model and great accuracy cannot therefore be obtained. However, it would appear that the most favoured arrangements would be as shown in fig. 6a. It was not possible to decide whether one chain was the enantiomorph of the other, as identical chains appeared to give as good results as different ones. The figure has, however, been drawn in both ways. The chains may in reality be somewhat tilted, but the general picture with a structure based on this type of repeating unit seems clear.

FIG. 7



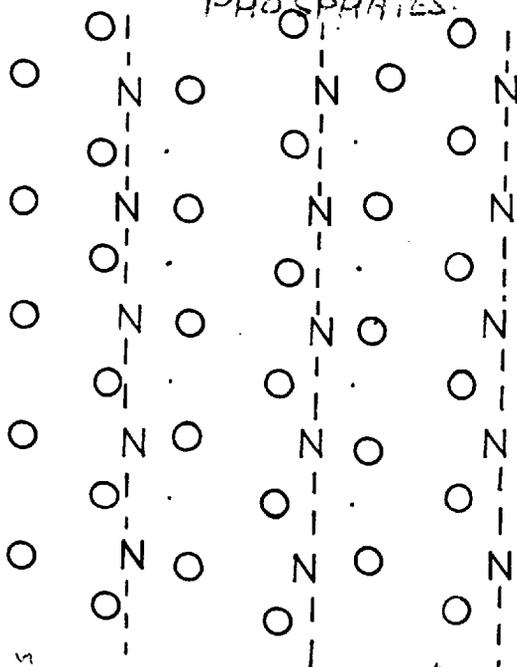
LAYOUT OF POLYPHOSPHATE SHEETS,
SHOWING TWOFOLD EXCESS OF FAVOURABLE
SITES FOR AMINE HEADS.

A planar configuration for the polyphosphate chain also seems possible, however. This is illustrated in Fig. 6b, all of the atoms being in the plane of the paper except for the "free" oxygen atoms. The alternate chains would either be displaced relative to one another, or inverted and displaced. The hydrogen bonding possibilities of these chains are excellent. The repeat distance down each chain is found to be 4.55 Å, using the angles of rubidium K.S. The repeat distance across pairs of chains is found to be 13.5 - 14 Å approx. or slightly less, using angles of 100 and 130°.

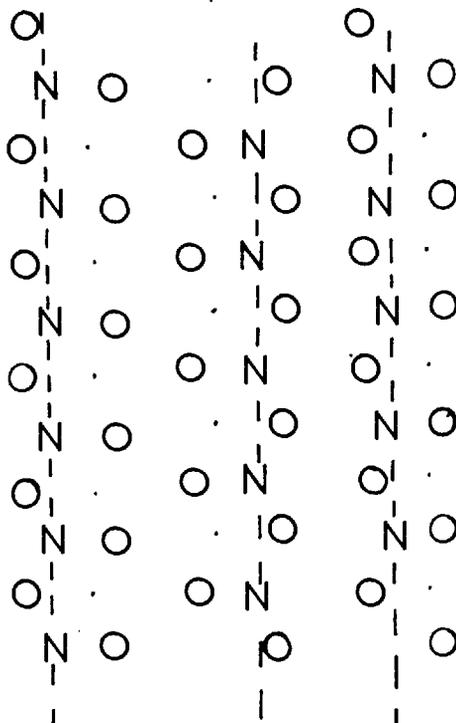
In both of the chain types considered, the position of the amine heads would be similar, as can be seen most easily with a model. As the "planar" polyphosphate chains provide the simplest case, however, this will be the only one considered here.

Each free oxygen atom can be considered as carrying half of a negative charge, and as taking part in hydrogen bonding. Each amine head can make three hydrogen bonds, and each of these can be considered as involving one-third of a positive charge. It will be seen therefore that each pair of free oxygen atoms attached to a common phosphorus atom should have a total of three hydrogen bonds. It may, however, be seen from fig. 7 that there is a twofold excess of "favourable" sites for hydrogen bonding of amine heads over the number required for electrical neutrality. It may also be observed that some of these sites allow free oxygen atoms to have two hydrogen bonds at an angle of about 120°. This would be a particularly favourable situation for hydrogen bonding. However, if both free oxygens on a given phosphorus atom were bound in this way, there would be $\frac{4}{3}$ of a positive charge to each negative charge. According

ARRANGEMENTS OF AMINE HEADS IN POLY- PHOSPHATES.



"EQUAL SEPARATION"
CONFIGURATION



"UNEQUAL SEPARATION"
CONFIGURATION

"FREE"
OXYGEN
ATOMS,

NITROGEN
ATOMS OF
AMINE HEADS,

ABOVE
PLATE N

BELOW
PLATE

FIG.8

to evidence given later, amine heads are present above and below each plate in equal numbers. Of each pair of free oxygen atoms on each phosphorus atom, one is above the plane of the polyphosphate plate and one below. It follows, therefore, that if the amine heads of one layer are so disposed as to hydrogen bond one oxygen atom twice, the amine heads of the next layer must be so disposed as to bond the corresponding oxygen atom on the other side of the polyphosphate sheet only once. As there are equivalent "favourable" positions for hydrogen bonding of the amine heads on both sides of the sheets, this may be arranged in one of the arrangements shown in fig. 8. It may be noted that two almost equally favourable dispositions of the ammonium heads are possible, with different arrangements of hydrogen bonding. One of them puts the heads in evenly spaced parallel rows, and the other in which the rows, though also parallel, are unevenly spaced. As the even spacing would allow the "head" ends of the cations to remain undistorted with close packing of the alkyl chains, this arrangement is presumably the case in unisorbed materials. Evidence will be presented to show that on sorption the uneven spacing is likely to be adopted, in at least some cases.

However, it is possible that an uneven spacing of rows of amine heads may be provided by the movement of polyphosphate chains, without any rearrangement of hydrogen bonding. This is discussed in section 9.2.

The thickness of a plate approximately 2.6 \AA for the "flat" configuration (to the centres of the oxygen atoms out of plane) and about the same for the potassium K.S. type chain. It appears, therefore, that it is not at present possible to determine which of the

possible structures is the correct one.

Since, as shown in the experimental section, products made by ion exchange of the high temperature form of sodium Maddrell's salt were identical with those from potassium K.S., it is of interest to refer to the structure of Maddrell's salt (M.S.). This was determined by Dornberger-Schiff, Liebau and Thilo (100).

This work shows M.S. to contain long unbranched chains of interconnected PO_4 groups. The repeating unit along the chains consists of three PO_4 tetrahedra, two of which can be regarded as being on a line, the other being off it. The structure is rather similar to that of β wollastonite (101).

Since, on ion exchanging this material, the same organic polyphosphates were produced as from potassium K.S. it follows that Maddrell salt chains are drastically reorganised on exchange. As preparations from polyphosphate solutions also gave the same products, it would appear that the chain arrangement is governed by the energetics of the product, and is not affected by the arrangement in the parent materials.

This conclusion is borne out by the fact that the repeat distance along the b axis of aryl and di alkyl ammonium polyphosphates is different from that of both parent materials.

It has been found in the present work that as an exchange proceeds, the intermediate state of the polyphosphate mass is that of a mixture of unexchanged and fully exchanged materials, and that gradual changes of axes from those of the parent material to those of the product do not occur. This is also consistent with a

drastic reorganisation of polyphosphate chains on exchange rather than preservation of their original arrangement.

In diagram 9 several different types of ~~polyphosphate~~ phosphate chains are compared. These are from lithium polyphosphate (102), rubidium polyphosphate (97), high-temperature sodium M.S. (100), and sodium K.S. type A (104). It may thus be seen that considerable variety in the arrangement of the polyphosphate chain is possible. Structures have also been published of silver polyphosphate (103) and of type B of sodium K.S. (109); these both have chains which spiral having four tetrahedra per turn as do those of sodium K.S. type A.

B. Arrangement of the alkyl chains in primary ammonium polyphosphates: The unit cells of compounds in this series increase in volume as the homologous series is ascended. From the increase in volume which was observed to occur, the volume occupied by each CH_2 group added to the ends of existing chains could be calculated.

A graph showing the increase of sheet separation with increase in chain length is shown in fig. 10. It will be noted that the graph is almost linear. This implies that the volume occupied by each additional CH_2 group is almost constant as the chains are increased. When this volume is calculated it is found to be about 29.3 \AA^3 for each CH_2 group.

Sydow (105) has determined from crystallographic data the volumes of the subcells in normal fatty acids in solid state which contain one CH_2 repeating unit of the hydrocarbon chain. These range from 23.3 \AA^3 to 24.7 \AA^3 with orthorhombic subcells and are 25 \AA^3 for two materials

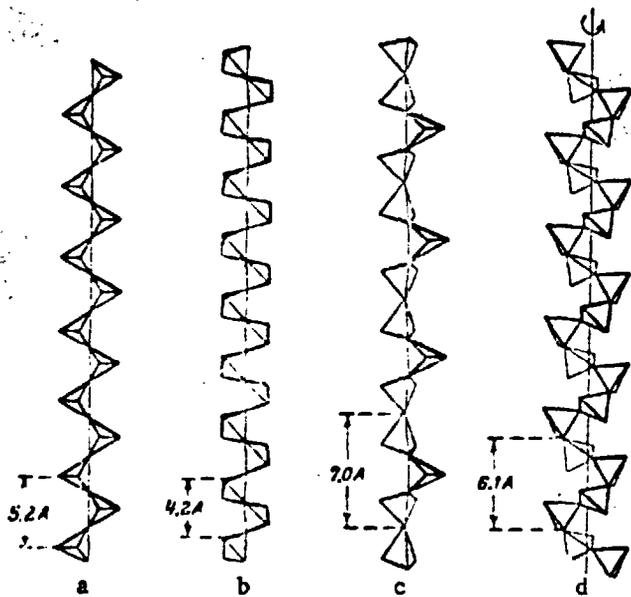


Fig. 9. Chains in polyphosphates: a) $(\text{LiPO}_3)_x$, low-temperature form; b) $(\text{RbPO}_3)_x$; c) Maddrell's salt, high-temperature form; d) Kurrol's salt, A form; $(\text{NaPO}_3)_x$.

with triclinic subcells. Vand and Bell (106) investigated trilaurin (a tri-ester of glycerol with lauric acid) and found a triclinic subcell for the CH_2 groups of 23.7 \AA^3 volume. Bunn (107) and Vainshtein and Pinsker (108) found orthorhombic subcells of 23.1 and 23.3 \AA^3 per CH_2 group respectively for n hydrocarbons.

The volumes of CH_2 units in the liquid state have been briefly calculated in this work, using density data for liquid long chain hydrocarbons, and neglecting the effect of the chain ends. The values of CH_2 volumes from this source appear to be about 29 \AA^3 .

In so far as the volume data can be used as evidence, it would seem probable that there is a certain amount of disordering of hydrocarbon chains in the unsorbed state of polyphosphates. There is a certain amount of evidence for the ordering of the alkyl chains of early members of the homologous series, however, based on the following data, which are derived from X-ray evidence.

It has been noted by Weiss and Michel (29) that the (100) repeat distance of the homologous primary alkyl ammonium series increases unevenly as the series is ascended. For the short chain length members of the series it was noted that the (100) spacing increased more when going from an even to an odd member than when going from an odd to an even member. This may be explained as follows. Since alkyl chains zig-zag, if they lie in an ordered array at an angle to the sheets, the end CH_3 groups will stick up in the case of the odd alkyl chains, and lie flat in the case of even numbered ones. This would account for the uneven increments in plate separation, since according to the evidence following there are two counterlayers of alkyl chains present which would lie

together more tightly in the case of chains with even numbers of C atoms. This may be seen more clearly in figs. 11a and 11b. The inference from this is that the chains are fairly ordered near to the plates.

Weiss and Michel (17) suggested that the alkyl chains would be arranged as a double layer between the polyphosphate sheets because the plate separation of primary alkyl ammonium polyphosphates increases by an average value of 1.8(9) Å per CH₂ group added. This compares with a C-C bond distance in an aliphatic chain of 1.54 Å, the C-C bonds being arranged in a zigzag manner. The length of such an alkyl chain is about 1.26Å per CH₂ unit (107). It thus appears that the alkyl chains are not long enough to reach across the gap between the plates. Presumably, therefore, a double layer is formed, some amine ions being attached to one plate and the others to the one opposite. The chains would not be vertical, but would lie against one another so as to produce close packing, as shown in fig. 12. Weiss and Michel calculated that if the chains were straight they would lie at an angle of 49° (approx.) to the sheets. The density considerations previously referred to would imply a more random arrangement of the alkyl chains than this, however possibly with a certain amount of interpenetration of alkyl chains into their counterlayers in the longer chain members of the series. The high volume per CH₂ unit of the early members of the series may be due to difficulties in securing close packing of the alkyl chains, due to their ends being fixed to the polyphosphate sheets.

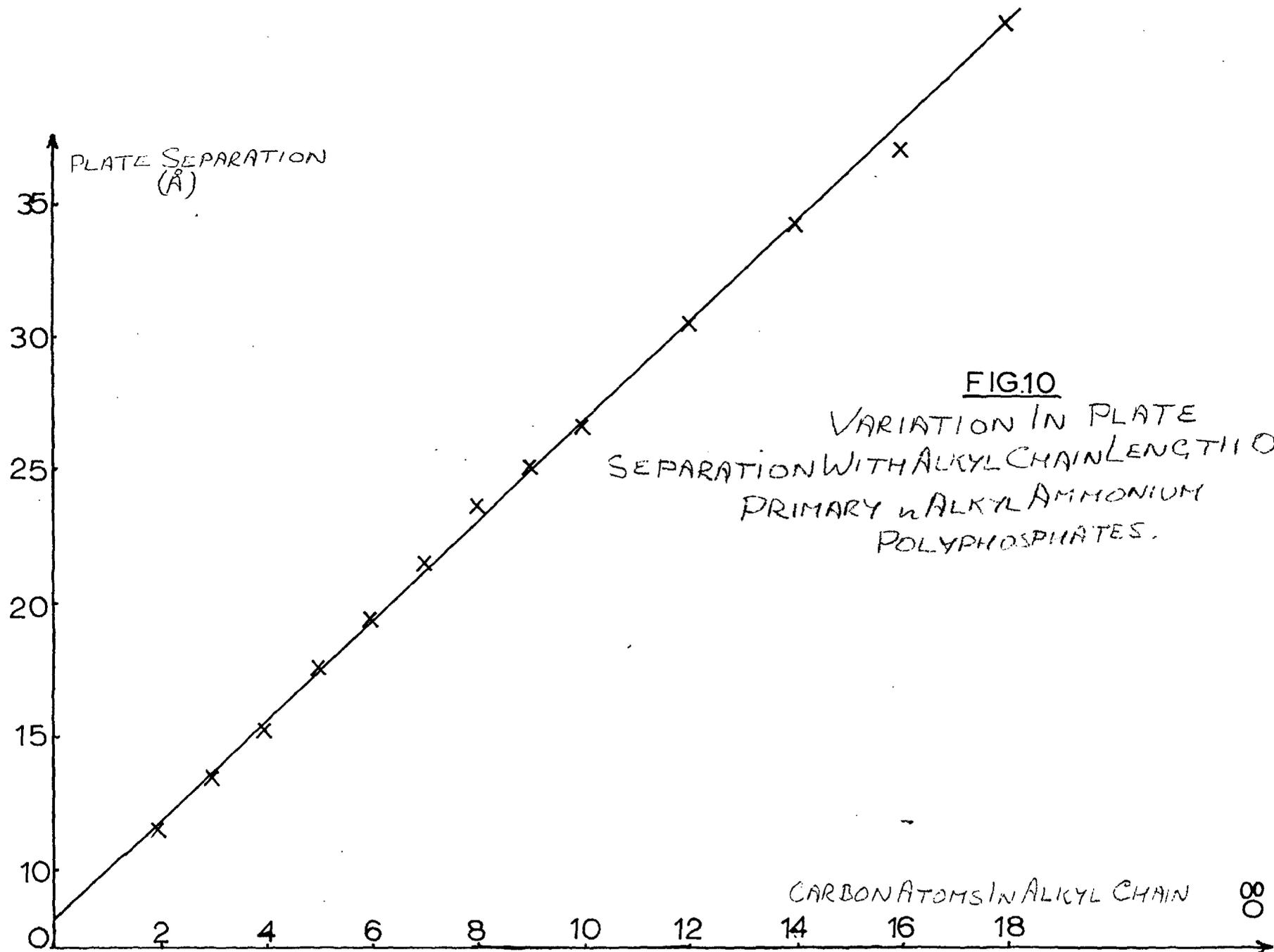


FIG.10
VARIATION IN PLATE SEPARATION WITH ALKYL CHAIN LENGTH OF PRIMARY & ALKYL AMMONIUM POLYPHOSPHATES.

8.3. Structure of a ω diammonium polyphosphates

These compounds are similar in structure to the primary polyphosphates. The ions, however, appear to form a single layer between the sheets, the amine heads at either end lying against different polyphosphate sheets. Evidence has been adduced from exchange equilibria to suggest that the members of this series with even numbers of carbon atoms are more stable than those with odd numbers. This, it has been suggested, is due to the difficulty of forming three hydrogen bonds at each end of the molecule in the case of odd numbered members, due to steric factors. Infrared data has also been quoted in support of this view (29).

From the polyphosphate axis repeat distance, one would imagine that the polyphosphate chains are arranged much as they are in the primary materials.

8.4. The structure of aryl and dialkyl ammonium polyphosphates

The b repeat distance of these polyphosphates appears to be elongated to about 5 Å. Presumably, therefore, the polyphosphate chains are stretched in these cases. They probably tend to become "flat" in form as they are extended, and their structure would be likely to correspond to a flat chain as illustrated in fig. 6b, with the angles distorted in order to increase the repeat distance.

Double layers appear to be formed in the case of both of these groups of materials.

8.5. The structure of quaternary ammonium polyphosphates

These materials have tetragonal unit cells in two cases. There is a repeat distance of about 4.8 \AA along one axis in the case of cetyl trimethyl ammonium polyphosphate, and 4.5 \AA approx. in the case of octadecyl pyridinium polyphosphate. The two axes perpendicular to this have repeat distances equal to one another (17).

It is therefore reasonable to suppose that the one repeat distance lies along the polyphosphate chain, and that the organic matter is disposed around this so as to provide two other equal repeat distances. In the present work it was found that in the case of dimethyl dioctadecyl ammonium polyphosphate, one repeat distance is about 4.5 \AA (though the lines giving this value are rather diffuse) and the two repeat distances perpendicular to this are respectively 33 \AA and 36 \AA . Thus there appears to be some departure from exactly tetragonal symmetry in this case, the general picture being, however, much the same as in the previous two cases.

It appears, therefore, that when quaternary ammonium polyphosphates are formed, the fact that there is no longer any possibility of hydrogen bonding results in the polyphosphate chains (which, in these circumstances, can no longer be cross-linked) separating from one another by a considerable distance.

9. SORPTIVE PROPERTIES OF PRIMARY AMMONIUM
POLYPHOSPHATES

9.1. Sorption of hydrocarbons on primary ammonium
polyphosphates

The sorption of hydrocarbons in the primary ammonium series of polyphosphates presented few difficulties compared with some of our other sorption work. Reproducibility of the amount sorbed was better than 20% in every case where sorption was not negligible. The isotherms were, in most cases, limited to the range 0 - 75% relative vapour pressure of sorbate, as this appeared to give better reproducibility and was simpler to cover experimentally than a more extended range.

No permanent sorption occurred with hydrocarbons on amyl, heptyl, nonyl and dodecyl ammonium polyphosphates or on anilinium polyphosphate. Hysteresis did not occur to any great extent and when it did occur it sometimes appeared to be associated with an increase in sorptive capacity during the run. However, reductions as well as increases in sorptive capacity were also found to occur, no very obvious cause of this being found. Possibly the rate of attainment of previous equilibria may affect the physical state of the sorbent and thus its sorptive capacity.

Details of isotherm reproducibilities: At 60°C the following work was carried out. Firstly, isotherms were obtained for benzene on two samples of heptyl ammonium polyphosphate, one of which had been used only to sorb nitromethane, the other being an unused sample. The two isotherms were identical within experimental error.

Repetition of benzene isotherms at this temperature for nonyl and amyl ammonium polyphosphates also gave agreement within experimental error. Likewise, on repetition of sorption of n-heptane and cyclo-hexane on nonyl amyl and heptyl ammonium polyphosphates identical isotherms were obtained.

At 30°C benzene sorption remained unchanged for three consecutive isotherms with amyl, heptyl and dodecyl ammonium polyphosphates. However, in nonyl ammonium polyphosphate, maximum divergencies were found of about 8% in the amount sorbed, the last isotherm having values intermediate between those of the first two. In anilinium polyphosphate benzene gave the same sorption for three successive isotherms at 30°C.

For cyclohexane, isotherms were measured and then, after other sorption studies on the given sorbent an attempt was made to reproduce points on the original isotherms. It was found that nonyl ammonium polyphosphate sorbed an average of about 17% less, heptyl ammonium polyphosphate about 4% more, and amyl ammonium polyphosphate about 20% less. Sorption was very small in the latter case, and experimental errors might have been about 15%, but even so it appears that less cyclohexane was sorbed the second time. The only non-hydrocarbon sorbate used between the two runs referred to above was water.

It was found, however, that with iso-octane and benzene the isotherms both preceding and following sorption runs with other hydrocarbon sorbates, were virtually unchanged. In this connection it is of interest to refer to the results obtained with water between the initial and the final runs with cyclohexane. It was observed that little sorption occurred. The sorbent

which took up most water was heptyl ammonium polyphosphate which sorbed only 0.7% of its own weight at 60% relative vapour pressure. No hysteresis was found except with heptyl ammonium polyphosphate, though, due to the small amounts sorbed and the limited number of results, this observation is not very certain. All of the water was removed from the samples by outgassing; no irreversible chemical reaction could have occurred, therefore.

If the physical state of the sorbent were altered appreciably by water sorption, (which would account for the subsequent alteration of the cyclohexane isotherm) one would perhaps expect some hysteresis in the water isotherm. This may have occurred undetected because, due to the small total amounts sorbed, the experimental error is estimated to be 30% in the region where the greatest hysteresis would have been expected.

In order to make the sorbents used in this section of the work as nearly as possible equivalent to one another, they were all prepared in the same way, by ion exchange of potassium Kurrol's salt, this being the most generally suitable method. Details are given in section 7.

Conclusion: It may be concluded from the foregoing results that the sorbents are somewhat labile, and their exact state is dependent on their history. Possibly the changes may be due to an increased ordering or disordering of the organic matter, or perhaps, in those cases where the polyphosphate plates move apart appreciably, with a tendency for the plates to buckle, or to be displaced relative to one another.

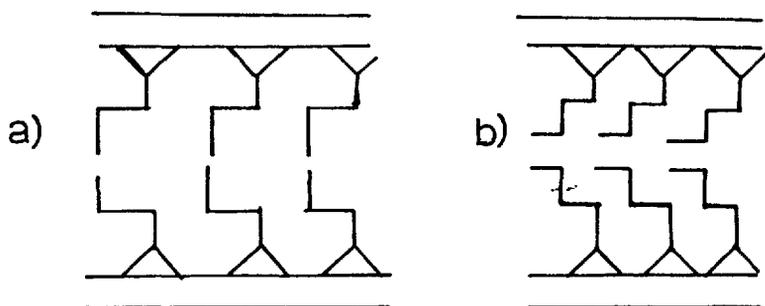


Fig.11 TO SHOW HOW EVEN NUMBERED ALKYL CHAINS FIT TOGETHER MORE COMPACTLY THAN ODD ONES.

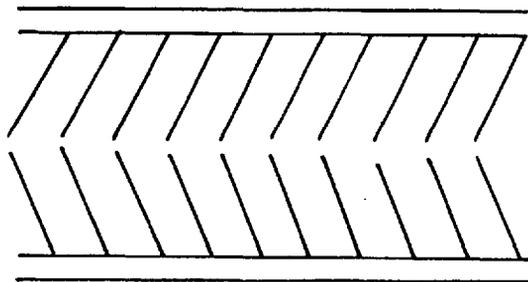
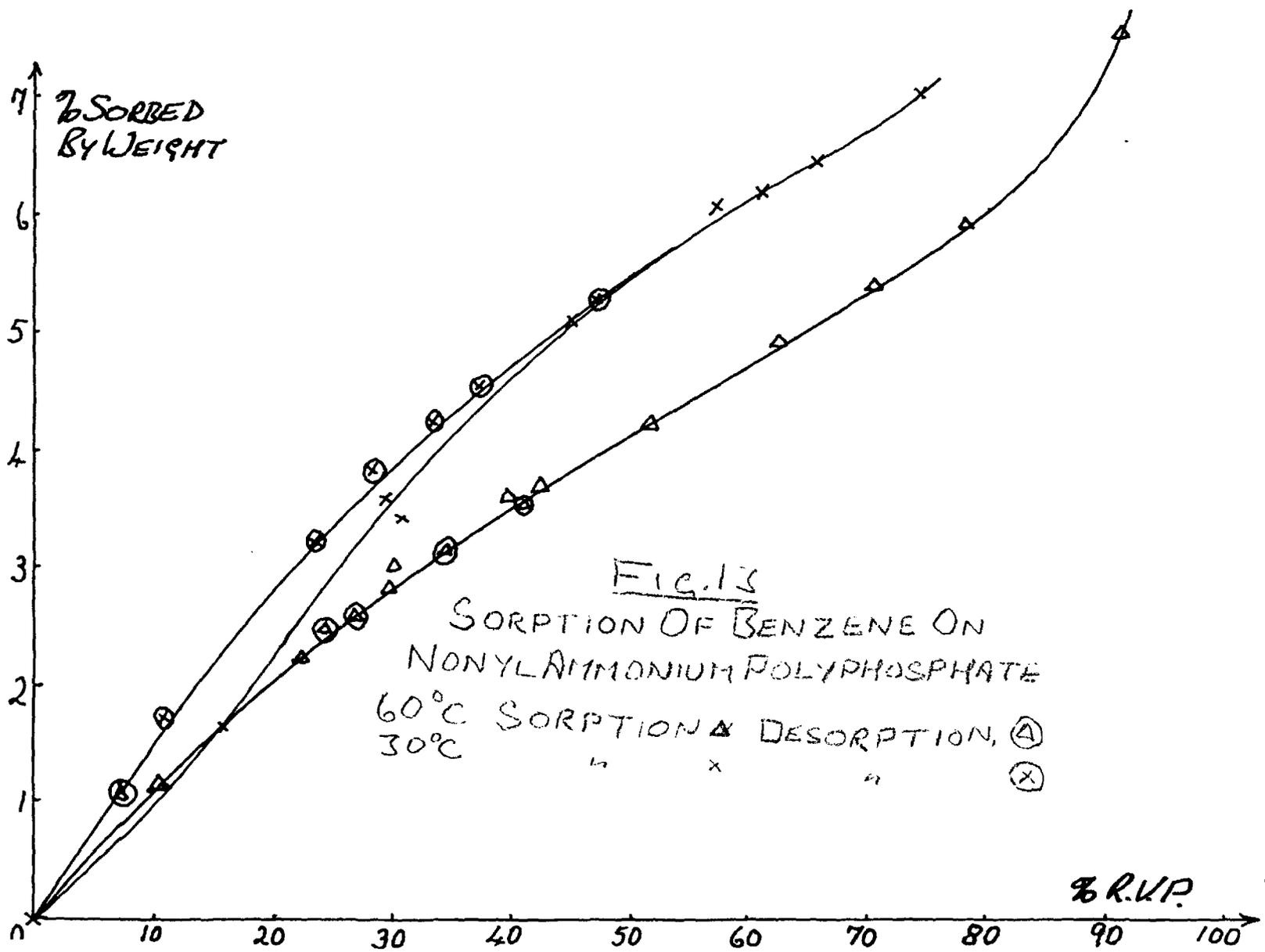
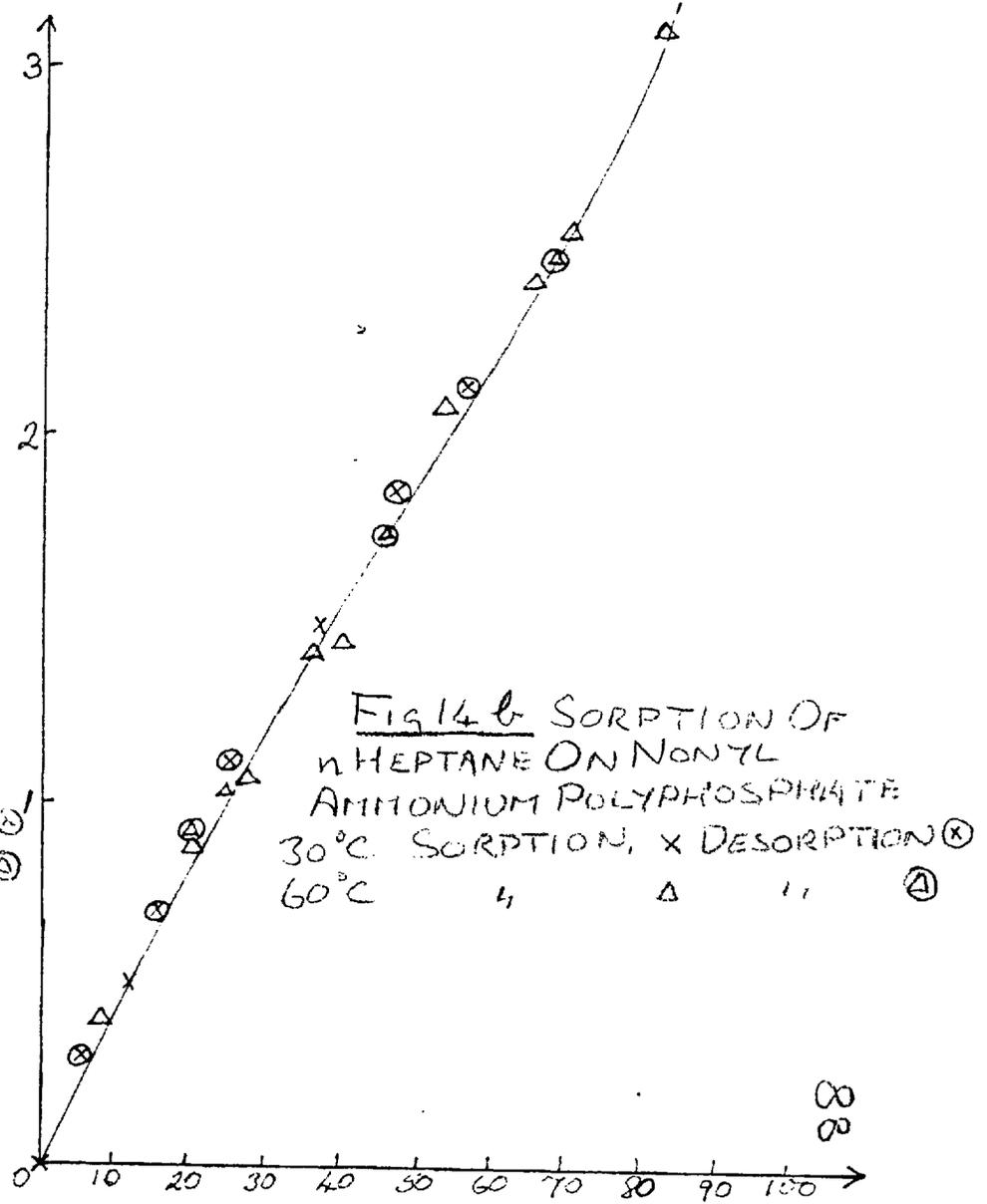
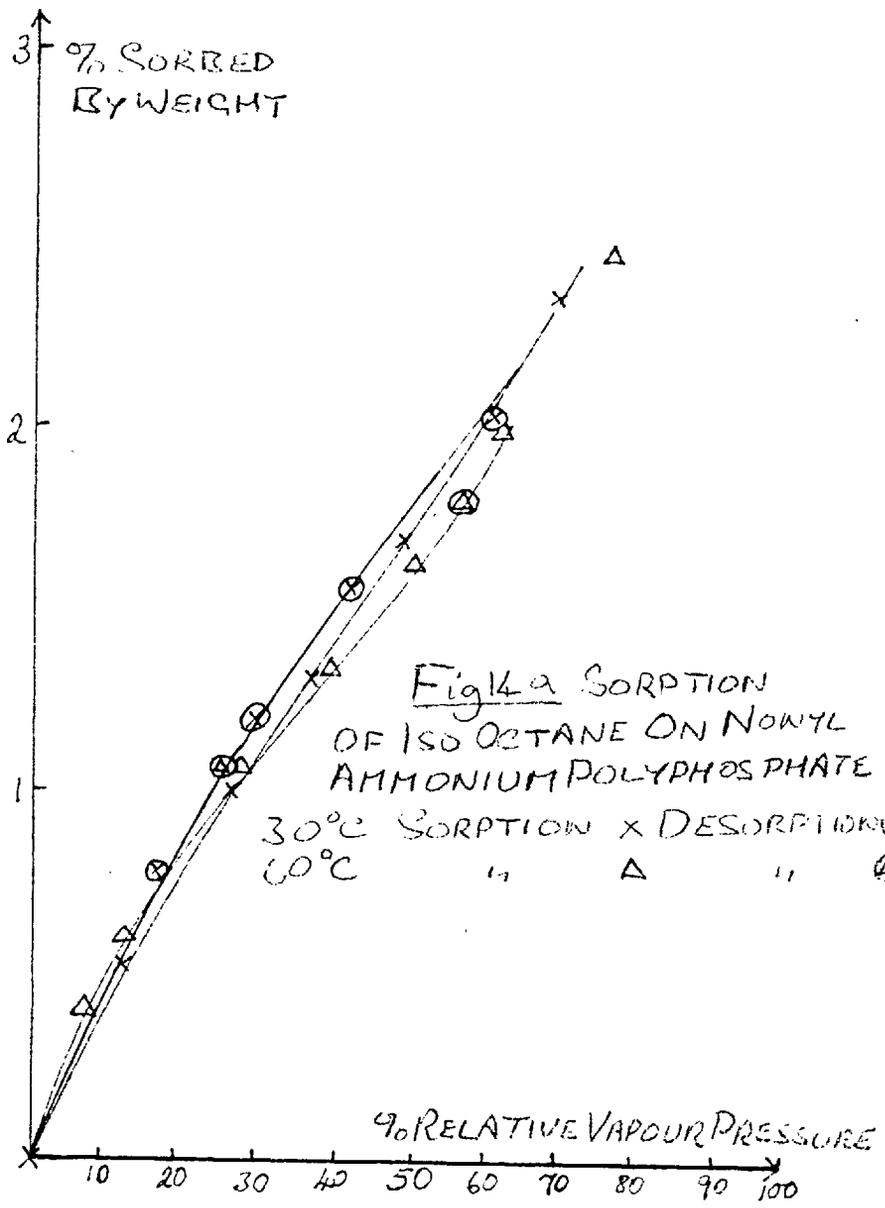
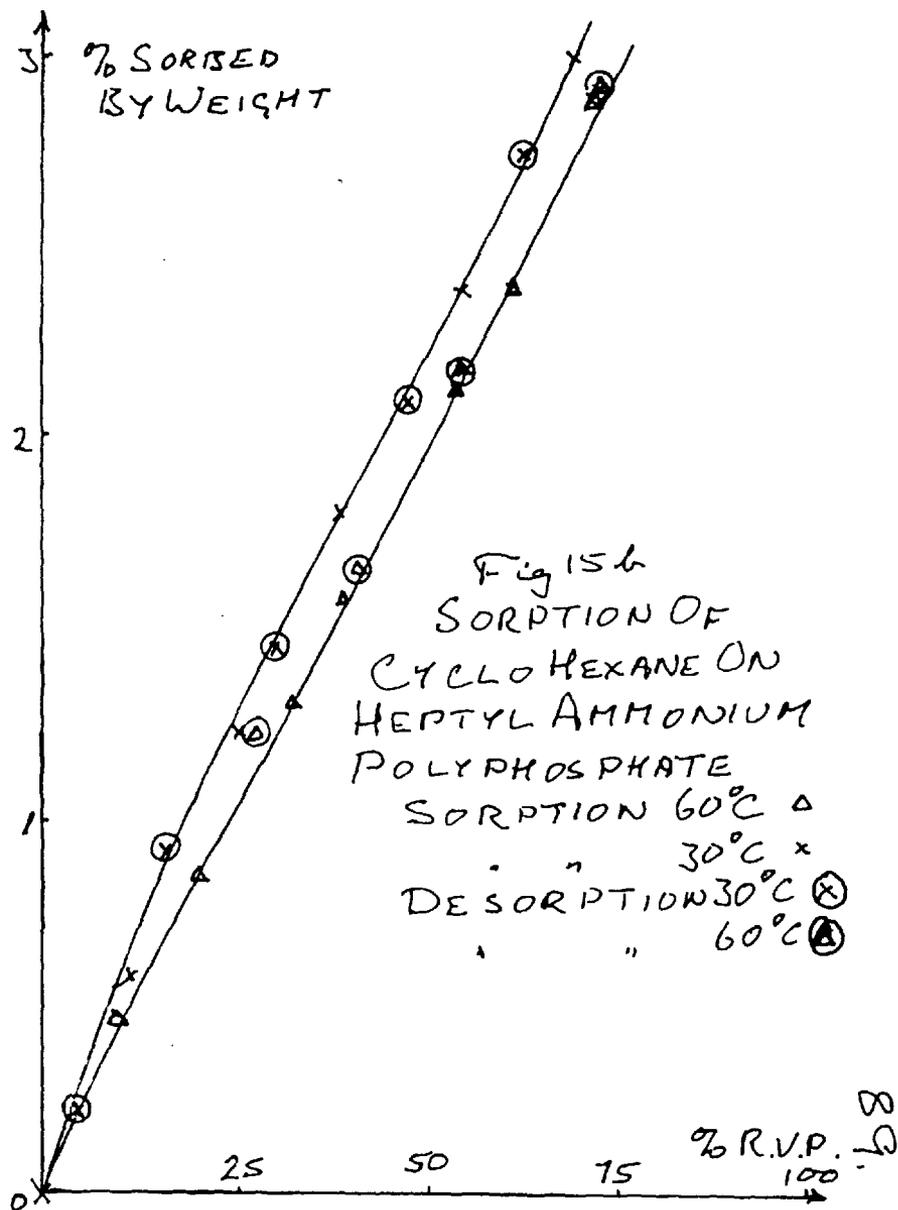
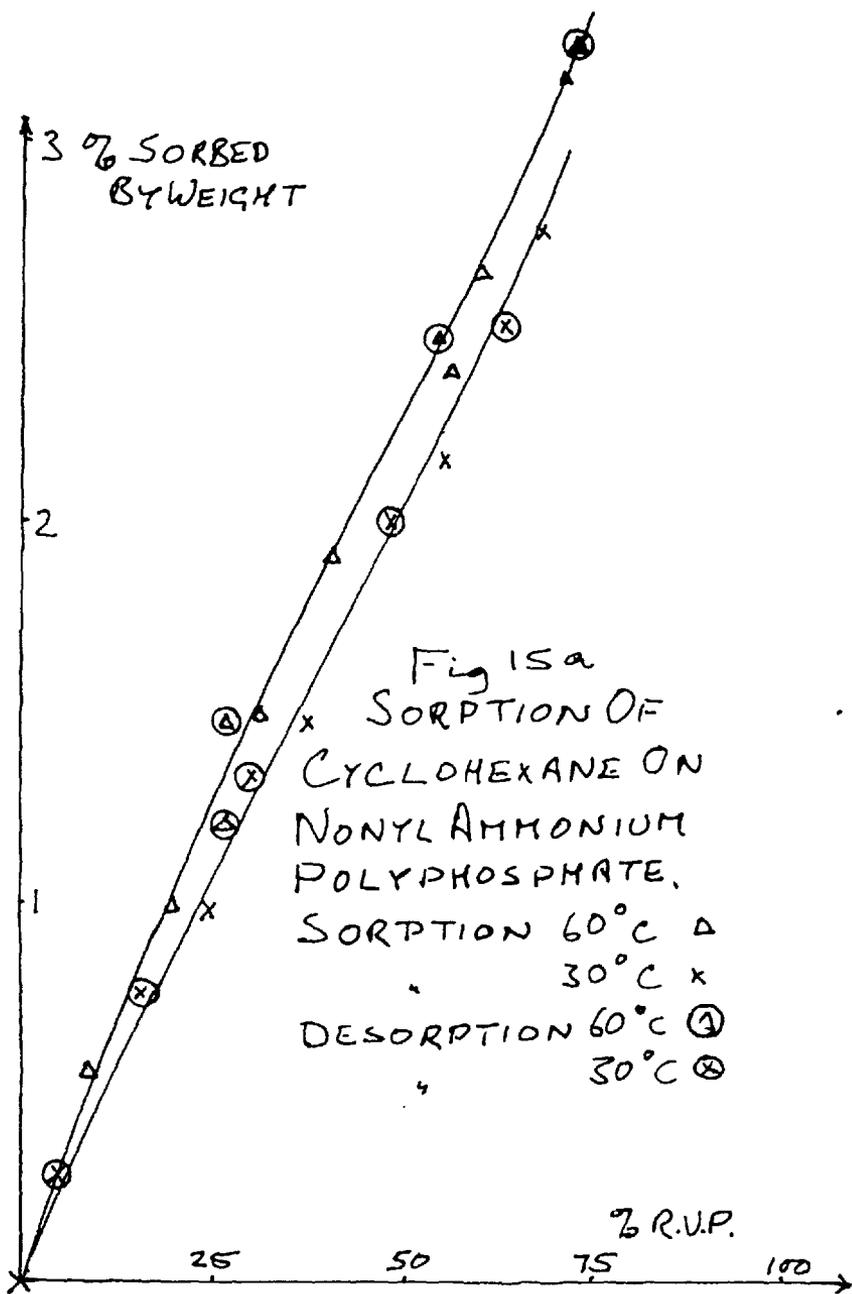
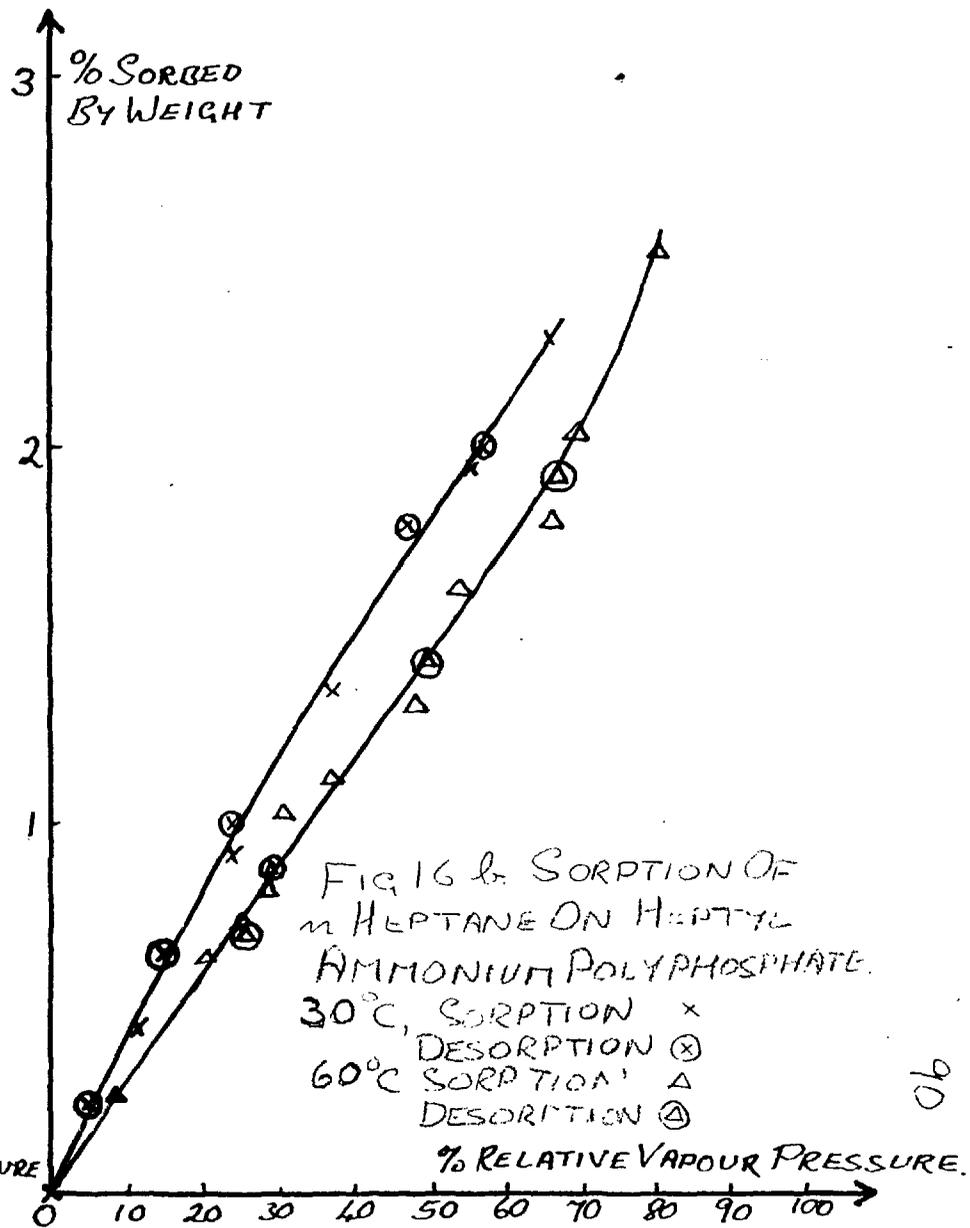
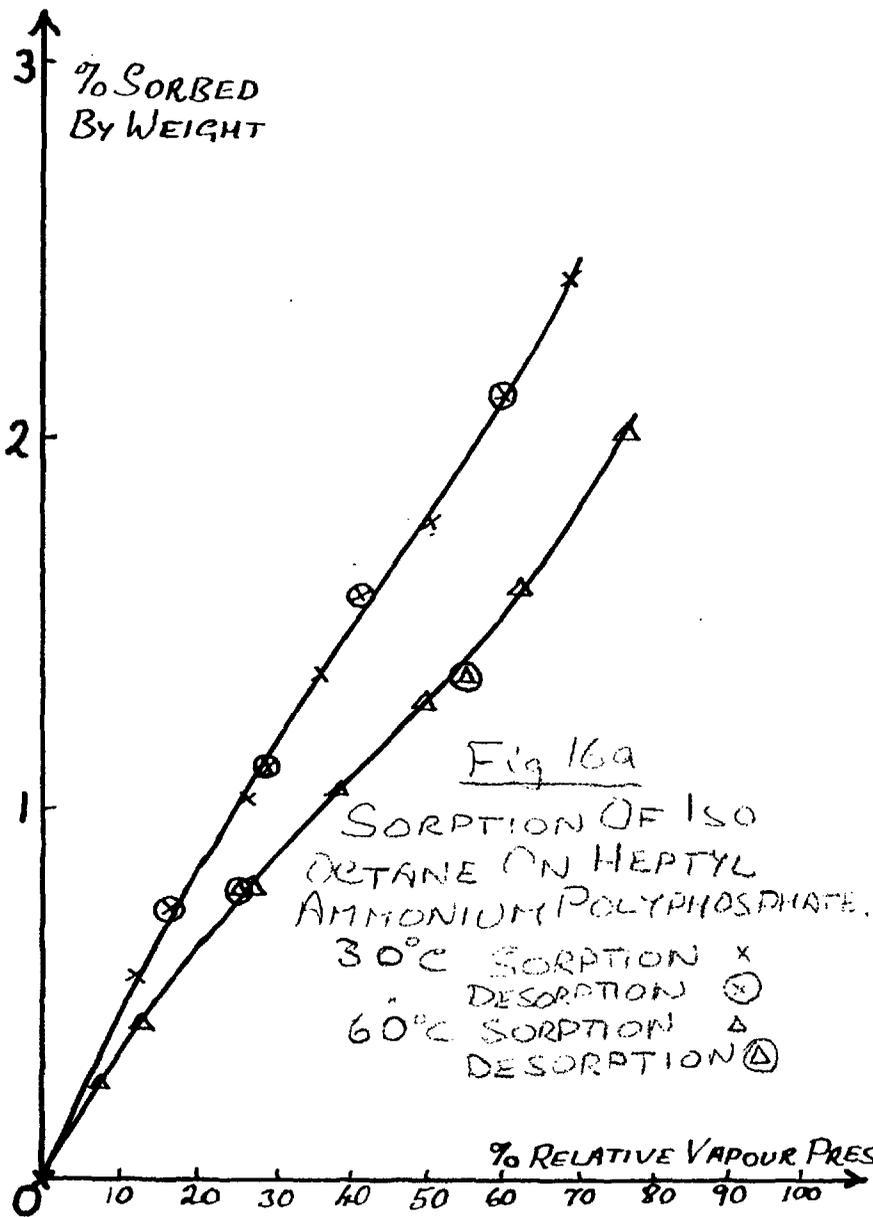


Fig.12. SHOWING DOUBLE LAYER OF ALKYL CHAINS, LYING AT AN ANGLE.

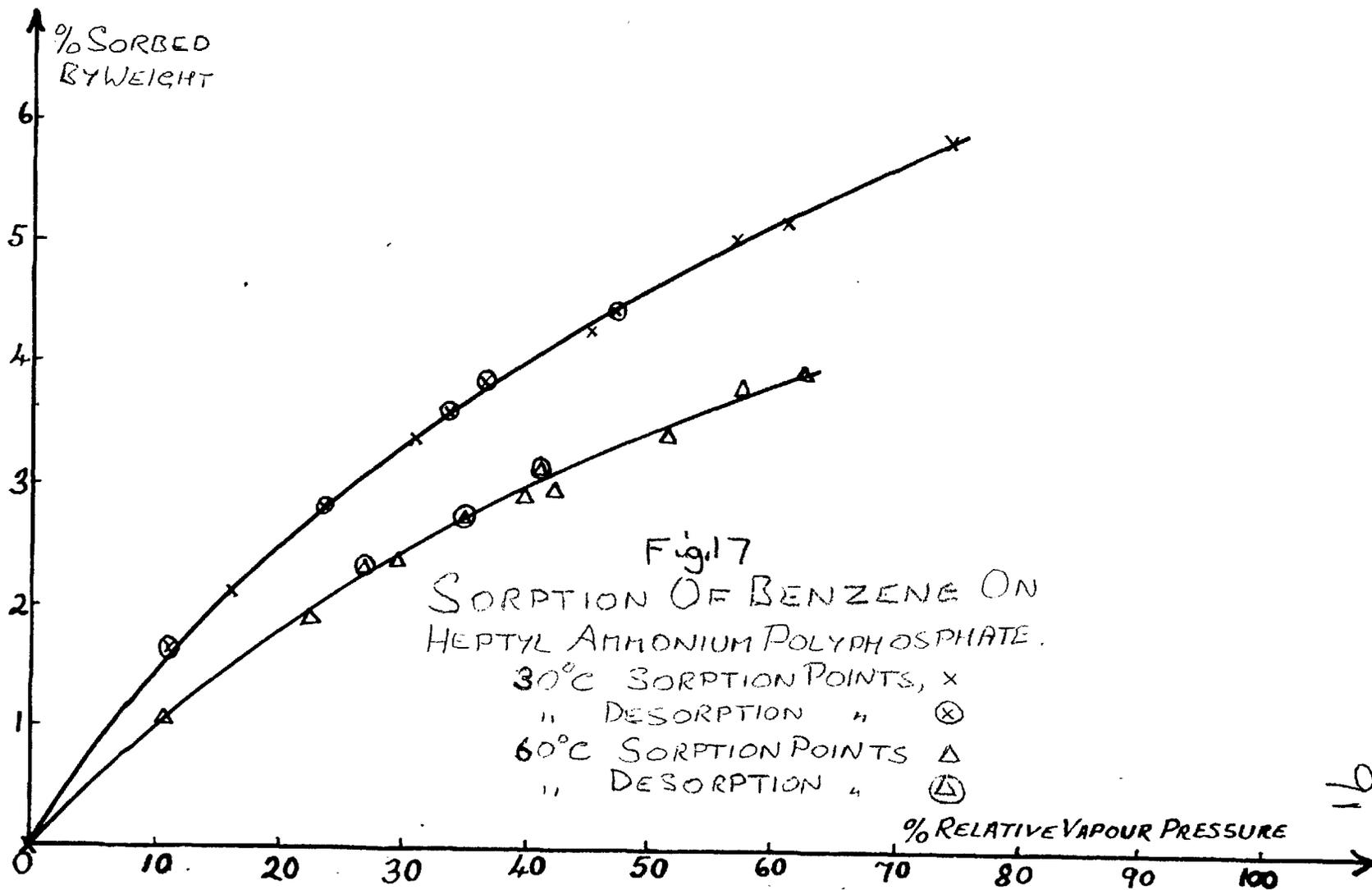


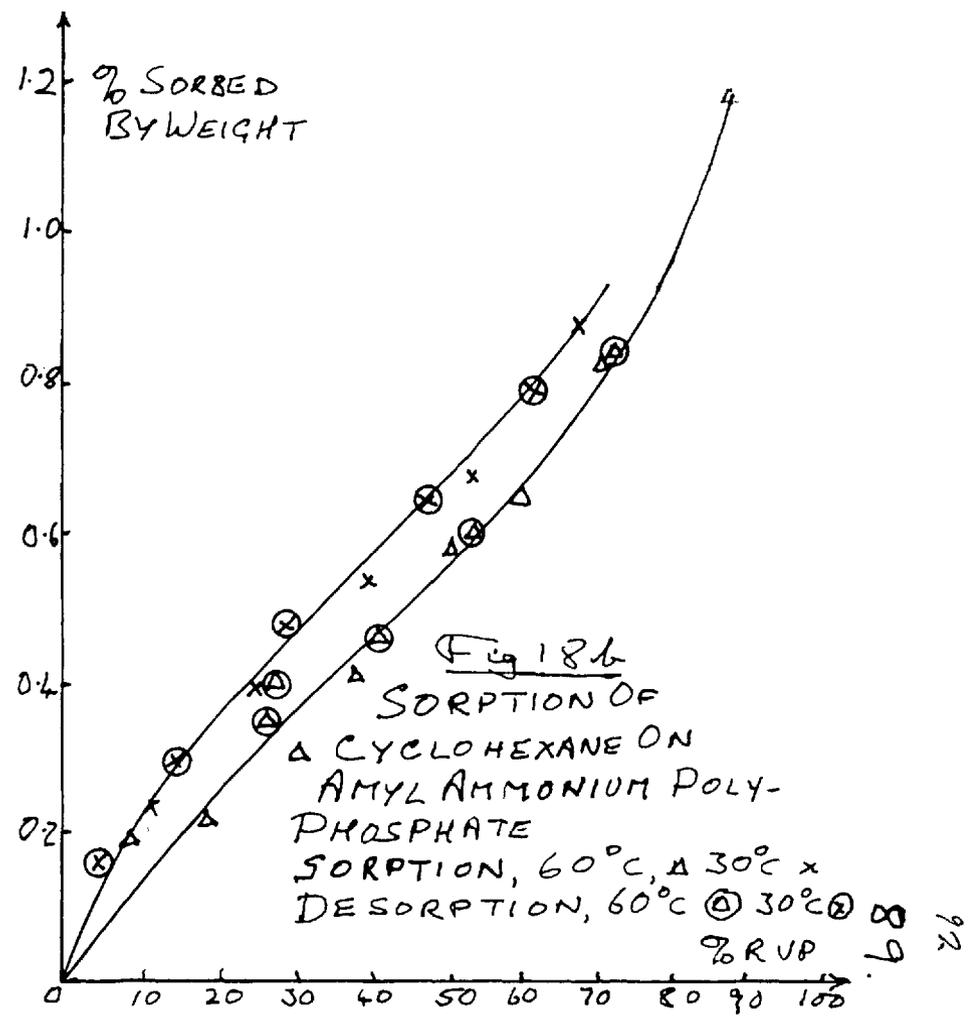
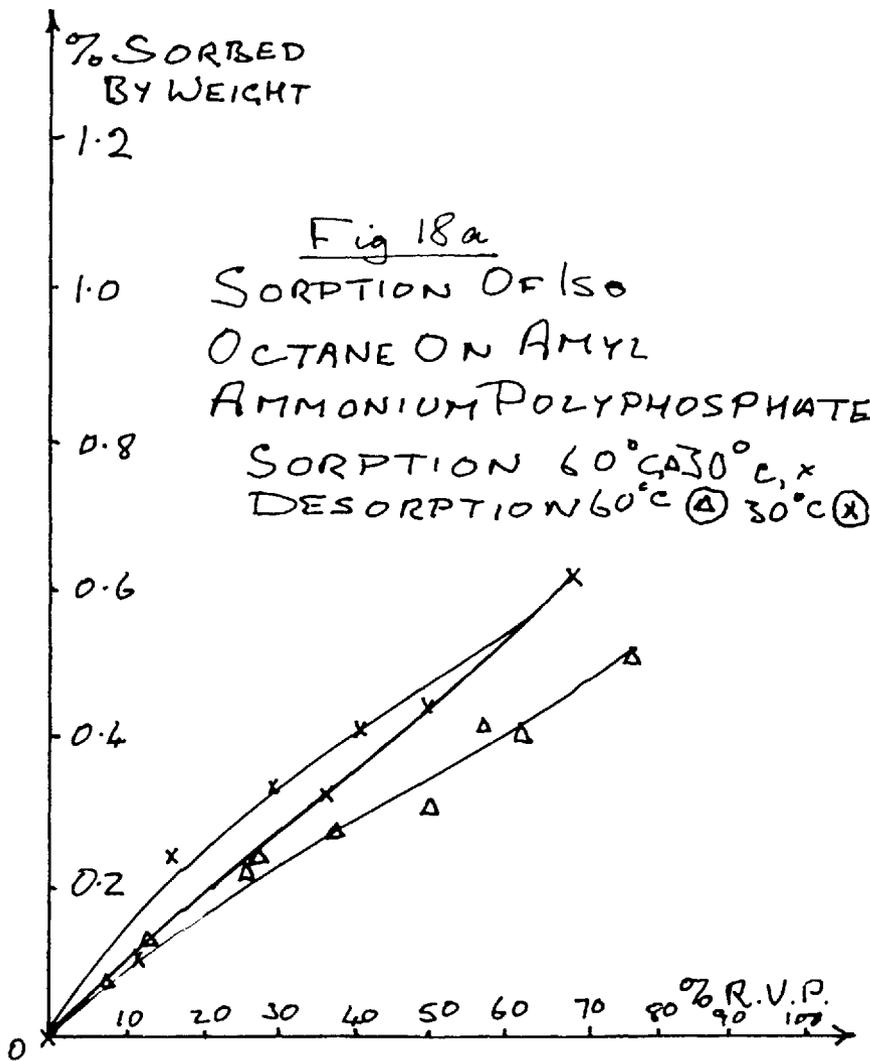


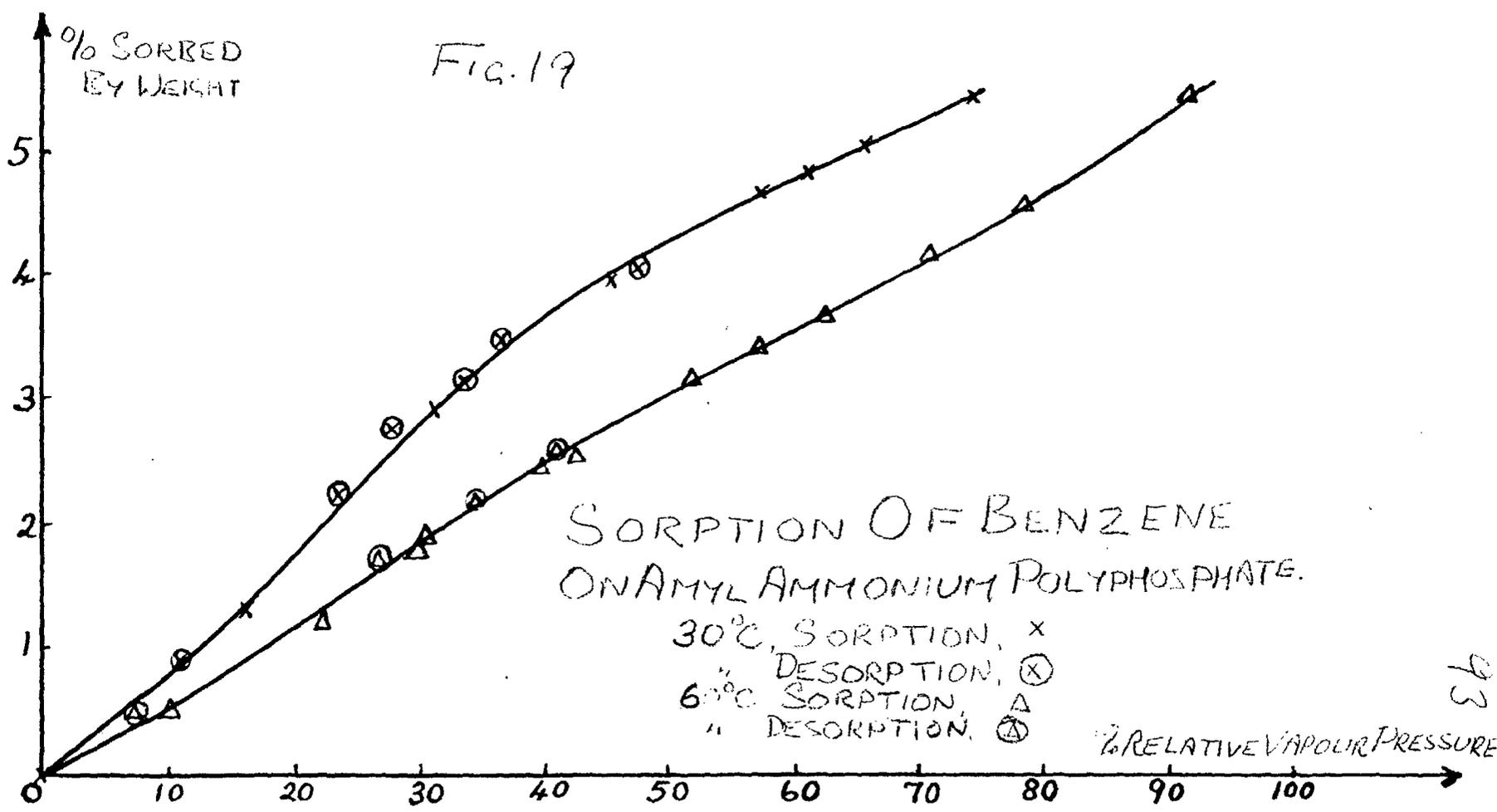


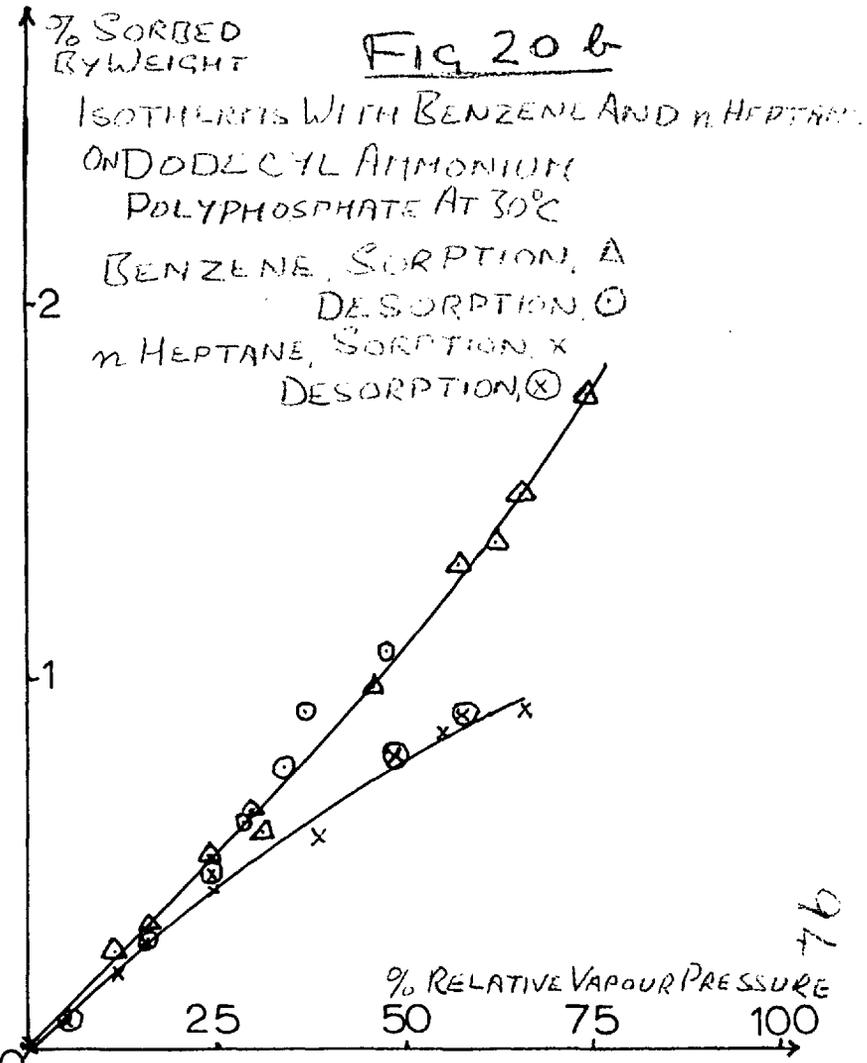
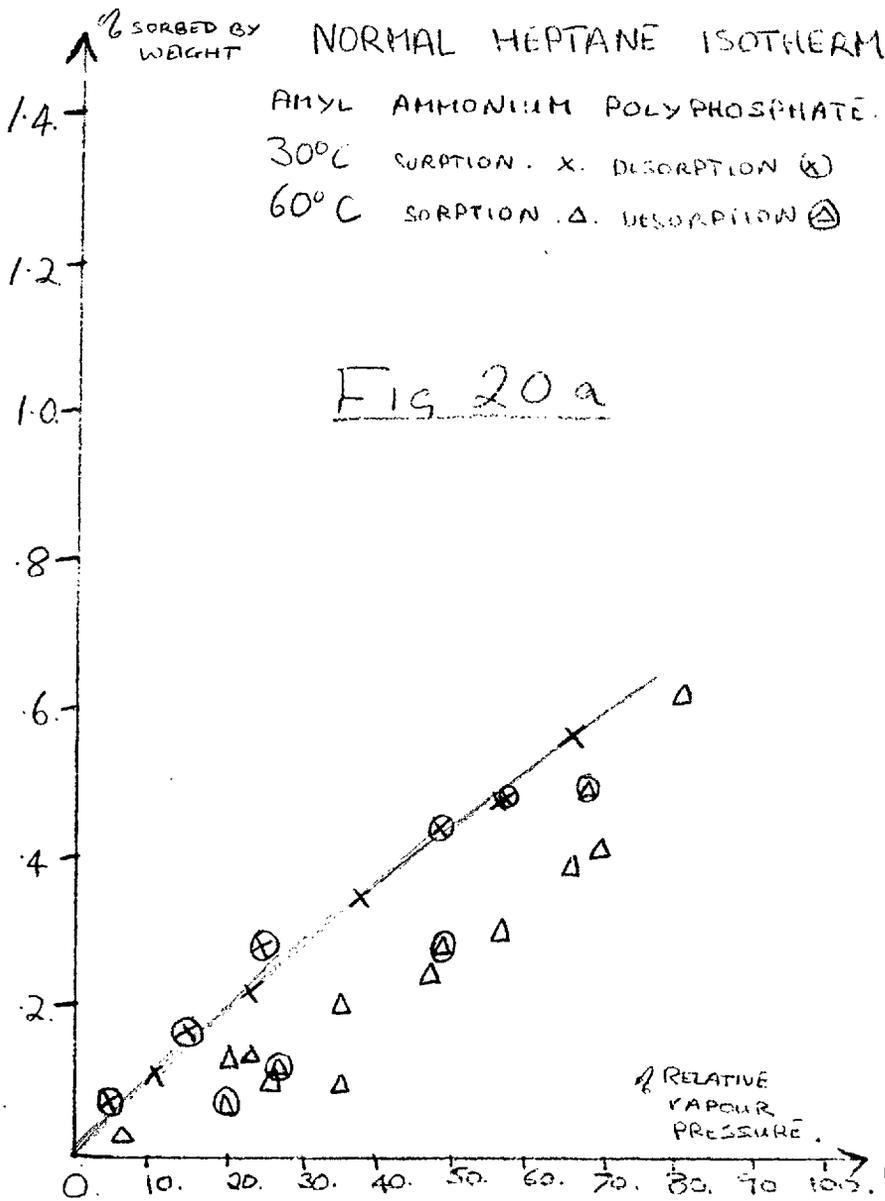


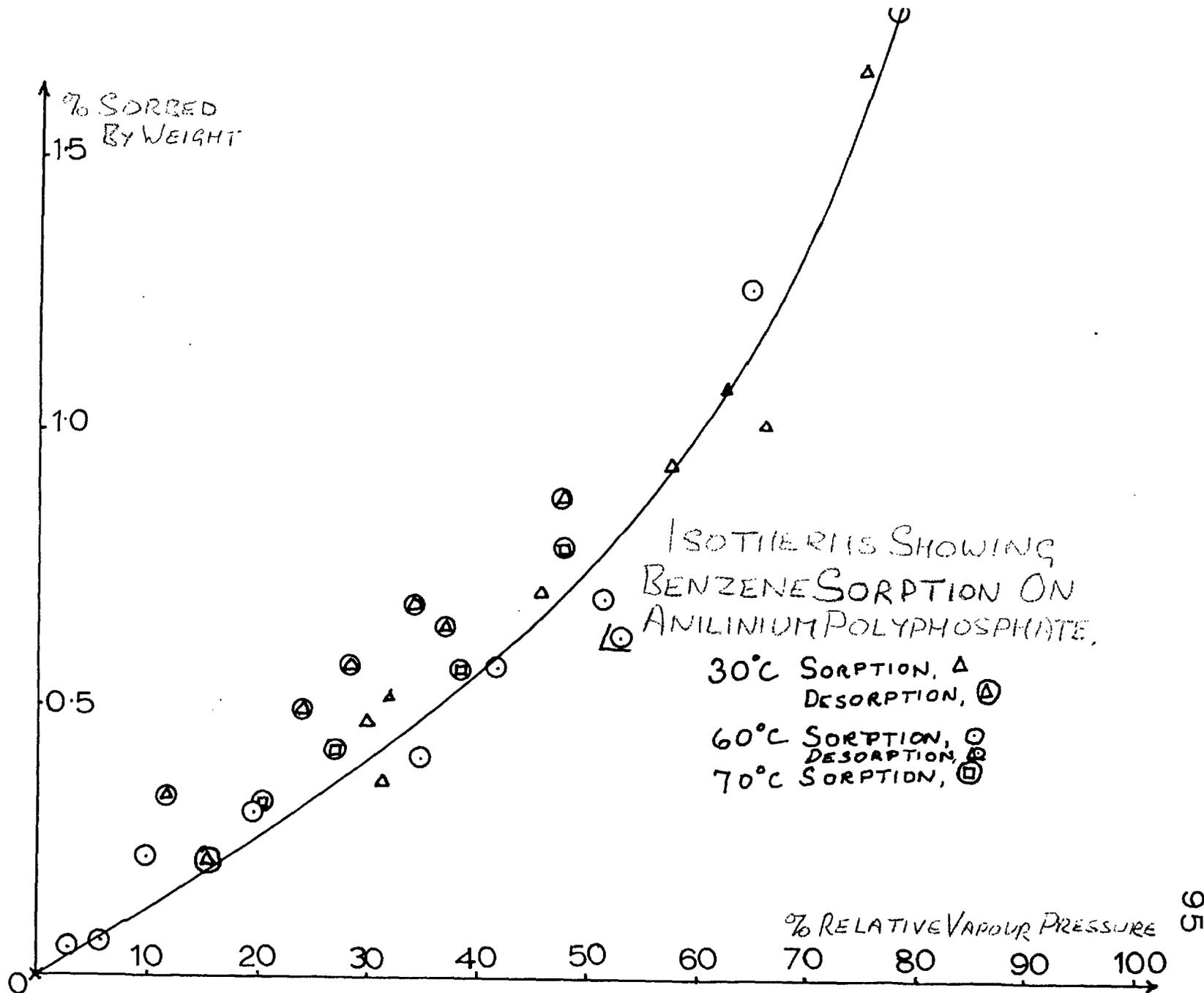
016











Behaviour of individual sorbents:

1. Nonyl ammonium polyphosphate

Isotherms were obtained using this sorbent for the four hydrocarbons, benzene, cyclohexane, n-heptane and iso-octane, at two different temperatures. These isotherms are represented in figs. 13, 14 and 15a.

At 60°C nonyl ammonium polyphosphate gives almost linear isotherms. The deviations from linearity are towards a type II isotherm in Brunauer's classification. It will also be noted that the sorptive capacity for benzene is (at 50% relative vapour pressure) about twice that for cyclo-hexane and nearly three times that for iso-octane. The n-heptane isotherm is intermediate between those of cyclohexane and iso-octane. No hysteresis occurs in any of these isotherms.

At 30°C all the isotherms show a little hysteresis, and except for benzene, they appear to be more linear. Once again, benzene is sorbed to a greater extent than the three paraffinic sorbates, by a factor of about three in each case at 50% relative vapour pressure. At 30°C the three paraffinic materials appear to be sorbed almost equally, n-heptane being sorbed a little less than the other two. However, on a sample of nonyl ammonium polyphosphate which had a different sorptive history cyclohexane and iso-octane were less strongly taken up than by the first specimen of this sorbent. For this polyphosphate too much reliance should not, therefore, be placed on the apparent order of sorptive capacities indicated by the isotherms shown.

The benzene and iso-octane isotherms were lower at 60°C than at 30°C, the former by an average of about

23% and the latter by about 15%. The n-heptane isotherms were identical throughout, but the cyclohexane isotherm was about 10% higher at 60°C. This latter result was anomalous in so far as all other isotherms of other paraffins with primary alkyl ammonium polyphosphates were lower at 60°C than at 30°C. It appears that in the cases of iso-octane and benzene the sorption is exothermic, but due to hysteresis at the lower temperatures the exact values cannot be calculated. The thermodynamics of sorption by these and other materials are discussed later.

2. Heptyl ammonium polyphosphate: Isotherms obtained for this sorbent with benzene, n-heptane, cyclohexane and iso-octane at 60°C and 30°C are shown in figs. 15b, 16 and 17).

Benzene was sorbed most strongly, by a factor of about two at both temperatures. No significant hysteresis was shown on any of the isotherms, which were very reproducible compared with those of nonyl ammonium polyphosphate.

At 60°C cyclohexane was sorbed more than n-heptane, which, in turn was sorbed more than iso octane (in terms of weight). At 30°C cyclohexane was again sorbed most, n-heptane and iso-octane being sorbed almost equally. Cyclohexane was sorbed more than other paraffins at both temperatures for amyl as well as heptyl and nonyl ammonium polyphosphates. However, in the case of dodecyl ammonium polyphosphate it is sorbed to roughly the same extent than iso-octane, though much more than n-heptane. Less information is available for this sorbent, and less reliance should be placed on this evidence than may be placed on that for amyl, heptyl and nonyl ammonium polyphosphates.

All of the isotherms for heptyl ammonium polyphosphates appear to be fairly linear. Divergences appear to be towards a type II isotherm in Brunauer's classification with benzene at 60°C and 30°C, and with the paraffins at 60°C. The paraffin isotherms are nearly linear at 30°C.

Amyl ammonium polyphosphate: This material is most notable for its selective sorption of benzene. This is sorbed (at 75% RVP) to about five times the extent of cyclohexane and eight times the extent of n-heptane and of iso-octane at 60°C. At lesser vapour pressures of benzene, the ratios are even greater. At 30°C and 70% relative vapour pressure the ratio of sorption of benzene to sorption of paraffin is about $6\frac{1}{2}$ with cyclohexane, and about $8\frac{1}{2}$ with n-heptane and iso-octane. Benzene and n-heptane appear to show slight hysteresis at 30°C. No hysteresis was observed at 60°C, but in view of the small amounts of paraffinic materials sorbed the hysteresis may be less than experimental error. The isotherms again appear to be almost linear although the deviations seem significant in the case of benzene at 30°C, where sorption is almost linear at low pressures, but falls off as the pressure is increased, until the capillary condensation region is reached. This is shown, with other isotherms for this sorbent in figs. 18, 19 and 20a.

Cyclohexane is sorbed more than other paraffins in amyl ammonium polyphosphate.

Dodecyl ammonium polyphosphate: Isotherms were obtained in this material with benzene and normal heptane, and a few sorption points were also obtained with iso-octane and cyclohexane. This part of the sorption by dodecyl

ammonium polyphosphate was performed at 30°C.

The benzene results appeared to be fully reproducible in three successive runs. One point on the graph was checked after the polyphosphate had been used for sorbing n-heptane and iso-octane. No change was noted. No checks were made on the reproducibility of paraffin sorption.

No hysteresis was observed with benzene or n-heptane. The isotherms tended to diverge from linearity towards form III in Brunauer's classification for benzene, and towards type I with n-heptane. Up to 50% relative vapour pressure, benzene appeared to be sorbed to the extent of about 30% more than n-heptane. Beyond that pressure, however, the ratio of amounts of the two materials sorbed became progressively greater.

The isotherms of cyclo-hexane and iso-octane were linear and were located in much the same positions as with n-heptane. The results indicate that the paraffins are sorbed to the extent of about 1% at 70% relative vapour pressure, and benzene slightly more. Thus, dodecyl ammonium polyphosphate is not a good sorbent for any of these hydrocarbons. The isotherms for n-heptane and benzene sorption are shown in fig. 20b.

Anilinium polyphosphate: Isotherms for benzene were obtained at three temperatures (70°, 60° and 30°C) using this material, but at 30°C only with n-heptane. They are shown in fig. 21. Some isotherm points at 30°C were also obtained with cyclohexane and iso-octane. None of these hydrocarbons were sorbed to any great extent. The position of the benzene isotherm changed very little with temperature. Hysteresis occurred, and the isotherms were

of type III in Brunauer's classification. Hysteresis was not observed with n-heptane, which also gave a type III isotherm. The weights sorbed per gram of sorbent of benzene and n-heptane were approximately the same up to 70% relative vapour pressure. Iso-octane was taken up rather more strongly, while only one-third as much cyclohexane was sorbed.

These results are very interesting, as they provide a complete contrast to those obtained using alkyl ammonium polyphosphates, which sorbed benzene most strongly, and paraffins almost equally.

Of the paraffins, cyclohexane, which is sorbed to the greatest extent by the primary alkyl ammonium polyphosphates, was sorbed least by anilinium polyphosphate. The explanation for these phenomena is not immediately apparent.

In the case of benzene, sorption appears to remain unchanged as the temperature is increased. This indicates that the heat of sorption from the liquid state is negligible. The isotherms are of type III in Brunauer's classification. These facts would be explained if the affinity of the benzene molecules for benzene liquid were greater than their affinity for the sorbent, so that benzene molecules would tend to cluster. Alternatively, sorption of benzene on one site may make other sites energetically more favourable for sorption. The small total amount sorbed shows that such groups of sites would be few in number.

Conclusion: Whatever the explanation may be it is interesting to see that anilinium polyphosphate sorbs some aliphatic materials as much as or more than it does benzene,

and that its sorption of paraffins is strongly dependent on molecular shape. Alkyl materials, however, sorb benzene much more than they do paraffins, and have a markedly different order of affinity between paraffins.

9.2. Thermodynamics of hydrocarbon sorption

9.2.1. General principles:

The sorption processes in the layer polyphosphates which were investigated in the present work, can be considered in terms of the following steps.

(1) Removal of sorbate molecules from their liquid to the vapour phase.

(2) Creation of sites for sorption. Sorption took place between the sheets for all those materials which sorbed significantly, as was shown by X-ray measurements. This process can therefore be divided into the following stages:

(a) Additional separation of sheets.

(b) Re-arrangement of cation chains to provide "holes" for sorbate molecules.

(c) Re-arrangement of polyphosphate chains, where necessary to allow process (b). The sum of the above two stages will be endothermic, and probably endentropic.

(3) Insertion of sorbate molecules from the vapour into the sites provided. This process will be exothermic and exentropic.

When a "mixing" mechanism is referred to in the following pages, it is meant that sorbate molecules are arranged in a somewhat random fashion among the cation chains, and that their interactions are essentially with

paraffinic chains, not with highly polar polyphosphate sheets. The energetics of this type of process may be expected to resemble those of a mixing process of two hydrocarbon liquids, rather than that of the sorption of a hydrocarbon on a polar surface.

The subsequent discussion of the thermodynamics of sorption is directed to suggesting mechanisms by which the sorption can occur. Having established these, it is intended to refine the structural ideas flowing from the thermodynamic values in order to account for the various selectivities found in the work described in the previous section. The thermodynamics of the sorption of benzene are discussed separately from those of the paraffins for the sake of clarity.

9.2.2. Sorption of benzene:

The sorption of benzene on the three polyphosphates for which calculations were made gave rise to the thermodynamic values tabulated below. The differential heats and entropies of sorption for the sorbates are shown for each percentage by weight sorbed. The standard state was liquid benzene in each case. Three specimen calculations were carried out for entropies based on Bering and Serpinski's method for deriving thermodynamic values from single isotherms using the Polanyi potential theory (117). This treatment is obviously invalid for the systems investigated. The reasons for this are probably that the intercalated benzene is not in a liquid-like state, and that the structure of the sorbent is strongly affected by the presence of benzene. The calculated values vary in the wrong sense and have completely wrong magnitudes.

TABLES 12-14: Thermodynamic values for benzene sorption

TABLE 12.

On nonyl ammonium polyphosphate.

p/p_0 %60°C	% Sorbed	ΔH kcal (range)	ΔS eu (60°C)
13.5	1.5	-0.8 ± 1.8	
19.0	2.0	-1.3 ± 1.3	
31.5	3.0	-2.3 ± 0.7	
47.0	4.0	-2.5 ± 0.4	"Orthodox" Bering and Serpinski Method
64.5	5.0	-2.4 ± 0.2	$-5.7 \pm 0.6 - 0.7$
79.5	6.0	-1.9 ± 0.1	$-5.1 \pm 0.3 - 0.8$
89.0	7.0	-1.0 ± 0.1	$-2.7 \pm 0.3 - 1.2$

TABLE 13.
On heptyl ammonium polyphosphate

P/p_0 %60°C	% sorbed (by wt.)	ΔH kcal	ΔS eu (30°C)
16.5	1.5	-2.7 ± 1.0	
23.5	2.0	-2.6 ± 0.6	-4.8 ± 1.8
31.6	2.5	-2.9 ± 0.2	-6.4 ± 0.6
41.0	3.0	-3.0 ± 0.2	-7.1 ± 0.6
52.0	3.5	-3.0 ± 0.2	-7.6 ± 0.6
62.0	4.0	-2.8 ± 0.2	-7.3 ± 0.6
71.0	4.5	-2.1 ± 0.2	-5.4 ± 0.6

TABLE 14.
On amyl ammonium polyphosphate

P/p_0 %60°C	% sorbed (by wt.)	ΔH kcal	ΔS eu (60°C)
10.0	0.5	$+0.8 \pm 0.5$	$+7.2 \pm 1.5$
16.4	1.0	-1.9 ± 0.2	-2.1 ± 0.6
25.0	1.5	-2.5 ± 0.2	-4.7 ± 0.6
31.7	2.0	-2.8 ± 0.2	-6.1 ± 0.6
40.0	2.5	-2.8 ± 0.2	-6.5 ± 0.6
48.7	3.0	-2.8 ± 0.2	-6.9 ± 0.6
56.0	3.5	-2.6 ± 0.2	-6.8 ± 0.6
67.0	4.0	-2.5 ± 0.2	-6.6 ± 0.6
76.0	4.5	-2.2 ± 0.2	-5.9 ± 0.6
85.0	5.0	-1.7 ± 0.2	-4.7 ± 0.6
93.0	5.5	-1.2 ± 0.2	-3.5 ± 0.6
97.5	6.0	-0.8 ± 0.2	-2.3 ± 0.6

The entropy decrease on freezing benzene may be calculated from the latent heat and freezing point data given by Timmermans (112) to be about 8 eu. This would be due to a loss of thermal entropy, due mainly to a reduction in rotational and rocking effects, and an elimination of translational effects, and an increase in the order of the molecules in the crystals. The magnitude of the entropies of sorption indicates a similar loss of thermal entropy by the benzene molecules on sorption into a restricted interlamellar environment, and probably a fixing of the orientations of the benzene molecules in the sorbed state.

There is also an exothermal differential heat of sorption from the liquid state of up to 3 kcal/mole. It is suggested that the benzene molecules approach closely edgewise to the polyphosphate plates, where the highly polar environment results in an evolution of heat, partly as the result of dipole/induced dipole interaction.

The reasons for this suggestion are as follows. The structure of the polyphosphates can be divided into two regions, one being near to the polyphosphate sheets, where the environment is highly polar. The other is the region further from the sheets where the environment is exclusively composed of alkyl chains. Sorption in the first region would tend to be similar to sorption on a polar surface, and in the second region it would be analogous to sorption into rubbers. The sorption of hydrocarbons into rubbers usually takes place with small positive heats and with positive entropies. However, the sorption of hydrocarbons into ethyl cellulose occurs with negative heats and entropies. This has been attributed to sorption into pre-existing holes in the polymer (36).

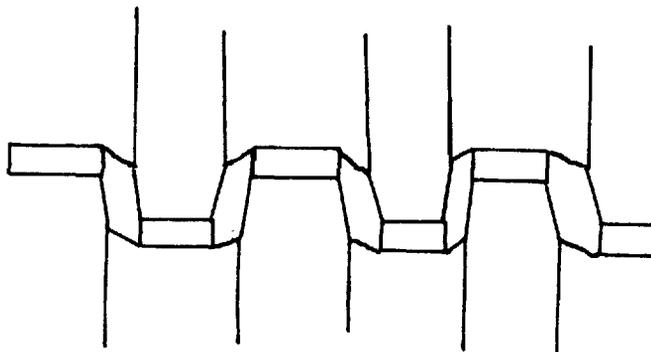
The negative heats and entropies encountered in this work, therefore, require that sorption should occur mainly in the neighbourhood of the polyphosphate sheets, where, by analogy with sorption work on aluminosilicates and other polar sorbents, one would expect negative heats and entropies (Section 3.1). This conclusion is arrived at because even if it were supposed that the ends of the alkyl chains in the sorbent were rigid enough to hold the benzene almost as firmly as it is held in the crystalline state (which would account for the entropy values), it would still not explain the negative heats given on sorption. It should be noted that (as shown in Section 8.2) the interlamellar space is completely filled with alkyl chains if the volume of a CH_2 group is taken as being the same as it is in a liquid paraffin. No holes of any sort would be left between the alkyl chains on this basis.

Since, as will be shown in the subsequent discussion, the neighbourhood of the polyphosphate sheets is accessible, it is reasonable to postulate that this region is a main area in which sorption occurs. It was shown in section 8.2 that the cation heads probably lie in rows in planes above and below the polyphosphate sheets (see Fig. 8). The rows would be parallel to one another, and could exist in one of two arrangements. The first would be for all of the rows on one side of a polyphosphate sheet to be equally separated from one another. The second would be for each row to be separated from its neighbour on one side by a centre to centre distance of about 8.1 \AA , and from the neighbour on the other side by a distance of about 5.6 \AA . The figures given are based on a "flat" configuration for polyphosphate chains lying in a plane. The positions of

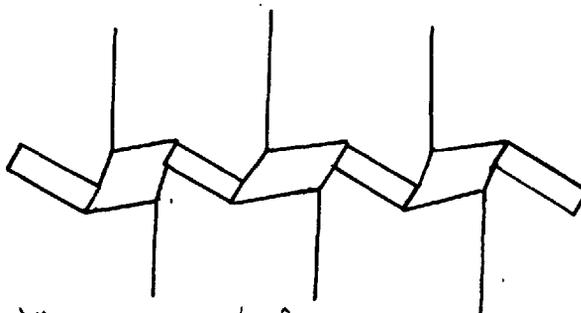
the amine heads with the "three dimensional" chains discussed in section 8.2 seem, from the models which were made of such chains, to be very similar.

The alkyl chains of the cations would presumably be more perpendicular to the sheets in the presence than in the absence of the sorbate in order to allow sorbate to enter between them. It would probably be necessary to reorganise the polyphosphate chains to allow this, as the amine heads of the cations are effectively tetrahedra which are tilted at an angle of about 35° to their alkyl chains. If the chains are to be vertical, therefore, either the amine heads have to hydrogen bond at an angle, or several bonds of the alkyl chain would have to be distorted in order to make the chains vertical some distance away from the sheet. As shown in fig. 22, two possible ways of achieving this would be for all of the polyphosphate chains to be tilted somewhat (a), or for alternate chains to be moved out of the plane of their neighbours, so that they would lie in a new plane (b). As the polyphosphate chains are only crosslinked by hydrogen bonding to common amine heads, this process should not, in itself, be energetically unfavourable.

The degree to which the reorganisation of the polyphosphate chains would affect the separations of the amine heads would depend on which process occurred. The "two plane" arrangement would clearly make the separations much more unequal, while the "tilt" arrangement would have much less effect. Either process of reorganising the polyphosphate chains would either result in a shortening of the repeat distance across the polyphosphate chains (i.e. the c axis), or a stretching of bonds in order to maintain this repeat distance. As this dimension is the

FIG.22

g) "TWO PLANE" ARRANGEMENT
OF POLYPHOSPHATE CHAINS



g') "TILTING" ARRANGEMENT
OF POLYPHOSPHATE CHAINS

critical one in deciding whether sorbate molecules can approach the plates, it may be more reasonable to suppose that the polyphosphate chains move only slightly, and that any movement of alkyl chains to a completely vertical position is accompanied by the slight distortion of a large number of bonds in the polyphosphate chains, the amine heads and in the alkyl chains. The c axis is, in fact, found by X-ray measurements to increase very slightly on sorption (29). With the "two plane" arrangement of polyphosphate chains, the amine heads become unequally separated without any rearrangement of the hydrogen bonding, as must be postulated for the other model. Indeed, if the chains are made vertical without distortion of bonds with the hydrogen bonding arrangement postulated for the unsorbed material, the nitrogen atoms of nearest rows of amine heads would be only about 3.1 Å apart. Since this would probably produce electrostatic repulsion, a reorganisation of hydrogen bonding might occur which would partially counteract the movement of amine heads brought about by the polyphosphate chain rearrangement. The separation of the closest rows of amine heads brought about by this means would still be only 3.9 Å, however, which would presumably also involve unfavourable electrostatic interactions.

It is clear, however, that a small movement towards a "two plane" arrangement of the polyphosphate plates could significantly reinforce any "unequal separation" effect of the amine heads due to hydrogen bonding, while not requiring much distortion of bonds in order to maintain the c axis repeat distance. This process would also allow the alkyl chains to become more vertical. The gaps thus afforded between rows of cations might be

sufficient to allow entrance of sorbate molecules without requiring any further distortion of bonds. In the tilted arrangement the separation of alternate rows of amine heads would be achieved by rearranging the hydrogen bonds. In order to make the alkyl chains sufficiently vertical it would probably be necessary to distort bonds, as well as making use of the tilting of the polyphosphate chains.

Although the foregoing possibilities will be kept in view, the subsequent discussion will be given in terms of the positions of the amine heads with undisturbed polyphosphate sheets, since the real situation is a matter of some doubt. The position chosen for the discussion can be regarded as a rather unfavourable one compared with a "two plane" arrangement of polyphosphate chains, but roughly corresponding with the "tilted" arrangement.

In the flat configuration of polyphosphate chains the longer distance of 8.1 Å between amine heads is sufficient to allow the edgewise approach of a benzene molecule close to the polyphosphate sheets. This conclusion is based on the following molecular dimensions.

Peybold models give a minimum thickness for an alkyl chain of 3.8 Å, and a width of 4.3 Å. The product of these gives a cross-sectional area for an alkyl chain of 16.2 Å². This is less than the cross-sectional area of 18.5 Å² derived from crystallographic data. Pauling (113) gives 2.0 Å as the radius of a methylene group, and Bunn (107) states from X-ray studies that the two lines of carbon atoms in an alkyl chain are displaced vertically from each other by 0.85 Å. These results would give cross-sectional dimensions of 4.0 and 4.85 Å for an alkyl chain. The product of these is 19.4 Å². Owing to the

possibility of zigzagging alkyl chains fitting into one another, the actual cross-sectional area could be less than the value of the product of these distances since, if the chains fit together, this would in effect reduce the 4.85 Å distance.

An X-ray diffraction determination of the structure of benzene was published in 1958 by Cox (114). It is not possible to tell from this what is the length or the width of the benzene, but the sum of length plus width can be calculated to be 10.25 Å. Peybold models give a length of 6.8 Å and a width of 3.1 Å, which gives a sum of 9.9 Å; Courtauld models (on which molecular dimensions used by previous workers have been based) give values of 3.7 and 6.9 Å. The sum of these is 10.6 Å. Both sets of values should thus be corrected, and if the mean values are taken, the width of the benzene molecule appears to be about 3.4 Å. On any of the sets of values referred to it should be easy to accommodate a benzene molecule between rows of alkyl chains by arranging the chains with their long cross-sectional dimension in the direction of the polyphosphate chains, or moving them slightly to one side.

It is possible to calculate the maximum weight of benzene which could be accommodated in the sites suggested by the following method. Benzene molecules would lie end to end in straight lines between the widely separated amine heads. If the length of such lines per unit weight of sorbent is calculated and divided by the length of each benzene molecule, the answer obtained will be the largest conceivable number of benzene molecules which could be accommodated on such sites. The result of this calculation is equivalent to the sorption of

about 15.7% of benzene by weight on amyl ammonium polyphosphate, and a little less on higher homologues. Thus, the maximum observed sorption (about 7% by weight) was equivalent to filling about half of such sites.

So far as reliable information is available, amyl, heptyl and nonyl ammonium polyphosphates all show the same type of variation in $\Delta\bar{H}$ and $\Delta\bar{S}$, the amount of benzene sorbed. The behaviour of all three will therefore be discussed together.

For small amounts sorbed the entropy change appears to be positive, though the errors involved in the first part of the graphs are large. The entropy change rapidly becomes negative as more benzene is sorbed, and reaches a minimum value of about -7 eu at about $3\frac{1}{2}\%$ sorption, after which it becomes less negative. Zero entropy change occurs at 100% RVP, where one is in effect condensing liquid benzene on to the sorbent. The same type of variation appears to occur for the heats.

The variation may be interpreted as follows. In the case of the entropies, the initial positive value may be the result of placing a few benzene molecules on a large number of available sites, which would lead to a positive configurational entropy. In addition to this the possibility must be taken into account that two sorption processes may occur simultaneously. One of these may involve a mixing process of benzene molecules with hydrocarbon chains. The driving force for this would be the positive configurational entropy resulting from the formation of a weak "solution" of benzene in the paraffinic material. If these effects resulted in entropy increases equal to or greater than the loss of

thermal entropy involved in the first process, a net zero or positive entropy would result. The subsequent increase in the negative entropy would result from the decline in the importance of the configurational contribution which would result from increased filling of the available sites in the sorbent.

The subsequent increase to zero entropy change on sorption at 100% RVP may result from two processes. One of these corresponds more and more as the relative vapour pressure approaches saturation, to the transference of benzene from its liquid to thickening and eventually liquid like adsorbed films of benzene on external surfaces of the polyphosphate. This process would become dominant over all others at saturated vapour pressure. However, it is possible that a second process might contribute to the increase in entropy. As the available sorption sites are increasingly filled, a squeezing effect close to the sheets may cause some benzene molecules to find an equilibrium position further away from the plates. These would presumably have more thermal entropy and be less ordered than those close to the plates.

The heats of information may be explained as follows.

- (1) One row of sites may be created by the movement of each row of amine heads to an "unequally spaced" position (see fig. 8). This movement would involve a similar displacement of the corresponding row of amine heads on the opposite side of the polyphosphate sheet in order to obtain electrical neutrality of both PP chains, involved in creating a row of sorption sites there also. (See section 8.2).
- (2) Although the "unequally spaced" position would provide

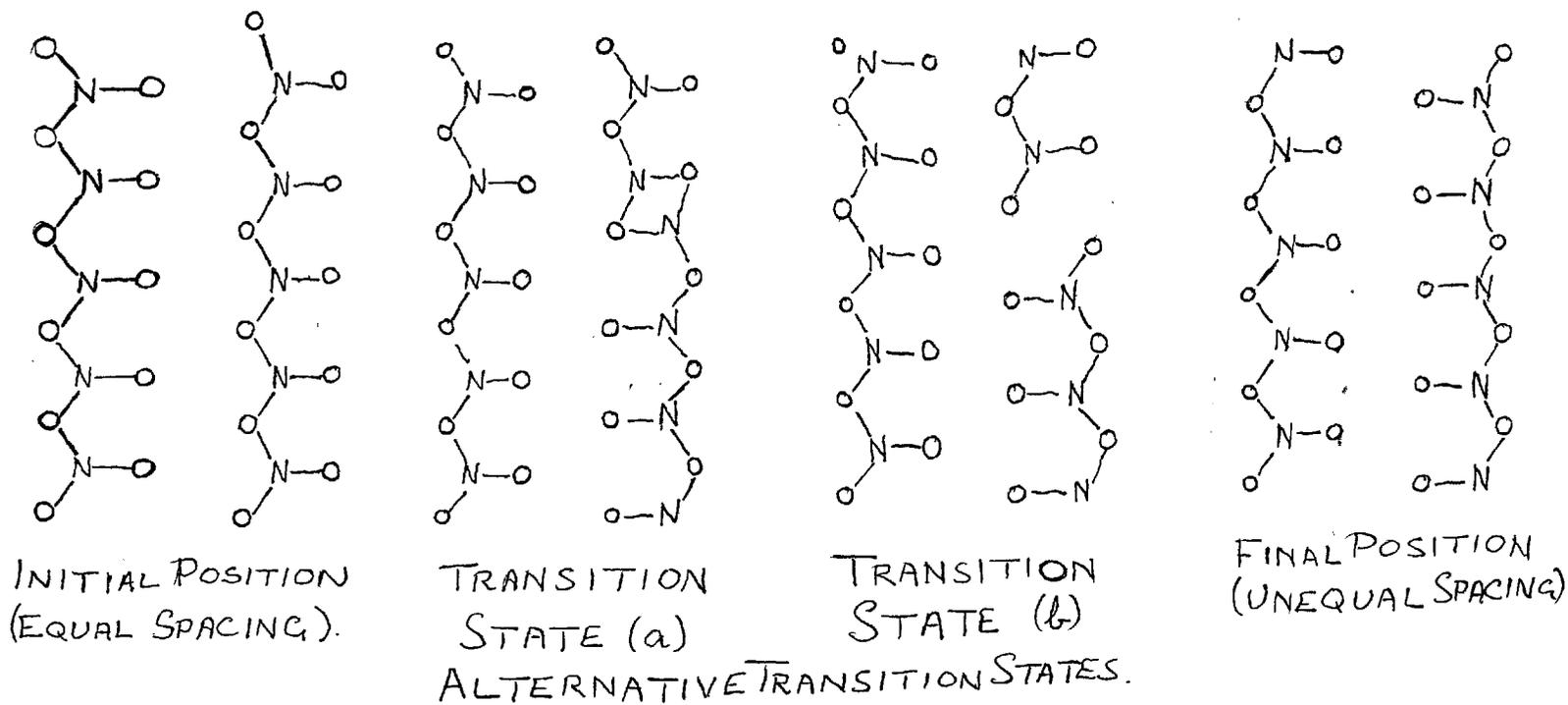
a situation for hydrogen bonding and electrostatic forces between the amine heads and the polyphosphate sheets nearly as satisfactory as that obtaining in the "equally spaced" arrangement, the transition state between the two arrangements would involve the disorganisation of hydrogen bonding and electrostatic attractions, as shown in Fig. 23. Positions (a) and (b) of the transition state would probably occur on opposite sides of the polyphosphate sheet in order to obtain electrical neutrality.

(3) Since the first few benzene molecules sorbed would have to initiate the displacement of such rows of amine heads, it is probable that their sorption would involve a greater expenditure of energy in this way than would the sorption of subsequent molecules.

Movement of polyphosphate chains to an arrangement in two planes may contribute to creating openings for sorption, between rows of amine heads, as shown earlier. It is, however, difficult to see how a significant contribution to the positive heats of sorption for the first benzene molecules taken up in each row of sites could be expected from this phenomenon.

The evolution of heat on further sorption can be explained on the basis of interaction of the benzene molecules with the sheet dipoles. The final stage, where reduction in the heat evolution occurs as P/p_0 approaches unity is associated with the tendency in this region for the benzene to be increasingly in liquid-like externally sorbed films. The possibility, previously referred to in the discussion of entropies, that the occupation of a proportion of the sites may squeeze the vacant ones and cause the incoming benzene to approach the sheets less

FIG. 23. SUGGESTED MOVEMENT OF AMINE HEADS DURING THE SORPTION PROCESS.
 OXYGEN ATOMS OF POLYPHOSPHATE CHAINS SHOWN THUS, O
 NITROGEN ATOMS OF AMINE HEADS SHOWN THUS, N



closely might also account for a proportion of the decline in heat emission.

9.2.3. Sorption of paraffins

It is proposed in this section to discuss the values of $\Delta\bar{H}$ and $\Delta\bar{S}$ for the sorption of paraffins. Reliable values for the thermodynamic functions were available only for heptyl ammonium polyphosphate. Less reliable information for the nonyl and amyl compounds will be used for comparison with the values for heptyl ammonium polyphosphate.

The changes in thermodynamic properties of cyclohexane on sorption into heptyl ammonium polyphosphate are given below.

TABLE 15.

Thermodynamics of sorption of cyclohexane/polyphosphate
into heptyl ammonium \rightarrow

% sorbed by wt.	$\Delta\bar{H}$ (k cal)	$\Delta\bar{S}$ (30°C) eu
0.5	$-0.35 \pm .4$	$+3.7 \pm 1.2$
1.0	$-1.0 \pm .2$	0 ± 0.6
1.5	$-0.8 \pm .15$	-0.4 ± 0.5
2.0	$-0.7 \pm .1$	-0.75 ± 0.3
2.5	$-0.55 \pm .1$	$-0.75(4) \pm .3$
3.0	$-0.50 \pm .1$	$-0.9(2) \pm .3$
3.5	$-0.35 \pm .1$	$-0.75(6) \pm .3$

The behaviour revealed here is very similar to that shown by benzene (section 9.2.2). The explanation of the sorption would be similar in both cases, within the range of relative vapour pressures investigated.

Calculations of values of $\Delta\bar{H}$ and $\Delta\bar{S}$ for sorption of iso-octane on heptyl ammonium polyphosphate gave the following results.

TABLE 16.

Thermodynamics of sorption of iso octane into heptyl ammonium polyphosphate

% sorbed by wt.	$\Delta\bar{H}$ k cal	$\Delta\bar{S}$ (30°C) eu
.5	-2.2 \pm 1	-2.4 \pm .3
.75	-2.3 \pm .5	-4.1 \pm 1.5
1.0	-2.6 \pm .2	-5.6 \pm .6
1.25	-2.7 \pm .1	-6.7 \pm .3
1.5	-2.3 \pm .1	-5.9 \pm .3
1.75	-2.2 \pm .1	-6.0 \pm .3
2.0	-1.8 \pm .1	-4.7 \pm .3
2.25	-1.2 \pm .1	-3.0 \pm .3
2.4	-0.7 \pm .1	-1.55 \pm .3

The picture for iso-octane sorption is similar to that for cyclohexane. The major differences from cyclohexane are the more negative values of heats and entropies. There may be more interaction with the plates in the case of iso octane, as discussed later, which would account for the differences in heats. In the liquid state, iso octane would have intramolecular

free rotations, which cyclohexane would lack. Loss of some of this rotational freedom on sorption into a "cage" of alkyl chains may account for the relatively higher entropy loss of iso-octane on sorption. The entropy losses on freezing the sorbates are 13 eu per mole for iso-octane, and 2.25 eu per mole for cyclohexane. These values would lead one to expect a greater entropy loss for iso-octane on sorption.

The following values have been calculated for n-heptane sorption on heptyl ammonium polyphosphate.

TABLE 17.

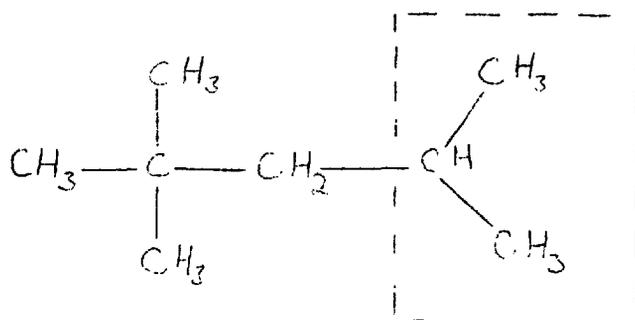
Thermodynamics of n-heptane sorption into heptyl ammonium polyphosphate.

% sorbed by wt.	ΔH kcal	ΔS eu
0.5	-2.7 ± 1	-4.2 ± 3.0
1.0	-1.6 ± 0.5	-2.7 ± 1.5
1.5	-1.5 ± 0.2	-3.1 ± 0.6
2.0	-1.2 ± 0.1	-2.9 ± 0.3
2.5	-1.0 ± 0.1	-3.1 ± 0.3

It would be possible, by assuming that the maximum experimental error occurred for the first values quoted, to obtain a picture for the sorption of this material which would be similar to that found with the other sorbates. However, as the n-heptane molecule differs from the other three hydrocarbon molecules used in that it is flexible and long, it may not be justifiable to assume that its sorption is identical. The first few n-heptane molecules

sorbed may, for instance, lie flat along the polyphosphate plates, thus interacting throughout their length. This would provide a large evolution of heat and a high degree of order in the sorbed state.

The portion of the other paraffin molecules which can approach closely to the sheet has been estimated with models. Iso-octane can be considered as a straight chain three carbon atoms long which is attached to a bulky group.



It seems that the small chain could approach closely to a sheet with the remainder of the molecule lying in an environment of alkyl chains away from the sheet.

Cyclohexane can exist in chair, half boat, or boat forms. In the last two forms, two CH₂ groups could approach closely to the plate. In the boat form only one could do so, however. The boat form is more stable in the free state by about 5.5 kcal per mole, as estimated by Johnson et al (115). Whether the additional interaction energy which might be provided by another form would be sufficient to cause inter-conversion is unknown.

In view of the low proportion of the cyclohexane and iso-octane molecules which can interact with the sheets, and the high proportion of the n-heptane molecule which can do so, it seems advisable to leave the interpretation of the thermodynamic evidence concerning n-heptane sorption on heptyl ammonium polyphosphate open.

In comparing the thermodynamic aspects of sorption in heptyl and nonyl ammonium polyphosphates, one would expect to find a greater contribution from "mixing" phenomena in the latter case, since its alkyl chains are longer. In fact, the heat and entropy changes of the sorbates on sorption are more positive in the case of nonyl- than of heptyl-ammonium polyphosphate. The quantities derived using nonyl ammonium polyphosphate as sorbent are so uncertain, however, as to make any further interpretation highly speculative. Accurate calculations from the data have been made only for cyclohexane, rough values only having been estimated for iso-octane and n-heptane.

The results for sorption of cyclohexane on amyl ammonium polyphosphate seemed to justify a calculation of heat and entropy changes of the sorbate. (see Table 18).

The apparent trends revealed in the values may, as inspection of the figures for estimated errors will indicate, be misleading as the thermodynamic evidence is not certain. The entropy change on freezing for cyclohexane is, as noted earlier, about 2.25 eu per mole; since the entropy of sorption could hardly be greater than that, the early values of heat and entropy changes should be reduced within the experimental error in order to give more realistic values for entropy changes.

TABLE 18

Thermodynamics of cyclohexane sorption on amyl ammonium polyphosphate

% sorbed by wt.	ΔH kcal	ΔS 30°C
0.40	-1.6 \pm 1.5	-2.6 \pm 5
0.45	-1.4 \pm 0.9	-2.5 \pm 3.0
0.50	-0.9 \pm 0.7	-1.1 \pm 2.3
0.55	-0.7 \pm 0.6	-0.7 \pm 2
0.60	-0.4 \pm 0.55	0. \pm 1.8
0.65	-0.35 \pm 0.5	+0.3 \pm 1.7
0.70	-0.15 \pm 0.5	+0.6 \pm 1.7
0.75	0 \pm 0.45	+1.0 \pm 1.5
0.80	0 \pm 0.45	+0.6 \pm 1.5
0.85	+0.1 \pm 0.4	+0.9 \pm 1.3
0.90	+0.1 \pm 0.4	+0.8 \pm 1.3

It would be reasonable in this case, in view of the smallness of the amounts sorbed, to expect sorption on the external surfaces of the particles to be an important contributor to the total result. However, the evidence on which to base an explanation of sorption in this system is lacking.

9.2.4. Thermodynamic properties of the sorbents

Some partial molal thermodynamic properties of the sorbents in the sorbent-sorbate mixture are given for amyl and heptyl ammonium polyphosphates in Appendix II.

The calculations are subject to considerable error for high amounts sorbed, but the general trends seem to be accurately represented.

These results are shown in graphical form in figs. 24 - 26. For heptyl ammonium polyphosphate, the results with benzene cover a smaller range of relative vapour pressures than do those for the same sorbent with cyclohexane, and of amyl ammonium polyphosphate with benzene.

All of the isotherms show initial increases from zero in both heats and entropies and the more extended ones then show sharp declines to large negative values of both quantities.

As a direct interpretation of these results is not possible, since the values of thermodynamic functions for the sorbent are a property of both sorbent and sorbate, the results will be compared with those obtained previously by Barrer and Reucroft (116). These workers performed similar calculations for sorption of perfluoro-methane, -ethane, and -propane and sulphur hexafluoride on faujasite. In each case only the first part of the vapour pressure range was covered. Owing to the lack of data for the saturated vapour pressures of the sorbates at the temperatures studied it is only possible to form an estimate, but it seems probable that about one third of the pressure range was covered in each case. Typical graphs obtained by them are shown in a thesis presented by Reucroft (116).

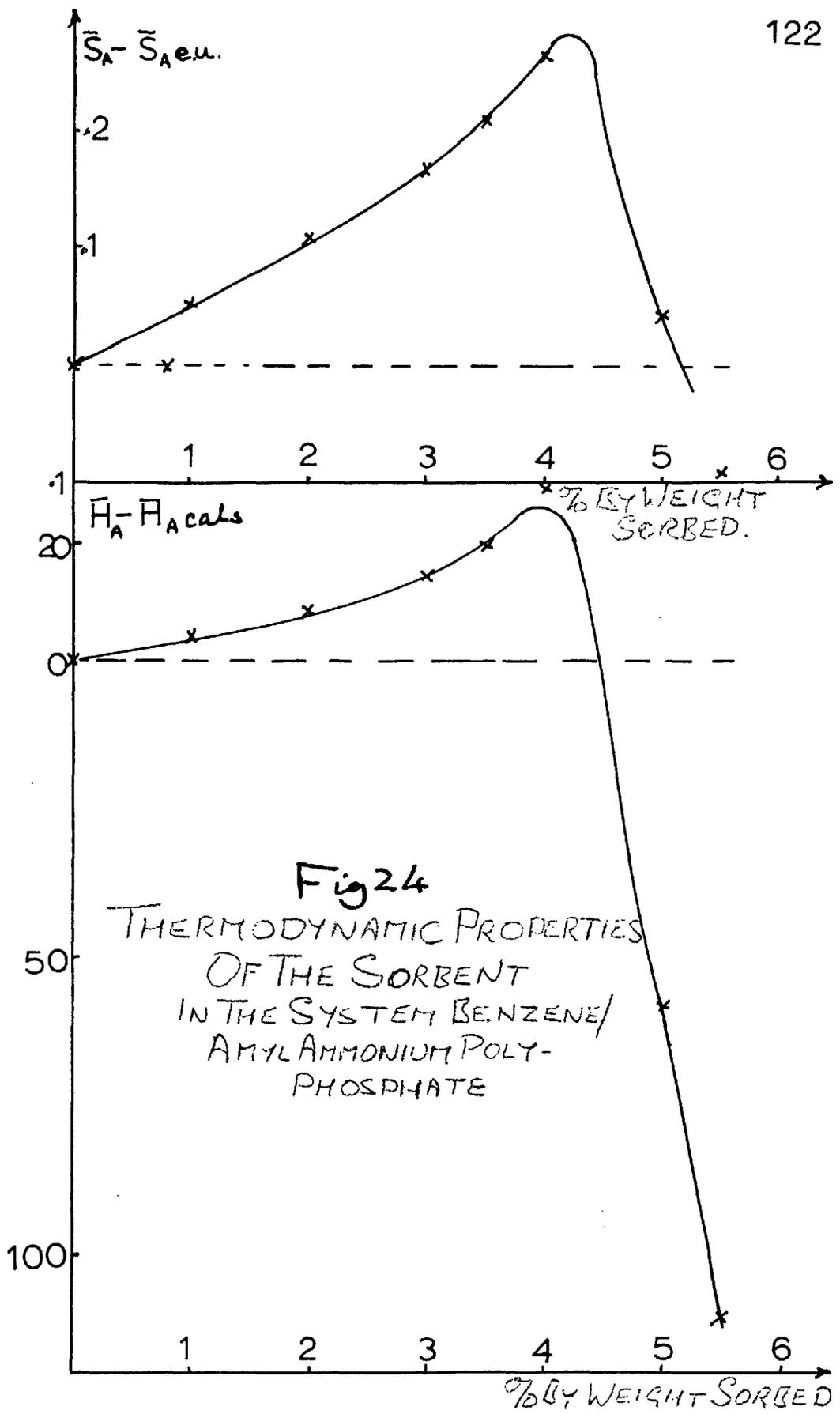


Fig 24
THERMODYNAMIC PROPERTIES
OF THE SORBENT
IN THE SYSTEM BENZENE/
AMYL AMMONIUM POLY-
PHOSPHATE

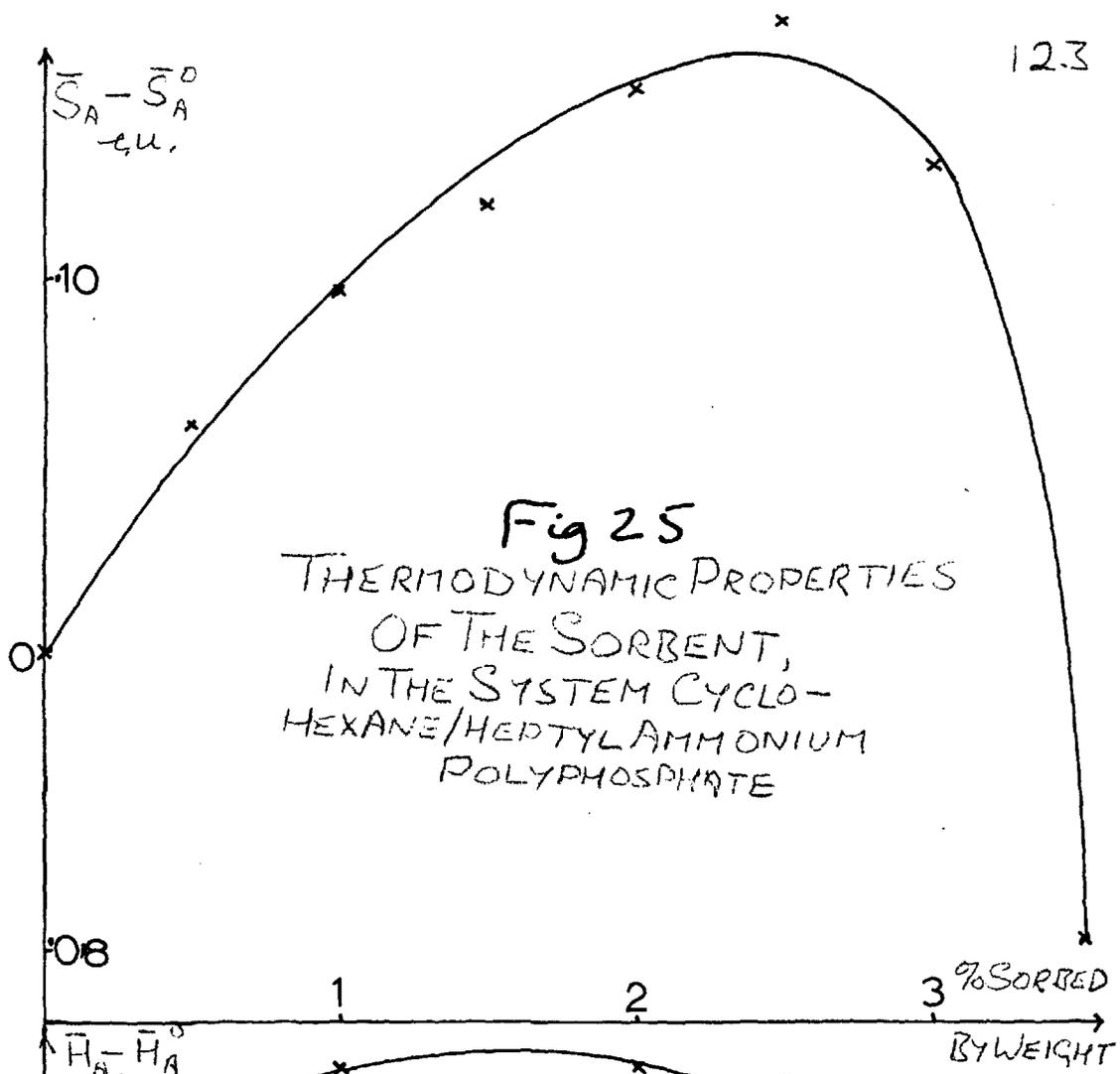


Fig 25
THERMODYNAMIC PROPERTIES
OF THE SORBENT,
IN THE SYSTEM CYCLO-
HEXANE/HEPTYLAMMONIUM
POLYPHOSPHATE

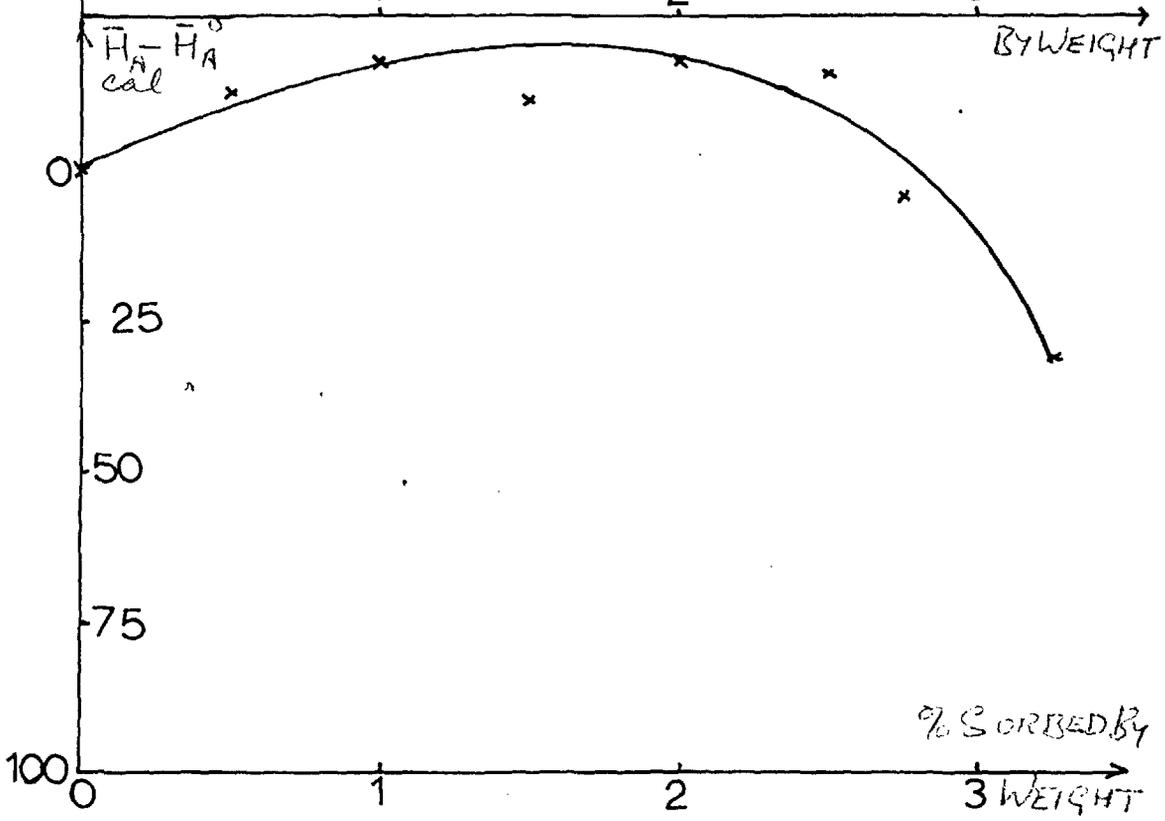
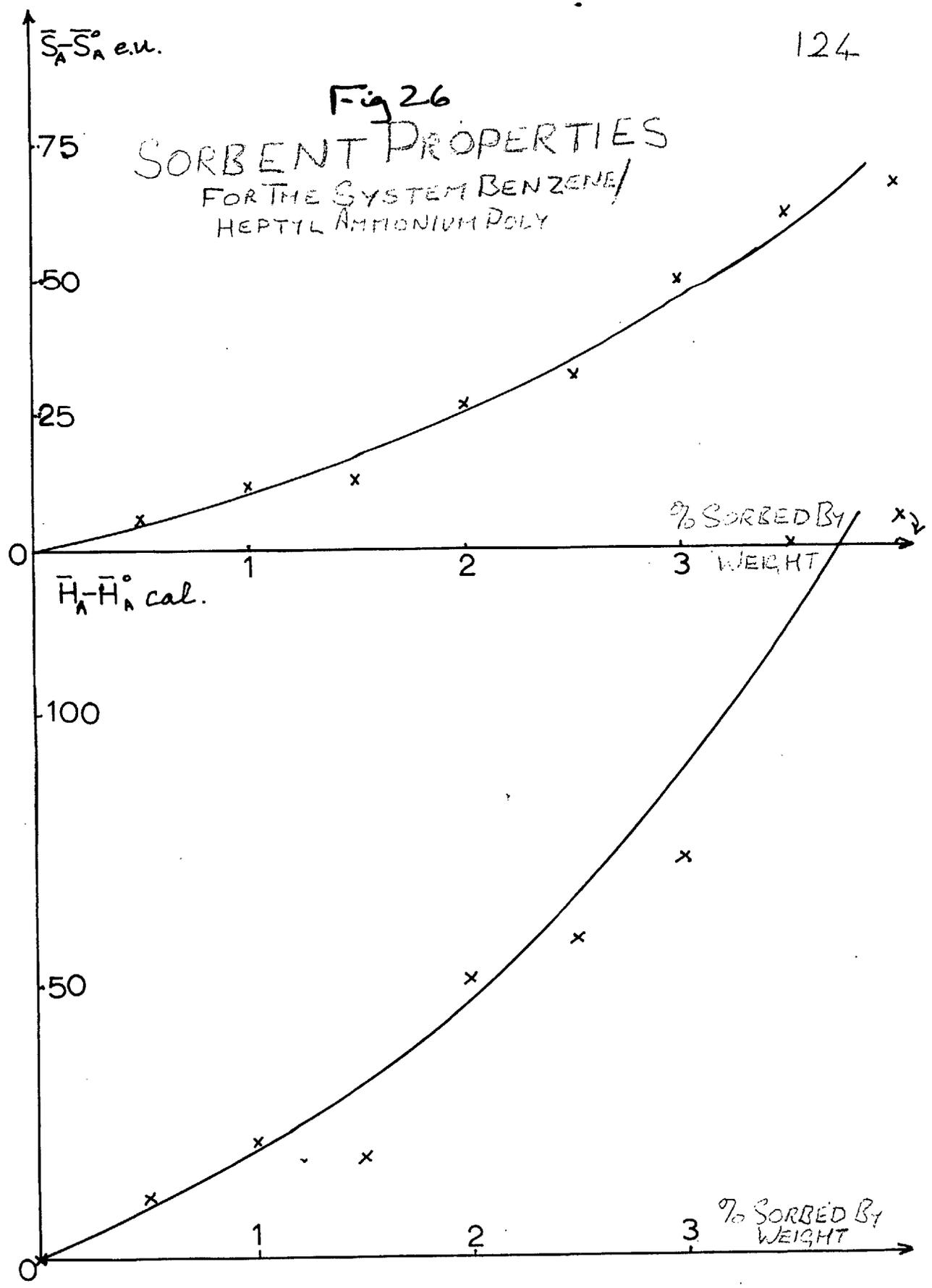


Fig 26

SORBENT PROPERTIES FOR THE SYSTEM BENZENE/ HEPTYL AMMONIUM POLY



Their graphs are very similar to those obtained in the present work, but as they lack values for the higher relative vapour pressure it is not possible to tell if the steep descent of the graphs to negative values, which was shown in this work, occurred in their systems also. It seems unlikely that the structure of the sodium faujasite investigated could have been significantly altered by sorption, whereas on any conceivable hypothesis the structure of the polyphosphates must have been affected to some extent. It appears, therefore, that the similarity of the graphs is coincidental, and no interpretation of them will be attempted.

Summary

(a) Thermodynamic quantities for the sorbates:

Every system for which reliable values are available shows negative differential heats and entropies of sorption for the sorbates over most of the range which has been studied. Departures from this behaviour seem to occur only when the amounts sorbed are very small; explanations for both the positive heats and positive entropies sometimes found at low coverage have been suggested.

The negative partial heats and entropies found over most of the range have been explained in terms of interactions between the sorbate molecules and highly polar polyphosphate sheets and amine heads. It has been shown from structural considerations that such interactions are possible, and that they would give rise to the effects found.

The errors involved in the calculated thermodynamic quantities make detailed explanations of the

results difficult. The general picture appears reasonably clear, however.

(b) Thermodynamic quantities for the sorbents:

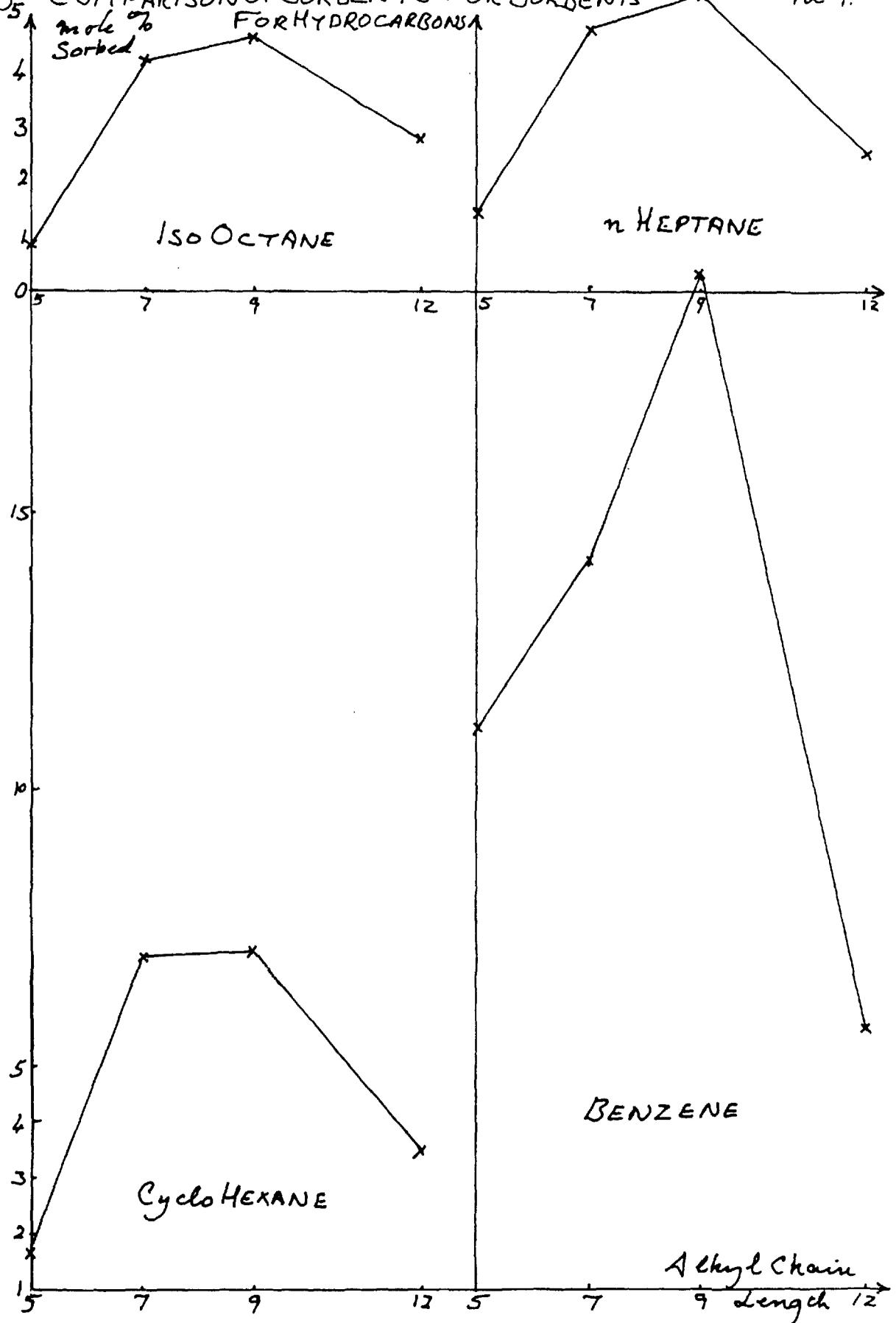
From a comparison of the results obtained with those of Barrer and Reucroft (116) it was decided that it was not possible to interpret them.

9.3. Comparison of alkyl ammonium polyphosphates as sorbents for hydrocarbons

Graphs are given in fig. 27 for the primary alkyl ammonium series showing the variation in the uptake of various sorbates with the alkyl chain length of the sorbent. In each case the uptake of the sorbate refers to 70% relative vapour pressure and 30°C. However, because the sorption isotherms were nearly linear the graphs also reflect the relative uptakes of the sorbates at lower pressures, while from incomplete data for sorption at 60°C it seems probable that the graphs would not be greatly different at that temperature. The uptake of sorbates is given in terms of moles sorbed per mole of sorbent.

In this section the data on selectivities shown in the graphs will be used to support certain ideas about the structures of the sorbents in the presence of sorbate. Before considering other explanations for the data, the following facts should be noted concerning the dodecyl ammonium compound. Firstly, it was the only member of the primary alkyl ammonium polyphosphate series with an even number of carbon atoms in the chains. This would not be expected to affect its sorptive properties

Fig 27. COMPARISON OF SORBENTS FOR HYDROCARBONS 127.



significantly as the total chain length is so long, but some minor effect might well occur due to packing considerations. Secondly, it was the only sorbent in the series prepared with ethanol in the exchange solution. It will be shown in section 9.4 that sorption of ethanol at 60°C can affect the sorptive properties of polyphosphates. However, this influence was found to be small with dodecyl ammonium polyphosphate at 60°C and would probably be smaller at the temperature of preparation (about 20°C).

It seems, therefore, that an explanation of the sorptive capacities of dodecyl ammonium polyphosphate must be based on its structure, rather than on its mode of preparation. Despite the thermodynamic evidence discussed in sections 9.2.2, 9.2.3, which suggests that the predominant mode of sorption is at sites next to the polyphosphate sheets, it would be surprising if no sorption occurred by "mixing" sorbates with the alkyl chains of sorbents. This type of sorption would be greatest when the cohesive energy densities of sorbate and sorbent were equal. Suppose, therefore, the cohesive energy density of the polyphosphate is altered by introducing different alkylammonium ions. Then the uptake of a given sorbate should go through a maximum at that chain length of the alkylammonium ion for which the cohesive energy density of the sorbate equals that of its environment in the polyphosphate.

This may well account for part of the observed effects, since the graphs of fig. 27 show maxima. The importance of this contribution to sorption is unknown, but is almost certainly small, because $\Delta\bar{H}$ and $\Delta\bar{S}$ are negative. In order to account for the chain length dependence of sorption, and the similar sorptive behaviour with three paraffins of very different structure, the

following model for the sorbed state may be postulated. This model can at least partly explain the phenomena encountered, and be consistent with the thermodynamic behaviour which was found though it is not possible to offer any direct proof of the structure suggested. The structure is based on the following considerations.

1. The paraffins sorbed were of different shapes.
2. All of the paraffins could have been sorbed in a "compact" configuration, but two (cyclohexane and iso-octane) cannot exist in an extended state. In some compact states, all three paraffin molecules have similar cross-sectional dimensions and the volumes of the three molecules are approximately equal.
3. Although the thermodynamic values must be treated with caution, they suggest that the mechanism of sorption would be similar for all three paraffins in heptyl ammonium polyphosphate. This is the only good sorbent for paraffins for which reasonably reliable thermodynamic values are available (see section 9.2.3). This thermodynamic evidence indicated that sorption occurred in the neighbourhood of the polyphosphate plates, as discussed in that section.

A possible model satisfying the above requirements is as follows. Sorption would occur for each sorbate molecule in sites which could be created by rearrangement of the alkyl chains of the sorbent. Such sites would allow a sorbate molecule of limited cross section or volume to be included close to the polyphosphate sheet. Either such sites would not exist or their cross sections would be very small in the case of amyl ammonium polyphosphate, but they would be much larger for heptyl ammonium polyphosphate and larger still for nonyl ammonium polyphosphate. The sites would be so large that none of the molecules could

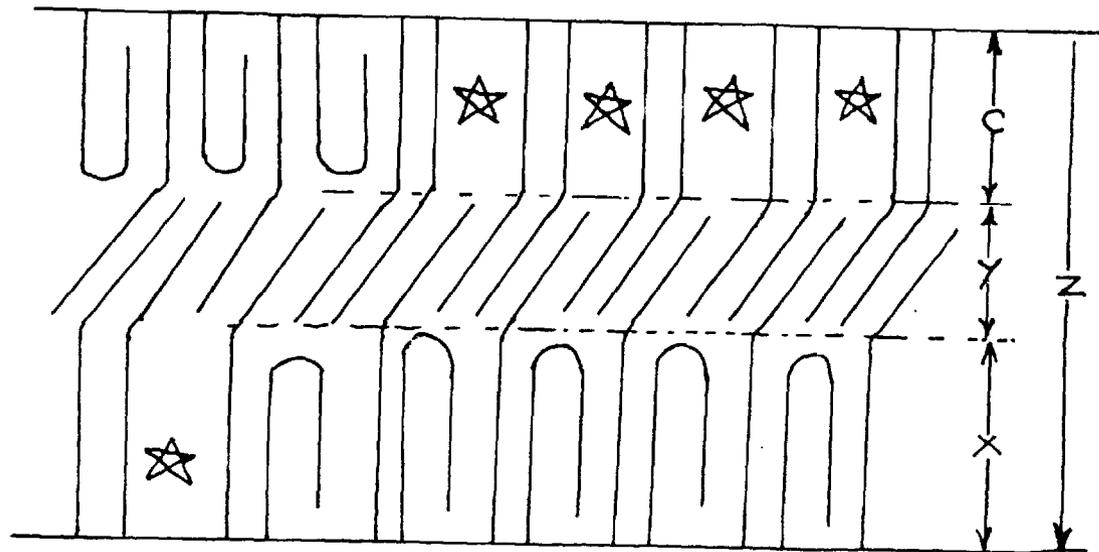
fill them completely in the case of dodecyl ammonium polyphosphate.

Since the alkyl chains are closely packed in the polyphosphate free of sorbate, (see section 8.2), the energy required to form the sites would include a large term for the loss of interaction energy on moving the alkyl chains apart to create "holes".

On filling such a hole with a paraffinic sorbate molecule energy would be released by interactions between the sorbate molecule and the polyphosphate sheet, as well as with the alkyl chains. If the molecule completely filled the cavity, such a release of energy would probably be greater than that required to create the site, but if the cavity was not filled completely, the reverse might be the case. In such circumstances, little sorption would occur. The plausibility of this model may be judged by whether it is sterically possible; and by whether the dimensions of the sites provided are suitable for inclusion of sorbate molecules in each of the sorbents. One possible structure of the polyphosphates containing sorbate, based on the foregoing principles, is shown in fig. 28. Although its steric requirements can apparently be satisfied (as judged from measurements on Peybold models), it should not be taken as giving more than a qualitative picture of the actual structure. In a situation as complex as that considered here it is not feasible to consider every modification. The chosen structure is based on sites of limited cross-sectional area. Structures with sites of limited volume would also explain the selectivities, but are not considered here.

The bent alkyl chains shown in the diagram occupy sites the dimensions of which can be estimated. The width

FIG. 28.



POSSIBLE STRUCTURE OF POLYPHOSPHATES
IN THE SORBED STATE, SHOWING SITES FOR
SORBATE MOLECULES.

X = HEIGHT OF BENT ALKYL CHAINS.

C = " " " " CAVITIES (SORPTION SITES).

Y = VERTICAL COMPONENT OF PART OF ALKYL CHAINS

Z = X + Y + C = PARAFFIN LAYER THICKNESS.

available to each is the longer of the separation distances between rows of amine heads, which is probably at least 8.1 Å (section 8.2). The thickness will be the repeat distance between one amine head and its neighbour in the same row, that is, at least 4.5 Å. The bunched heptyl chain has dimensions of 6.3, 8.2 and 4.7 Å as determined from Peybold models, the 6.3 Å dimension being vertical to the plates. It can thus be seen that the chain could fit into the space suggested if the available height were 6.3 Å. It is difficult to estimate this height independently, as the chains bounding the height would be more easily pushed away than those forming the other two boundaries.

The heights of the cavities have been estimated as follows. The structure of the polyphosphate may be regarded as a "sandwich" of paraffinic material between polyphosphate sheets. The thickness of the polyphosphate sheets may be estimated by plotting the total sheet separation in primary alkyl ammonium polyphosphates against the number of carbon atoms in their alkyl chains. The extrapolated value for the sheet separation when this number of carbons is zero can be considered as the thickness of the ammonium polyphosphate sheets with no alkyl material between them. By subtracting this value from the total sheet separation for any polyphosphate, an estimate of the thickness of the paraffinic layer in it may be made. Any expansion due to sorption should be added to this thickness. By subtracting the vertical component of the length of the extended alkyl chains from this thickness, the height of the cavities may be determined.

A specimen calculation is given as follows, for heptyl ammonium polyphosphate:

Thickness of the outgassed paraffin layer $\approx 13 \text{ \AA}$
 + Swelling under sorbate ($\approx 1 \text{ \AA}$) $\approx 14 \text{ \AA}$

Height of bent alkyl chains (as estimated
 from Peybold models) $\approx 6 \text{ \AA}$
 (= X in Fig. 28)

Actual length of heptyl chains (as $\approx 10.5 \text{ \AA}$
 estimated from Peybold models)

\therefore Sloping length of chains = $10.5 - 6 \text{ \AA} = 4.5 \text{ \AA}$

If the sloping parts of the chains are assumed completely to fill the space available to them they will lie at an angle of 28° because then the cross-sectional area of the chains will equal the area of the plates multiplied by $\cos \theta$, where θ is the angle of the chains to the plates.

\therefore Vertical projection of sloped portion $\approx 4 \text{ \AA}$
 (= Y in Fig. 28)

\therefore Height of sorption site (C) $\approx 14 \text{ \AA} - X - Y = \underline{4 \text{ \AA}}$

If some of the sorption sites are empty the chains next to them will presumably not be held vertical, and the dimensions measured from the models are only approximate, so there is considerable uncertainty in the estimate of the heights. The sorption sites produced could have infinite length as channels might be formed running through the crystals, but their cross section would be only about $4 \text{ \AA} \times 4 \text{ \AA}$ as the height is about 4 \AA and the gaps between the alkyl chains are about 4 \AA (section 8) on the above reckoning. This distance would vary as the polyphosphate swelled. The cyclohexane molecule in the chair form is about 4.7 \AA thick and about 7 \AA long; it would therefore fit into such a site only with considerable distortion. The same conclusion applies to the boat form. Such sorption was found to occur quite readily.

The height of a bent alkyl chain does not increase so quickly as its chain length whereas the thickness of an alkyl layer increases more rapidly. Thus the height of the cavities alters markedly with the alkyl chain length of the polyphosphate. One would not expect the small cavities which could occur in amyl ammonium polyphosphate to allow such copious sorption. This was found to be the case. Sorption would probably be easier into nonyl ammonium polyphosphate, which would have larger cavities than heptyl ammonium polyphosphate.

These cavities in dodecyl ammonium polyphosphate could easily have heights greater than 9 \AA . The greatest extended length of the n-heptane molecule (the longest one used) is about $8-9 \text{ \AA}$. This would suggest, if the model gives a valid picture, that the cavities in this material would not have been filled by the sorbates used, and thus the energetics of site formation would probably have been unfavourable. This may be the reason why sorption did not occur so freely as in the heptylammonium polyphosphate. Possibly alkanes of greater molecular size might be sorbed more copiously if the above hypothesis is correct. It has been found for instance that dodecyl ammonium polyphosphate will sorb dodecyl alcohol more than heptanol (29). Since it is not a good sorbent for benzene or the aliphatics used, it seems possible that dodecyl ammonium polyphosphate is in a particularly stable energetic state, perhaps due to it being in a "self sorbed" condition, some of its chains being bent back to their sheets and interacting with them, thus blocking sorption.

Data to prove that the foregoing explanation of selectivity is correct are lacking, but the explanation seems to have some justification.

9.4. Other sorption studies on primary ammonium polyphosphates

The sorption of ethyl alcohol, amyl alcohol, nitromethane, water and butyric acid was studied on a variety of primary ammonium polyphosphates. Except with the system heptyl APP/amyl alcohol, all of the isotherms obtained were linear or of type III in Brunauer's classification. Each of the sorbates will be considered separately in the following discussion.

The sorption of ethanol:

Sorption of ethanol was carried out on anilinium and amyl, heptyl and dodecyl ammonium polyphosphates. Their behaviour is described separately.

(a) Anilinium polyphosphate: With anilinium polyphosphate three isotherms were measured at 60°C. One of these was obtained on an entirely fresh sample, and two on a sample which had previously been used for benzene sorption only. Hysteresis was found for the only isotherm for which desorption was attempted. The shape of the isotherms was the same in each case, but the amounts sorbed at any given vapour pressure varied markedly. The chart below shows the percentage of ethanol sorbed by weight at each of three relative vapour pressures. The graphs are shown in Figs. 29 - 31.

%RVP	% by weight sorbed at 60°C		
	Fresh sample Isotherm (A)	Sample previously exposed to C ₆ H ₆ 1st Isotherm (B)	Repeat Isotherm (C)
30	0.85	1.0	2.3
60	1.9	2.35	6.0
75	2.8	4.15	9.0

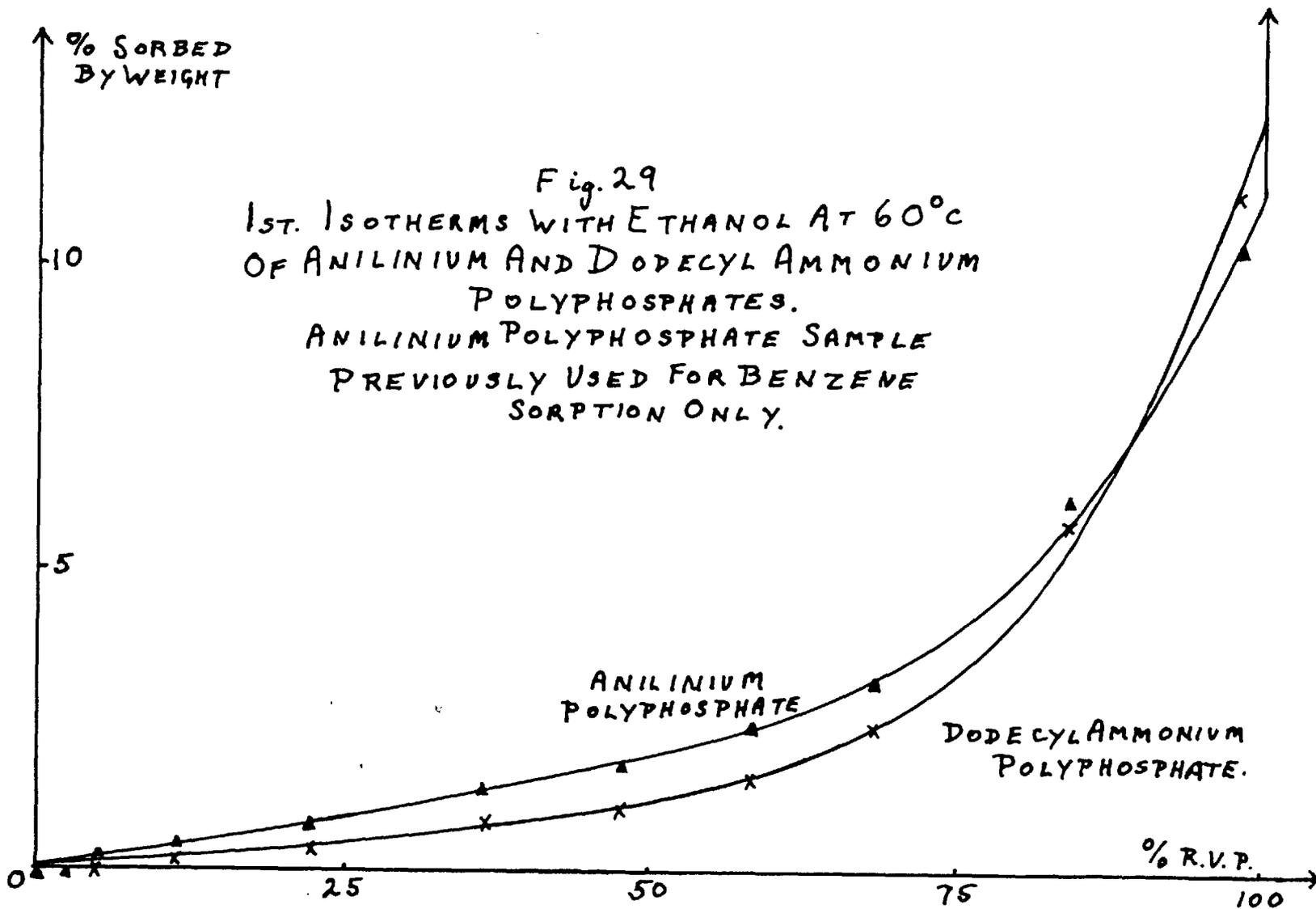
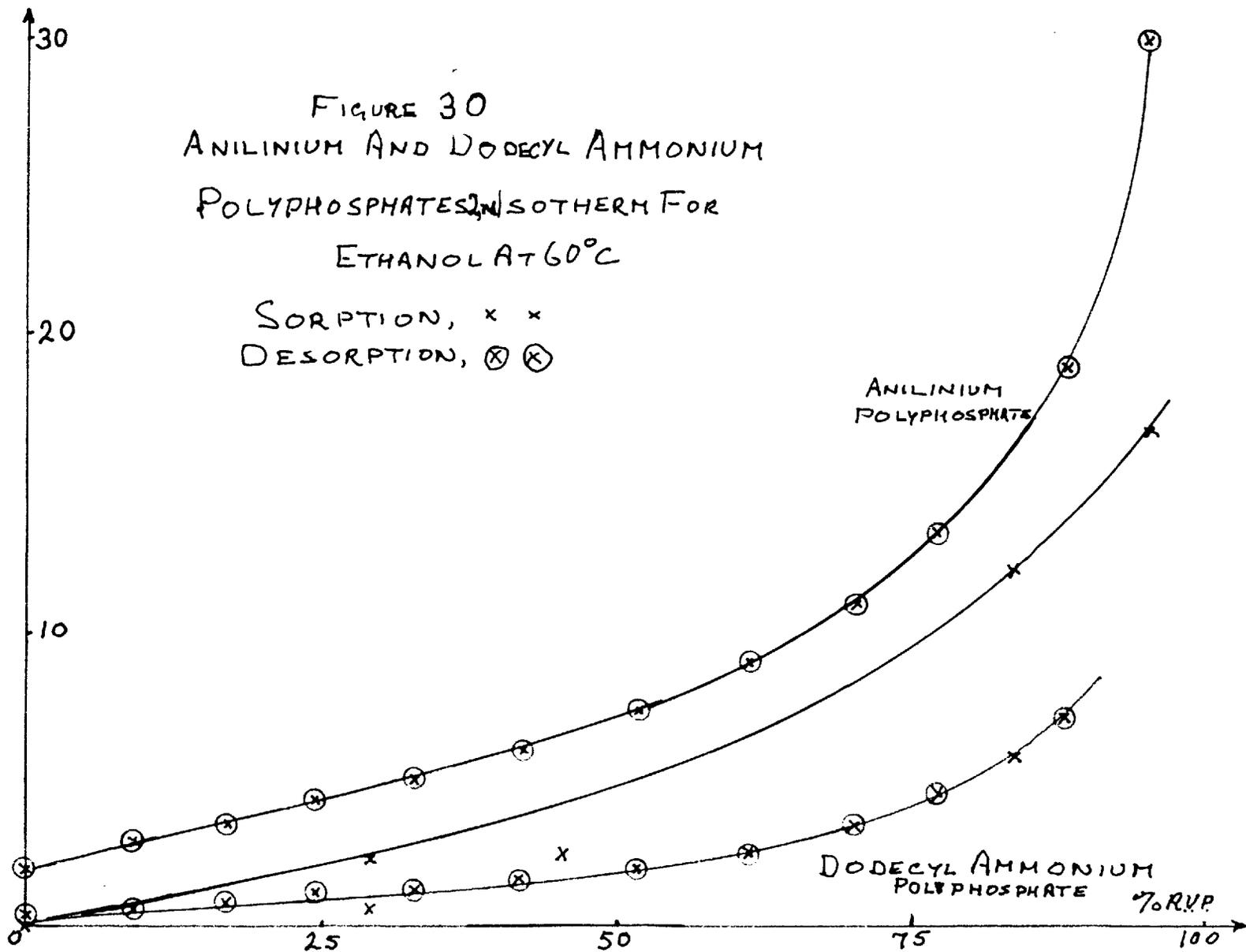
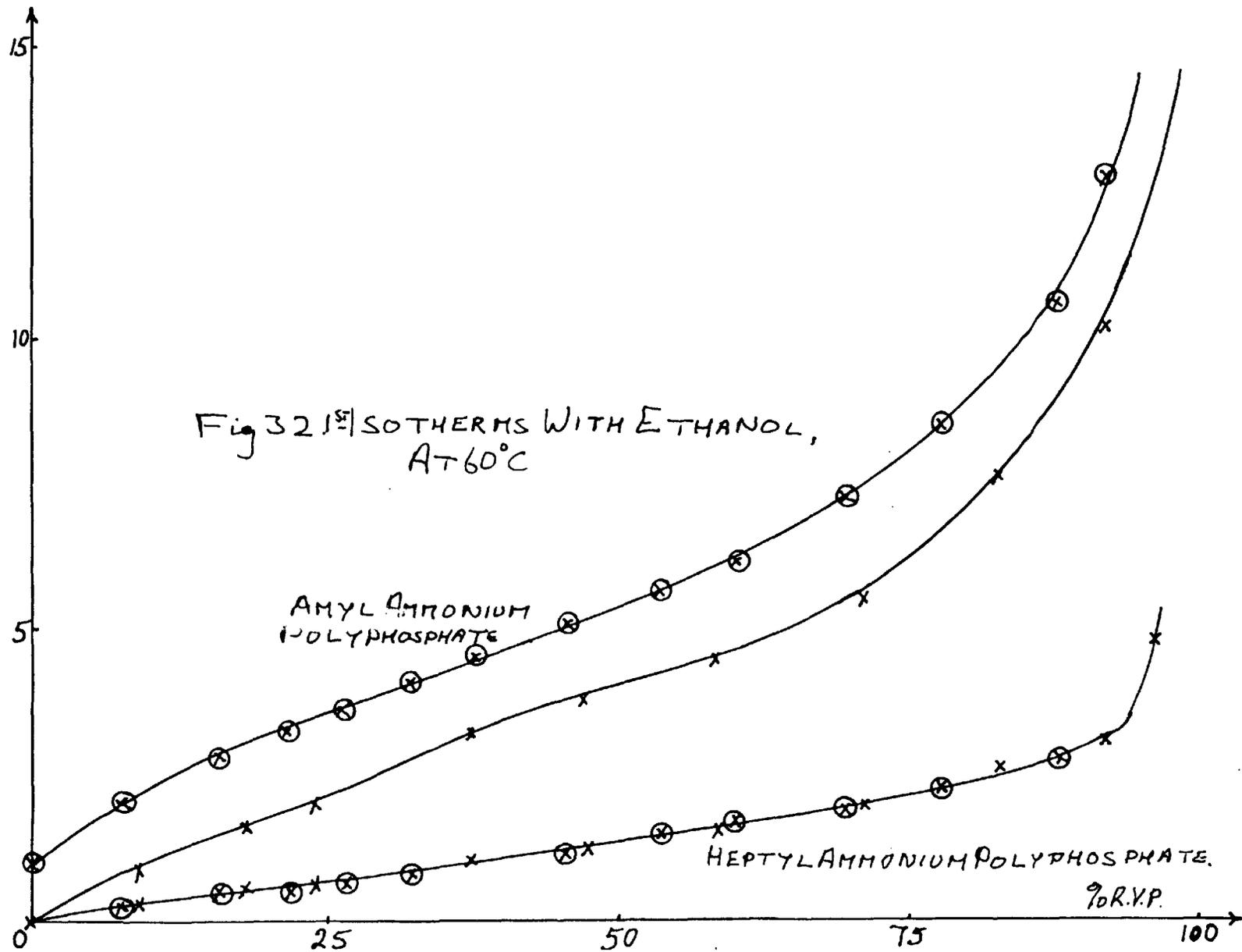
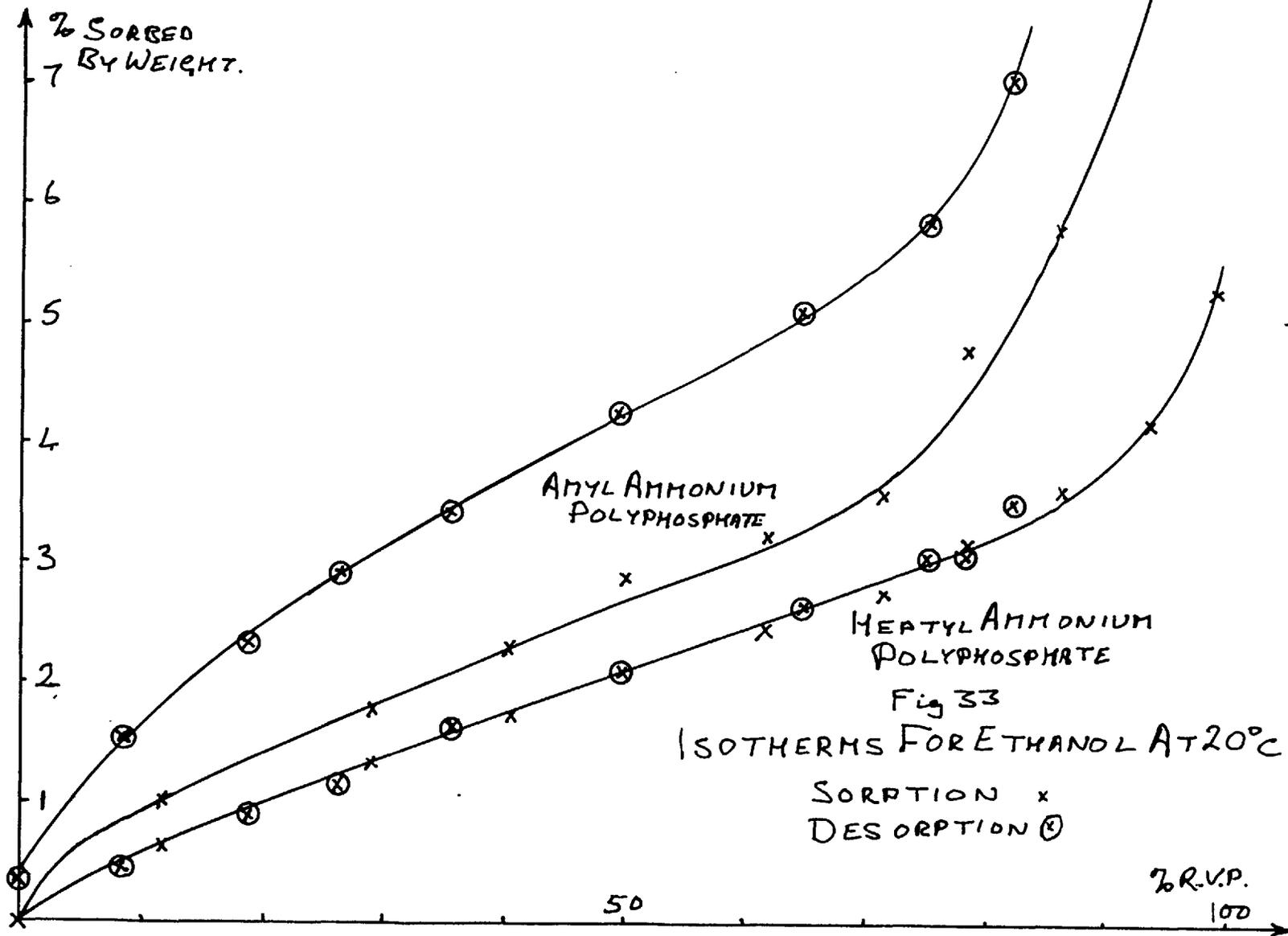


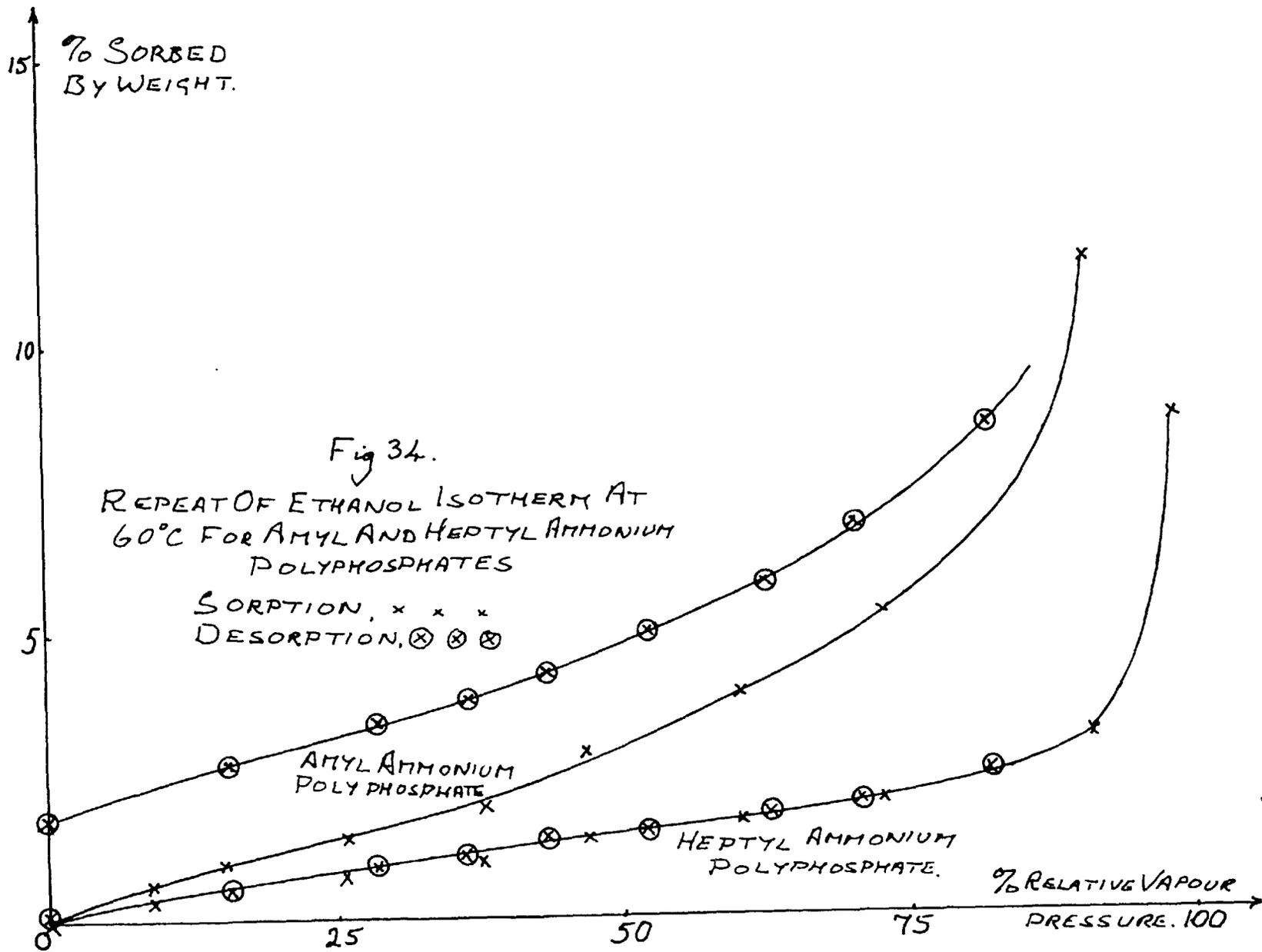
FIGURE 30
 ANILINIUM AND DODECYL AMMONIUM
 POLYPHOSPHATES ISOTHERM FOR
 ETHANOL AT 60°C

SORPTION, x x
 DESORPTION, (x) (x)









The impression given, by these results, that prior exposure to benzene increased the sorptive capacity of anilinium polyphosphate for ethanol, may be misleading. Repetition of the ethanol isotherm with the second sample more than doubled its sorptive capacity. Due to experimental difficulties, the second sample had been left exposed to ethanol vapour for considerable periods before most of the isotherm results were obtained. This may have increased the sorptive capacity of the sample.

At this point one may refer to the shortcomings of the method used to determine when equilibrium had been reached. The extension of the springs was measured at intervals until constant values were obtained. It was found that the reading after half an hour was the same, within the experimental error, as that obtained after three and a half hours. A reading taken under such conditions was assumed to give an equilibrium point, but a very slow process leading to a further uptake of sorbate would be undetected if the change in readings due to the process were less than the experimental error.

Small irreversible increases in the weight of the solid were recorded after these isotherms; it is probable, therefore, that a slow chemical reaction occurred during the course of an isotherm which was accompanied by an increase in the sorptive capacity of the sorbent.

The conclusions, therefore, seem to be as follows.

1. The pure sorption process occurred quite rapidly (usually within an hour).
2. A slow reaction occurred between ethanol and the sorbent. This increased the sorptive capacity of the sorbent, while changing its nature. As judged by the

irreversible increases in weight of the sample divided by the length of time taken up in obtaining an isotherm, the time taken to produce a change equal to the experimental error by the slow process was between nine hours and two days. The largest irreversible sorption occurring in one isotherm was 1.9% by weight. The nature of the slow reaction process with alcohols will be considered later (see pp. 150-2).

(b) Dodecyl ammonium polyphosphate: Three isotherms were also measured at 60°C using dodecyl ammonium polyphosphate as sorbent. Only one sample was used. A table of amounts sorbed at three pressures in the three isotherms is given below.

% Relative Vapour Pressure	% by weight sorbed		
	1st Isotherm	2nd Isotherm	3rd Isotherm
30	0.5%	0.9%	0.7%
60	1.5%	2.3%	1.86%
75	3.4%	3.8%	3.4%

The isotherms were of type III in Brunauer's classification as shown in Figs. 29-31, and no hysteresis was detected in the second isotherm, which was the only one for which desorption results were obtained. There appeared to be very slight irreversible increases in the weight of the samples which, however, were greater than the estimated error in the cathetometer readings in one case only.

The sorption of ethanol does not significantly affect dodecyl ammonium polyphosphate, although the first isotherm is lower than either repeat isotherm. In the

study of hydrocarbon sorption on homologues of this compound a similar alteration in sorptive capacities was found (9.1). This phenomenon could not be ascribed in the case of the hydrocarbons to any reaction between the sorbent and sorbate.

Heptyl ammonium polyphosphate

Three isotherms were obtained for this sorbent, using the same sample in each case. The first isotherm was at 60°C, the next at 20°C, and the last again at 60°C. The first and last isotherms were identical, all three were nearly linear, and no hysteresis was shown. In these circumstances the thermodynamics of sorption could be considered.

The differential heat of sorption, $\Delta\bar{H}$, of the liquid sorbate was approximately -2.3 kcal per mole throughout the range up to 80% relative vapour pressure. The differential entropy change $\Delta\bar{S}$ was negative throughout the range of sorption, steadily increasing in magnitude from -5.7 eu with 0.5% of ethanol sorbed by weight to -7.2 eu with 3% of ethanol sorbed, as shown in table 19.

TABLE 19.
Thermodynamics of ethanol sorption on heptyl ammonium polyphosphate

% ethanol sorbed (by weight)	$\Delta\bar{H}(=\bar{H}_S-H_L)$ kcal	$\Delta\bar{S}(=\bar{S}_S-S_L)$ eu
$\frac{1}{2}$	$-2.3^{\pm.2}$	$-5.7^{\pm.6}$
1	$-2.3^{\pm.2}$	$-6.4^{\pm.6}$
$1\frac{1}{2}$	$-2.3^{\pm.2}$	$-6.9^{\pm.6}$
2	$-2.3^{\pm.2}$	$-7.2^{\pm.6}$
$2\frac{1}{2}$	-1.6	$-5.9^{\pm.6}$
3	-0.9	$-2.8^{\pm.6}$

The thermodynamic behaviour is similar to that discussed with benzene (section 9.2.2). For similar reasons to those given in that discussion sorption in this system may be supposed to take place in the region of the polyphosphate plates. In such an environment the ethanol would be able to form hydrogen bonds easily.

Amyl ammonium polyphosphate: This polyphosphate sorbed substantially more ethanol than either dodecyl or heptyl ammonium polyphosphate. Three isotherms were measured, all using the same sample. The first was at 60°C, the second at 20°C, and the third at 60°C. The last was somewhat lower than the first.

Considerable hysteresis was shown by all of the isotherms, and irreversible sorption occurred. For these reasons, no thermodynamic information could be obtained. As shown in figs. 32-34 the uptake of ethanol was much greater on amyl than on heptyl ammonium polyphosphate. Comparison with figs. 29-31 will show that it was also much greater than on dodecyl ammonium polyphosphate.

The sample used for these isotherms and for the isotherm with amyl alcohol was made by the neutralisation of polyphosphoric acid, as described in section 7. The heptyl- and dodecyl ammonium polyphosphate samples used for the sorption of ethanol were prepared by ion exchange of potassium K.S. Amyl ammonium polyphosphate prepared by neutralisation was different in appearance from the same sorbent prepared by ion exchange (it was papery instead of powdery), and its X-ray pattern gave more diffuse lines. This may have been because the sample was composed of extremely small crystallites, either randomly stacked together or embedded in a matrix of amorphous material.

It seems possible, therefore, that the differences between its sorptive properties and those of heptyl ammonium polyphosphate may result from differences in its texture brought about by their different methods of preparation. However, as shown by Weiss and Michel (29) polyphosphates of this series tend to take up alcohols which have approximately the same alkyl chain lengths as the sorbents. There may thus be a tendency for amyl ammonium polyphosphate to sorb alcohols of short chain length more than do heptyl- and dodecyl ammonium polyphosphate, even if prepared by the same method.

The effects of ethanol sorption on the polyphosphates investigated are summarised in table 20.

TABLE 20.

Effect of ethanol sorption on polyphosphates.

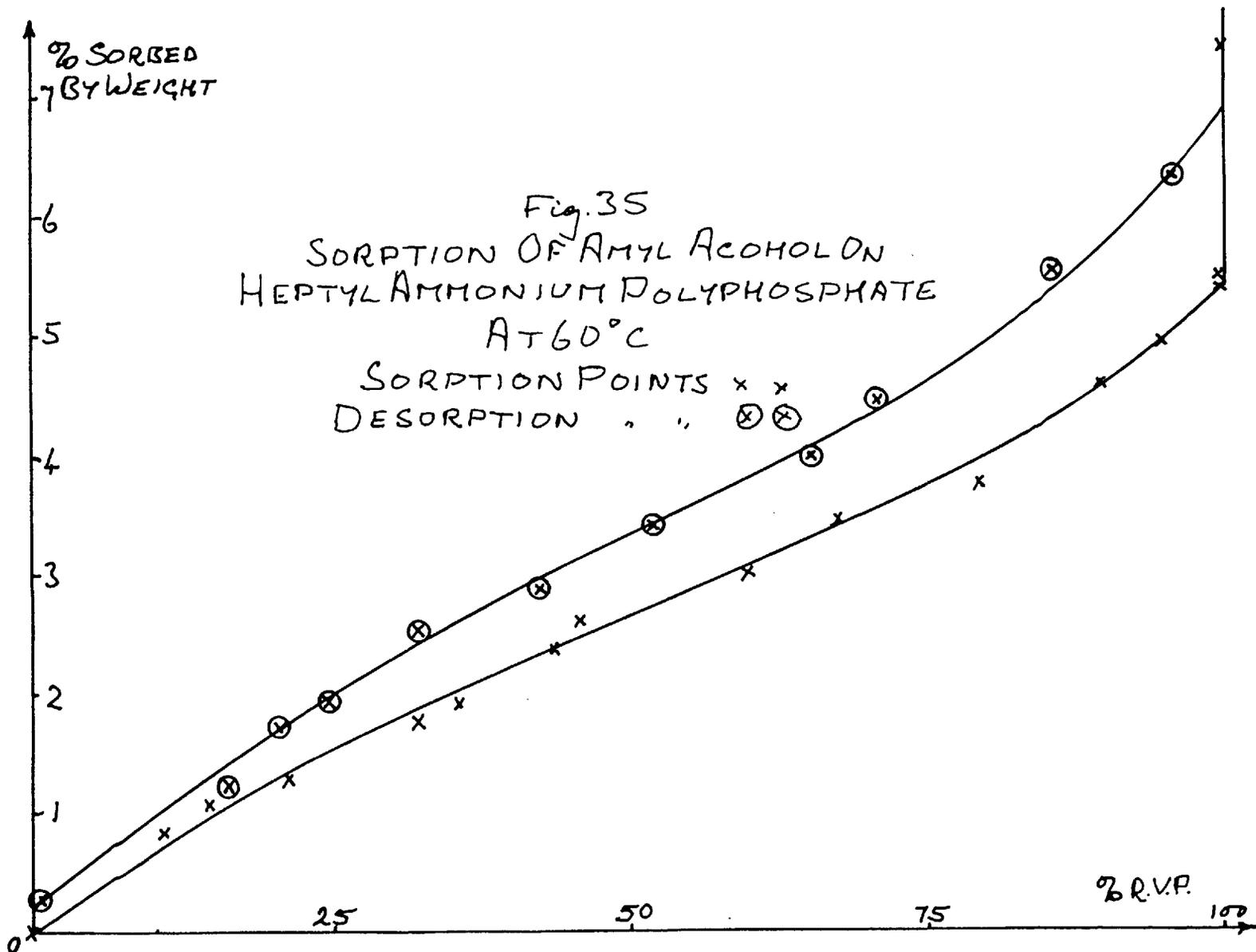
Sorbent	Hysteresis	Irreversible reaction	Change in sorptive capacity on repetition of isotherms
Anilium Polyphosphate	Yes	Yes	Increase of 100%+
Dodecyl Ammonium Polyphosphate	No	Probably very slight reaction	Tends to increase slightly. Not very significant.
Heptyl Ammonium Polyphosphate	No	No	No
Amyl Ammonium Polyphosphate	Yes	Yes	Small reduction

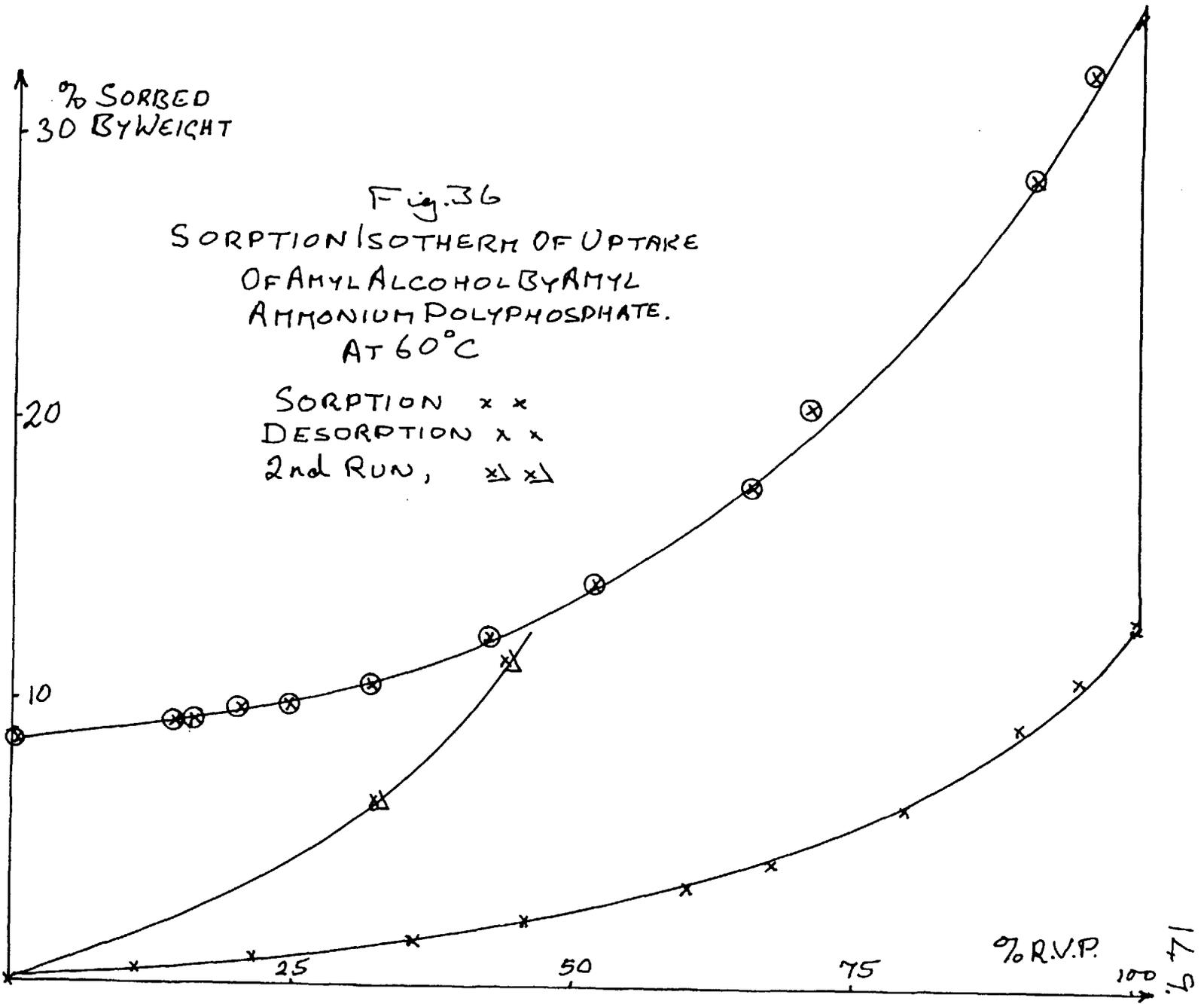
Amyl alcohol: Two isotherms were obtained with this sorbate, one of them with amyl ammonium polyphosphate and the other with heptyl ammonium polyphosphate. Both isotherms were measured at 60°C, and they are shown in figs. 35 and 36 respectively.

Heptyl ammonium polyphosphate showed an isotherm which tended in shape towards the second type in Brunauer's classification, but was nearly linear. It showed hysteresis throughout, the hysteresis becoming less with smaller amounts sorbed. A little irreversible sorption occurred, but when a few of the sorption points were repeated, the first results were confirmed. It appears, therefore, that this sorbent was not affected permanently by exposure to amyl alcohol.

The sample of amyl ammonium polyphosphate used for the amyl alcohol isotherm was that which had been previously used for the sorption of ethanol. Between the runs with ethanol the sample had been outgassed as gently as ^{was} consistent with the removal of the bulk of the ethanol, in the region of 100°C, but it was not possible to remove all the ethanol by this means. For this reason the sample was outgassed at 120°C for about 24 hours before the isotherm with amyl alcohol was commenced. As reported in section 6 this treatment is likely to have partially vaporised the sample and probably altered its physical state.

Very considerable hysteresis and irreversible sorption were shown in the isotherm. Both sorption and desorption curves were of type III in Brunauer's classification. After evacuating the apparatus but without raising the temperature, some alcohol was found to be irreversibly sorbed. Further amyl alcohol vapour was





% SORBED
BY WEIGHT

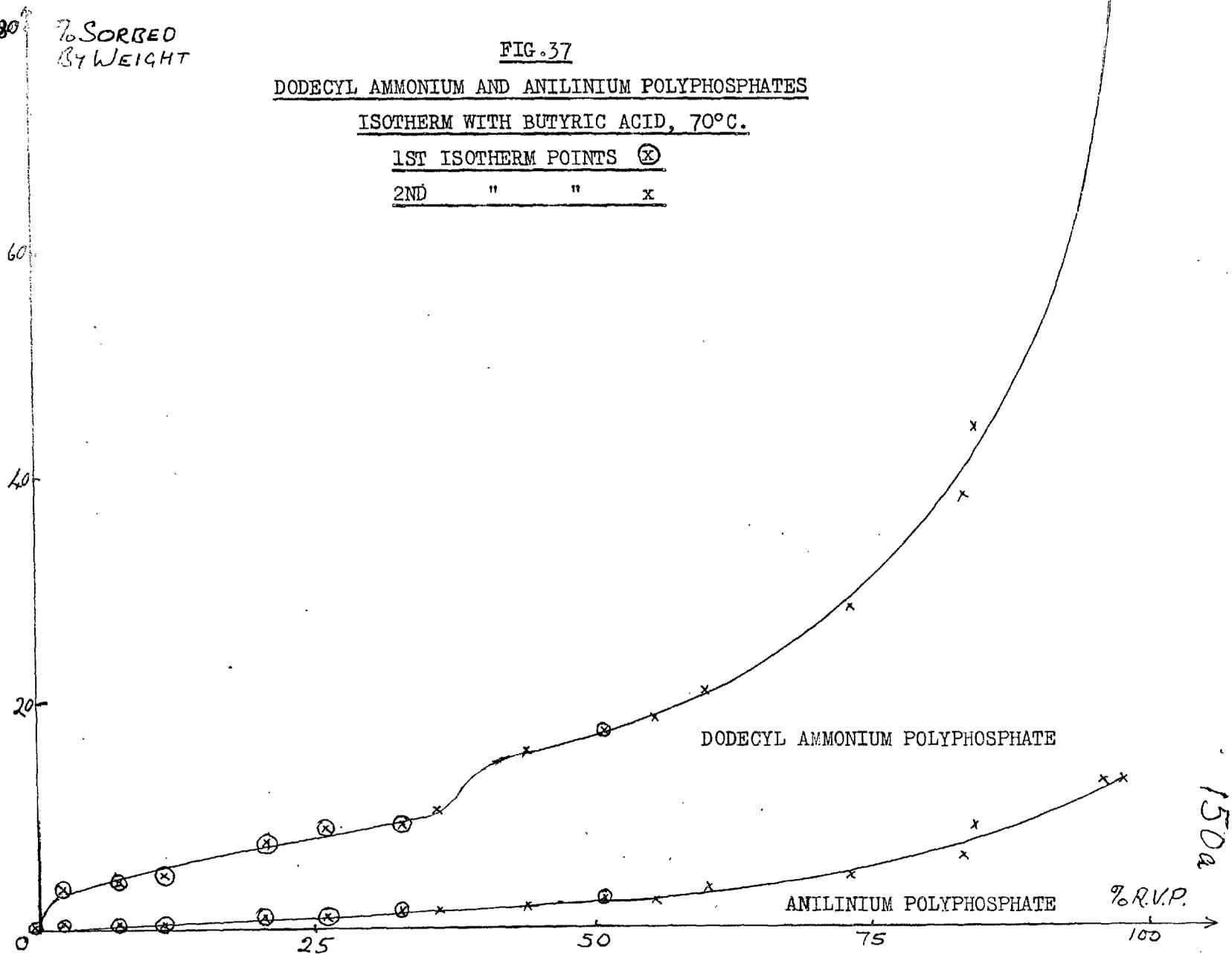
FIG. 37

DODECYL AMMONIUM AND ANILINIUM POLYPHOSPHATES

ISOTHERM WITH BUTYRIC ACID, 70°C.

1ST ISOTHERM POINTS (⊗)

2ND " " (x)



DODECYL AMMONIUM POLYPHOSPHATE

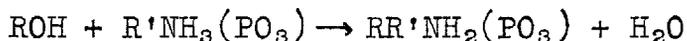
ANILINIUM POLYPHOSPHATE

% R.V.P.

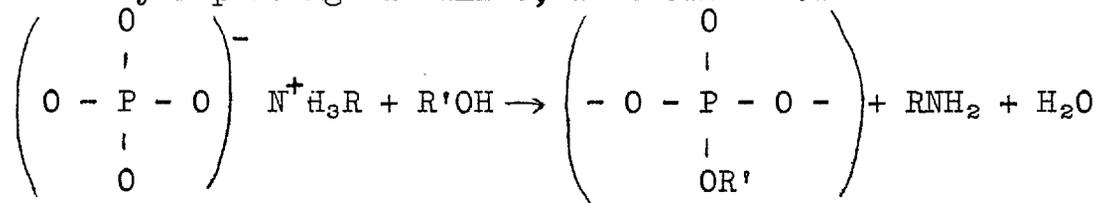
150a

reaction occurs the alcohol is held in similar sites. The OH group of the alcohol would thus be near to both the amine heads and to the polyphosphate chains.

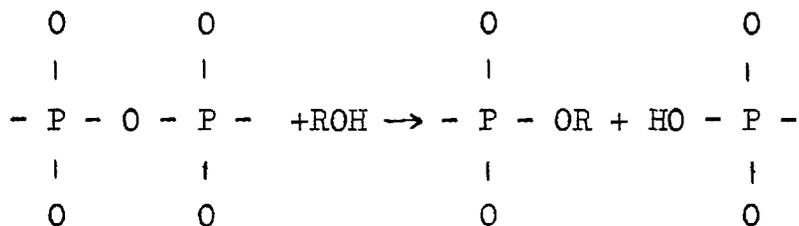
There are three reactions which are likely to occur between an alcohol and a primary ammonium polyphosphate. One of these is the formation of a secondary ammonium polyphosphate, according to the reaction:



which would lead to an increase in weight of the sample, as found experimentally. The second is the formation of an ester by replacing the amine, as shown below:



which would have led to a decline in weight for all of the systems investigated. For this reason it can be assumed that this reaction did not occur. The third possible reaction would be for the formation of a polyphosphate ester to take place with rupture of the polyphosphate chain, as shown below:



This reaction would also lead to an increase in the weight of the sample.

The effect of these reactions on the sorptive capacity of the sample is difficult to predict. If such

a reaction blocked favourable sorption sites the sorptive capacity of the sample would presumably be reduced; if, however, it caused buckling of the sheets, breaking the polyphosphate chains and opening up holes in the structure of the sorbent the sorptive capacity would presumably be increased.

The sorption of butyric acid: It has been shown by X-ray work that an expansion in the unit cell of dodecyl ammonium polyphosphate occurs when it is exposed to butyric acid (29). It was decided, therefore, to measure an isotherm for the butyric acid/dodecyl ammonium polyphosphate system and to see if any correlation could be found between the sorption and the X-ray results. The isotherm obtained is shown in fig. 37. It will be noted that there is a sudden increase in the amount sorbed at about 40% R.V.P.; the amount sorbed at the top of the sudden rise was 15½% by weight which is approximately that calculated from the expansion in the unit cell (16%). Since the temperature of the isotherm was 70°C and the X-ray work was presumably carried out at room temperature such good agreement seems fortuitous. An isotherm was also obtained with anilinium polyphosphate for the same sorbate. This is also shown in fig. 37. The isotherms are both of type III in Brunauer's classification.

Apart from the fact that dodecyl ammonium polyphosphate was a rather poor sorbent for everything else which was tried with it (ethanol, various hydrocarbons, water and nitromethane), and yet sorbed 30% by weight of butyric acid at 75% relative vapour pressure, there is nothing else worthy of note about these isotherms.

The samples were discarded after this run, as

exposure to butyric acid was almost certain to have altered them considerably.

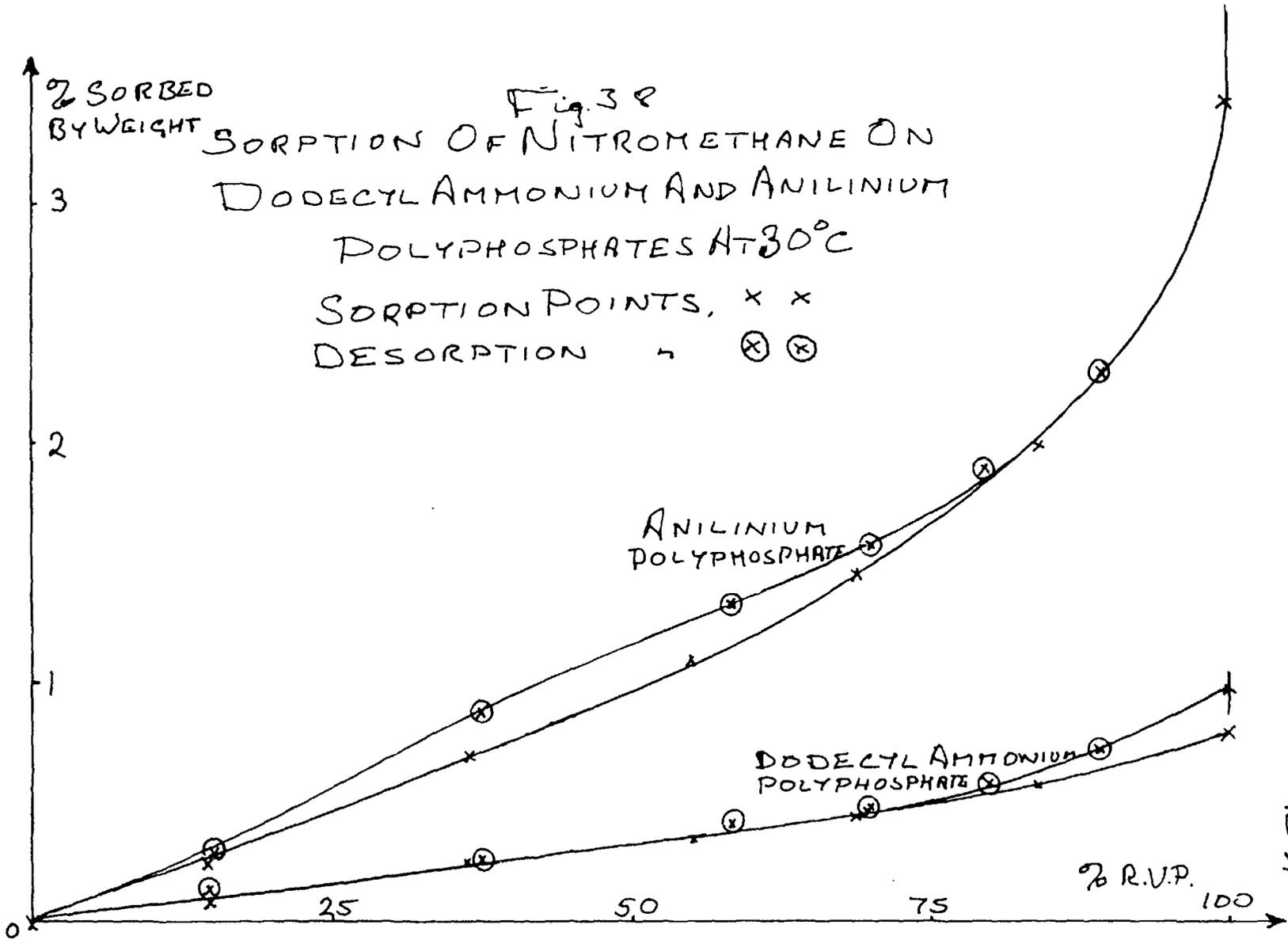
The sorption of nitromethane: Isotherms were measured at 30°C and 60°C with this sorbate using anilinium and dodecyl ammonium polyphosphates as sorbents. These isotherms are shown in figs. 38 and 39. Both samples had previously been exposed to ethanol, which reacted with the former but apparently not with the latter.

All of the curves were of type III in Brunauer's classification, but were nearly linear. The ones with anilinium polyphosphate showed hysteresis, but those with dodecyl ammonium polyphosphate did not.

The isotherms with anilinium polyphosphate are not significantly temperature dependent, but a very small amount of irreversible sorption seemed to occur at 60°C; this was not much greater than the experimental error and may have been due to a faulty reading. It is believed (135-143) that the treatment with ethanol affected the sorptive capacity of this polyphosphate. The above results therefore are probably not comparable with other sorption data using this sorbent.

The isotherms with dodecyl ammonium polyphosphate on the other hand were strongly temperature dependent, indicating that the sorption was endothermal. Little hysteresis was shown, and as this sorbent was probably not affected significantly by the previous ethanol sorption (143-144) the results referred to above may probably be compared directly with other data for this sorbent.

The above results are of considerable interest as they provide the only example of strongly endothermal



3
% SORBED
BY WEIGHT

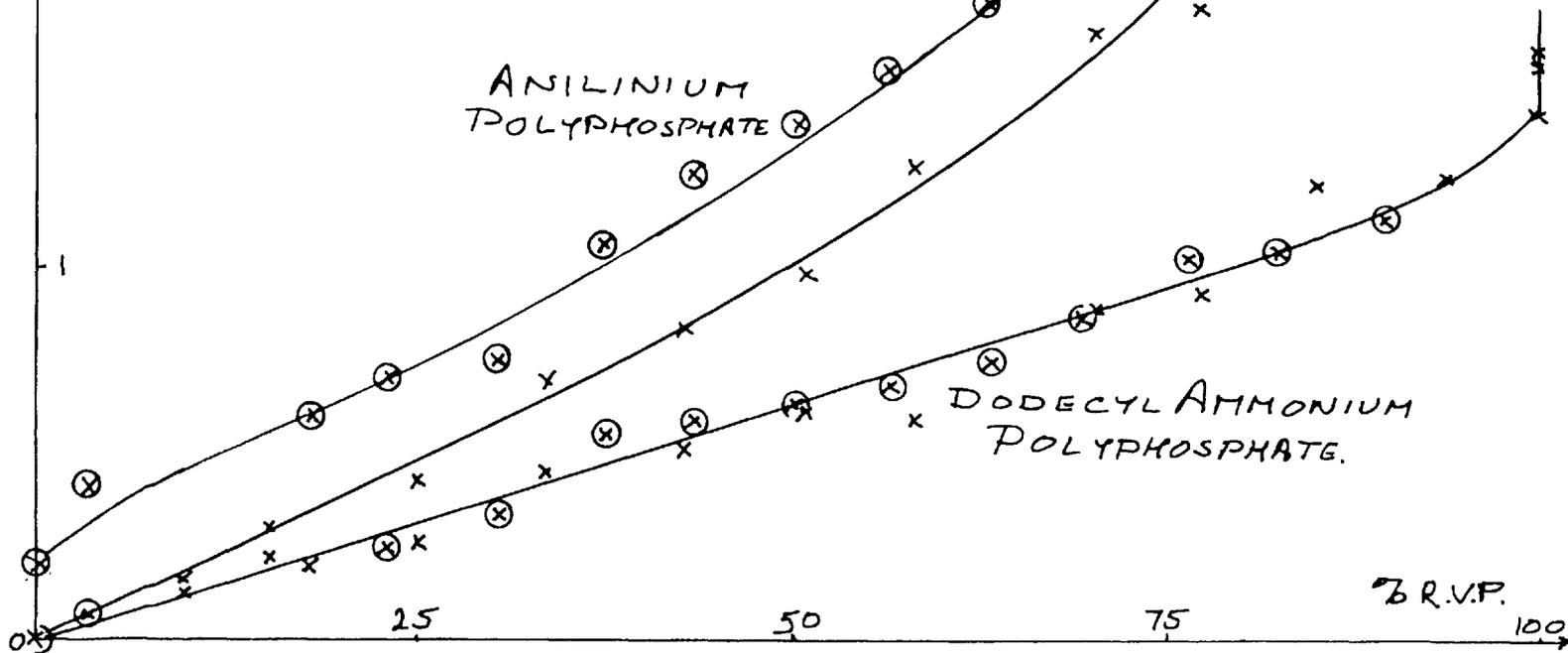
Fig. 39

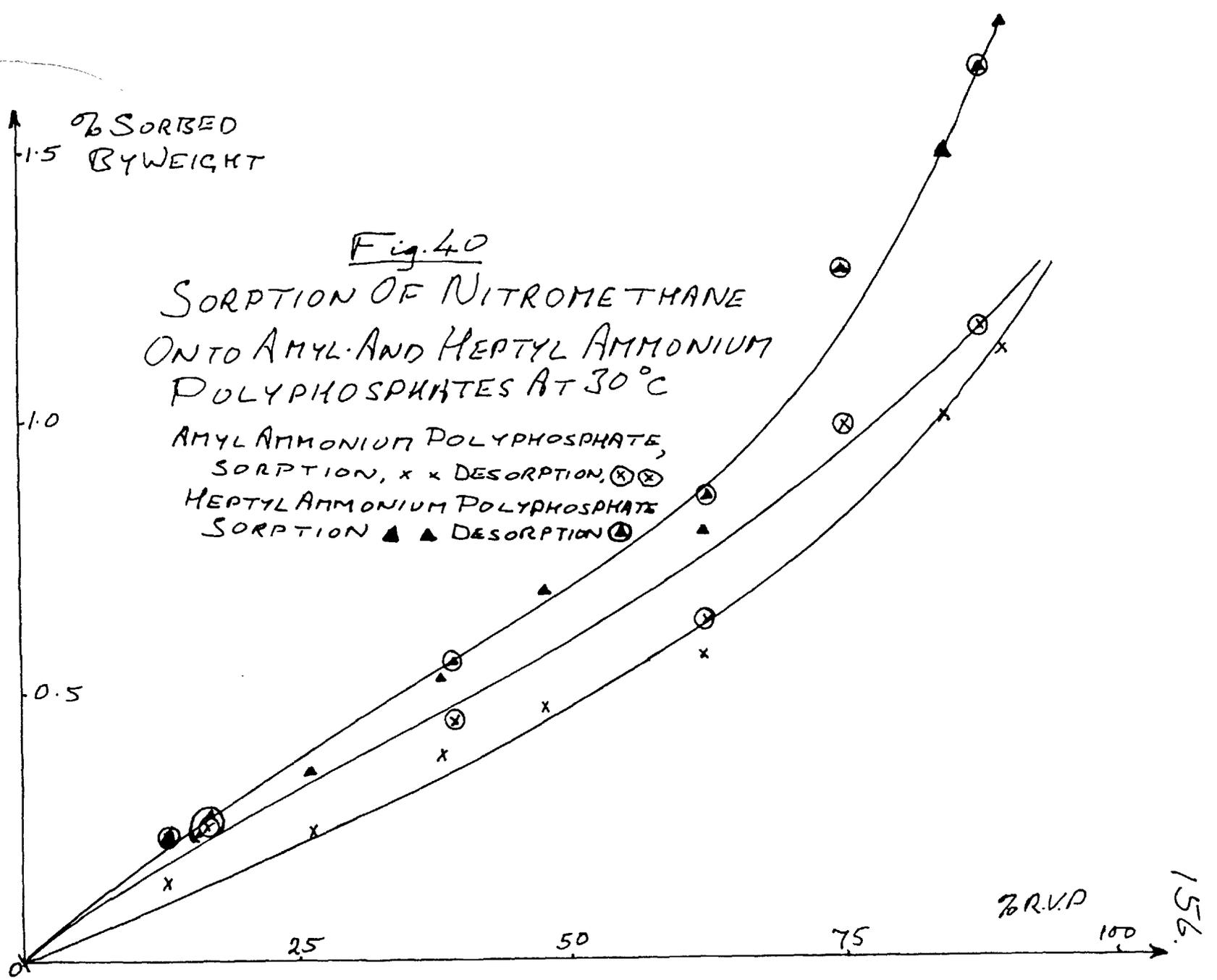
SORPTION OF NITROMETHANE AT
60°C BY DODECYLAMMONIUM AND
ANILINIUM POLYPHOSPHATES.

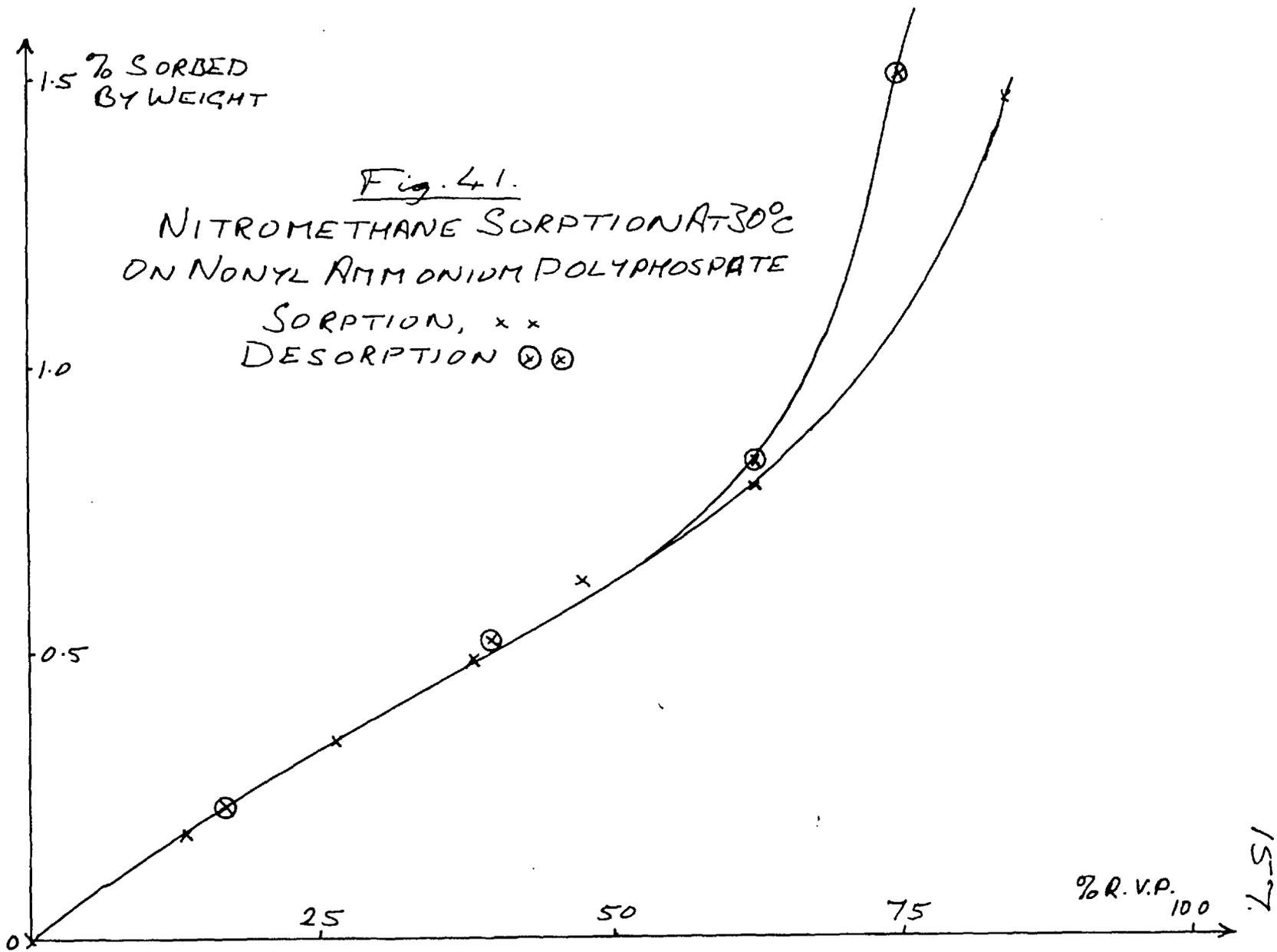
SORPTION, x x
DESORPTION, ⊗ ⊗

ANILINIUM
POLYPHOSPHATE ⊗

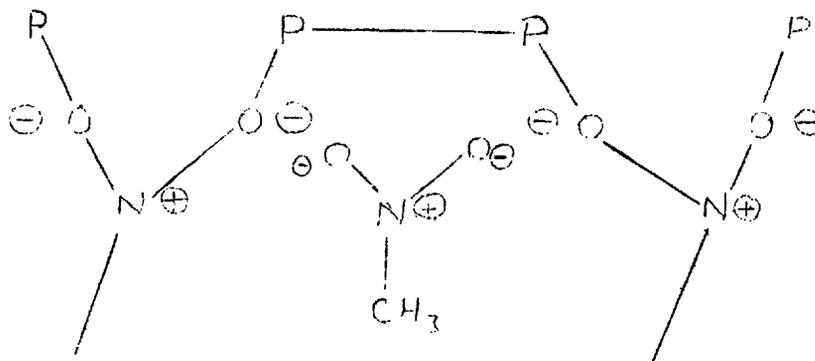
DODECYLAMMONIUM
POLYPHOSPHATE.







sorption recorded among the polyphosphates investigated. The very high cohesive energy density of nitromethane ($12.6 \text{ (cal/cc)}^{\frac{1}{2}}$) may have been a factor in this. The amount of sorption which was found was very low (1% at 80% RVP at 60°C , and 0.55% at 80% RVP at 30°C). The dipole of the nitromethane would be in the same direction as that of the polyphosphate sheets with the nitromethane



Nitromethane molecule approaching
polyphosphate plate

in the sorbed state, as shown above. This would provide a repulsion between the two permanent dipoles.

Isotherms were also obtained with nonyl, heptyl and amyl ammonium polyphosphates at 30°C . These are shown in figs. 40 and 41. The amyl ammonium polyphosphate was prepared by ion exchange from potassium Kurrol's salt. The isotherms with nonyl and amyl ammonium polyphosphates show hysteresis, the former in the high relative vapour pressure region only, and the latter throughout its range.

The sorbates took up nitromethane in the order anilinium > heptyl > nonyl > amyl > dodecyl at 30°C. Apart from the anilinium polyphosphate results, which should be accepted with reservation, the order of sorption is very similar to that applying with paraffin sorption (9.1 and 9.2).

Sorption of water: Isotherms for the sorption of water at 60°C by anilinium and dodecyl ammonium polyphosphates were measured. Both samples had been exposed to ethanol vapour at 60°C previously, and the comments of the previous section on this apply in the present case also. The isotherms are shown in fig. 42. A few points were also measured at 30°C with samples of anilinium ~~ammonium~~ polyphosphate and dodecyl, nonyl, heptyl and amyl ammonium polyphosphate which had not been exposed to ethanol vapour. These indicated that sorption occurred with little or no hysteresis. Except for nonyl ammonium polyphosphate, which gave a linear isotherm, all of the curves both at 60°C and at 30°C were of type III in Brunauer's classification. At 30°C water was sorbed in the order dodecyl > heptyl > anilinium > amyl ammonium polyphosphates. Nonyl ammonium polyphosphate occupied a position intermediate between anilinium ~~ammonium~~ polyphosphate and heptyl ammonium polyphosphate for the first part of the isotherm, and then was intermediate between anilinium ~~ammonium~~ polyphosphate and amyl ammonium polyphosphate. Above about 60% relative vapour pressure it became the least sorptive material.

If the results for dodecyl ammonium polyphosphate at 60°C and 30°C can be directly compared, the sorption of water does not seem to occur with a significant heat in this system.

15
% SORBED
BY WEIGHT

Fig 42. SORPTION OF WATER
BY ANILINIUM POLYPHOSPHATE (x) AND
DODECYL AMMONIUM POLYPHOSPHATE (⊗)
AT 60°C

10

5

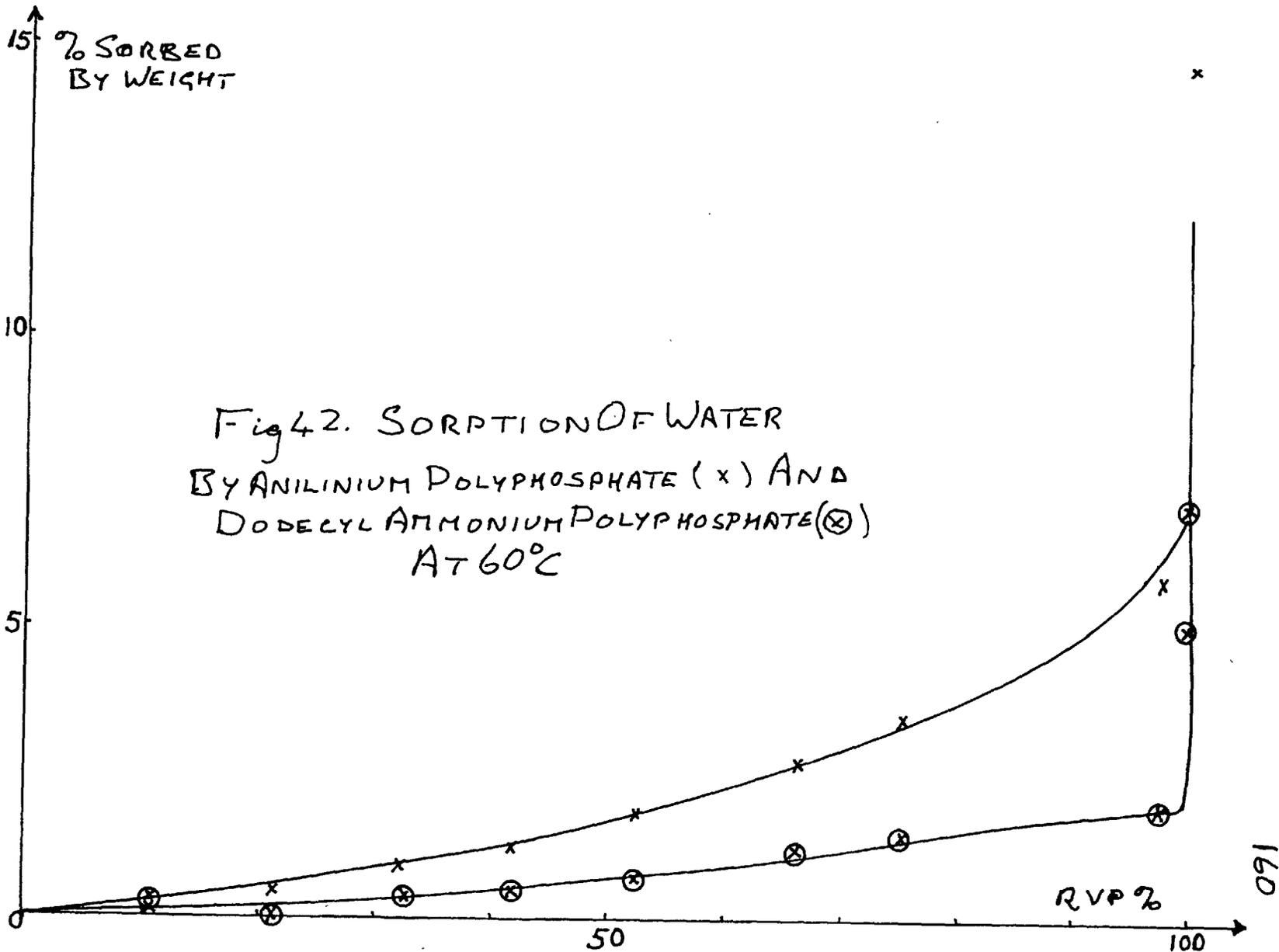
0

50

100

RVP %

160



Swelling during sorption: The swelling effects of alcohols, carboxylic acids and aldehydes on polyphosphates have been extensively investigated by Weiss and Michel, as discussed in section 3.2.

In the present work some further X-ray studies have been carried out by filling capillaries with certain sorbents and exposing them to varying pressures of sorbate vapour. The capillaries were then X-rayed on a flat plate camera, and the repeat distance was determined along the a axis, which is subject to major variations (29), with an estimated accuracy of $\pm 0.3 \text{ \AA}$. Weiss and Michel (29) showed that the c axis also varied by about 0.4 \AA , but lines due to this were too faint to be detected on our photographs.

It was found that the a axis of anilinium polyphosphate was unaffected by exposure to ethanol, even when saturation vapour pressure was reached. However, this sorbent takes up very little ethanol in any case so little change in the axis was expected.

The exposure of amyl ammonium polyphosphate to ethanol gave the following results:

Relative Vapour Pressure (%)	d_{100}^0 (Å)	% sorbed by weight
0	17.2	0
50	17.5	3.5
75	17.7	5
100	18.5	very large, mostly on external surfaces.

The d_{100} spacings are compared in column 3 with the sorption of ethanol at 20°C by a second, less crystalline sample of the sorbent. If the probable variation in the c axis under these conditions is taken into account, the above data indicate that the sorption of ethanol is essentially interlamellar. However, it is not possible to tell by this method whether any vacant space close to the polyphosphate plates is filled.

The results obtained when cyclohexane and n-heptane were sorbed into nonyl ammonium polyphosphate indicated that no increase in the d_{100} spacing occurred until the relative vapour pressure of these sorbents was increased to the saturation value. In view of the failure to detect such swelling at 75% RVP when approximately 3% by weight of each of these sorbates was taken up, it could be inferred that some filling of vacant interlamellar space took place. The error in the d_{100} spacing is equivalent to 1.2% sorption, however, and the fact that the other two axes are unknown makes this conclusion tentative. Sorption on the surface of the particles may also contribute to the total amount of sorption observed.

Benzene was found to increase the d_{100} distance of nonyl ammonium polyphosphate as follows:

% RVP	$d_{100}(\text{Å})$	% sorbed
0	24.6	0
50	25.0	5.6
80	26.5	7.5
100	27.5	very large, mostly on external surfaces.

At 50% RVP the expansion in the d_{100} spacing is not sufficient to account for sorption over 5% of benzene, whereas at 80% RVP the increase in the sheet separation seems quite sufficient. When benzene was sorbed into amyl ammonium polyphosphate the following results were obtained:

% RVP	d_{100} (Å)	% sorbed (est.)
0	17.2	0
25	17.5	2.8
50	18.0	4.9
80	18.5	6.0
100	18.5	very great, mostly on external surfaces

At each pressure below saturation the expansion in the d_{100} spacing is sufficient to account (within the experimental error) for the uptake of sorbate.

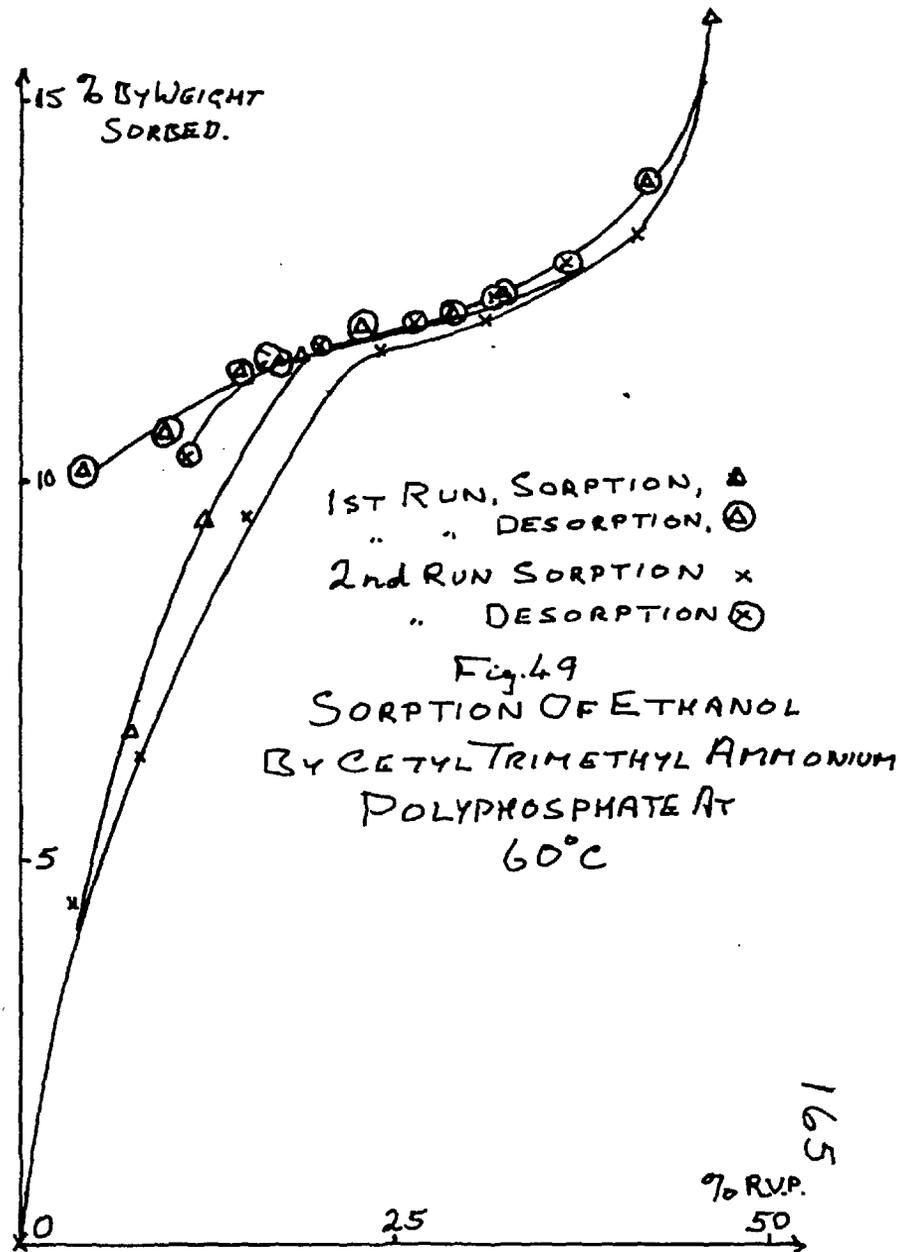
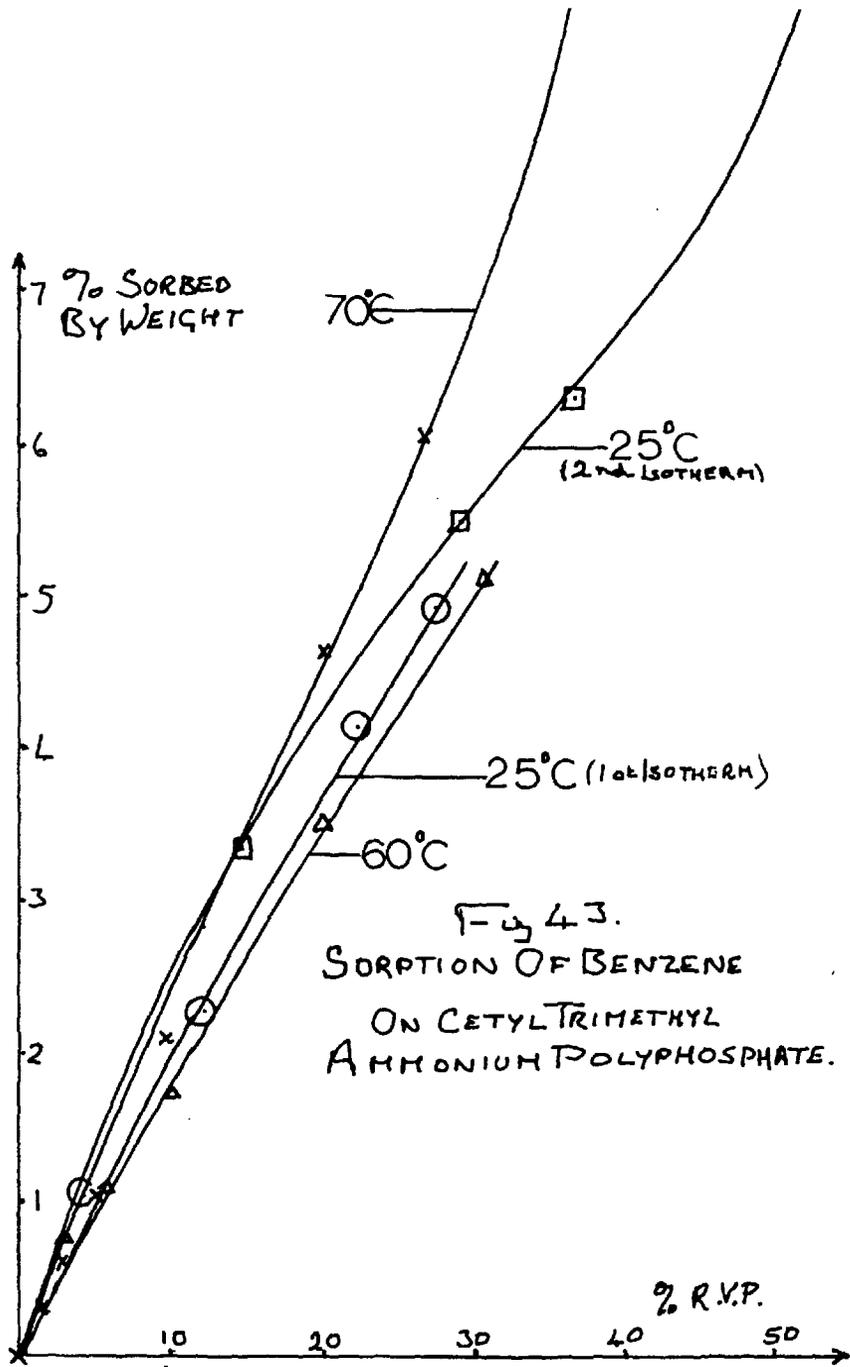
Conclusions: It seems from the above studies that interlamellar sorption occurs with the primary alkyl ammonium polyphosphates. It is not possible to tell with certainty whether sorption involves some pre-existing interlamellar spaces.

10. SORPTION OF CETYL TRIMETHYL AMMONIUM POLYPHOSPHATE

Isotherms were measured for this material with benzene, n-heptane, cyclohexane, iso-octane, and ethanol. With benzene and ethanol it was found that the polyphosphate tended to dissolve in the sorbate as the pressure was increased. Subsequent isotherms were therefore limited to the first part of the pressure range.

Linear isotherms with considerable hysteresis were obtained with hydrocarbons. Since the upper limit of the pressure was dictated only by the tendency for the sorbent to dissolve, the desorption curves must be regarded as scanning curves of bigger hysteresis loops.

Isotherms for benzene were measured at three temperatures, 25°C, 60°C and 70°C, the isotherm at 25°C being determined twice. The low pressure regions of these isotherms are shown in fig. 43, no desorption points being included. No definite trend of sorptive capacity with temperature is revealed, since the two 25°C isotherms lie between those for 60 and 70°C. The two isotherms at 25°C diverge from each other quite markedly, despite the fact that the second was measured immediately after the first, on the same sample at the same temperature. Since the isotherms cannot be reproduced at the same temperature, isotherms at different temperatures may not be strictly comparable. This is the more likely since, in the case of the present isotherms, the sample which had been used at 70 and 60°C dissolved at the latter temperature and was therefore replaced before isotherms were measured at 25°C. In addition, as hysteresis was shown in this system, it is not possible to calculate heats of sorption from the isotherms. It seems probable, however, that large heat



165

effects are not involved.

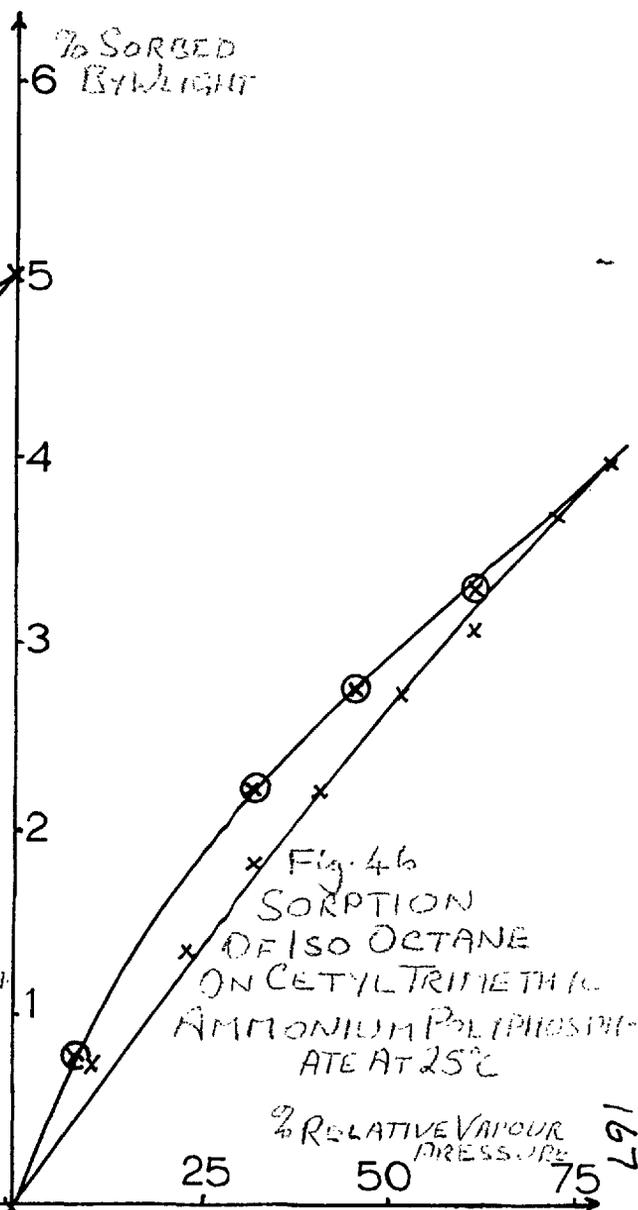
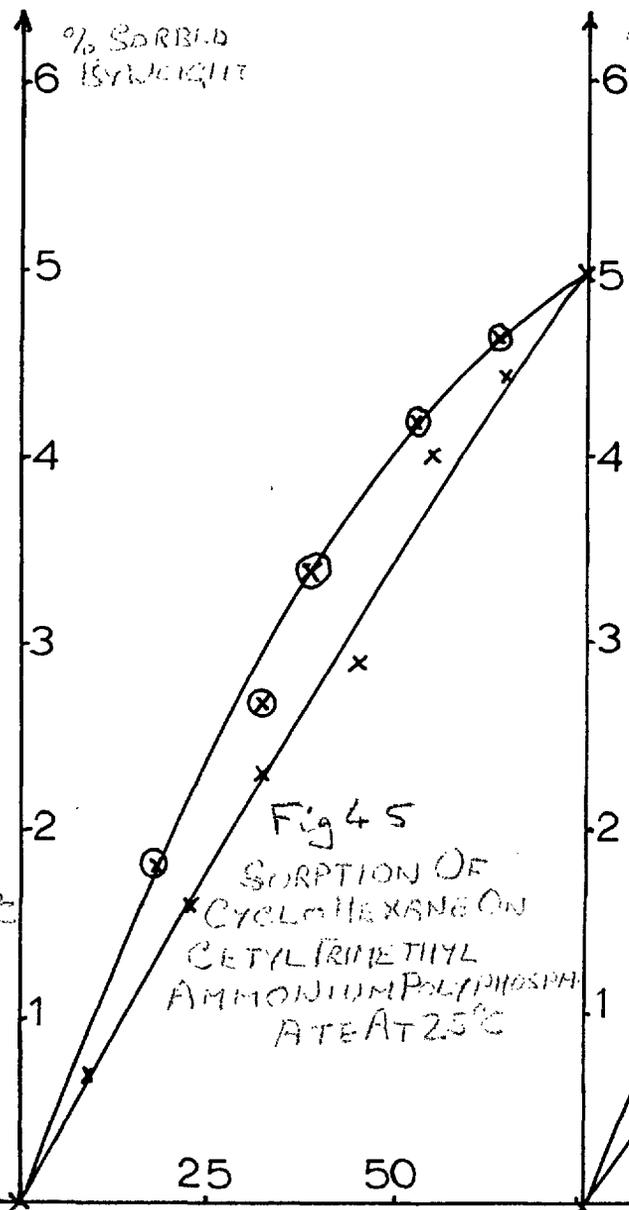
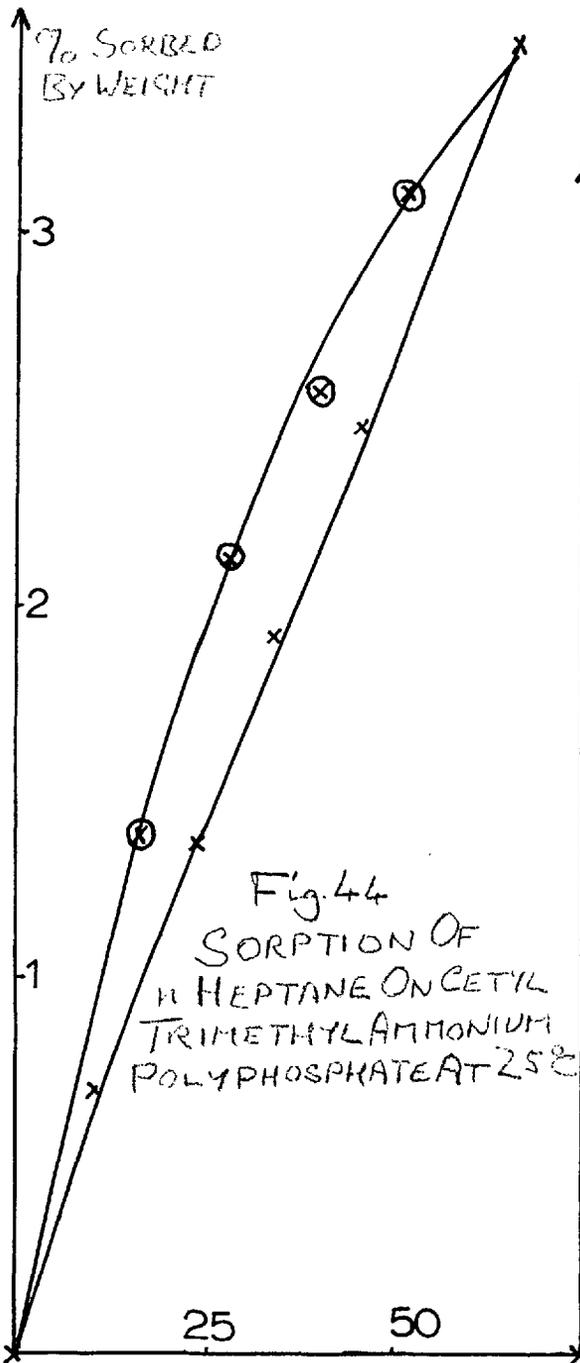
The isotherms with the other hydrocarbons were obtained only at 25°C, and are shown in figs. 44 - 46. The extent of sorption at this temperature was in the order benzene > cyclohexane > n-heptane > iso-octane.

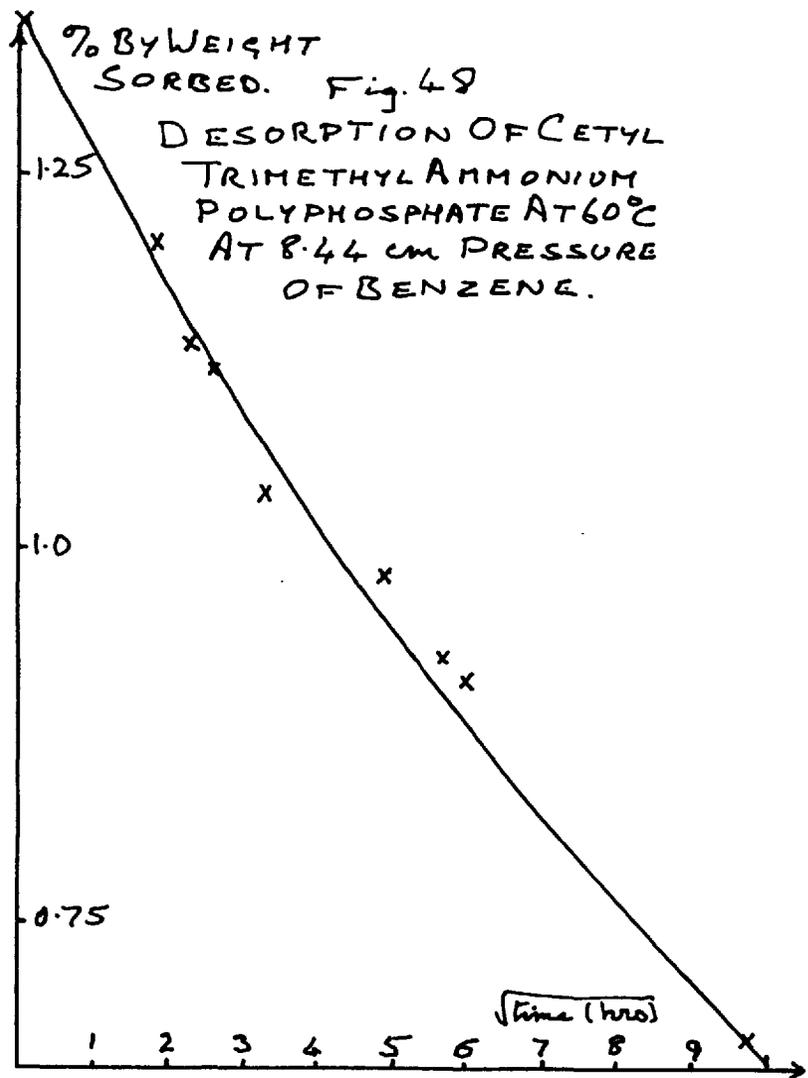
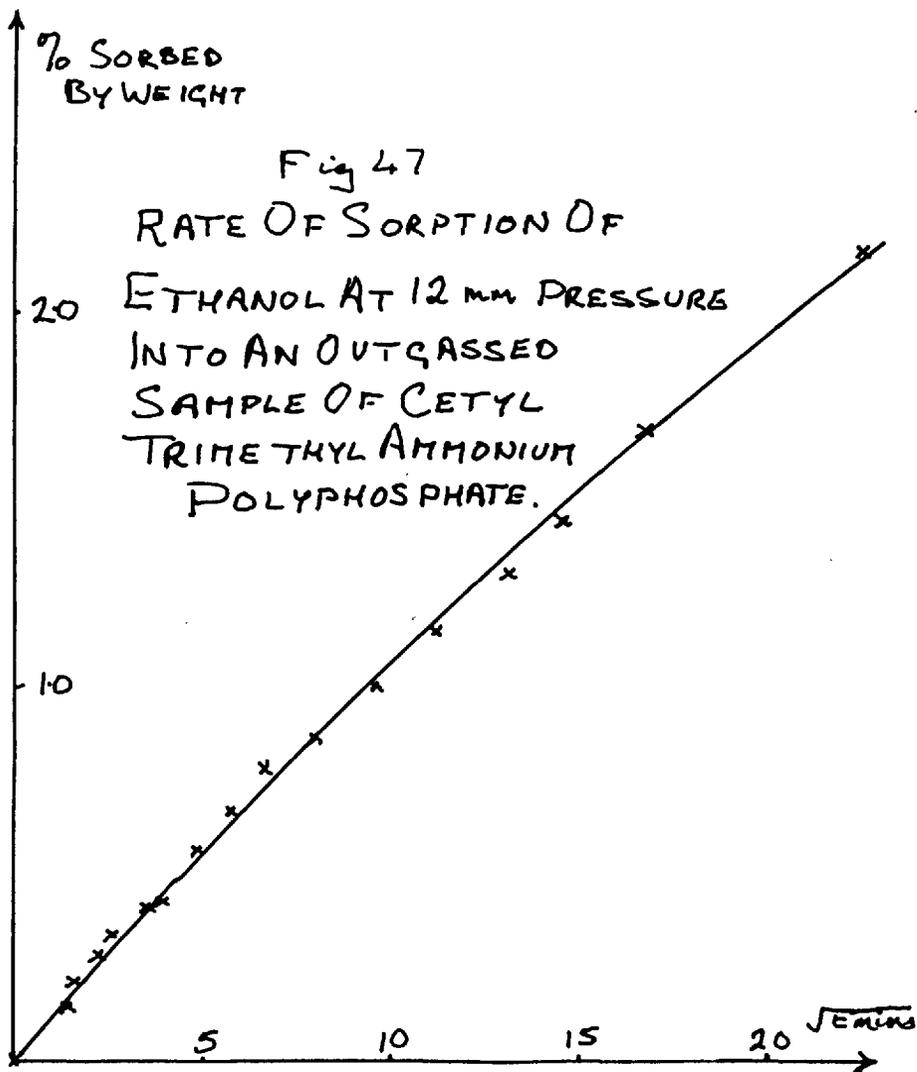
If it is assumed that the sorption occurs without significant heat change, then the entropies of sorption would be positive, corresponding to sorption by mixing. That is, that sorbate molecules are rather randomly arranged in an environment of partially randomised alkyl chains, in the sorbed state. This hypothesis is supported by the shape of the isotherms, which tend to be that of such mixtures as C₄ paraffins dissolving in rubber. The comparatively large amount of alkyl material present in the sorbent and the absence of cross-linking of polyphosphate chains in the structure suggests that mixtures of this kind should be easily formed.

The order of affinity for the various hydrocarbons also supports the "mixture" hypothesis, as the order experimentally obtained is that of declining cohesive energy densities of sorbates.

However, the fact that sorption tends to increase sharply with the formation of a visible solution at high relative pressures of benzene, suggests that the polyphosphate chains, which had at lower relative pressures tended to limit sorption to some extent, are eventually moved apart and disordered to such an extent as to allow a true solution to be formed.

Sorption of ethanol was measured at 60°C only, Fig.49. The form of the isotherm in this case was entirely different from that found for hydrocarbons. The isotherm





measurements were repeated, and although there was some alteration in the low pressure region, the "plateau" region, where about 12% of ethanol was sorbed, was reproduced in both isotherms on sorption and desorption. This percentage by weight represents 0.95 molecules of ethanol sorbed per monomer unit of the sorbent. One can assume from this therefore that the state corresponding to one ethanol molecule sorbed per repeating unit of sorbent is very stable, and it is interesting to consider what this suggests about the structure of the sorbed state. On the basis of the discussion given in section 8, it is safe to assume that the cation heads are attracted to the "free" oxygen atoms in the polyphosphate chains by electrostatic forces. Two such oxygen atoms, each carrying $\frac{1}{2}$ a negative charge, were shown in section 8 to be bonded to each phosphorus atom. As the head of the quaternary cation is very bulky, it may be supposed that it has a "shielding" effect on any free oxygen atoms to which it is attracted.

Each head would be attracted to two oxygen atoms, however, so it seems probable that the shielding effect on one of the atoms is insufficient completely to prevent it from taking part in hydrogen bonding. If this is so, there would be one negatively charged oxygen atom per monomer unit of sorbent which might be able to form a single hydrogen bond. Each molecule of ethanol would be able to form one hydrogen bond, and so, as observed, one such molecule would be expected to sorb in each monomer unit of sorbent.

Equilibrium was established very slowly with cetyl trimethyl ammonium polyphosphate for all the sorbates. Kinetic data were therefore obtained for some sorption and desorption points. The data always gave linear graphs of

amount sorbed against $\sqrt{\text{time}}$. Examples of such graphs are shown in figs. 47 and 48. The fact that such graphs are linear may imply that the rate of sorption is diffusion controlled.

SUMMARY

Isotherms have been measured for the sorption of a wide range of vapours on four primary alkyl ammonium polyphosphates and anilinium polyphosphate. In addition, the sorptive properties of cetyl trimethyl ammonium polyphosphate with ethanol and four hydrocarbons have been studied. Approximately linear isotherms were found for the primary alkyl ammonium polyphosphate series with cyclohexane, n-heptane, iso-octane and benzene. As little hysteresis was found with these isotherms, and as equilibrium was attained fairly rapidly, this series may have potential chromatographic uses. A wide range of selectivities were found in the uptake of the various hydrocarbons. Where possible, thermodynamic data have been derived for these systems and the implication of such data have been discussed in structural terms. Sorption was usually found to take place close to the highly polar regions of the sorbents.

The reproducibility of isotherms with hydrocarbons was sometimes poor, but the chief difficulty was found in reproducing isotherms with ethanol. In this case the sorbate was found to react with the sorbent, thus altering its sorptive capacity. Considerable reaction was found to occur with amyl alcohol and butyric acid.

It was found that water and nitromethane did not react with the primary alkyl ammonium series. Nearly all the isotherms measured with non-hydrocarbons with this series of sorbents were of type III in Brunauer's classification.

Anilinium polyphosphate sorbed ethanol and butyric acid freely but was a poor sorbent for hydrocarbons. Its

isotherms tended to be particularly non-reproducible, and it degraded more readily than the other sorbents on prolonged heating, thus making satisfactory outgassing more difficult.

Cetyl trimethyl ammonium polyphosphate gave linear isotherms with hydrocarbons until the material started to dissolve. Equilibrium was attained very slowly, and the isotherms showed hysteresis. It seems possible that it sorbs hydrocarbons by a mixing process occurring between its alkyl chains and sorbate molecules. With ethanol, a 1:1 mole ratio of sorbate to sorbent seems to be particularly stable.

X-ray diffraction data have been obtained for polyphosphates in their sorbed states, and the implications of such information discussed. Various methods of preparation of substituted ammonium polyphosphates have been considered, and the unit cells of products made by some of these methods have been determined. Such data for unit cells has in general confirmed that of Weiss and Michel (17, 29).

APPENDIX

The results for each sample of sorbent are arranged in chronological order. Replacement of samples is indicated in the correct places in the results.

SORPTION WITH DODECYL AMMONIUM POLYPHOSPHATE:Ethanol 60°C. Ist IsothermWater Isotherm 60°C

<u>R.V.P. %</u>	<u>% sorbed by wt.</u>	<u>R.V.P. %</u>	<u>% sorbed by wt.</u>
0	0	0	0
4.7	0	10.71	.28
12.2	0.2	21.42	.0
22.2	0.45	32.46	.37
36.5	0.72	41.84	.48
47.5	1.0	52.48	.69
58.0	1.5	66.20	1.15
68.3	2.4	75.31	1.43
84.0	5.7	97.8	1.91
96.0	11.1	100.3	2.28
100	16.2.	100.4	3.27

Nitromethane 60°C

<u>R.V.P. %</u>	<u>x(wt. sorbed %)</u>	<u>R.V.P. %</u>	<u>x(wt. sorbed %)</u>
0	0	99.967	1.545
9.55	.136	89.55	1.136
17.79	.227	82.455	1.045
25.20	.273	76.517	.863
33.89	.454	68.60	.863
42.92	.522	63.15	.750
50.98	.613	56.67	.682
58.37	.591	50.45	.636
70.39	.886	43.60	.591
77.30	.931	37.64	.545
85.00	1.227	30.47	.34
93.71	1.249	24.89	.13
99.60	1.567	23.24	.25
100.034	1.408	18.0	.20
100.19	1.567	3.5	.07
		0	0.0

Nitromethane 30°C

<u>R.V.P. %</u>	<u>x(wt. sorbed %)</u>	<u>R.V.P. %</u>	<u>x(wt. sorbed %)</u>
0	0	100	.97
14.47	.1	89.4	.70
36.4	.25	79.6	.56
55.1	.34	70.0	.48
68.7	.43	58.5	.41
83.9	.57	37.4	.27
100	.77	14.9	.14
		0	.1

Ethanol 60°C Repeat Isotherms

<u>R.V.P. %</u>	<u>% sorbed by wt.</u>	<u>R.V.P. %</u>	<u>% sorbed by wt.</u>
0	0	24.1	1.1
29.0	.59	16.7	.80
45.4	2.43	8.9	.66
83.8	5.77	0	.39
95.2	18.76	0	0
100	34.1	11.5	.22
96.7	33.5	19.5	.42
93.9	16.1	35.2	.81
86.2	7.1	49.5	1.29
77.3	4.6	59.7	1.82
70.4	3.45	70.5	2.71
61.1	2.57	82.7	4.88
51.8	1.95	93.9	10.58
41.7	1.61	100	very great
32.7	1.39	82.5	5.25

Butyric Acid Isotherm 70°C

<u>R.V.P. %</u>	<u>% sorbed by wt.</u>	<u>R.V.P. %</u>	<u>% sorbed by wt.</u>
0	0	36.4	10.34
2.4	3.40	44.1	15.75
7.4	4.08	51.4	17.41
11.2	4.82	60.1	21.11
20.8	7.68	73.1	28.41
26.3	8.77	83.1	38.17
32.5	9.19	84.4	44.4
55.6	18.59	96.5	88.0
		93.5	121.0

Fresh Sample - Benzene Isotherm 30°C

<u>R.V.P. %</u>	<u>% sorbed by wt.</u>	<u>R.V.P. %</u>	<u>% sorbed by wt.</u>
0	0	16.5	.33
31.1	.57	31.66	.66
66.0	1.48	45.85	.97
28.2	.61	62.4	1.36
0	0	74.6	1.75
29.6	.64	47.6	1.07
57.5	1.29	33.9	.75
36.7	.90	23.9	.57
0	0	11.1	.26
		0	0

n-Heptane 30°C

<u>R.V.P. %</u>	<u>% sorbed by wt.</u>	<u>R.V.P. %</u>	<u>% sorbed by wt.</u>
0	0	57.7	.89
11.97	.21	48.7	.78
24.5	.41	24.8	.46
38.32	.57	15.1	.28
56.4	.86	5.4	.08
66.9	.90	0	0

30°C Isotherms

R.V.P. % % sorbed by wt. R.V.P. % % sorbed by wt.

Iso-octane

0	0
48.4	.74
70.5	1.16
0	0

Cyclo-hexane

0	0
32.8	.41
70.9	1.09
0	0

Benzene

0	0
52.8	1.06
0	0

Water

0	0
22.6	.299
61.5	1.20
35.0	.43
0	0

SORPTION WITH NONYL AMMONIUM POLYPHOSPHATE:Benzene 60°C

<u>R.V.P. %</u>	<u>x (% sorbed)</u>	<u>R.V.P. %</u>	<u>x (% sorbed)</u>
0	0	0	0
10.603	1.192	0	0
22.358	2.251	10.7	1.17
29.526	2.842	30.2	2.90
40.030	3.615	0	0
42.327	3.729	0	0
51.869	4.254	57.4	4.511
62.623	5.007	66.4	4.998
70.940	5.494	41.2	3.472
78.403	6.457	34.65	3.119
91.597	7.554	26.8	2.546
24.442	2.480	7.50	1.068
		0	0

Normal Heptane 60°C

<u>R.V.P. %</u>	<u>x (% sorbed)</u>	<u>R.V.P. %</u>	<u>x (% sorbed)</u>
0	0	36.956	1.469
7.53	.439	47.774	1.755
20.833	.868	56.774	2.079
24.088	1.040	69.747	2.5845
35.548	1.402	80.852	3.119
66.013	2.422	67.636	2.632
20.536	.906	49.727	2.003
27.497	1.097	27.9896	1.164
		0	0

Cyclohexane 60°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>	<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0	Pressure taken up to 73%, then	
9.936	.553	54.753	2.413
20.028	.963	40.689	1.860
31.343	1.421	27.80	1.02
39.381	1.850	0	0
53.283	2.289		
61.749	2.585		
72.355	3.0997		
88.976	4.216		
72.59	3.185		
26.674	1.288		

Iso-octane 60°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>	<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0	63.735	1.993
8.412	.429	76.658	2.480
13.690	.629	57.576	1.812
27.629	1.087	26.468	1.049
38.662	1.354	0	0
50.503	1.640		

Iso-octane 30°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0
12.079	.531
26.472	.996
36.651	1.309
50.032	1.698
69.460	2.334
60.825	2.030
41.730	1.556
29.889	1.205
16.254	.788
0	0

Cyclo-hexane 30°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0
11.859	.550
25.174	.996
39.499	1.518
55.948	2.106
69.197	2.770
63.555	2.562
48.152	2.011
30.552	1.385
16.761	.778
5.617	.285
0	0

Nitro-methane 30°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0
13.151	.1803
26.386	.342
38.193	.484
47.814	.617
62.163	.731
84.116	1.452
89.578	1.850
Pressure raised to 100% R.V.P. then:	
87.376	2.078
75.146	1.499
62.688	.825
39.474	.512
16.680	.228
0	0

Benzene 30°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0
31.103	3.359
65.986	6.442
28.208	3.833
0	0
29.630	3.586
57.489	6.072
36.75	4.52
0	0
16.517	1.622
31.655	3.643
45.848	5.085
62.433	6.214
74.642	7.030
47.585	5.266
33.886	4.232
23.88	3.188
11.102	1.689
0	0

Normal Heptane 30°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>
11.973	.5123
24.494	.930
38.320	1.461
56.365	1.992
66.880	2.343
57.720	2.125
48.749	1.831
24.803	1.091
15.146	.6931
5.437	.313
0	0

Iso-octane 30°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>
48.413	1.556
70.540	2.324
0	0

Benzene 30°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0
52.754	5.702
0	0

Water 30°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>
22.63	.161
61.509	.455
0	0

Cyclo-hexane 30°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0
32.8	1.051
70.9	2.58

SORPTION WITH HEPTYL AMMONIUM POLYPHOSPHATE:Ethanol Isotherms60°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>	<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0	87.91	2.774
8.660	.303	77.98	2.271
17.6797	.536	69.70	1.958
23.921	.660	60.47	1.714
37.3780	1.100	53.83	1.550
47.104	1.264	46.39	1.183
58.562	1.509	13.446	.884
71.252	1.999	11.449	.829
84.860	2.611	9.539	.721
91.988	3.100	7.776	.534
96.110	4.705	5.530	.503
91.95	4.665	2.692	.245
		0	0

20°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>	<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0	99.14	5.288
11.666	.6165	82.32	3.493
29.03	1.329	75.24	3.082
40.310	1.712	64.35	2.630
49.911	2.000	49.71	2.096
62.10	2.466	35.68	1.616
71.13	2.767	26.28	1.137
78.373	3.1097	18.97	.890
86.41	3.603	8.49	.425
93.74	4.151	0	0

Ethanol Isotherm (contd.)60°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>	<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0	82.05	2.478
8.807	.318	70.49	1.9798
15.031	.443	62.55	1.7445
25.526	0.706	52.16	1.4953
37.531	0.983	43.32	1.371
46.725	1.351	36.37	1.066
60.436	1.648	28.34	.914
72.73	1.980	15.53	.568
90.92	3.032	0	.125
98.32	3.570		<u>Outgassed</u>
93.36	3.517	0	0

Amyl Alcohol 60°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>	<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0	71.019	4.453
10.836	.819	55.564	3.9677
21.309	1.290	51.855	3.399
36.000	1.9283	42.400	2.886
45.928	2.594	32.03	2.358
60.473	3.010	24.182	1.9283
67.564	3.454	20.291	1.7061
74.092	3.760	16.291	1.221
89.855	4.564	8.536	.2497
94.910	4.925	0	0
99.637	5.385	32.469	1.712
99.637	5.369	43.777	2.39
100.15	7.491	100.	14.9
96.001	6.312	100.	19.5
90.801	5.535	38.505	2.73
		0	0

Normal Heptane 60°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>	<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0	36.956	1.137
7.53	.290	47.774	1.340
20.833	.643	56.774	1.634
24.088	.740	69.747	2.059
35.548	1.040	80.852	2.552
66.043	1.866	67.636	1.991
20.536	.686	49.727	1.4180
27.497	.8145	27.9896	.8619
		0	0

Benzene Isotherm 60°C

After nitromethane run:

Rerun (fresh sample):

<u>R.V.P. %</u>	<u>x(% sorbed)</u>	<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0	0	0
4.146	1.107	10.7	1.000
22.358	2.251	30.3	2.50
29.526	2.842	59.4	3.807
40.030	3.615	66.4	4.386
42.327	3.729	41.2	3.120
51.869	3.491	34.465	2.745
62.623	3.974	26.8	2.316
		7.50	.9972
		0	0

Cyclo Hexane 60°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>	<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0.	72.355	2.98
9.936	0.48	88.976	4.10
20.028	0.86	72.598	3.03
31.34	1.31	26.674	1.23
39.381	1.63	54.753	2.22
53.283	2.17	40.6898	1.71
61.749	2.45	27.80	1.26
		0	0

Iso-Octane60°C30°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>	<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0	0	0
8.412	.2900	12.079	.534
13.690	.4611	26.476	1.025
27.629	.8150	36.651	1.377
38.662	1.083	50.032	1.794
50.503	1.3297	69.460	2.424
63.735	1.6430	60.825	2.114
76.658	2.048	41.730	1.602
57.576	1.448	29.889	1.185
26.468	.804	16.254	.758
0	0	0	0

Cyclo Hexane 30°CNitro Methane 30°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>	<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0	0	0
11.859	0.59	13.151	.224
25.174	1.23	26.386	.342
39.499	1.80	38.193	.512
55.948	2.38	47.814	.673
69.197	3.04	62.163	.779
63.555	2.78	84.116	1.473
48.152	2.14	89.570	1.719
30.552	1.46	87.276	1.623
16.761	.89	75.146	1.2560
5.617	.22	62.688	.843
0	0	39.474	.5445
		16.680	.235
		0	0

Benzene 30°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0
31.103	3.3953
65.986	5.403
28.208	3.289
0	0
29.630	3.246
57.489	5.018
36.75	3.825
16.517	2.103
45.848	4.281
62.433	5.157
74.642	5.851
47.585	4.442
33.886	3.609
23.88	2.797
11.902	1.676
0	0

Normal Heptane 30°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0
11.973	.459
24.494	.929
38.320	1.388
56.365	1.986
66.880	2.328
57.720	2.018
48.749	1.815
24.803	1.004
15.146	.673
5.437	.278
0	0

Iso-Octane 30°C

48.413	1.623
70.540	2.530
0	0

Benzene 30°C

0	0
52.754	4.70
0	0

Water 30°C

0	0
22.63	.192
61.509	.673
35.0	.352
0	0

Cyclo Hexane 30°C

0	0
32.8	1.48
70.9	3.13
0	0

SORPTION WITH AMYLAMMONIUM POLYPHOSPHATEEthanol Isotherms60°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>	<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0	87.91	10.541
8.660	.9596	77.98	8.491
17.6797	1.599	69.70	7.255
23.921	1.9773	60.47	6.194
37.3780	3.242	53.83	5.685
47.104	3.795	46.39	5.074
58.562	4.4925	37.73	4.536
71.252	5.4812	32.13	4.10
84.860	7.1691	26.77	3.664
91.988	10.148	21.82	3.228
96.110	20.980	15.52	2.850
91.95	12.780	7.554	2.094
		0	0

20°C

0	0	99.14	50.25
11.666	1.0138	82.32	7.0086
29.03	1.763	75.24	5.833
40.310	2.292	64.35	5.10
49.911	2.7035	49.71	4.25
62.10	3.218	35.68	3.42
71.13	4.761	26.28	2.91
86.41	5.774	18.97	2.307
93.74	7.934	8.49	1.543
		0	0

Ethanol Isotherms (contd.)60°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>	<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0	93.36	18.090
8.808	.573	82.05	9.405
15.031	.940	70.49	6.774
25.526	1.395	62.55	5.760
37.531	1.8957	52.16	4.952
46.725	2.8501	43.32	4.276
60.436	3.821	36.37	3.791
72.73	5.129	28.34	3.365
90.92	11.315	15.53	2.630
98.32	33.931	0	1.749

Amyl Alcohol60°C

0	0	71.019	20.487
10.836	.445	65.564	17.667
21.309	.920	51.855	14.193
36.000	1.529	42.400	12.307
45.928	2.227	37.20	10.541
60.473	3.415	24.182	9.947
67.564	4.365	20.291	9.6450
79.092	5.627	16.291	9.323
89.8	9.219	.7636	8.536
94.910	10.882	32.469	6.497
99.637	12.782	43.777	11.506
99.637	13.183	100	50.569
100.15	34.5	100	65.388
96.001	32.440	38.505	16.259
90.801	28.697	0	0

Benzene Isotherm 60°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>	<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0	10.7	.648
4.146	.554	30.3	1.94
22.358	1.226	0	0
29.358	1.835	59.4	3.456
40.032	2.499	58.076	3.118
42.327	2.633	41.2	2.573
51.869	3.211	34.65	2.1798
62.623	3.733	26.8	1.6840
70.940	4.231	7.50	.4531
78.403	4.642	0	0
91.597	5.512		

Normal Heptane 60°C

0	0	36.956	.154
7.53	.034	47.774	.256
20.833	.154	56.774	.316
24.088	.154	69.747	.427
35.548	.2137	80.852	.633
66.043	.402	67.636	.521
20.536	.0855	49.727	.2991
27.497	.120	27.9896	.1368
		0	0

Cyclo Hexane 60°C

0	0	72.355	0.94
9.936	0.21	88.976	1.33
20.028	0.23	72.591	1.01
31.343	0.36	26.674	0.39
39.381	0.48	54.753	0.68
53.283	0.67	40.6898	0.53
61.749	0.72	27.80	0.44
		0	0

<u>Iso-Octane</u>			
<u>60°C</u>		<u>30°C</u>	
<u>R.V.P. %</u>	<u>x(% sorbed)</u>	<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0	0	0
8.412	.077	12.079	.110
13.690	.137	26.476	.265
27.629	.256	36.651	.316
38.662	.259	50.032	.436
50.503	.316	69.460	.615
63.735	.436	60.825	.487
76.658	.547	41.730	.410
57.576	.427	29.889	.333
26.468	.231	16.254	.239
0	0	0	0

<u>Cyclo Hexane 30°C</u>		<u>Nitro Methane 30°C</u>	
0	0	0	0
11.859	.222	13.151	.145
25.174	.3758	26.386	.239
39.499	.521	38.193	.376
55.948	.666	47.814	.461
69.197	.863	62.163	.555
63.555	.786	84.116	.999
48.152	.641	89.570	1.128
30.552	.461	87.876	1.162
16.761	.290	75.146	.982
5.617	.154	62.688	.624
0	0	39.474	.436
		16.680	.248
		0	0

Benzene 30°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0
31.103	2.853
65.986	5.001
28.208	2.742
29.630	2.793
57.489	4.689
36.75	3.47
16.517	1.333
31.655	2.913
45.848	3.946
62.433	4.843
74.642	5.416
47.585	4.049
33.886	3.152
23.88	2.264
11.902	.8713
0	0

Water 30°C

0	0
22.63	.111
61.509	.461
35.0	.205
0	0

Normal Heptane 30°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0
11.973	.111
24.494	.214
38.320	.350
56.365	.487
66.88	.572
57.720	.4701
48.749	.453
24.803	.299
15.146	.179
5.437	.077
0	0
<u>Iso-Octane 30°C</u>	
0	0
48.413	.427
70.540	.641
52.754	.399
0	0

Cyclo-Hexane 30°C

0	0
32.8	.333
70.9	.769
0	0

SORPTION WITH ANILINIUM POLYPHOSPHATE

<u>Benzene 70°C</u>			
<u>R.V.P. %</u>	<u>x(% sorbed)</u>	<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0	20.836	.563
5.234	0	26.090	.789
10.975	.316	0	0
14.684	.417		
<u>Benzene 60°C</u>			
0	0	89.1	2.907
2.609	.056	100	9.754
5.889	.067	100	10.03
10.004	.224	100	9.08
19.650	.303	90.5	4.65
30.47	.404	78.4	2.95
41.77	.572	62.5	2.099
51.466	.696	52.64	1.897
64.856	1.268	36.30	1.04
77.699	1.578	0	0
<u>Ethanol 60°C</u>			
0	0	47.86	1.33
2.357	0.	58.33	1.72
5.066	.09	68.49	2.33
11.14	.27	84.19	3.12
22.246	.495	98.28	6.13
36.52	.732	100	10.3
		100	14.23
<u>Water 60°C</u>			
0	0	52.48	1.801
10.71	.225	66.20	2.713
21.42	.462	75.31	3.434
32.46	.878	97.80	5.877
41.84	1.204	100.28	14.682
		100.41	21.809

<u>Nitromethane 60°C</u>			
<u>R.V.P. %</u>	<u>x(% sorbed)</u>	<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0	99.967	6.020
9.55	.166	89.55	2.701
17.79	.308	82.455	2.405
25.20	.438	76.517	2.097
33.89	.699	68.60	1.896
42.92	.841	63.15	1.718
50.98	.983	56.67	1.540
58.37	1.268	50.45	1.386
70.39	1.623	43.60	.591
77.30	1.896	37.64	.545
85.00	2.180	30	.758
93.71	2.618	24.89	.557
99.60	8.174	23.24	.711
100.034	6.421	18.01	.616
100.19	5.818	3.52	.415
		0	.20

<u>Nitromethane 30°C</u>			
0	0	100.02	6.59
14.67	.248	89.39	2.30
36.41	.689	79.57	1.877
55.11	1.010	70.04	1.570
68.74	1.480	58.53	1.32
83.90	1.995	37.45	.874
100.00	3.42	14.95	.28
		0	0

Second Ethanol Isotherm 60°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>	<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0	71.4	1.10
29.54	.223	61.5	.885
45.5	.25	52.5	.735
88.4	1.24	42.5	.602
90.01	1.662	33.45	.505
100.01	3.44	24.54	.420
96.5	3.34	17.5	.385
95.01	3.01	9.54	.25
88.5	1.85	0	.109
77.5	1.32	0	0

New Isotherm. Ethanol 60°C

0	0	70.531	2.532
11.511	.2979	82.741	3.779
19.522	.5957	93.873	7.503
35.200	.9774	100	16.709
49.490	1.3776	100	19.967
59.697	1.8224	100	21.689
		82.537	4.217

Butyric Acid 70°C

0	0	36.43	1.4862
2.4	.28398	44.09	1.9689
7.4	.3597	51.37	2.527
11.3	.42597	60.137	3.313
20.78	.861	73.12	4.619
26.30	.9655	83.12	6.342
32.535	1.3253	84.42	8.709
55.59	2.3665	96.5	14.852
		93.51	74.669

Benzene 30°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>	<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0	31.655	.512
31.103	.366	45.848	.702
65.986	1.170	62.433	1.083
28.208	.570	74.642	1.668
29.630	.468	47.585	1.878
57.489	.936	33.886	.688
36.75	.640	23.88	.497
16.517	.2163	11.102	.336
		0	0

Normal Heptane 30°C

0	0	57.760	.9656
11.973	.307	48.749	.688
24.494	.336	24.803	.395
38.320	.512	15.146	.205
56.365	.863	5.437	.146
66.880	1.156	0	0

Iso-Octane 30°C

48.413	.746
70.540	1.536
0	0
52.754	.629

Water 30°C

22.68	.146
61.509	.5546
0	0

Cyclo-Hexane 30°C

32.8	.116
70.9	.553
0	0

ISOTHERMS WITH CETYL TRIMETHYL AMMONIUM POLYPHOSPHATE

New sample of sorbent.

Ethanol 60°C

<u>R.V.P. %</u>	<u>x(% sorbed)</u>	<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0	4.182	10.621
2.35	5.994	0	0
9.348	8.613	3.4052	4.452
12.030	9.428	7.6099	6.353
18.716	11.6877	15.325	9.505
25.846	11.959	23.737	11.726
31.429	12.182	31.506	12.386
46.649	16.014	41.39	13.210
42.002	13.948	36.801	12.851
32.291	12.423	31.128	12.434
22.782	12.202	26.193	12.085
17.01	12.085	19.811	11.784
14.800	11.5324	16.732	11.667
9.589	11.486	11.343	10.291
		0	1.949*

* not equilibrium point.

Benzene 70°CBenzene 60°C

0	0	0	0
1.39	.33	2.609	.796
2.82	.605	5.889	1.108
5.15	1.079	10.004	1.753
9.55	2.097	19.6450	3.536
20.0	4.647	30.47	5.127
26.8	6.05	41.777	11.009
38.1	9.345	54.866	19.107
47.6	12.339	77.699	23.014
0	0		

<u>Benzene 25°C</u>			
<u>R.V.P. %</u>	<u>x(% sorbed)</u>	<u>R.V.P. %</u>	<u>x(% sorbed)</u>
0	0	0	0
4.225	1.065	14.466	3.328
11.056	2.2633	29.334	5.525
22.366	4.177	36.821	6.307
27.59	4.909	52.504	9.369
20.28	4.344	37.54	7.622
11.607	3.045	22.719	5.542
5.697	1.797	11.99	3.428
		0	0
<u>Normal Heptane 25°C</u>			
0	0	66.26	3.5115
10.65	.716	51.35	3.112
24.2	1.365	40.22	2.563
34.02	1.930	28.26	2.1135
45.22	2.4797	16.305	1.3815
48.92	2.846	0	0
<u>Cyclo Hexane 25°C</u>			
0	0	74.586	4.893
8.823	.699	63.637	4.626
22.05	1.548	52.960	4.1605
31.99	2.296	38.741	3.378
42.397	2.879	32.189	2.713
55.148	3.977	18.167	1.781
64.148	4.410	0	0
<u>Iso-Octane 25°C</u>			
0	0	72.061	3.478
10.727	.749	79.374	3.778
22.67	1.365	62.343	3.312
31.616	1.831	45.616	2.746
40.4505	2.213	32.222	2.230
51.576	2.746	7.6566	.799
61.717	3.112	0	0

APPENDIX II

THERMODYNAMIC PROPERTIES OF THE SORBENTS

AMYL AMMONIUM POLYPHOSPHATE/BENZENE HEPTYL AMMONIUM POLYPHOSPHATE/BENZENE

<u>% Sorbed</u>	<u>$\Delta \bar{S}$ e.u.</u>	<u>$\Delta \bar{H}$ cal</u>	<u>% Sorbed</u>	<u>$\Delta \bar{S}$ e.u.</u>	<u>$\Delta \bar{H}$ cal</u>
0.7	0.0	- 8.5	0.5	0.057	10.3
1.0	+ 0.053	+ 4.2	1.0	0.113	20.2
2.0	+ 0.107	+ 8.7	1.5	0.127	17.5
3.0	+ 0.167	+14.5	2.0	0.26	50.2
3.5	+ 0.207	+19.6	2.5	0.31	57.0
4.0	+ 0.263	+29.0	3.0	0.49	72.4
5.0	+ 0.043	-58.4	3.5	0.61	130
5.5	- 0.093	-110.3	4.0	0.66	135

HEPTYL AMMONIUM POLYPHOSPHATE/CYCLOHEXANE

<u>% Sorbed</u>	<u>$\Delta \bar{S}$ e.u.</u>	<u>$\Delta \bar{H}$ cal</u>
.5	0.061	12.2
1.0	0.097	16.1
1.5	0.11	11.5
2.0	0.15	16.3
2.5	0.17	14.4
3.0	0.13	- 5.4
3.5	- 0.077	-31.9

REFERENCES

1. Van Wazer and Kroupa, J.A.C.S., 78, 1772 (1956).
2. Hill, Faust and Reynolds, Amer.J.Sci., 242, 457,
542 (1944).
3. Van Wazer, "Phosphorus and Its Compounds, Vol. 1",
437 (1958)
Interscience Publishers.
4. McCullough, Van Wazer and Griffith, J.A.C.S.,
78, 4528 (1956).
5. Graham, Phil.Trans., 123, 253 (1833);
Ann.Physik., 32, 33 (1834).
6. Maddrell, Annalen, 61, 63 (1847);
Phil. Mag., 30, 32 (1847).
7. Partridge, Hicks and Smith, J.A.C.S., 63, 454 (1941).
8. Tamman, Prakt. Chem., 45, 417 (1892).
9. Osterheld and Audrieth, J.Phys.Chem., 56, 38 (1952).
10. Pascal, Chem.Reviews, 178, 1542 (1924);
180, 665 (1925).
11. Iler, J.Phys.Chem., 56, 1086 (1952).
12. Van Wazer, "Phosphorus and Its Compounds, Vol. 1",
454 (1958)
Interscience Publishers.
13. Powney, Nature, 152, 76 (1943).
14. Steigmann, J.Soc.Chem.Ind., 66, 355 (1947).
15. Ebel and Colas, Chem.Reviews, 239, 173 (1954).
16. Tayler, British Patent 798,600 (1958).
17. Weiss and Michel, Z.anorg.Chem., 296, 313 (1958).
18. Barrer and MacLeod, Trans.Faraday Soc., 50, 980 (1954);
19. 51, 1290 (1955).

20. Reay, Ph.D. Thesis, University of London (1956).
21. Kelsey, Ph.D. Thesis, University of London (1959).
22. Weiss, Chem.Ber., 91, 487 (1958).
23. Weiss, Mehler and Hofmann, Z.Naturforsch.,
11b, 431 (1956).
24. Weiss, Mehler and Hofmann, Z.Naturforsch.,
11b, 435 (1956).
25. Weiss and Weiss, Angew.Chem., 72, 413 (1960).
26. Weiss, Hartl and Hofmann, Z.Naturforsch.,
12b, 351 (1957).
27. Hartl and Weiss, Naturwiss., 49, 10 (1962).
28. Weiss, Michel and Fodues, Naturwiss., 49, 11 (1962).
29. Weiss and Michel, Z.anorg.Chem., 306, 277 (1960).
30. Weiss and Michel, Z.Naturforsch., 17b, 133 (1962).
31. Weiss and Michel, Z.Naturforsch., 15b, 807 (1960).
32. Weiss and Michel, Appl.Sci. and Tech. in Germany,
Serial 5, April 1961.
33. Volkova and Vol'kenshtein, Soviet Physics-JETP,
1705 (1960).
34. Flory, J.Chem.Phys., 17, 223 (1949).
35. Parker and Michaels, Thesis, Mass.Inst.Tech. (1958),
quoted by Platt, Ph.D. Thesis, University
of London, p.182 (1959).
36. Barrer, Barrie and Slater, J.Polymer Sci., 27,177(1958).
37. Hill, Adv.Catalysis, IV, 211 (1952).
38. Hill, J.Chem.Phys., 17, 520 (1949).
39. Hill, J.Chem.Phys., 18, 246 (1950).
40. Everett, Trans.Faraday Soc., 46, 453 (1950).

41. Everett, Trans.Faraday Soc., 46, 942 (1950).
42. Drain, Sci.Progress, 42, 608 (1954).
43. Freundlich, Z.physikal.Chem., 57, 385 (1906).
44. Langmuir, J.A.C.S., 40, 1361 (1918).
45. Volmer, Z.physikal.Chem., 115, 253 (1925).
46. Fowler, Proc.Camb.Phil.Soc., 31, 260 (1935).
47. Langmuir, J.A.C.S., 54, 2798 (1932).
48. Hill, J.Chem.Phys., 14, 441 (1946).
49. Tompkins, Trans.Faraday Soc., 46, 569 (1950).
50. Polanyi, VerhI.d.D.Phys.Ges., 15, 55 (1916).
51. Goldman and Polanyi, Z.physikal.Chem., A132, 321
(1928).
52. Bulkley, J.Res.Nat.Bur.Standards, 6, 89 (1931).
53. Bastour and Bowden, Proc.Roy.Soc., A151, 220 (1935).
54. Cohan and Meyer, J.A.C.S., 62, 2715 (1940).
55. Bowden and Throssel, Proc.Roy. Soc., A.209, 297(1951).
56. Folman and Shereshefsky, J.Phys.Chem., 59, 607 (1955).
57. Halsey and Taylor, J.Chem.Phys., 15, 624 (1947).
58. Brunauer, Emmett and Teller, J.A.C.S., 60, 309 (1938).
59. Hill, J.Chem.Phys., 14, 263 (1946).
60. Brunauer, "The Adsorption of Gases and Vapours.
Vol. I. Physical Adsorption", (1944), O.U.P.
61. Hill, J.Chem.Phys., 15, 767 (1947).
62. Halsey, J.Chem.Phys., 16, 931 (1948).
63. Barrer, Mackenzie and MacLeod, J.Chem.Soc., 1736 (1952).
64. Barrer, Mackenzie and MacLeod, J.Chem.Soc., 4184 (1953).

65. Harkins and Jura, J.A.C.S., 66, 1366 (1944).
66. Rao, J.Phys.Chem., 45, 500 (1941).
67. Brown and Foster, Research, 3, 97 (1950).
68. Carman and Raal, Proc.Roy.Soc., 209A, 59 (1951).
69. Gregg, "Surface Chemistry", p.205 (1949), Butterworths.
70. Pierce and Smith, J.Phys.Colloid Chem., 54, 784 (1950).
71. Wylie, Austral.J.Sci.Res., A5, 288 (1952).
72. Urquhart, J.Text.Inst., 20, 125 (1929).
73. Barkas, Nature, 148, 629 (1941).
74. Barkas, Trans.Faraday Soc., 38, 194 (1942).
75. White and Eyring, Text.Res.J., 17, 523 (1947).
76. Barrer, Drake and Whittam, Proc.Roy.Soc., A219, ³²₍₁₉₅₃₎.
77. Everett and Whitton, Trans.Faraday Soc., 48, 749(1952).
78. Everett and Smith, Trans.Faraday Soc., 50, 187 (1954).
79. Everett, Trans.Faraday Soc., 50, 1077 (1954).
80. Everett, Trans.Faraday Soc., 51, 1551 (1955).
81. Enderby, Trans.Faraday Soc., 51, 835 (1955).
82. Enderby, Trans.Faraday Soc., 52, 106 (1956).
83. Flory and Krigbaum, Ann.Rev.Phys.Chem., 2, 383 (1951).
84. Flory, J.Chem.Phys., 10, 51 (1942).
85. Flory, "Principles of Polymer Chemistry", Cornell University Press (1953).
86. Hildebrand and Scott, "The Solubility of Non-Electrolytes", 3rd Edit., Reinhold (1950).
87. Scatchard, Chem.Reviews, 8, 321 (1931).

88. Gee and Treloar, Trans.Faraday Soc., 38, 147(1942).
89. Gee and Orr, Trans.Faraday Soc., 42, 507 (1946).
90. Gee, Trans.Faraday Soc., 38, 276 (1942).
91. Gee, Trans.Faraday Soc., 38, 418 (1942).
92. Scott and Magat, J.Polymer Sci., 4, 555 (1949).
93. Weiss and Michel, private communication.
94. Seidel and Linke, "Solubilities of Organic Compounds,"
Supplement to 3rd Edit., Van Nostrand (1952).
- 95a Murray & Hartley, Trans.Farad.Soc. 31 183-9 (1935)
- 95b McBain and Bakr, J.A.C.S., 48, 690 (1926).
96. Jost, Naturwiss., 49, 229 (1962).
97. Corbridge, Acta.Cryst., 2, 308 (1956).
98. Romers, Ketelaar and MacGillavry, Acta Cryst.,
4, 114 (1951).
99. Hampson and Stosick, J.A.C.S., 60, 1814 (1938).
100. Dornberger-Schiff, Liebau and Thilo, Acta Cryst.,
55, 8, 752 (1955).
101. Buerger, Proc.Nat.Acad.Sci., 42, 113 (1956).
102. Hilmer, Acta Cryst., 2, 87 (1956).
103. Jost, Acta Cryst., 14, 779 (1961).
104. Jost, Acta Cryst., 14, 844 (1961).
105. Von Sydow, Arkiv för Kemi, BD.9, Nr. 19, (1956).
106. Vand and Bell, Acta Cryst., 4, 465 (1951).
107. Bunn, Trans.Faraday Soc., 35, 482 (1939).
108. Vainshtein and Pinsker, Dokl.Akad.Nauk.SSSR,
72, 53 (1950).
109. Thilo and Jost, Soviet Phys.Cryst., Vol.6, No.6,
670 (1962).

110. Andress and Fischer, *Z.anorg.Chem.*, 273, 193 (1953).
111. Corbridge, *Acta Cryst.*, 8, 520 (1955).
112. Timmermans, "Physico Chemical Constants of Pure Organic Compounds", Elsevier (1950).
113. Pauling, "The Nature of the Chemical Bond", 3rd edit., Cornell U.P., O.U.P. (1960).
114. Cox, *Revs.Mod.Physics*, 30, 159 (1958).
115. Johnson, Bauer, Margrave, Frisch, Dreger and Hubbard, *J.A.C.S.*, 83, 606 (1961).
116. Barrer and Reucroft, Ph.D. Thesis, University of London (1959).
117. Bering and Serpinski, *Doklady Akad.Nauk SSSR*, 114, 1254 (1957).