

APATITE SURFACES MODIFIED BY REACTION WITH ALIPHATIC
DIAZO COMPOUNDS

A Thesis submitted for the degree of
Master of Philosophy
in the University of London,
by John David Wynne Hudson, B.Sc.

Physical Chemistry Laboratories

June, 1970.

Imperial College of Science and Technology,

South Kensington,

London, S.W.7.

ABSTRACT

Stoichiometric and calcium deficient apatites have been treated with ethereal solutions of aliphatic diazo compounds in attempts to bring about chemical reactions with the surfaces of these salts.

Isotherms of nitrogen and water have shown that the diazo reaction forms a stable chemisorbed monolayer on the apatite and these modified salts are less hydrophilic than their parent apatites.

The nature of the diazo reaction at the surface of apatites has been elucidated by an analysis of results obtained from sorption studies, chemical analysis, infra-red spectroscopy and X-ray, powder diffraction photography. A mechanism for this reaction, consistent with the surface chemistry and geometry of apatites and with the chemistry of aliphatic diazo compounds, is presented.

ACKNOWLEDGEMENTS

The author wishes to express his sincere gratitude to Professor R.M. Barrer, F.R.S., and to Mr. R. Ash for their guidance throughout the course of this work.

Thanks are due to Dr. I.S. Kerr for the X-ray powder diffraction photography measurements, and to the technical staff of Imperial College for their indispensable assistance.

This work would not have been possible without the continued support and encouragement of my wife and parents, to whom sincere thanks are given.

Finally, gratitude is acknowledged to the S.R.C. for financial support during the period October, 1966, to September, 1968.

CONTENTS

	Page.
Abstract	2
Acknowledgements	3
Contents	4
Chapter 1 Introduction	8
Chapter 2 Materials and Literature Survey	21
2.1 The Apatites	21
2.1.1 Hydroxyapatite and related salts	21
2.1.2 The crystal structure of	23
hydroxyapatite.	
2.1.3 The crystal structure of non-	36
stoichiometric apatite.	
2.1.4 Some surface properties of apatites.	55
2.2 Aliphatic diazo compounds	62
2.2.1 Introduction	62
2.2.2 Structure of the diazoalkanes	64
2.2.3 Properties of the diazoalkanes	66
Chapter 3 Theory	76
3.1 Introduction	76
3.2 Theoretical aspects of adsorption	78
3.2.1 Physical adsorption	78
3.2.2 Chemisorption	89
3.3.1 Infra-red spectroscopy	90
3.3.2 X-ray powder diffraction	104.

	Page.
Chapter 4	Preparation of Materials 105
4.1	Preparation of apatites and related salts. 105
4.1.1	Hydroxyapatite 105
4.1.2	Non-stoichiometric apatites 109
4.1.3	Octa-calcium phosphate 111
4.1.4	The pyrolysis of calcium phosphate 112
4.1.5	Materials obtained from other sources. 114
4.2	Preparation of aliphatic diazo-compounds 114
4.2.1	Preparation of disubstituted derivatives of diazomethane 115
4.2.2	Preparation of an ethereal solution of diazomethane 115
4.2.3	Preparation of an ethereal solution of ethyl diazoacetic ester 116
4.2.4	Preparation of ethereal solutions of the higher homologues of diazomethane. 118
4.2.5	Preparation of ethereal solutions of the higher homologues of diazomethane 120
4.3	Preparation of surface modified apatites and related salts 123
Chapter 5	Experimental Techniques 128
5.1	Sorption apparatus 128

	Page.
5.1.1 Pumping system	128
5.1.2 Volumetric sorption apparatus	130
5.1.2.1 Measurement of isotherms	133
5.1.3 Gravimetric sorption apparatus	136
5.1.3.1 Measurement of isotherms	138
5.2 Other apparatus and techniques involved in this study	139
5.2.1 Chemical analysis	140
5.2.1.1 Calcium phosphate materials	140
5.2.1.2 Aliphatic diazo compounds	140
5.2.1.3 Surface modified materials	141
5.2.2 Infrared spectroscopy	141
5.2.3 X-ray powder diffraction	143
Chapter 6 Results and Discussion	145
6.1 Characterisation of materials	145
6.1.1 Nitrogen sorption studies	145
6.1.1.1 Determination of the specific surfaces of materials studied in this work	151
6.1.1.2 The c parameter of the B.E.T. equation	159
6.1.1.3 Heats of adsorption	163
6.1.2 Chemical analysis	166
6.1.2.1 Chemical analysis of apatites	166

	Page
6.1.2.2 Chemical analysis of aliphatic diazo compounds	170
6.1.2.3 Chemical analysis of modified apatites	171
6.1.3 Infrared spectroscopy	175
6.1.3.1 Infrared spectra of apatite and related salts	175
6.1.3.2 Infrared spectra of modified apatites	184
6.1.4 X-ray powder diffraction	186
6.1.5 General survey of some of the characteristics of these apatites and modified apatites	188
6.2 Water sorption results	189
6.2.1 Water sorption isotherms	189
6.2.2 Comparison of water sorption results	194
6.2.3 The parameter c of the B.E.T. equation	206
6.2.4 Kinetics of adsorption	211
6.2.5 General discussion of the water sorption results	211
Chapter 7 Conclusions	217
References	220

CHAPTER I

INTRODUCTION

Various attempts have been made to find adhesives which will bond permanently to both dentine and enamel¹⁻⁵, since restoratives in current use are limited by their lack of adhesion, in vivo, to the tooth structure. Although the problems associated with cementation are complex, they are most probably centred around the fact that the bond with the tooth structure has to survive in continuous contact with water.

Much attention has been paid to the properties of the component tissues of teeth. (The approximate compositions of samples of enamel, dentine, cementum and bone are given in Table 1.) Enamel is very largely inorganic in its composition. It forms the hard, non-vital covering of teeth over the softer, vital dentine, with bone, the third hard, calcified tissue of the body, differing from enamel and dentine in acting as a store of calcium and phosphorus. The inorganic component of the skeletal tissues is an apatite whose x-ray diffraction pattern differs little from the mineral hydroxyapatite. Enamel contains rod-shaped apatite crystals, elongated in the direction of the c-axis and having dimensions of

Table 1

Chemical composition of enamel, dentine, cementum and bone⁶.

	<u>Enamel</u>	<u>Dentine</u>	<u>Cementum</u> <u>Compact Bone</u>
Water	2.3%	13.2%	32%
Organic matter	1.7%	17.5%	22%
Ash	96.0%	69.3%	46%
In 100g of ash			
Calcium	36.1g	35.0g	35.5g
Phosphorus	17.3	17.1	17.1
Carbon dioxide	3.0	4.0	4.4
Magnesium	0.5	1.2	0.9
Sodium	0.2	0.2	1.1
Potassium	0.3	0.07	0.1
Chlorine	0.3	0.03	0.1
Fluorine	0.016	0.017-	0.015
Sulphur	0.1	0.2	0.6
Copper	0.01		
Silicon	0.003		0.04
Iron	0.0025		0.09
Zinc	0.016	0.018	
Lead	0.037	0.037	0.02
Together with traces of:			
Ce, La, Pr, Ne, Ag, Sr, Ba, Cr, Sn, Mn, Ti, Ni, V, Al,			
B, Cu, Li, Se.			

the order of 2000 x 500 Å. The crystals in dentine and bone are similarly elongated but their size is reduced to about 500 x 100 Å. An organic matrix of the protein collagen surrounds the inorganic component of bone and dentine, but little is known of the organic portion of enamel. Apatite and organic protein fractions are the only crystalline phases ever observed in healthy bone, dentine and enamel, and bonding to tooth material may involve either or both of these.

The name 'apatite', coined by Werner in 1790 from the Greek 'to deceive'⁷, remains an accurate description of the salt. The elucidation of the crystal chemistry of biological apatites is still a major problem^{8,9}. Until recently, the position of carbon dioxide in the biological apatites was a subject of much speculation. From a review of the literature on the mineral phase of bone⁹ it was concluded that, although carbonate or possibly bicarbonate ions are located on the surface of apatite crystals and carbon dioxide may be located elsewhere, it could not be present as a separate carbonate phase. Later considerations of the location of carbon dioxide have placed it in the form of carbonate ions bonded to surface calcium or magnesium ions¹⁰, and replacing orthophosphate ions¹¹. An infra-red and

x-ray crystallographic study¹² has recently revealed that carbonate ions in dental enamel are in two different environments. One location is very probably the substitution position of certain hydroxyl ions and accounts for a small fraction of the carbonate ions, the remainder are apparently adsorbed onto the surface of the apatite crystals.

The problem of the carbonate-containing apatites is associated with the structure of non-stoichiometric homologues for in the basic region of the $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$ system, crystalline phases may be precipitated which yield X-ray diffraction patterns typical of hydroxy-apatite whilst deviating considerably from the composition of this salt. Non-stoichiometric apatites have been reported with compositions over a range of Ca/P molar ratios from $\frac{4}{3}$ to $\frac{5}{3}$ ¹³. It was thought that phosphate ions adsorbed onto the surface of apatites accounted for low calcium contents^{14,15}, but synthetic apatites have been prepared with surface areas far too small for their non-stoichiometry to be achieved by surface adsorption^{16,17}. Apparent calcium deficiencies may result from the simultaneous presence of brushite (dicalcium phosphate dihydrate), monetite (anhydrous dicalcium phosphate) and octacalcium phosphate in the precipitated solids¹⁸.

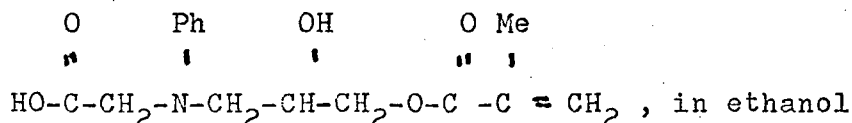
There are two models which represent current opinion as to the structure of non-stoichiometric apatites. One is based on epitaxial intergrowths of hydroxyapatite and octacalcium phosphate,¹⁹ and the other describes a continuous series of compositions with defects in the apatite lattice²⁰⁻²⁵. Both will be examined further in Chapter II.

Adhesion of restoratives to the tooth structure may be considerably influenced by the high proportion of apatite, an energetic water adsorbent²⁶. An adhesive possessing a greater affinity than water for this salt is therefore necessary. A search for molecules which might react with the apatite surface to give stable, chemisorbed films is needed, the aim being to reduce permanently the hydrophilic nature of the apatite and yield a surface which would adhere to various polymeric materials. The systematic approach to the problem of finding molecules which would not be displaced by water includes an investigation of the suitability of certain surface-active agents to cause preferential wetting of powdered tooth tissues by the organic phase of a water/*n*-butanol system⁴. These normally hydrophilic powders became organophilic when the surface-active agent had an adequate hydrocarbon portion and when its polar group

had the ability to compete successfully with water for the powder surfaces.

Calcium ions on the apatite surface form rather weak chelate linkages with suitable polar groups²⁷. Surface active compounds containing groups theoretically capable of forming an amphoteric five-atom chelate ring with apatitic calcium ions are effective in competing with water for the surface⁴. The uptake of tetracycline by mineralised bone is probably due to the formation of β -diketone to calcium links²⁸. Proteins and other amino acids may be chromatographically separated by hydroxyapatite, an effect which is probably attributable to amino acid-calcium complexation.

A surface-active compound which is able to co-ordinate with apatitic surface calcium ions and to react or copolymerise with the monomer of a restorative polymer would form a useful intermediate between the two phases. Recent investigations of these 'surface-active comonomers' have led to certain fairly successful treatments^{29,30}. The addition-reaction product of N-phenylglycine and glycidyl methacrylate provides an example of this type of compound. A 5% solution of the comonomer,



was applied to dentine prior to the application of methacrylate resin and significantly improved subsequent adhesion of the restorative²⁹.

Tooth surfaces pretreated with dilute mineral acids have bonded well with acrylic restorative materials³⁰⁻³⁴. Dentine treated with either dilute acid or base adheres well to methacrylate restoratives, especially if a surface active comonomer was also applied after rinsing and drying the dentine³⁰. Clinical trials of enamel surfaces restored with a filled methyl-2-cyanoacrylate have shown³⁰ that pretreatment of the tooth with a phosphoric acid conditioning agent aided adhesion, but further restorative was needed after only eight months. Adhesion to dentine under oral conditions has not been achieved by this method. Contact angle measurements on human tooth surfaces have shown that, before acid treatment, these surfaces are hydrophobic, yet water and epoxy resins gave zero contact angles, indicating hydrophilicity, after treatment with phosphoric acid³⁵. This result suggests that enamel is not extensively exposed on the tooth surface but may be covered with a thin film of organic material. Acids other than phosphoric have similar effects on the tooth surface. Adhesion of acrylic restoratives to enamel is improved by the application of dilute hydrochloric acid

to the tooth surface³⁴,

Attention has been paid recently to restorative systems containing homopolymers and copolymers of methyl methacrylate³⁴. There are many advantages of using fast-setting acrylic adhesives for bonding plastic attachments to human tooth surfaces. Setting times may be varied over a wide range; desirable properties can be built into the acrylic systems by the incorporation of suitable comonomers into polymer and monomer-polymer mixtures; acrylic systems are easy to mix and apply and can be prepared as to have reasonably long shelf-lives; the acrylic adhesives are a familiar clinical system; and most polymers based on methyl methacrylate show very low oral toxicity. Polymerisation of methyl methacrylate monomer may be initiated by a very low concentration of benzoyl peroxide, and N, N-dimethylaniline may be used to accelerate the reaction. Setting times may accordingly be adjusted by variation of benzoyl peroxide and N, N-dimethylaniline concentrations. Polymer or copolymer may be added to monomer to minimise shrinkage, which for a typical acrylic monomer on polymerisation is about 20%. Variations in the amount of additive effectively control the degree of shrinkage, which should ideally be avoided altogether to increase the strength of adhesive joints. The optimum molecular weight for polymer

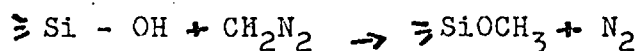
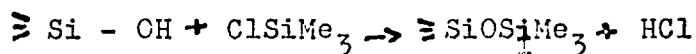
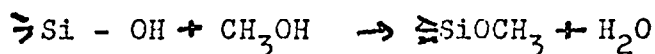
additives is about 20,000 : a 40% polymer solution in methyl methacrylate monomer gave an adhesive of acceptable viscosity and 12.4% shrinkage during setting.³⁴ Adhesives with poor physical properties generally resulted from use of lower molecular weight additives.

Quartz fillers of acrylic adhesive systems have been investigated as a potential means of reducing shrinkage during polymerisation. An improvement in the bond strength was noted with the addition of powdered quartz to acrylic monomer³⁴, but no significant improvement in the bond strength was found if a methacrylate substituted, silane coupling agent was used in quartz-filled acrylic polymers. Coupling agent without added quartz actually decreased the joint-strength substantially.

Water has been found to have a deleterious effect on bond strengths in acrylic restorative systems with the breakdown in strength proportional to the logarithm of the time of immersion after peak strength has been attained³⁴. Although a copolymer of 80% methyl methacrylate with methacrylic acid has reasonably good bond strength with the tooth surface after a period of immersion of one year at 37°C, continued immersion would doubtless result in the eventual breakdown of the bond.

Siliconising treatments are known to produce profound

changes in the hydrophilic character of the various silicas. Methanol³⁷, trimethyl chlorosilane³⁸ and diazomethane³⁹ form hydrophobic monolayers of chemisorbed groups on hydroxylated silicas, resulting from the following reactions at the silica surface:



Trimethyl silyl groups provide a surface on silica which is both durable in contact with liquid water⁴⁰ and thermally stable⁴¹. A substantial reduction in the hydrophilic character of aerosil silicas, after prior treatment with hexamethyl disilazane, has also been noted⁴².

Reactions between zinc oxide and some n-alkyl thiols⁴³, between chromia and methanol and ethanol⁴⁴, and between alumina and ethanol⁴⁵ all yield monolayers of chemisorbed organic groups.

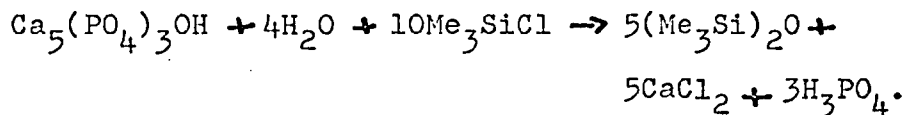
The grafting of long alkyl chains to apatite surfaces might promote adhesion to polymers since the chains could become entangled with the polymer. This suggests that the surface of teeth or synthetic apatites may react to yield hydrophobic monolayers if suitable reagents could be found. A carious tooth might then be restored in such

a way that good adhesion would result between it and a polymer of suitable physical properties. Polymer-surface modified apatite composites might also be prepared with good cohesion by the preparation of restorative materials with reduced thermal expansion and improved bulk strength. The filler would also reduce shrinkage during curing.

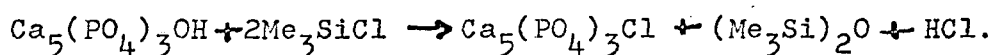
Dry samples of synthetic apatite powder have been treated with silane derivatives such as Me_2SiCl_2 , Me_3SiCl , $\text{C}_{18}\text{H}_{37}\text{SiCl}_3$ and $(\text{Me}_3\text{Si})_2\text{NH}$, either dissolved in solvents or as the pure reagents, in open and sealed vessels and at temperatures ranging from 20°C to 200°C ⁴². These treatments altered the subsequently measured adsorption isotherms of water, but the changes were not permanent and progressive sorption runs gave isotherms which tended to return towards the curve for pure apatite. When two evacuated gravimetric sorption units were interconnected, material distilled from a modified apatite in one unit to a pure apatite in the second. This could be followed by the approach of the initially different water sorption isotherms to a mean curve.

Treatment of apatite with liquid trimethyl chlorosilane at 60°C yielded a hygroscopic product, found to be a mixture of calcium chloride and dicalcium phosphate

dihydrate by X-ray examination, and although no hydroxy-apatite was found in the product, an examination by mass spectrometry indicated the presence of the silyl ether, $(\text{Me}_3\text{Si})_2\text{O}$, in a trimethyl chlorosilane solution⁴². Hydroxyapatite may have decomposed according to the equation:



Some calcium chloride may then have reacted with phosphoric acid and water to produce the calcium phosphate found present. The removal, by evacuation, of water from apatite prevented the occurrence of bulk decomposition, nevertheless no stable chemisorbed alkyl silane layers were formed and the materials modifying the surface were considered to be silyl ethers:



The formation of silyl ether liberates a little hydrochloric acid which may further attack the apatite surface. Silyl ethers are volatile liquids so that lack of permanence of the surface films and the previously noted easy transport in vacuo from sample to sample is readily understood.

The lack of success in achieving stable surface groups by the treatment of apatites with silane derivatives points to the difficulty of forming an Si-O-P

bond. It is noteworthy in this connection that hydrothermal reactions involving alkaline magmas with phosphate, aluminium hydroxide and colloidal silica⁴⁶ yielded aluminophosphates and aluminosilicates but never any silicophosphates containing such a bond.

Silica, alumina and hydroxyapatite have been treated with ethereal solutions of diazomethane⁴². These normally hydrophilic sorbents were all rendered substantially less hydrophilic and the surfaces were stable to outgassing at 100°C and to repeated water sorption measurements. The reaction of diazomethane, and other aliphatic diazocompounds, with the surface of various synthetic apatites has accordingly been made the subject of this work.

CHAPTER 2

MATERIALS AND LITERATURE SURVEY2.1 The Apatites2.1.1 Hydroxyapatite and related salts.

The apatite series, an important phosphate group crystallising in the hexagonal system and insoluble in water, is the chief mineral source of phosphorus in the chemical and fertiliser industries.

Stoichiometric apatites may be represented by the formula $M_{10}X_2(RO_4)_6$ where all cation sites (M) may be occupied by divalent ions of lead, strontium, zinc or cadmium as well as of the more usual calcium. Provided electrical neutrality is maintained, some cation sites may contain other species such as sodium, potassium, manganese, magnesium, iron, aluminium, water and cerium. Anions of fluorine, hydroxide, chlorine and carbonate occupy sites (X), and phosphate, arsenate, vanadate and silicate can fill sites RO_4 , although the divalent ions of carbonate and sulphate may be found at this normally trivalent site.

Naturally occurring apatites are divided into two main groups, with only small amounts of exceptional materials: apatite is reserved as the name for calcium containing salts such as hydroxyapatite, fluorapatite,

francolite and dahlite while the pyromorphite series contains lead as the dominant cation and includes pyromorphite, mimelite and vanadite. The calcium series contains fluorine and hydroxyl ions in X positions.

Hydroxyapatite, belonging to the calcium series, and other similar substances are of principal interest in this work, and a brief survey of the members of this series will first be made.

Fluorapatite, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, occurs in igneous rocks as small prismatic crystals of hexagonal section, fine examples occurring at Durango, New Mexico. Chloride ions often replace some of the fluoride ions to give slightly variable refractive indices. Hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ occurs as a rare mineral at Hospenthal, Switzerland⁴⁷, and in the hydrothermal deposits at Holly Springs, Georgia, U.S.A.⁴⁸

Francolite, a crystalline fluorapatite-like mineral containing up to 6% carbon dioxide, has been found as a thin, colourless, confusedly crystalline crust on a fibrous quartz mass at Wheal Franco, Tavistock, Devon⁴⁹; while specimens of francolite occurring in sedimentary

ironstone from the Yorkshire coalfields have been described which were up to one millimetre diameter, hexagonal plates, consisting of the basal plane and a low pyramid, twined in six triangular sectors.⁵⁰ It can also come from sources such as hydrothermal ore deposits, marine phosphates, or freshwater sediments. At Bamle, Norway, dahlite, a carbonate-containing, fluorine-free apatite mineral has been found⁵¹, occurring as a pale yellow crust on apatite. Some well formed hexagonal crystals of about 2mm in diameter and containing no fluorine have been found in Podolia, Russia⁵², and have been assumed to be dahlite⁵³. It has been suggested that francolite is merely dahlite in which the fluorine content exceeds 1%⁵⁴.

2.1.2 The crystal structure of hydroxyapatite.

The space group of fluorapatite, $P6_3/m$, was determined from X-ray diffraction photographs in 1923⁵⁵, two authors, independently, confirmed this space-group and suggested structures of the material⁵⁶⁻⁵⁸. The position of the fluorine atom in the crystal lattice was the only difference in the suggested structures and although a choice between the two possibilities is difficult to make, later authors^{59,60} have accepted and improved upon the Naray-Szabo⁵⁶ analysis, with fluorine at $00\frac{1}{4}$, $00\frac{3}{4}$. Mehmel^{57,58}, in suggesting that the fluorine positions

were 000 , $00\frac{1}{2}$, proposed a structure similar to the one now accepted⁵⁹ for the chlorine positions in chlorapatite.

Anions X occur on the rotation axis through calcium triangles and the anions are not essential for the determination of the main structure. Although these interstices are usually filled in some regular way by various ions, as suggested above, such filling is not always necessary (it has been reported that $\text{Pb}_5(\text{PO}_4)_2\text{SiO}_4$ ⁶¹ and $\text{Ba}_{10}(\text{PO}_4)_5\text{BO}_4$ ⁶² have apatite-like structures in which these channels are, ostensibly, empty.) Because of the largeness of these channels and the fact that they are supported by the rest of the structure, one is led to expect that they may provide easy diffusion paths. It is known that F replaces OH in fossil bone and, more significantly, it has been shown⁶³ that a single crystal of synthetic chlorapatite may be changed, by a diffusion process at 1200°C , into a single crystal of hydroxyapatite, the resulting crystal containing only 6 per cent of its original chlorine.

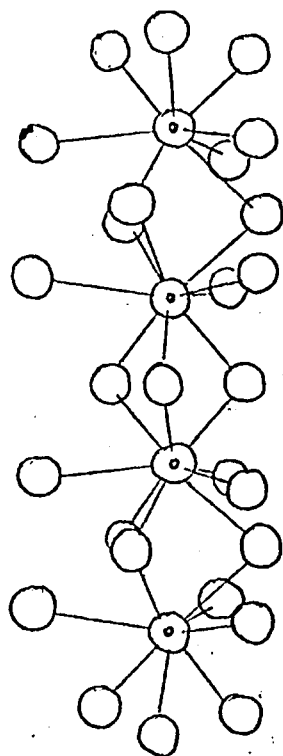
A more recent study of the fluorapatite structure⁶⁰ gives hexagonal lattice constants of $a = 9.37 \text{ \AA}$, $c = 6.88 \text{ \AA}$, with the lattice containing two different kinds of calcium ions and three different kinds of oxygen. Situated along each of the three-fold axes, half the height of a unit

cell apart, is a column of calcium ions. Adjacent calciums, in each column, are bonded by means of three shared oxygens which lie in a horizontal plane of symmetry (see figure 2.1a), in addition to which each of these calcium ions is bonded, at greater distance, to three other oxygen atoms which lie in a plane almost at the same height. This arrangement of calcium and oxygen ions forms a continuous vertical column with each calcium co-ordinated with nine oxygen atoms. That there is not an identical repeat of the oxygen arrangement around successive calcium ions, but rather for alternate calciums, is because each set of three shared oxygens is rotated about the chain axis. Furthermore, the sets of oxygen atoms linked to only one calcium ion, although accurately coincident when viewed down the c-axis, are alternately raised and lowered in a direction parallel to the c-axis so that some of the oxygen atoms are closer than others. This approach enables each close pair to become oxygen atoms of the same phosphate ion, a third oxygen of this ion is one of those shared by two calcium ions in a column. The fourth oxygen of the phosphate ion projects outwards from the column; this and like oxygens link adjacent calcium-oxygen columns together (see figure 2.1b) and constitute shared oxygens of the adjacent column. Neighbouring columns are related to each other by a

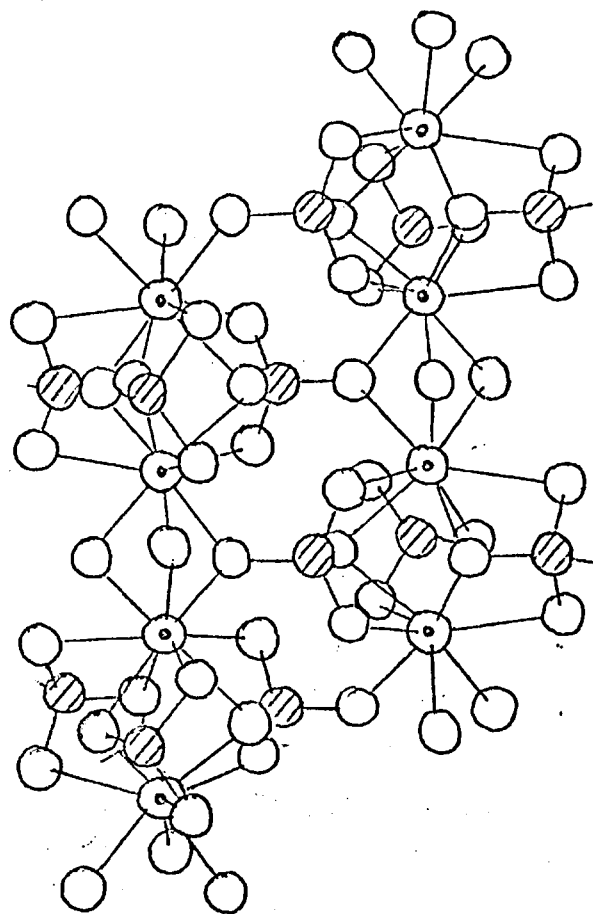
Figure 2.1.

Calcium ion columns

(a.)



(b.)



○ Oxygen

● Calcium

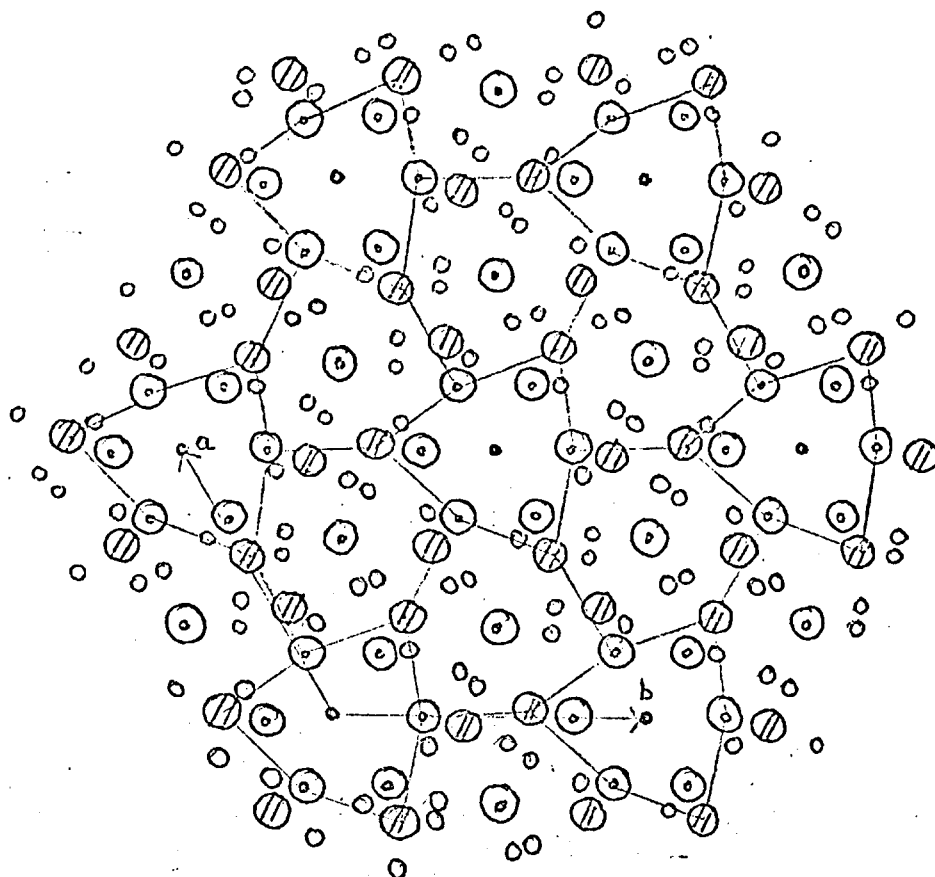
▨ Phosphorus

two-fold screw axis placed midway between them, and the columns, linked in the manner described above, result in a hexagonal honeycomb with channels extending throughout the structure. The walls of these channels are lined with oxygen atoms, the arrangement being such that there are, in the wall of each channel, six cavities per unit cell length. Additional calcium ions are fitted into these cavities, one calcium going about halfway into each. The addition of a fluorine atom at $(00\frac{1}{2})$ and $(00\frac{3}{2})$ (which are the centres of each triangular array of the 'cavity' calciums) completes the fluorapatite lattice (see figure 2.2).

The space group and unit cell dimensions, obtained from X-ray data, of a mineral sample of hydroxyapatite mined in Holly Springs, Georgia, U.S.A., have been found⁶⁴ to be $P6_3/m$ and $a = 9.432\text{\AA}$, $c = 6.881\text{\AA}$. The overall structure is indicated in figure 2.3.

Neutron diffraction data have been used more recently⁶⁵ to determine the position of the hydrogen atom of the hydroxyl group, the oxygen atom of the group is located about $0.3\text{\AA}$ (on the average) above or below the triangle of calcium ions on the mirror planes at $z = \frac{1}{4}$, $z = \frac{3}{4}$. The geometry is approximately similar to that found in calcium hydroxide, but each side of this triangle is $4.09\text{\AA}$ in

Figure 2.2

Fluorapatite lattice viewed along the c axis

● Fluorine

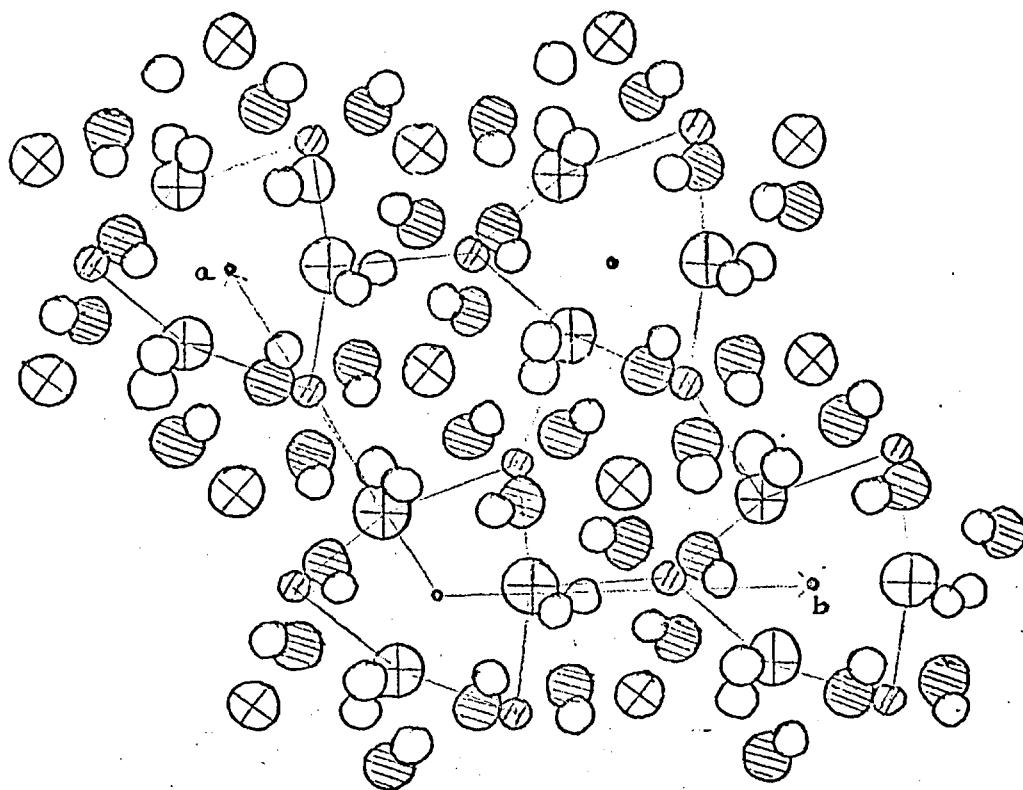
○ Oxygen

⊙ Calcium

⊘ Phosphorus

Figure 2.3

Hydroxyapatite lattice viewed along the c axis



- | | | | |
|---|------------------|---|-----------------------|
| • | Hydroxyl group | ● | Oxygen |
| ⊗ | Columnar calcium | ⊘ | Phosphorus |
| ⊕ | Hexagonal " | ○ | Atoms in other planes |

length as compared with $3.59\text{\AA}$ in the hydroxide. A distance of $2.38\text{\AA}$ for the $\text{Ca}-\text{O}_\text{H}$ distance in hydroxyapatite is comparable with the distance of $2.37\text{\AA}$ in calcium hydroxide, and this may be explained by a simple study of the geometry of this environment. The hydroxyapatite hydroxyl group could drop closer to the calcium plane by an expansion of the calcium triangle, the $\text{Ca}-\text{O}$ distance is maintained the same as for the smaller calcium triangle of the hydroxide.

Motion of the hydroxyl ion in hydroxyapatite, in the c direction, would be almost perpendicular to the $\text{Ca}-\text{O}_\text{H}$ direction and therefore such motion may become relatively large without appreciably changing the $\text{Ca}-\text{O}_\text{H}$ length. This has been born out by neutron diffraction studies which also indicated that, perpendicular to the c direction, thermal motion of the O_H is relatively small while motion of the H is quite large. Such large vibrational motion of the hydrogen about the centre of mass of the hydroxyl group is consistent with the generally open nature of the structure in this neighbourhood.

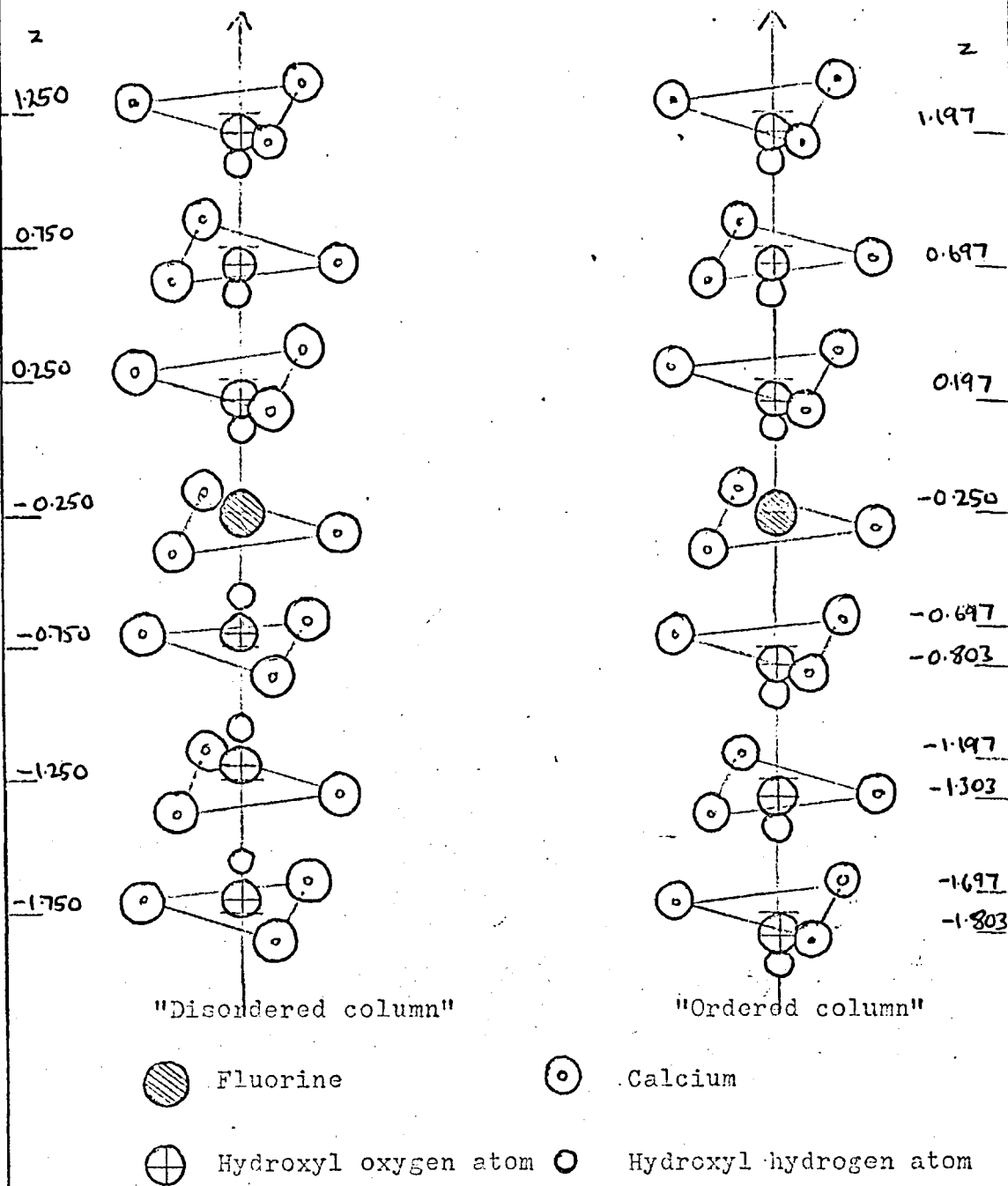
The displacement of the hydroxyl oxygen atoms from the mirror planes $z = \frac{1}{4}, \frac{3}{4}$ leaves a distance of $0.7\text{\AA}$ between half oxygens, implying a configuration in which only one of the two possible positions is filled. Neutron

diffraction data has shown that the hydroxyl groups do not straddle the mirror plane, thus two models for the hydroxyl group position are indicated. In the 'disordered column' model the orientation of hydroxyl groups is reversed at various places within a column, whereas in the 'ordered column' model all the groups in a given column are oriented in the same way, although the choice of orientation is random (see figure 2.4). Some special structural circumstances may occur at such places where the direction of the O-H group is reversed in the 'disordered column' model.

Several possibilities have been suggested as causes for reversals in hydroxyl ion direction^{65,66}, since present data are inadequate for the determination of structural detail as fine as a reversal mechanism, for this need operate only in a relatively small number of unit cells. If hydroxyl groups were to extend towards each other from the mirror planes $z = \frac{1}{4}, \frac{3}{4}$, the hydrogen atoms would be very close. In the case of pure synthetic hydroxyapatite it seems either that vacancies must exist at these reversal points to prevent close approach of hydroxyl groups or that the ordered column model should apply, but it may be possible for an occasional O-H to be placed across the mirror plane or for an occasional hydroxyl pair to be pointing generally toward each other from adjacent mirror

Figure 2.4

"Disordered column" and "ordered column" models for the hydroxyl group position.



planes while individual ions make a substantial angle with the c axis⁶⁶.

Some fluorine has always been found in mineral hydroxyapatite. An atom of fluorine at the centre of a calcium triangle might have some attraction for the hydrogen of neighbouring hydroxyl groups, and such an impurity might even be expected to produce disorder within the column. At the least such an impurity would accommodate disorder. Present structure determinations of the fluorine in fluorapatite place it at $z = \frac{1}{4}$, $\frac{3}{4}$, or at the centre of the calcium triangles⁵⁶. A polar moment with fluorine is not made up by the triangle as with a hydroxyl group, or a chlorine in chlorapatite, and the lack of such a moment may contribute to the greater chemical stability of fluorapatite; for example its lower solubility and greater resistance to dissolution in acids. Recent in-vivo bone apatite growth-rate investigations have demonstrated^{67,68} that fluoride-containing bone apatite grows more rapidly and to larger crystallite size than the fluoride-free specimens, an effect which may be interpreted as being due to the stability difference between ordered and disordered column models for hydroxyapatite. Several authors have suggested that the reduction in the rate of dissolution of dental enamel when small amounts of fluoride

are present may be caused by fluorine hindering the transport of hydroxyl ions along the 6_3 -axis⁶⁶.

NMR experiments on a mineral sample of hydroxyapatite from Holly Springs have been useful in the elucidation of the crystallography of linear chains of hydroxyl ions in apatites⁶⁶. The sample contained about one fluorine atom for every eleven hydroxyl ions. Recordings of the fluorine resonance line for H_O parallel to the c-axis were considered to consist of the superposition of a triplet and a doublet. The configuration H-F-H gives rise to the triplet while the H-F-vacancy configuration produces the doublet. These results showed that the H to F distance in the H-F-vacancy configuration is $2.12 \pm 0.03 \overset{O}{\text{Å}}$ while the H to F distance in the H-F-H configuration is $2.18 \pm 0.02 \overset{O}{\text{Å}}$ and compare most favourably with the H-F distance calculated from neutron diffraction data, if it is assumed that the fluorine atom has the same position in hydroxyapatite as it has in fluorapatite, this distance is $2.13 \overset{O}{\text{Å}}$ (see figure 2.4). O-H-F hydrogen bonding is possibly the cause of the lower result for the H-F distance in the H-F-vacancy configuration, it being conceivable that such hydrogen bonding could account for the reduced mobility of hydroxyl groups adjacent to fluorine atoms. The existence of weak hydrogen bonds

may account for the additional infra-red adsorption band⁶⁹, near 3540 cm^{-1} , of mineral hydroxyapatite which according to recent measurements⁷⁰, is split into two separate peaks. The disordered column model for hydroxyapatite suggests that the hydroxyl ions are not in their lowest possible energy state, this particular contribution to the free energy of the crystal would be reduced if an ion were substituted into an ordered position. Preferential replacement of OH by F at ordinary temperatures may be partly due to fluorine substitution into ordered positions, but the large difference in the heats of formation of fluorapatite and hydroxyapatite makes it clear that statistical disorder cannot be the major source of energy difference.

The large rocking motion of the hydrogen atom perpendicular to the c-axis⁶⁶ suggests that the atom may be brought closer in turn to an oxygen atom on each of the three surrounding phosphate groups. If this was the case then a bifurcated type of hydrogen bonding would occur, which would result in a low frequency deviation of the band due to the hydroxyl ion stretching frequency.⁷¹ The observed value of 3566 cm^{-1} ⁷² for this mode is in fact slightly lower than the value predicted for a linear O-H.... OPO_3 arrangement⁷¹, namely 3578, and is substantially

lower than the values for this frequency in systems where no H-bonding occurs (water vapour, 3755cm^{-1} ⁷³; $\text{Ca}(\text{OH})_2$, 3644cm^{-1} ⁷⁴; $\text{Mg}(\text{OH})_2$, 3698cm^{-1} ⁷⁵; and LiOH , 3678cm^{-1} ⁷⁶).

The case for hydrogen bonding is substantially supported if the observed band at 633cm^{-1} ⁷² is assigned to a librational mode of the hydroxyl ion. This band is considerably higher than that in magnesium⁷⁷, calcium⁷⁸ and lithium⁷⁹ hydroxides for the same motion, namely 380cm^{-1} . This result suggests that hydrogen bonding to three phosphate groups in turn makes a large contribution to the librational force constant.

2.1.3 Crystal structure of non-stoichiometric apatites.

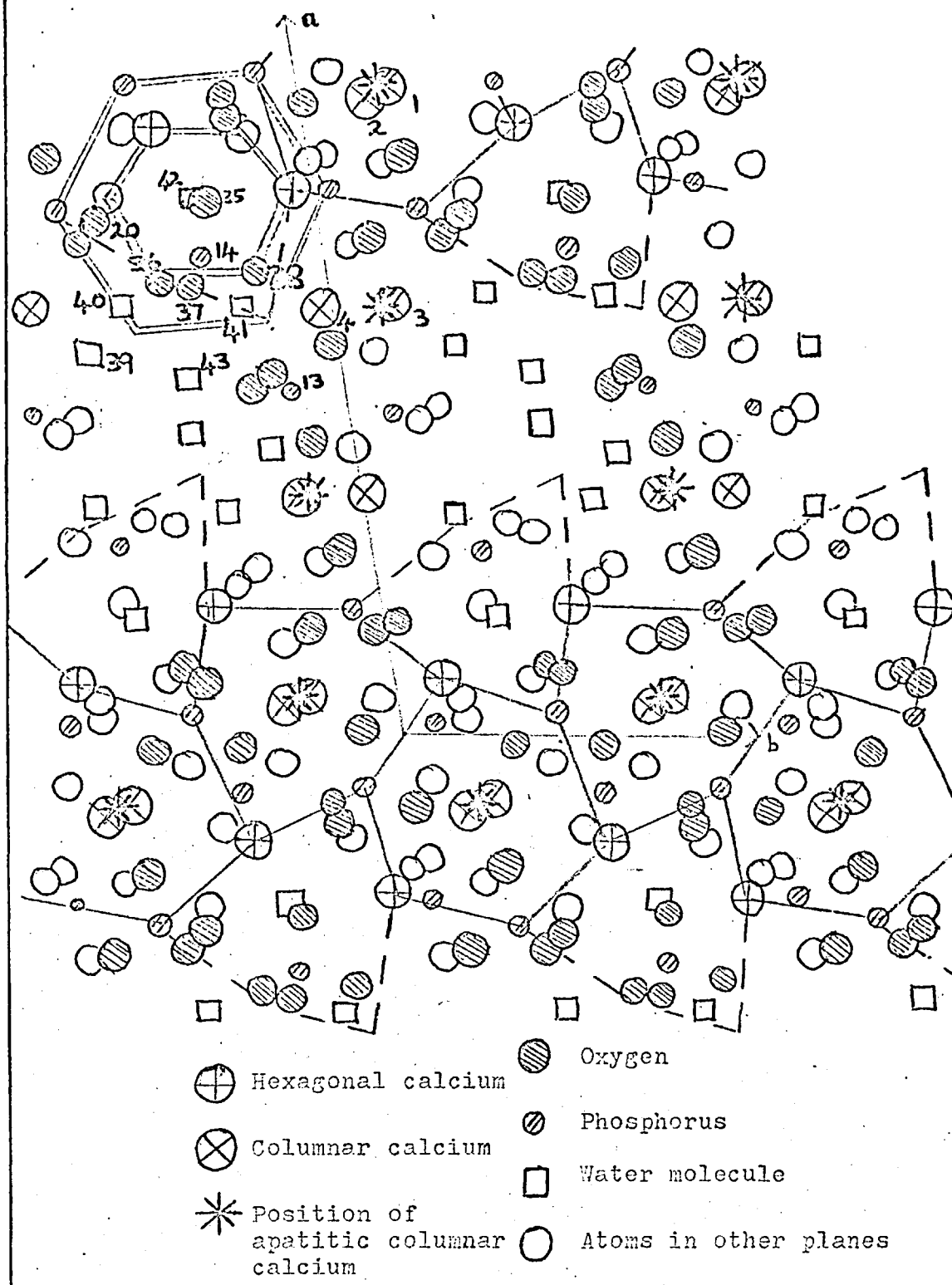
Octacalcium phosphate, also known as tetracalcium hydrogen triphosphate, occurs in some calcium phosphate systems which are more basic than dicalcium phosphate⁸⁰⁻⁸³, and although its existence as a distinct crystalline phase has been questioned^{10, 84}, it has now been established by single crystal⁸⁵ and powder-diffraction⁸⁶ X-ray studies. X-ray, optical and chemical properties have indicated that octacalcium phosphate is structurally related to hydroxyapatite although the two salts are not isostructural. It has been shown that octacalcium phosphate is composed of apatitic layers that are parallel to the bc plane and

separated by hydrated layers⁸⁵. The structural analysis of the salt⁸⁷ was based upon the following unit cell constants: $a = 19.87\text{\AA}$; $b = 9.63\text{\AA}$; $c = 6.87\text{\AA}$; $\alpha = 89^\circ 17'$; $\beta = 92^\circ 13'$; and $\gamma = 108^\circ 57'$. The centrosymmetric space group $P1$ which was assumed in this analysis was verified by the success of the structural determination. Constant numbers of waters of hydration were not yielded by the compositional analysis : water enters and leaves the octacalcium phosphate lattice with some ease. The unit cell was, however, assumed to be $2[\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}]$.

Figure 2.5 illustrates the structure of octacalcium phosphate, projected down the c-axis. Apatitic phosphorus sites are at the corners of the larger hexagon while calcium sites are shown by the corners of the smaller hexagon, only four of the sites on each hexagon are filled in this structure, the sites of the missing atoms being shown connected by the broken lines. One of the missing calcium ions seems to have been replaced by a water molecule O(41). One pair, Ca(1) and Ca(2), of the two pairs of apatitic column calciums, is in virtually the same position in octacalcium phosphate, with the corresponding apatitic positions one above and one in the position marked by the asterisk. The second pair of calcium ions is split, one, Ca(3), is quite near its apatitic site but the other,

Figure 2.5

Octacalcium phosphate lattice viewed along the c axis



Ca(4), is displaced by about 1.5Å parallel to the $\bar{b}$ -axis. The structure of octacalcium phosphate is close to the structure of hydroxyapatite⁶⁴ for small values of x , and the region defined approximately by $\frac{1}{2}x > -\frac{1}{4}$ is referred to as the 'apatite layer' while the portion defined by $\frac{1}{2}x > \frac{1}{4}$ is called the 'water layer'. Tying these layers together is the phosphate ion P(13), with the remaining phosphate P(14) lying in the region which in hydroxyapatite is occupied by two 'hexagonal' calciums. One of the oxygen atoms O(35) of P(14) lies in the centre of the hexagon, occupying the site of an apatitic hydroxyl ion. (A water molecule, O(42), occupies the other hydroxyl site.) Ease in losing water from octacalcium phosphate and the difficulty of establishing a definite degree of hydration are explained by the channel of the 'water layer'. The formula $2[\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}]$ assumes the water site O(43) is completely filled in the ideal compound. This site was found to be incompletely occupied in the crystal on which the X-ray intensity measurements were made, but there is sufficient room at the site for a water molecule, where it would be co-ordinated to eight oxygen atoms by distances of less than 3.5Å. There does not appear to be any space in the unit cell large enough to accommodate another water molecule.

The asymmetric octacalcium phosphate unit contains two non-water protons which may form inter phosphate hydrogen bonds. One such bond may be indicated by a distance of only 2.47Å between oxygen atoms O(20) and O(36), the other interphosphate oxygen to oxygen distances are greater than 2.9Å and a second interphosphate hydrogen bond cannot be located definitely on the basis of X-ray work.

Many investigators have reported that precipitated calcium phosphates which give apatitic X-ray patterns often have molar ratios of Ca to P less than in hydroxyapatite. Several explanations have been put forward to account for this apparent anomaly. Low Ca to P ratios have been described by some early workers as being due to surface absorption of phosphate ions^{14,15,88}, synthetic apatites of low calcium content have, however, been prepared with surface areas far too low to accommodate the excess phosphate required^{16,17}. An alternative proposal, that the simultaneous presence of brushite, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, monetite, CaHPO_4 , and octacalcium phosphate, $2[\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}]$, is the cause of low Ca to P ratios of these salts, has since been put forward.¹⁸

On the basis of the structure determination of octacalcium phosphate⁸⁷, it has been suggested that hydroxy-

apatite and octacalcium phosphate form crystalline interlayered or lamellar mixtures analogous in this respect to clays¹⁹. This proposal, it is argued, accounts not only for apatitic precipitates with calcium to phosphorus ratios less than that of hydroxyapatite but also explains observed chemical and physical properties of these basic calcium phosphates. The similarities between the structures of the two stoichiometric salts could allow epitaxial overgrowths of one compound on to the other to occur easily. Variations in the composition of the liquid phase in the immediate vicinity of a growing crystal, as in dropwise neutralisation, could cause alternate deposition of first one compound and then the other. Lamellar growth of this kind could result in multi-layered crystals.

Octacalcium phosphate and anhydrous dicalcium phosphate are difficult to detect by X-ray powder diffraction in the presence of an apatite, and may contribute to low calcium content in apatitic materials. Octacalcium phosphate has been found to hydrolyse progressively in boiling water to hydroxyapatite⁴⁷. Prolonged boiling of an octacalcium phosphate crystal resulted in a crystal whose X-ray pattern was essentially that of hydroxyapatite. Anhydrous dicalcium phosphate is sometimes

formed as a separate phase in the hydrolysis of octacalcium phosphate.

The rapid precipitation and subsequent alterations of octacalcium phosphate explain some of the complications in the chemistry of basic calcium phosphates. An experiment has been described in which dicalcium phosphate dihydrate was added to distilled water at 85°C with continuous stirring¹⁹. Within five minutes octacalcium phosphate crystals were observed as a separate phase, these crystals grew for about fifteen minutes until the dicalcium salt had nearly disappeared. At about this time, aggregates of fine acicular crystallites of hydroxyapatite appeared. That the continued precipitation of hydroxyapatite was maintained by dissolution of octacalcium phosphate was indicated by the subsequent rounding of edges of octacalcium phosphate crystals. The remaining octacalcium phosphate became converted to an apatite, mostly in situ, on cooling and standing overnight. From this experiment it may be seen that hydroxyapatite was apparently produced by two mechanisms: the direct precipitation produced an acicular habit whereas hydrolysis formed a platey habit. Repetition of the experiment at a lower temperature resulted in the formation of anhydrous dicalcium phosphate at the termination of the precipitation of octacalcium phosphate. It does in any case seem

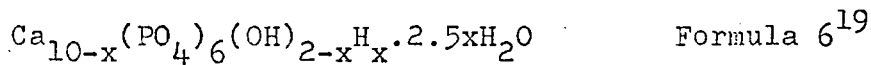
likely that octacalcium phosphate is important as a reaction intermediate in the precipitation of hydroxyapatite and may be present in calcium deficient apatites.

Other recent theories of the structure of calcium deficient apatites have been based on the concept of a continuous series of compositions modelled on a defect apatite lattice, various general formulae being proposed for such series. These are collected below:

$\text{Ca}_{10-x}\text{H}_{2x}(\text{PO}_4)_6(\text{OH})_2$	Formula 1	²²
$\text{Ca}_{10-x}\text{H}_x(\text{PO}_4)_6(\text{OH})_{2-x}$	"	²¹
$\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x-2y}$	"	²³
$\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x} \cdot x\text{H}_2\text{O}$	"	²⁴
$\text{Ca}_{9-x}(\text{HPO}_4)_{1+2x}(\text{PO}_4)_{5-2x}\text{OH} \cdot \text{H}_2\text{O}$	"	²⁵

where, in the cases of formulae 1, 2 and 3, $0 \leq x \leq 2$ and in formula 3, $y = 1 - \frac{x}{2}$, whereas in the cases of formulae 4 and 5, $0 \leq x \leq 1$.

It should be noted that the layer type structure could also be accounted for by formulae 2 or 4. In fact, a further general formula has been suggested to accommodate this structure:



where $0 \leq x \leq 2$. This formula, it was pointed out, must not be considered to represent an isomorphous series. A structure for a possible lamellar mixture of the two

salts, hydroxyapatite and octacalcium phosphate, is shown in figure 2.6. It was assumed that the compositional formulae 1, 2 and 3 were uniquely applicable over the whole range of observed compositions. The deficiency of calcium ions in the lattice would cause charge imbalance, and this may be seen to be compensated for by incorporation of protons in formula 1, by incorporation of protons and removal of hydroxyl ions in the formulae 2 and 3, and by incorporation of protons and water molecules and removal of hydroxyl ions in the formulae 4, 5 and 6. All of these formulae assume the inclusion of protons in the lattice, either in octacalcium phosphate for the lamellar model for the calcium deficient apatites or throughout the lattice for a defect model of the structure. Acid phosphates are known to condense in a number of ways, and work has been done to determine the reaction products on the gentle ignition of these calcium salts. Sodium acid phosphates condense into polymers, and the degree of polymerisation decreases as the starting material is made more basic⁸⁹. The dibasic salt forms largely the dimeric pyrophosphate. Calcium acid phosphates behave similarly, and the following reaction begins at about 300°C and proceeds rapidly at 400°C⁹⁰:

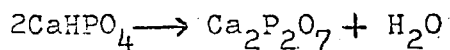
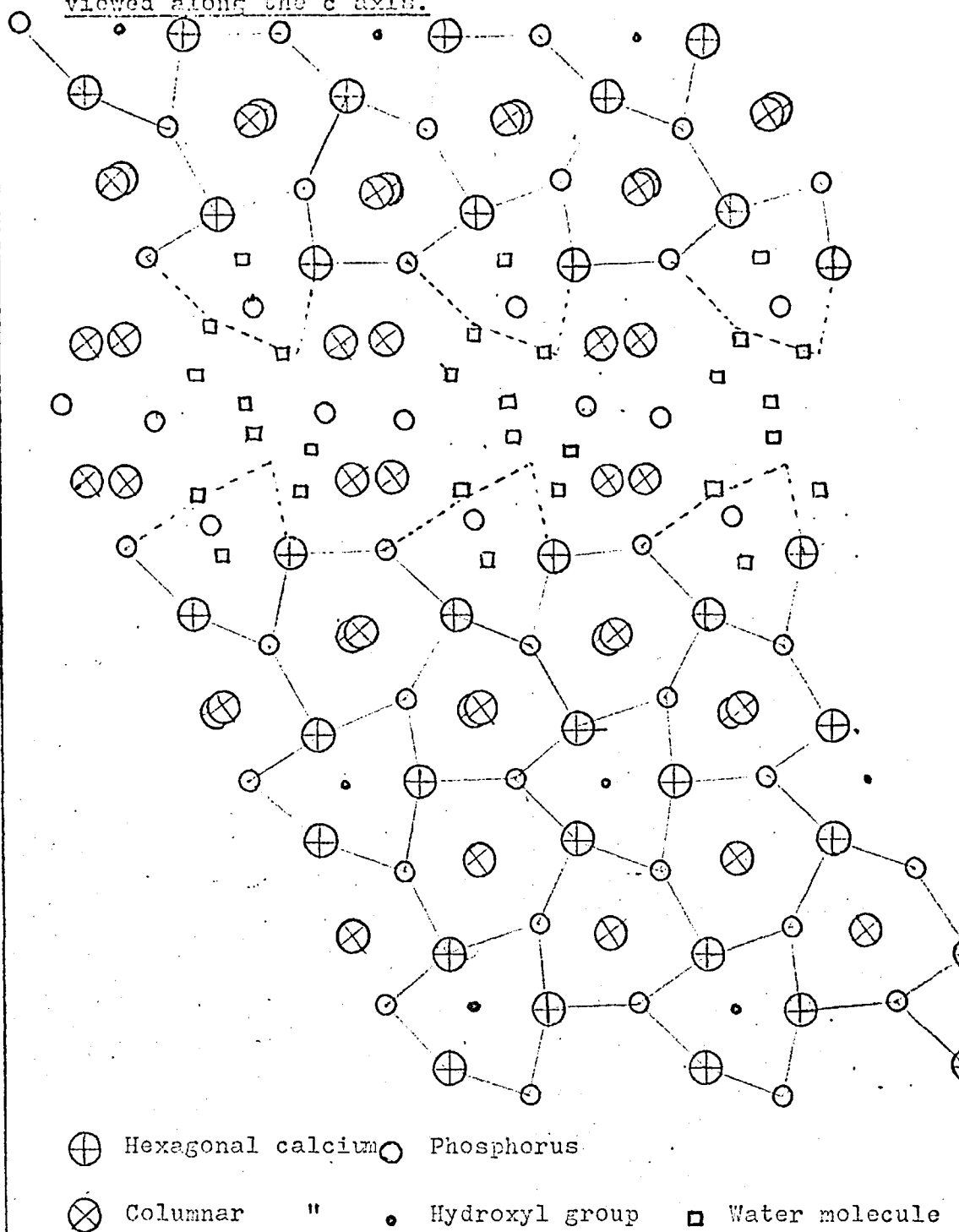


Figure 2.6

Octacalcium phosphate - hydroxyapatite lamellar structure
viewed along the c axis.

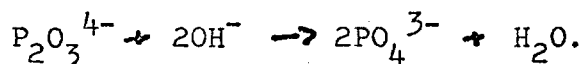


The existence of pyrophosphates in samples of ignited calcium deficient apatites may be confirmed by chemical separation as manganous pyrophosphate⁹¹. It was further shown⁹¹ that pyrophosphate is the predominant condensed form in ignited calcium deficient apatites.

The rate of formation of pyrophosphate in these apatitic materials is much slower than that observed for the condensation from pure, anhydrous dicalcium phosphate. This reaction first occurs at a measurable rate at a temperature which may not be higher for polymerisation of the apatite, but the rate up to 700°C has a much smaller temperature coefficient⁹¹. This low rate and small temperature coefficient suggest that the rate-controlling factor could be solid diffusion or surface migration of some reactant such as the protons.

Although the effect of ignition upon these salts is indicative of the presence of acid phosphate groups, it does not answer the question of where these may reside.

Above 800°C reaction between pyrophosphate and hydroxyl ions occurs to form orthophosphate ions⁹¹:



A useful method of verifying the suitability of the various general formulae has been provided by the polymer-

isation reaction at 600°C. Analysis of samples ignited at this temperature for their pyrophosphate content, and comparison of the results with the calcium to phosphorus ratio of each sample may indicate what proportion of the phosphate ions are associated with protons^{21,24,25,91,92}.

Figure 2.7 shows the theoretical curves calculated for each formula, for all the values of the calcium to phosphorus ratio between the two salts hydroxyapatite and octacalcium phosphate. The figure also shows some of the experimentally determined values, and these may be seen to be close to the theoretical curve for formulae 2, 3, 4 and 6 in the region of this ratio above 1.5, but tend to follow the curve for formula 5 below this ratio.

A study of the percentage weight loss between 750 and 900°C²⁴ has similarly indicated the validity of these general formulae, and supports the proposition that formula 5 alone describes accurately the region of the calcium to phosphorus ratio less than 1.5.

Ignition of the calcium deficient apatites may be represented by the following equations:

For Ca/P molar ratios between 1.67 and 1.5:

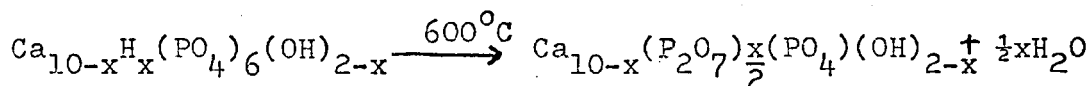
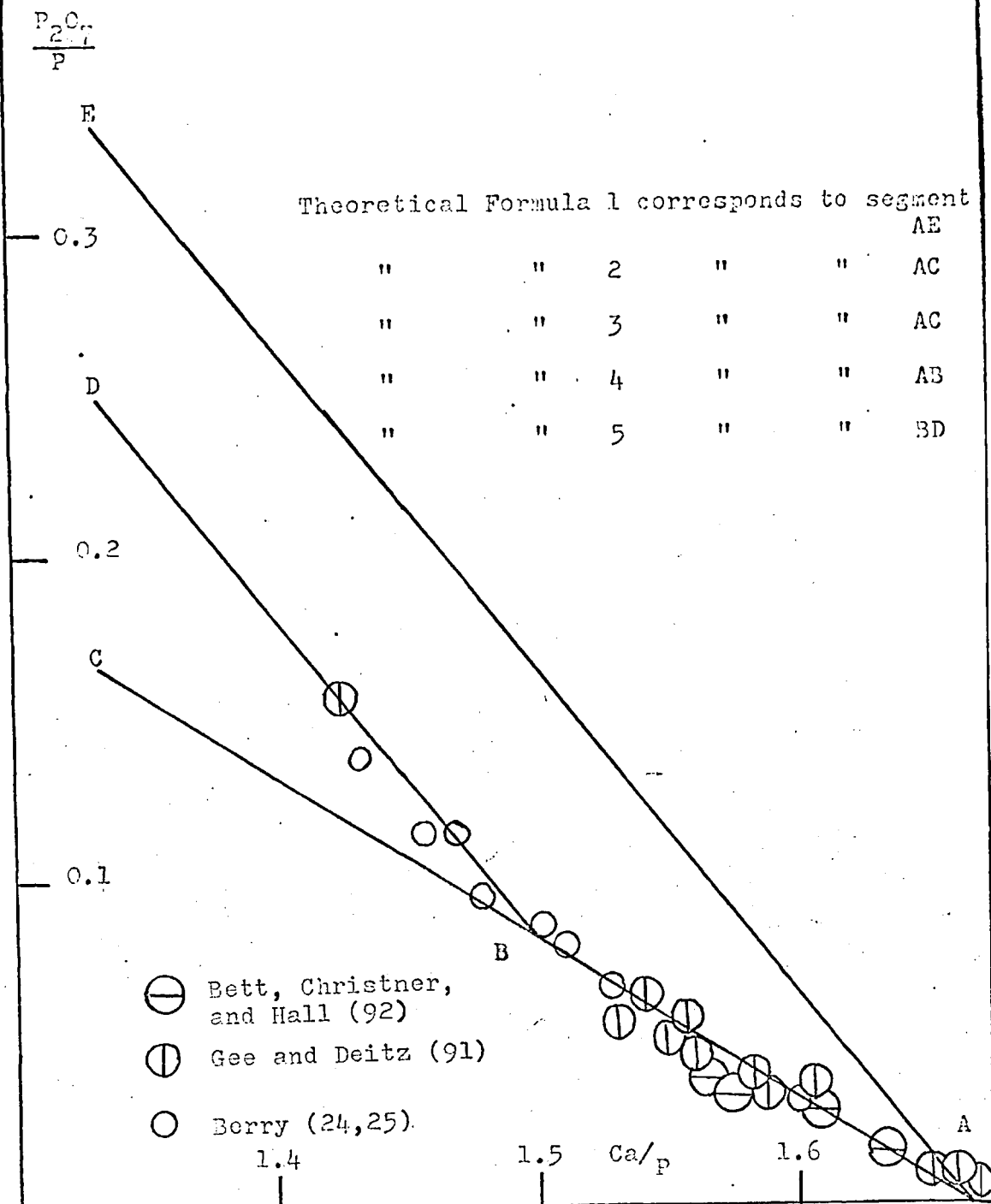
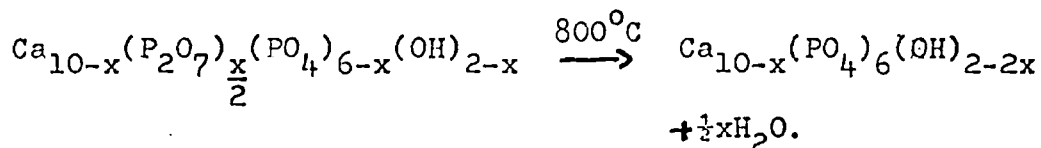


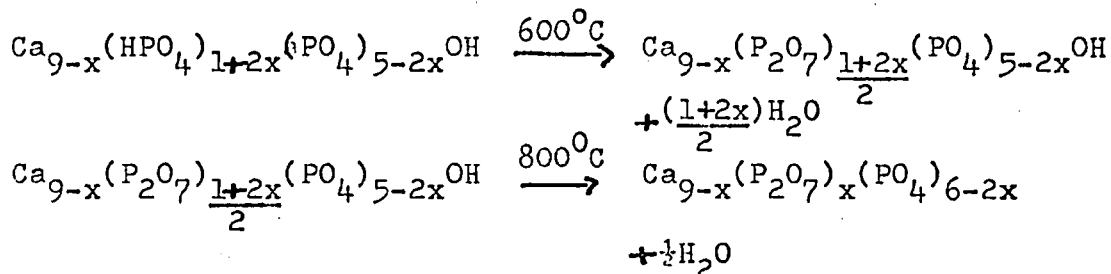
Figure 2.7

Pyrophosphate to total phosphate molar ratio after
heating apatites at 600°C for 120 hours versus calcium
to phosphorus molar ratio.





and for Ca/P molar ratios between 1.5 and 1.33 :



The degree of hydration of the calcium deficient apatites is at the present time not understood, and no clear observations have been made. Thermogravimetric analysis in general yields poorly resolved curves and these results together with differential thermogravimetric curves have led to a view that the weight loss occurring between 200 and 350°C corresponds to the evolution of lattice water⁹³. The data obtained for several samples of calcium deficient apatites, with calcium to phosphorus ratios greater than 1.5, have been in reasonable agreement with the degree of hydration proposed in formula 4. This correlation was indicated by a plot of calculated versus observed weight loss between 200 and 900°C. for apatites in this compositional region⁹³.

Much evidence for the defect hydroxyapatite model for the calcium deficient salts is based on infra-red data. Infra-red spectra of octacalcium phosphate⁹⁴⁻⁹⁶,

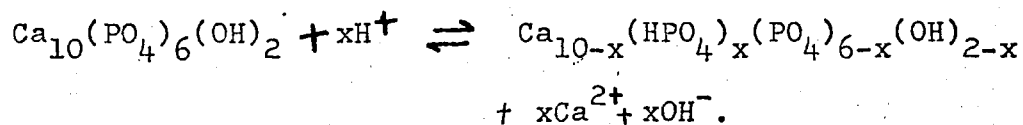
of various calcium deficient apatites^{24,25} and of stoichiometric hydroxyapatite^{94,96-98} have been determined, and the characteristic bands of each salt compared. In any such comparison the essential supposition is that, if any octacalcium phosphate units are present either as a separate phase or as lamellar structures with hydroxyapatite, then the absorption bands characteristic of each phosphate should be observed in spectra from mixed systems.

Infra-red spectra of hydroxyapatite and octacalcium phosphate have been discussed in relation to their crystal structure and observed spectra of each salt have been correlated with theoretically derived site group assignments of the orthophosphate ion in a crystalline state^{24,25}. Essentially similar crystal field environments acting upon orthophosphate ions in both hydroxyapatite and octacalcium phosphate cause the principal fundamental modes in both materials to occur at nearly identical frequencies. There are however a number of bands which, it was assumed, may be regarded as specific and characteristic of the octacalcium phosphate lattice⁹⁵, each of which serve to distinguish the spectrum of this salt from hydroxyapatite. Study of absorption bands characteristic of calcium deficient apatite samples revealed several bands which are distinct from those observed for the stoichiometric material but none of which correspond to the bands characteristic

of octacalcium phosphate^{24,25}. This data was interpreted as being consistent with a view that the calcium deficient apatites have a crystal lattice similar to hydroxyapatite, with calcium and hydroxyl ion site defects. Charge neutrality may be maintained by inclusion of protons which are probably involved in interphosphate hydrogen bonding. In anticipation of this structure, the extra bands noted for the calcium deficient material were assigned to O_3POH modes.

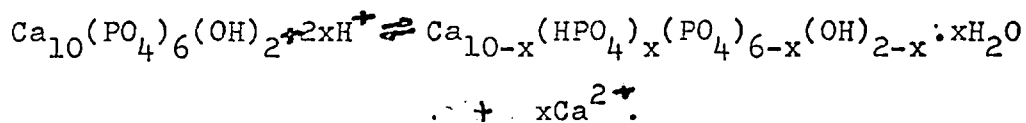
Differential thermal analysis of octacalcium phosphate and calcium deficient apatites has, according to one author, failed to show the presence of the former salt in the deficient apatites^{24,25}.

Simultaneous continuous variations in composition of both solid and solution phases in the basic region of the $CaO-P_2O_5-H_2O$ system may be consistent with a solid solution system⁸⁰ of the form



This suggestion is doubtful because of the necessity that hydroxyl sites may be unoccupied¹⁷. The inclusion of protons in defect apatites could, however, take one of two forms⁸⁶, either as hydrogen phosphate ions or through reaction with hydroxyl ions to form water. Presence of

hydrogen phosphate ions is indicated by both infra-red spectral data^{24,25} and by the formation of pyrophosphate ions on heating⁹¹. Retention of the spatial requirements of the apatite lattice would be achieved by the presence of water molecules. The solid-solution reaction may then be rewritten in the form²⁴:



An X-ray study of the precipitation of hydroxyapatite has shown that the ageing of freshly precipitated phosphates, prepared under the conditions described, can be divided into three stages⁹⁹. The first stage which commences immediately on mixing and continues for about five hours is characterised by x-ray scattering characteristic of amorphous material. Progression thereafter from a barely discernible apatitic profile to a fully developed apatite pattern with the complete absence of any underlying amorphous features is covered by the second stage, which lasts for about a further two hours. The third phase lasts indefinitely and covers the period following total conversion of the amorphous phase to a crystalline apatite.

The formation of 'non-crystalline' calcium phosphate

is a kinetic phenomenon⁹⁹. Rapid mixing of the reaction solutions creates strong interactions between Ca^{2+} and HPO_4^{2-} ions leading to irregular co-ordination complexes large enough in size to separate from solution. The molar calcium to phosphorus ratio of this amorphous phase, after washing, was well below the ratio of the overall reaction system and was found to be dependent on the calcium salt used in the preparation. (A lower value was found if chloride was used in place of calcium nitrate.) The fact that the molar calcium to phosphorus ratio did not vary under a given set of initial conditions suggests that the amorphous stage consists of a chemically well-defined local structural unit. No detectable amount of phosphate was found in either the reaction solution or wash waters after the precipitation. Nearly coincident with the emergence of a discernible diffraction profile was a more rapid decrease in solution calcium concentration, this indicates that the initial phase is metastable with respect to the more ordered apatite configuration. A sigmoid curve relating amount transformed with time strongly suggests that the conversion mechanism is autocatalytic. The interfacial surfaces of the emerging crystalline phase may act as sites for heterogeneous nucleation, thereby accelerating the rate of conversion. It is

interesting to note that the 'non-crystalline' calcium phosphate remains stable indefinitely if kept dry, indicating that water is needed for the process of nucleation to take place. The improvement in hydroxyapatite crystallinity during the third stage is typical of the gradual enlargement of mean particle size of many low-solubility precipitates as a result of re-precipitation in solution. This 'Ostwald ripening' is generally attributed to the dissolving of the smaller, more soluble crystals and re-deposition of the dissolved material on the growing faces of the larger, less soluble crystals¹⁰⁰. Although re-crystallisation may well be in progress from the earliest stages of conversion, the time interval in the second stage is insufficient for this gradual increase in crystal dimension to have a measurable effect on the crystallinity values measured during this period. A gradual decrease in solution of the calcium concentration indicated that perfection of the crystalline phase parallels the crystal growth.

Well crystallised, precipitated, calcium-deficient apatites have not shown any of the characteristics of octacalcium phosphate but this is no proof that octacalcium phosphate is not present in these salts. It should, however, be observed that several authors have detected

octacalcium phosphate/hydroxyapatite mixtures in some preparations, particularly at low pH^{93,101}. This detection of the presence of the more acidic phosphate was by X-ray powder diffraction, but in each case the precipitate was not well crystallised and was found to be inhomogeneous when examined by electron-microscopy.

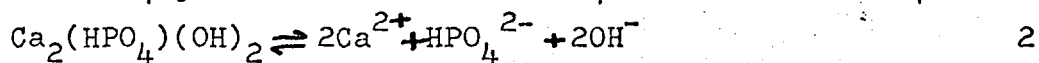
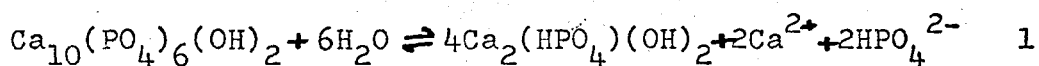
Two models for the calcium deficient apatites have been discussed but no determination of the structure of these salts has yet been conducted. X-ray powder diffraction photographs have shown evidence in favour of each model, but one important observation from the studies of two authors is that the a-axis increases, and the c-axis is reduced as the degree of calcium deficiency rises^{17,102}. On the basis of infra-red work, on well crystallised samples of calcium deficient apatites, it is most likely that the continuous series model is applicable but little information has been yielded on the nature of this series, and the various authors are not in agreement on the assignment of bands characteristic of the hydrogen phosphate modes^{22,24,94}.

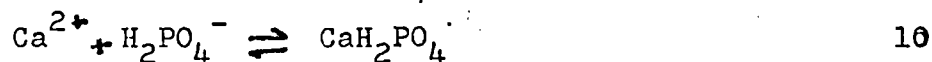
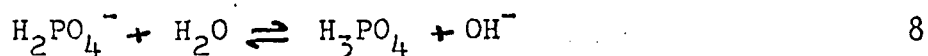
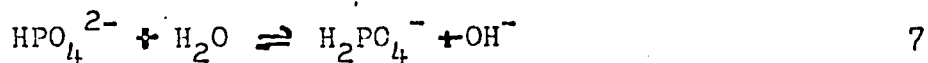
2.1.4 Some surface properties of apatites.

The acicular and platey habits of hydroxyapatite are such that the faces 100 could be the major contributors to the surface area of the crystals. Only after a

period of about 500 hours has equilibrium of this surface, in aqueous solution, been found to occur¹⁰³. The reasons for such time effects are not yet understood but it has been suggested that the adsorption process occurs essentially in two steps¹⁰⁴. Initially a rapid adsorption or desorption of protons occurs with change in pH after which a slow process occurs which may be attributed to structural rearrangements of hydroxo complex ions existing on the surface. At low pH the interface acquires a positive charge which decreases with increasing pH to zero at pH 7.4, the zero point of charge. It becomes increasingly negative at higher pH.

The observed charge changes may be qualitatively interpreted in terms of hydrolysis of terminal phosphate groups in accord with the theory of Rootare, Deitz and Carpenter¹⁰⁵. A surface complex, $\text{Ca}_2(\text{HPO}_4)(\text{OH})_2$ is proposed as a result of which the following reactions can occur.





Surface species would undergo hydrolysis according to these reactions and the extent of such hydrolysis for each species, depending on the pH, would essentially determine the surface charge. A thermodynamically identical mechanism would be the hydrolysis of such ions in bulk solution followed by adsorption at the interface. Non-stoichiometry of the apatite could also contribute to charge generation. In solutions at pH values above the zero point of charge, equilibria (2) (6) (7) and (8) would shift towards the left and equilibria (3) and (4) towards the right, the solid surface thus acquiring a net negative charge. In acid solutions the solid would acquire a net positive charge due to the shift of equilibria (6) (7) and (8) towards the right and equilibria (3) and (4) towards the left.

The surfaces of apatite samples precipitated at different pH under equilibrium conditions are, on the basis of this work, subject to hydrolysis mechanisms, the charge on the solid surface may have a critical effect on the properties of these materials.

An attempt was made to estimate the surface concentrations of acid phosphate protons from the spectra of suitable adsorbed indicators⁹². Triphenylcarbinol was added to pellets of calcium deficient apatites and a yellow colour developed. The measured spectra confirmed the formation of triphenyl carbonium ions, presumably by the reaction

$$\text{ROH} + \text{H}^+ \rightleftharpoons \text{R}^+ + \text{H}_2\text{O}.$$
 By using excess carbinol about four monolayers were formed, and by evacuation of the sample after equilibration, solvent and water of reaction were removed, the carbonium ion density then being a measure of the acid site density as the equation is driven to the right. The calculation of surface carbonium ion concentration showed that the values fell as the calcium to phosphorus ratio approached the stoichiometric value for hydroxyapatite, at which value it became too low to measure. As the temperature of pretreatment was raised, the carbonium ion concentration fell, until after evacuating at 500°C it was no longer detectable on any of the samples. Subsequent burning in oxygen at 530°C to remove organic material with exposure to 20 mm of water vapour at 350°C partially restored the surface reactivity to the material. Experiments using trianisylcarbinol, a much stronger base of $\text{pK}_a = +0.82$ compared to $\text{pK}_a = -6.6$ for triphenyl carbinol,

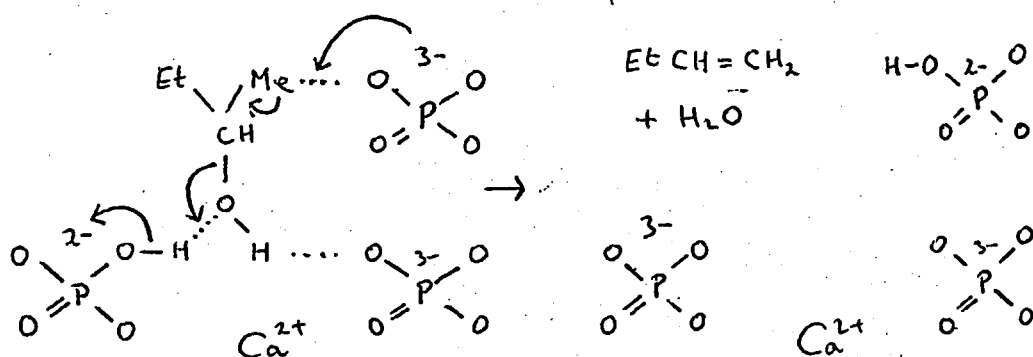
gave results in good qualitative agreement with triphenyl carbinol results. Measurable carbonium ion concentrations were found with this indicator even after pretreatment at 500°C but the concentration of carbonium ions still increased with calcium deficiency. Maximum ion concentration was obtained for the most calcium deficient apatite, of calcium to phosphorus molar ratio 1.58, after evacuation at 160°C. The site densities calculated from trianisyl carbinol were found to be about 5% of the proton density, assuming that unit cells at the surface contain about the same concentration of phosphatic hydrogen as internal unit cells. In fact the maximum observed concentration of trianisyl carbonium ions was close to the concentration of carbonium ions on a silica-alumina¹⁰⁶, it is possible that the carbonium ion concentration is limited in some way on the surface.

Rising temperature experiments have shown that the hydrogen of stoichiometric hydroxyapatite exchanged with deuterium at lower temperatures than with calcium deficient samples.⁹² Exchange did not become significant with the non-stoichiometric apatites until temperatures were reached where condensation of hydrogen phosphate to pyrophosphate was already considerable. Values of hydrogen content, measured after pretreatment at 550°C,

were nearly free of acid orthophosphate and so must have been close to the values of the free structural hydroxyl ion. The formula value of 12×10^{20} hydrogen atoms per gramme of stoichiometric apatite was approached with the hydrogen content falling off continuously as the molar calcium to phosphorus ratio was lowered. The results obtained were plotted against the calcium to phosphorus molar ratio and fell close to a theoretical curve derived from formula 4 discussed earlier.

Basic calcium phosphates have been found to effect the dehydrogenation and dehydration of alcohols¹⁰⁷ the selectivity for these reactions being controlled by the composition of the phosphate. More recent work has contributed to the understanding of this selectivity^{92,108}. The dehydration rates of 2-butanol for a series of calcium-deficient and stoichiometric apatites have been studied and compared on the basis of an equal surface area of the solids⁹². They indicate that the reaction is of zero order and that the rate constants increase as the molar calcium to phosphorus ratio decreases. Dehydration of alcohols in solution is acid catalysed and takes place at measurable rates in solutions of low acid strength. The activity of apatites for the dehydration of 2-butanol is therefore consistent with catalysis by acid protons. The butanol dehydration experiments took place over

apatites which had been pretreated at 550°C . From the results obtained from indicator adsorption experiments⁹² it would be predicted that only a very small number of protons could remain on the surface. Acid protons may have been generated by hydrolysis of pyrophosphate by water eliminated from the reaction. Trianisyl carbinol is probably protonated by orthophosphate hydrogen atoms which catalyse the butanol dehydration, and these are present in increasing concentrations as the molar calcium to phosphorus ratio falls. A mechanism, consistent with the surface chemistry and geometry of apatite has been suggested for the 2-butanol dehydrations⁹²:



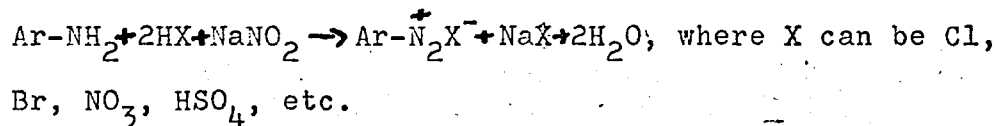
2.2 Aliphatic Diazo Compounds.

2.2.1 Introduction

Aromatic diazocompounds were discovered in 1858¹⁰⁹ at a time when modern organic chemistry was in its infancy. A contemporary advance had been the concept of the quadrivalence of carbon, while the structural theory of compounds did not exist. The only means of obtaining structural information about natural and synthetic products was by elementary analysis, hence the term 'diazo' was chosen because it was thought that two hydrogen atoms of the benzene ring had been replaced by the nitrogen atoms.

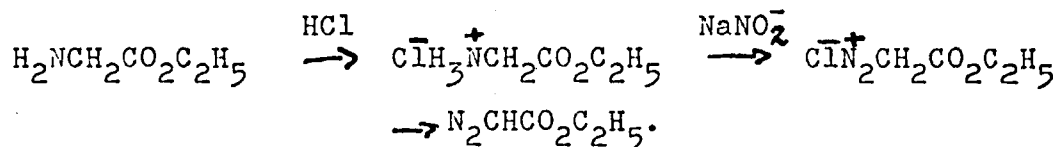
Usually, diazotization can be carried out by allowing sodium nitrite to act on a solution of a primary organic amine in mineral acid at a temperature of about 0°C.

The reaction may be represented as:

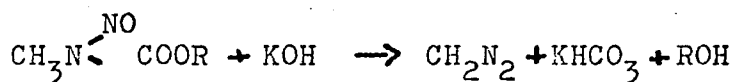


Aliphatic diazonium salts are incapable of existence because the >C-N= bond is not resonance stabilised, stable derivatives called diazoalkanes are formed by splitting of a proton from the α -carbon atom of the 'alkyldiazonium ion'. The earliest recorded preparation of a diazocompound was in 1883 by this method¹¹⁰ but diazotization can only be used for those amines which

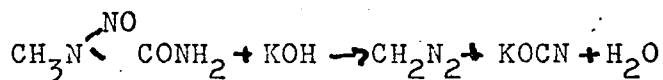
which carry a strongly negative substituent at the α -carbon atom. Ethyl diazoacetic ester may be prepared by direct nitrosation of amino acetic ester,



Later, diazomethane was prepared by the action of aqueous alkali on nitrosocompounds and two methods have been in general use. Nitroso-methylurethan evolves a yellow gas when treated with alkali¹¹¹ and a careful study of this reaction^{112,113} identified the composition of the gas as CH_2N_2 , diazomethane. The preparation follows the equation^{114,115}



The more popular method of preparing diazomethane employs nitrosomethylurea in place of the urethan^{116,117}



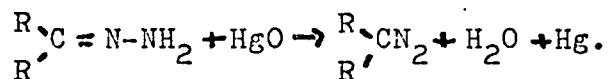
An ethereal solution of N-methyl-N-nitroso-p-toluene sulphonamide has been shown to be a particularly good reagent for the preparation of diazomethane¹¹⁸.

In the above cases, diazomethane is formed from a compound containing an N-methyl-N-nitrosamino group, but preparations are also known in which an alkane derivative

is treated with a nitroso compound^{119,120}.

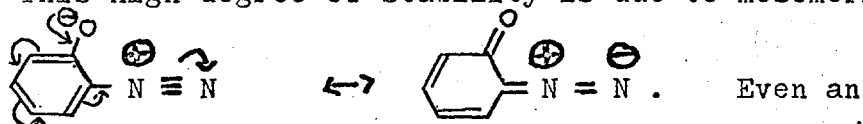
Most of these methods can be adapted for the synthesis of the homologues of diazomethane, but a particularly good method involves 4-methyl -4-alkylnitrosamino-2-pentanones¹²¹⁻¹²⁴.

One early preparation of diazoalkanes^{125,-127} has been evaluated thoroughly¹²⁸⁻¹³² and is perhaps the best way of preparing disubstituted derivatives of diazomethane. The method involves the oxidation, by mercuric oxide, of ketohydrazones:



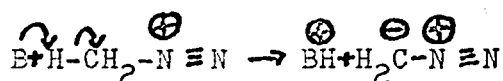
2.2.2 Structure of the diazoalkanes.

Electron-releasing substituents in the aromatic nucleus greatly reduce the tendency of aryldiazonium ions to lose molecular nitrogen. The o- or p- phenolate group confers such stability to an aryldiazonium ion that the names diazo oxide and quinone dioxide are sometimes used. This high degree of stability is due to mesomerism,

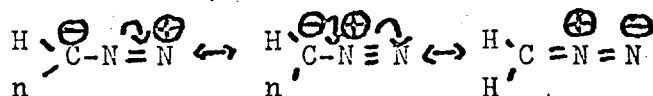


Even an unsubstituted phenyl group is able to stabilize a diazonium ion through mesomerism between the π -electrons of the nucleus and the $-\text{N}_2^+$ group.

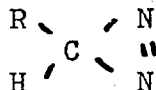
Mesomerism cannot occur in the methyldiazonium ion, and the splitting off of molecular nitrogen follows, the residual carbonium ion reacts with the solvent or loses a proton. Tetrahedral carbon is unable to take part in mesomerism, other than by hyperconjugation, and stabilization of a diazonium group bond to an sp^3 -hybridized carbon atom could only occur if the carbon atom becomes hybridized in the sp^2 -state. A proton would have to be removed from the α -carbon atom of the methyldiazonium ion leaving the electron pair of the broken bond on the atom,



Mesomerism can occur in this new compound, diazomethane, just as in the anyldiazonium ion,



The greater reactivity of diazoalkanes compared with aromatic diazocompounds led early workers to the view that cyclic structures^{112,133} could account for their known compositions,



Open structures were then suggested¹³⁴⁻¹³⁶ and steric similarities noted^{137,138} between diazoalkanes, ketenes and azides, and preceded the.

introduction of the zwitterionic form, $\text{R}-\overset{\oplus}{\text{C}}(\text{H})-\overset{\ominus}{\text{N}}\equiv\text{N}$. No evidence for optical activity has been found to support the open structures^{139,140} but electron diffraction results¹⁴¹ brought the final decision as these results can only be accounted for by the linear arrangement. The atomic distances and bond angles of diazomethane have recently been determined¹⁴² ($\text{C}-\text{H}=1.08$ Å; $\text{C}-\text{N}=1.32$ Å; $\text{N}-\text{N}=1.12$ Å; $\text{H}-\text{C}-\text{H}=127^\circ$) which, together with the observation¹⁴³ that the two nitrogen atoms were found not to be equivalent by N¹⁵ studies, supports the Zwitterionic form shown above. Infra-red spectra of diazoalkanes can only be interpreted on the basis of a linear formula¹⁴⁴⁻¹⁴⁸ and the correctness of this structure is thus not in doubt. Diazoalkanes exhibit a characteristic absorption band at 2010 to 2070 cm^{-1} which is assigned to the N-N link.

2.2.3 Properties of the diazoalkanes.

An examination of some physical properties of aliphatic diazocompounds (see Table 2) will show that lower diazoalkanes exist as gases at room temperatures, while the higher derivatives are liquid or solid.

Diazomethane and its homologues have reputations as explosives and are extremely poisonous¹⁴⁹⁻¹⁵². The lower diazomethanes are choking, irritating gases but

Table 2

Aliphatic group of diazocompound; >CN_2	Colour	Melting point or Boiling Point (pressure in mm,Hg)
H,H	Deep yellow	M.P. -145°C , B.P. -23°C (760)
H, CH_3	" "	B.P. -18°C (89.5)
H, C_2H_5	" "	B.P. -8°C (41.5)
CH_3 , CH_3	Red	B.P. -31°C (14)
H, C_3H_7	Deep yellow	B.P. -4.5°C (26)
H, isoC_3H_7	" "	B.P. 0°C (32)
H, Ph	Red-Brown	B.P. 81°C (15)
Me, Ph	Deep red	M.P. -10°C
Ph, Ph	Crimson	M.P. 29°C
-Ph-Ph-	Deep Orange	M.P. 95°C
H, PhCO	Yellow	M.P. 50°C
Ph, PhCO	Orange	M.P. 79°C
MeCO , MeCO	Yellow	B.P. 57°C (0.1)
MeCO , PhCO	Pale yellow	M.P. -62°C
PhCO , PhCO	Light "	M.P. 114°C
H, EtOCO	Yellow	B.P. 46°C (15)
MeCO , EtOCO	Light yellow	B.P. 83°C (12)
PhCO , EtOCO	Pale "	M.P. 84°C
EtOCO , EtOCO	" "	B.P. 108°C (11)

these toxic and explosive hazards are reduced when the materials are kept in solution. Continued exposure to the gases leads to an allergic oversensitivity, with symptoms similar to asthma, and large doses can be fatal. The dangers of poisoning may be considerably reduced if work is done in the fume cupboard during all stages of preparation and use of diazoalkanes, and safety is increased if solutions of the gases are used whenever possible.

The main application of diazoalkanes is in the alkylation of compounds bearing relatively strongly acid hydroxy groups, the preparation of methyl esters of carboxylic acids by means of diazomethane in ethereal solution being by far the best known. The reaction proceeds smoothly and rapidly, under mild conditions so that decomposition or other side reactions, which may occur under the more vigorous conditions required by other alkylating agents, are absent. Phenols and enols, as well as carboxylic acids, are alkylated by means of diazoalkanes, but, although they give good yields, the reactions are distinctly less rapid due to the lower acidity of these compounds. Conversion of alcohols to ethers by diazo alkylation is not normally possible unless there are neighbouring substituents in the alcohol with

negative mesomeric or inductive effects, thus the alcoholic group of tartronic acid, $\text{HO}_2\text{CCH}(\text{OH})\text{CO}_2\text{H}$ may be readily methylated.

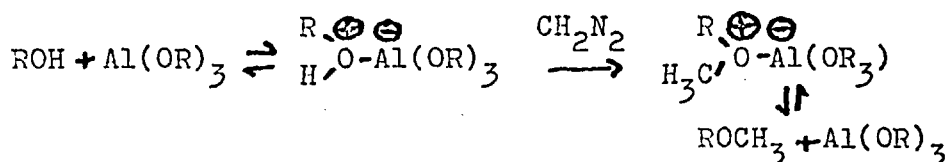
Compounds with weakly acid hydroxy groups may sometimes be alkylated if the reaction takes place in aliphatic hydrocarbons instead of ether^{48,153,154}. Thus trichloroethyl alcohol, which does not react at all in ethereal solution, is readily converted into the methyl ether by diazomethane in heptane. This effect may be caused by the slightly basic character of ether. Hydrogen bonding between the alcoholic hydroxy group as donor and the ether oxygen as acceptor could lower the acidity of the former still further. An alternative suggestion, that the addition of catalytic amounts of amphoteric solvents can speed up the alkylation, has been put forward¹⁵⁵: glycine, which does not react with diazomethane in dry ether, interacts vigorously on adding a little water or methanol to yield betaine,

$$\overset{\oplus}{\text{H}_3\text{N}} \text{CH}_2 \overset{\ominus}{\text{CO}_2} \xrightarrow{\text{CH}_2\text{N}_2} (\text{H}_3\text{C})_3\overset{\oplus}{\text{N}} \text{CH}_2 \overset{\ominus}{\text{CO}_2}$$

Under certain conditions, the hydroxy groups of carbohydrates can be methylated, for example methyl glucosides have been prepared by adding an ethereal solution of diazomethane to an aqueous methanolic solution of sugar¹⁵⁶.

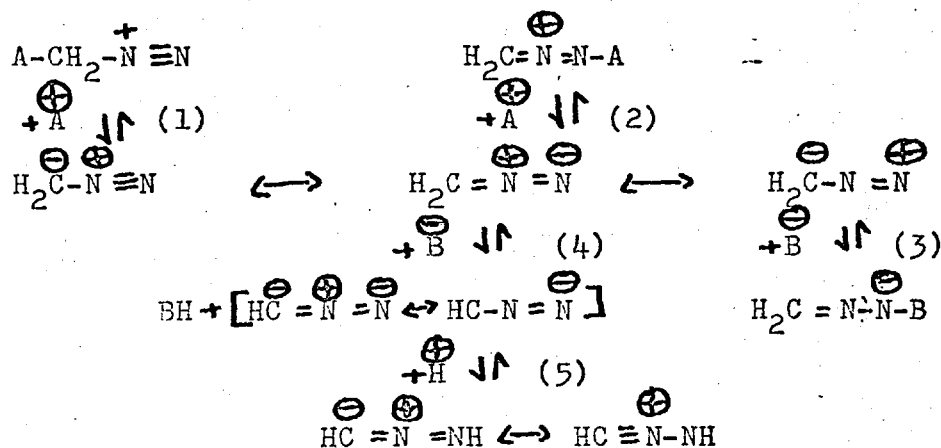
Complex formation can enhance the activity of

hydroxy groups and both aluminium alcoholate¹⁵⁴ and fluoborate^{157,158} have been used successfully. These Lewis acid catalysed reactions may take the form,



Ammonia, primary and secondary amines may be methylated with diazomethane in the presence of the Lewis acid boron trifluoride^{159,160}. This indicates that not only hydrogen attached to oxygen is liable to substitution.

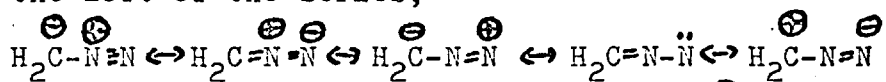
The primary process of most reactions of diazoalkanes is their addition as a molecule followed by the liberation of nitrogen from this addition compound. These reactions have been systematised¹⁶¹ by regarding the diazoalkanes in turn as bases, as Brönsted, and as Lewis acids:



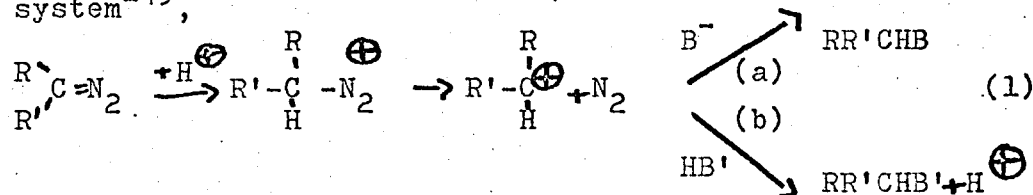
Alkylation reactions of the type just discussed have the form (1) while (2) and (3) represent the reactions of

diazoalkanes, with aldehydes and ketones and with systems containing double bonds, respectively. Reaction (4) in which the diazocompound behaves as a Lewis acid terminates in isodiazomethane, normally this tautomerism greatly favours diazomethane.

Diazoalkanes appear as the nucleophilic component of the alkylation reactions, the basic character of these molecules is derived from the first mesomeric form on the left of the series,



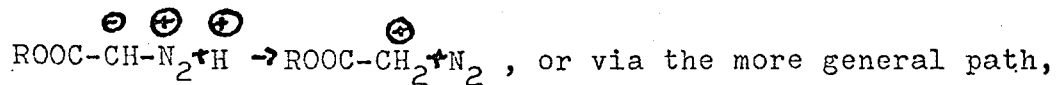
Reaction of this molecule with an acid A converts it into A $\text{CH}_2\text{N}_2^{\oplus}$ and addition of a proton yields the alkyldiazonium ion, $\text{H}_3\text{C}-\text{N}^{\oplus}=\text{N}$. Interaction with compounds bearing an acid hydrogen atom probably takes place initially by proton transfer to the diazoalkane, with the evolution of nitrogen, the highly reactive alkyldiazonium ion formed then yields a carbonium ion, which attacks the conjugate base, or any other base available in the system¹⁴⁹,

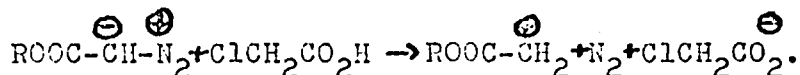


The concept of the intermediate formation of a diazonium ion may be supported by a number of observations,

for instance it has been known for some time¹²⁹ that the reactivity of diazoalkanes is dependent in a characteristic manner on the nature of the substituents R and R'. From diazomethane, where R = R' = H, the rate of reaction decreases as one or two of the hydrogen atoms are replaced by aryl groups, the basic character of the carbon atom of the mesomeric form $\text{H}_2\overset{\ominus}{\text{C}} - \overset{\oplus}{\text{N}} \equiv \text{N}$ being progressively reduced. Inductive and mesomeric effects of carbonyl and alkoxycarbonyl groups similarly lower the basicity and thus the nucleophilic reactivity of diazoalkanes, the difference in behaviour between diazomethane and diazoacetic ester is a good example of this.

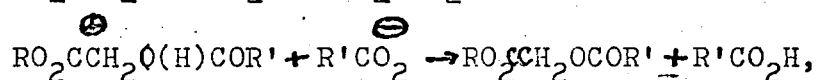
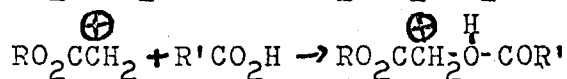
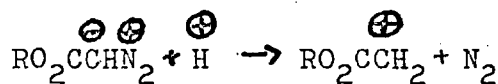
An investigation of the reaction of diazoacetic ester with phenol in a non-polar medium (of benzene)¹⁶² has provided some interesting information on the acid catalysis of this reaction. Phenoxycetic ester formation occurs only on addition of a relatively strong acid and the rate of reaction is proportional to the concentration of the latter, phenol itself being too weak an acid to be able to catalyse the reaction. Acid catalysis is certainly taking place but it was not until more recently that the nature of the reaction could be elucidated, for acid catalysis may occur by proton transfer,



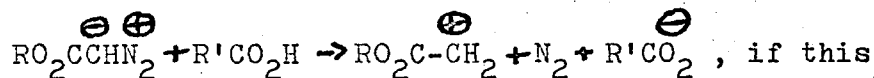


The rates of reactions catalysed by carboxylic acids are linearly related to the dissociation constants of the acids (determined in water) and this led to the supposition that the reactions were catalysed via the general mechanism. Dimerization equilibria of carboxylic acids in benzene solution would be superimposed upon the protolysis while for larger acid molecules, steric effects may play a part.

The reaction of diazoacetic ester with a carboxylic acid in benzene is of first order with respect to the diazocompound but of second order with respect to acid¹⁶². This may be reconciled with the mechanism,



although proton transfer may be replaced, as the first stage of the reaction, by general acid addition,



step occurs more rapidly than the second.

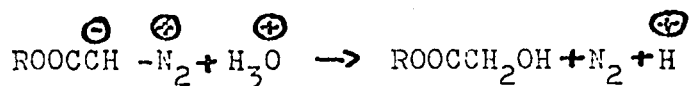
Corresponding reaction rates for aliphatic compounds free from carbonyl groups are directly proportional to

the concentration of the carboxylic acid¹⁶³⁻¹⁶⁶, and on this basis it can be assumed that in aprotic solvents general acid catalysis takes place.

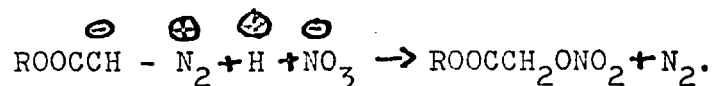
The reactions of aliphatic diazocompounds in an aqueous medium exhibit all the signs of specific proton catalysis. Before modern potentiometric means were available pH could be measured from the kinetics of the evolution of nitrogen from solutions of diazoacetic ester¹⁶⁷⁻¹⁶⁹.

The general equation (1) for the diazoalkane-acid reaction indicated that the alkyldiazonium ion $RR'CHN_2$ can interact with both the conjugate base of the acid HB used and of other acids HB'. Proton containing solvents come into consideration as sources of acids HB' and reactions involving them regenerate protons making the solvent a true catalyst. The choice between a stoichiometric and catalytic interaction of diazoalkanes with acids (that is (a) and (b), respectively, of equation (1)), is affected by the strength of the acids present¹⁴⁹. In aqueous medium and in the presence of strong mineral acids (perchloric, sulphuric) diazoalkanes uniformly follow the catalytic scheme (b), but the nitrate ion is able to compete successfully as a base with water. Diazoacetic ester yields glycollic ester with dilute

sulphuric acid in a clean reaction according to (b),

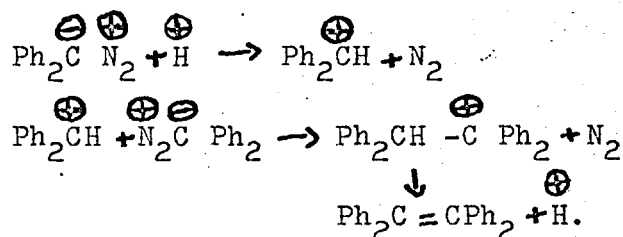


but the same concentration of acid in the presence of a large amount of potassium nitrate leads to the formation of the corresponding nitrate,



As this reaction consumes acid, the rate decreases until in time it stops completely¹⁶⁹. Analogously, the decomposition of diazoacetic ester catalysed by perchloric acid can be halted by the addition of halides, their effectiveness increasing with nucleophilic character in the order $\text{Cl}^- < \text{Br}^- < \text{I}^-$ ¹⁶⁸.

Strong acid catalysis, with toluenesulphonic acid, in a polar but aprotic medium of acetonitrile, of diphenyldiazomethane to form tetraphenyl ethylene¹⁷⁰ illustrates that extra diazoalkane competes successfully as a base,



CHAPTER 3

THEORY3.1 Introduction

Various chemical treatments have changed the character of the surface of synthetic apatites, some of which are considered in Chapter 1. If a modifying agent is held to a solid surface such as apatite by van der Waals' forces then this adsorption is classified as physical. Chemisorption on the other hand involves a transfer of electrons between adsorbent and adsorbate. Although the rate of desorption of a physically adsorbed phase may be retarded by diffusion effects such a layer is generally removed by reducing the pressure at the temperature at which adsorption took place. Rather more severe conditions may effect the removal of a chemisorbed material.

When the surfaces of two solid bodies are brought sufficiently close together, their fields of force overlap and so cause adhesion wherever the two solids are nearly or completely in contact. Such attraction between solid surfaces is of a similar origin to the physical adsorption described above, which may be conveniently classified as being brought about by forces associated with permanent

dipole moments in an adsorbed fluid, polarisation of an adsorbed fluid, dispersion energies and the short-range repulsive energies. It is clear from this that an apatite surface will have a different character when the solid is held ^{at low temperature} under a very low pressure from when it is surrounded by an atmosphere of nitrogen, for example. It is equally apparent, however, that a surface layer of adsorbed nitrogen molecules, which may be readily removed, is not an effective treatment if a permanent and durable surface layer is required. In a similar manner, a solid phase adhering to the apatite surface merely by means of physical forces would be unacceptable.

A process of chemisorption seems to be necessary to effect the surface characteristics which are required of a modified apatite. Once the hydrophilic nature of these salts has been substantially and permanently reduced the adhesion of other solids, such as polymer materials, to the apatitic surface may be considerably improved. It is likely that a chemisorbed monolayer on the apatitic surface, which could not only reduce its hydrophilic character but also provide a good basis for adhesion, is the best surface for the purpose of this work.

Since changes in the surface character, produced

by chemical treatments, and the stability of the resulting modified surfaces in a moist environment, may be evaluated by means of physical adsorption, it is pertinent to discuss some aspects of surface chemistry. Certain theories of adsorption of gases and vapours by solids will therefore be reviewed in section 3.2. This section will also deal briefly with the various inferences from the study of physical adsorption.

Various characteristics of the materials used in this work have been evaluated by means of infra-red spectroscopy; X-ray powder diffraction photographs have also been used in the analysis of the materials and a brief account of the principles underlying these techniques will be given in section 3.3.

3.2 Theoretical Aspects of Adsorption

3.2.1 Physical adsorption.

The interpretation of the adsorption isotherm is fundamental to the problem of characterising a solid surface. Determination of the surface area of the materials prepared in this work rests on the calculation from an isotherm of the monolayer capacity, i.e., the amount of adsorbate which can be held in a completed monolayer on the solid. Differences in the hydrophilic nature of

surfaces after modification may be conveniently assessed from water-vapour sorption isotherms.

A solid must first be freed from previously adsorbed gases by outgassing before measurements, at a fixed temperature, of adsorption and pressure may be carried out. Adsorption isotherms are usually represented graphically, with adsorptions as ordinates and pressures as abscissae. It is convenient, if the adsorbate is a vapour, to express the results in terms of relative pressures.

Five types of isotherm have been classified by Brunauer, Deming, Deming and Teller¹⁷¹. Isotherms of type 1 are associated with systems in which adsorption does not proceed beyond a monomolecular layer and are the only isotherms found in the adsorption of gases, i.e., fluids above their critical temperature. The other types refer to multimolecular layer adsorption. Isotherms measured in this work are all of type 2, which may be simply described as the rapid filling of a monolayer, the adsorbent having a greater affinity than the adsorbate for other adsorbate molecules, followed by the development of a multilayered system. At very low pressures and correspondingly low adsorptions all isotherms tend to a straight line, so that adsorption is proportional to pressure. This behaviour, reminiscent of Henry's law

for the solubility of a gas in a liquid, is sometimes referred to as the Henry's law region. Type 2 isotherms are likely if the adsorbent is non-porous, i.e. devoid of internal surface.

A general equation which applies to the various types of adsorption isotherm was introduced by Brunauer, Emmett and Teller¹⁷² and Brunauer, Deming, Deming and Teller¹⁷¹ and can be applied to the isotherms measured in this work. A simple procedure is developed for the determination of the monolayer capacity and also it claims to be able to reproduce with the same set of parameters the course of an isotherm at different temperatures and to calculate the heat of adsorption from a single isotherm.

The theory assumes that the equilibrium set up between the adsorbed gas and the adsorbent is a dynamic one, the rate at which molecules condense on to a fixed adsorption site being equated with the rate at which they re-evaporate from the occupied sites^{172,173}. If at a pressure p (dyn.cm.⁻²) the fraction of sites occupied is θ_1 and the fraction of sites empty is θ_0 (so that $\theta + \theta_0 = 1$), then the rate of condensation is $k p \theta_0$ molecules cm⁻² sec⁻¹, where k is a constant given by kinetic theory as $k = \frac{N}{(2\pi MRT)^{1/2}}$.

The re-evaporation of a molecule from the surface is essentially

an activated process, the rate of which will be given by the expression $z_m \theta_1 \nu_1 e^{-E_1/RT}$ where z_m is the number of molecules adsorbed per cm^2 in a completed monolayer; E_1 is the energy of activation for desorption, which may be identified with $-\Delta H_{\text{desorption}}$; ν_1 is the frequency of oscillation of the molecules perpendicular to the surface¹⁷⁴. Then at equilibrium

$$k p \theta_0 = z_m \theta_1 \nu_1 e^{-E_1/RT}$$

and similarly for successive layers

$$k p \theta_1 = z_m \theta_2 \nu_2 e^{-E_2/RT}$$

$$k p \theta_{i-1} = z_m \theta_i \nu_i e^{-E_i/RT}$$

Here θ_1 is the fraction of the surface covered with a single molecular layer, θ_2 that covered with a second, and so on; ν_i and E_i are the oscillation frequency and the heat of adsorption respectively of the molecules in the i^{th} layer.

Assumptions that the heat of adsorption in all layers beyond the first is equal to the latent heat of condensation L and that the average time of sojourn ($\frac{1}{\nu}$) of a molecule in all layers after the first is the same are made, so that $\nu_2 = \nu_3 = \dots = \nu_i$. Now the total number of molecules adsorbed per cm^2 of the adsorbent surface is $z = z_m \times (\theta_1 + 2\theta_2 + 3\theta_3 + \dots)$, and the total number of molecules

adsorbed on one gram. of adsorbent is Sz (where S is the surface area of one gram. of adsorbent); the corresponding number adsorbed in a completed monolayer is Sz_m and

so $\frac{x}{x_m} = \frac{Sz}{Sz_m} = \frac{z}{z_m}$, which may be rewritten $\frac{x}{x_m} = (\theta_1 + 2\theta_2 + 3\theta_3 \dots)$

The summation on the right-hand side of the above equation may be carried out after the further assumption is made that the vapour condenses on the adsorbent as a liquid when its pressure reaches the saturated vapour pressure.

The completed equation is of the form

$$\frac{p}{x(p_0 - p)} = \frac{1}{x_m c} + \frac{c-1}{x_m c} \cdot \frac{p}{p_0} \quad 3.2.1$$

where the constant c is given by

$$c = e^{(E_1 - L)/RT} \quad 3.2.2$$

According to equation 3.2.1, a plot of $\frac{p}{x(p_0 - p)}$ against $\frac{p}{p_0}$ should give a straight line of slope $\frac{(c-1)}{x_m c}$

and intercept $\frac{1}{x_m c}$; and application of this test to

experimental data obtained in this work shows that this equation does reproduce the course of most isotherms reasonably well, but only over the range approximately corresponding to $0.05 < \frac{p}{p_0} < 0.30$.

The failure of the equation at low relative pressures is ascribed by the authors to the non-uniformity of the surface. This would cause a variation in the value of E_1 from one region of the surface to another which cannot be corrected for quantitatively. The limited validity of a theory may, however, be due to shortcomings in the model itself, rather than to lack of knowledge of the parameters it employs. The assumption that the adsorbate has liquid-like properties after the first layer is hard to reconcile with the fact that, as shown by careful experiments, solids exposed to a saturated vapour often take up a strictly limited amount, and not the indefinitely large quantity postulated by BET. An important, and perhaps unjustifiable, assumption is that each molecule condensing in any layer after the first gives out its full latent heat of liquefaction whether it has horizontal neighbours or not. It has been pointed out¹⁷⁵ that in the absence of horizontal neighbours the co-ordination number is much less than twelve (the approximate value in a bulk liquid) and the heat evolved should be only a fraction of the latent heat. One equation has been developed which attempts to allow for the variation of co-ordination number in an empirical way¹⁷⁶. But an analysis of the BET mechanism in terms

of co-ordination showed it to be incapable of explaining any adsorption beyond a monolayer¹⁷⁷.

It is important to emphasise that the ability of an equation to reproduce experimental data does not, in itself, prove the correctness of a theory, and it is necessary to compare the values of the parameters obtained by application to the experimental data with independent estimates of them. In this instance it is possible to make the comparison for parameter c , and to a limited extent for x_m .

A value for the differential heat of adsorption can be calculated from the isotherm at a single temperature from the constant c by means of equation 3.2.2, if the theory is internally consistent. It must, however, be borne in mind that the BET model lays down that adsorption shall occur in the first and higher layers at the same time. When the total adsorption increases from x to $(x+\delta x)$, only a fraction, r , of the increment goes into the first layer with heat of adsorption E_1 , the remainder, $(1-r)$, going into the higher layers with heat of adsorption L , the latent heat of condensation of adsorbate in bulk. Thus, the heat of adsorption E^1 corresponding to adsorption x from this theory is $E^1 = rE_1 + (1-r)L$. E^1 should be

equal to the value $\Delta \bar{H}$ calculated from the Clausius-Clapeyron equation. The value, r , can be calculated from the model, and has the form¹⁷⁸

$$r = \frac{(1-p/p_o)^2}{1+(c-1)(p/p_o)^2}$$

Assuming that the adsorbate obeys the perfect gas laws, and that the volume of the adsorbed phase is negligible compared with that of the gas, the Clausius-Clapeyron equation can be written in the forms

$$\frac{d \ln p_o}{dT} = \frac{L}{RT^2} \quad \text{and} \quad \left(\frac{\partial \ln p}{\partial T} \right)_x = \frac{\Delta \bar{H}_x}{RT^2}$$

where $\Delta \bar{H}_x$ is the differential heat of adsorption at constant x . From these two expressions, it follows that

$$\left\{ \frac{\partial \ln p/p_o}{\partial T} \right\}_x = \frac{\Delta \bar{H}_x - L}{RT^2} \quad 3.2.3$$

The differentiation of equation 3.2.1 yields the equation

$$\left\{ \frac{\partial \ln p/p_o}{\partial T} \right\}_x = - \left\{ \frac{\partial \ln c}{\partial T} \right\}_x \cdot \frac{(1-p/p_o)^2}{(1+(c-1)(p/p_o)^2)} \quad 3.2.4$$

while differentiation of equation 3.2.2 yields the equation

$$\frac{\partial \ln c}{\partial T} = \frac{E_1 - L}{RT^2} \quad 3.2.5$$

If it is assumed that E_1 and L are constant for small ranges of temperature, a further expression is obtained

from equations 3.2.4 and 3.2.5

$$\left(\frac{\partial \ln p/p_0}{\partial T}\right)_x = \frac{E_1 - L}{RT^2} \cdot \frac{(1 - p/p_0)^2}{(1 + (c-1)(p/p_0)^2)} \quad 3.2.6$$

From equations 3.2.3 and 3.2.6 may be derived the following expression

$$\frac{\Delta \bar{H}_x - L}{RT^2} = \frac{E_1 - L}{RT^2} \cdot \frac{(1 - p/p_0)^2}{(1 + (c-1)(p/p_0)^2)}$$

which may be rearranged to become

$$\frac{\Delta \bar{H}_x - L}{E_1 - L} = \frac{(1 - p/p_0)^2}{(1 + (c-1)(p/p_0)^2)} \quad 3.2.7$$

$$\text{The expression } E^1 = rE_1 + (1-r)L, \text{ where } r = \frac{(1 - p/p_0)^2}{1 + (c-1)(p/p_0)^2}$$

may now be compared with equation 3.2.7 and it may be seen that $E^1 = \Delta \bar{H}_x$. The heat of adsorption calculated from a single isotherm fulfills thermodynamic requirements as expressed by the Clausius-Clapeyron equation. This test has been applied to a wide range of recorded data¹⁷⁸ and it was found that there was a qualitative correspondence but not always a quantitative agreement between the calculated and the measured values, discrepancies of the order of some hundreds of calories per mole being common. Even the qualitative correspondence is useful, for it enables a rough estimate to be made of the value of the

differential heat of adsorption from the shape of an isotherm. From the mathematical properties of equation 1 it follows that as c increases, the 'knee' of the curve moves closer to the x axis, so that an isotherm with a sharp bend corresponds to a high value of (E_1-L) .

Evaluations of x_m from isotherms on solids of known areas may be examined in order to calculate corresponding areas covered by each adsorbate molecule, A_m where these are related to each other by

$$S = \frac{x_m}{M} N \times A_m \quad S \text{ being the specific surface of}$$

adsorbent, N Avogadro's Number, and M the molecular weight of adsorbate. Values of A_m , obtained in this way from a selection of adsorbents of known specific surface, may be compared for any particular adsorbents. The numerical value of A_m will clearly depend on the way in which molecules are packed on the surface in the completed monolayer. In the type of model just discussed, since each molecule is anchored on a definite site on the surface, A_m should be determined by the lattice dimensions of the solid, and should therefore vary for a given adsorbate according to the nature of the solid. But if the adsorbed molecules are mobile, the value of A_m should be determined by the dimensions of the adsorbate molecule and with the exception

of a spherically symmetrical molecule would also vary according to its orientation relative to the surface. Knowledge of the effective dimensions of molecules and of the way they pack together in films is subject to much uncertainty. A formula relating A_m to the density ρ of the adsorbate in the ordinary liquid or solid form, assuming a packing in which a molecule has twelve nearest neighbours is $A_m = 1.091 \frac{(M)^2}{(\rho N)^{2/3}}$ and the results collected from this formula by using the liquid density¹⁷⁹ compare favourably with values derived from the monolayer capacity on an adsorbent of known specific surface¹⁸⁰.

S may not be known independently for many adsorbents but values of S from a number of different vapours on the same adsorbent should be similar. Experiments on a sample of silica gel¹⁷² have in this way demonstrated the consistency of these determinations. Again A_m values for each vapour were determined, using the formula shown above, from the liquid density. It is interesting to note that this formula does not satisfy the BET conditions that adsorption occurs on fixed sites on the solid.

The Clausius-Clapeyron equation, which has been applied as a test of the theory, is valid for thermodynamically

reversible processes only. The validity of the BET equation, when applied to irreversible sorption measurements, is therefore subject to doubt.

Irreversibility of sorption isotherms with non-porous rigid sorbents is not usual but has been noted in the low temperature sorption of nitrogen by a non-porous carbon black¹⁸¹ and explained by swelling of the sorbent. Work on an activated charcoal rod¹⁸², and on rods of porous glass^{183,184} have demonstrated that swelling normally occurs during sorption on these solids. On the basis of work mentioned in chapter 2 on the water apatite interface, it is likely that certain chemical effects may occur during water sorption by apatites.

3.2.2 Chemisorption

Chemisorption involves a displacement of electrons as between adsorbent and atoms or molecules of adsorbate. The adsorbed film is therefore a species different from either adsorbent or adsorbate but will be confined to a monolayer in thickness. The reaction between apatite surface and aliphatic diazo compounds should therefore be regarded as a process of chemisorption since the adsorbed layer is not removable by the normal process of outgassing, neither does it possess the characteristics

of diazoalkanes⁴².

3.3.1 Infra-red spectroscopy

The approach to absorption of infra-red radiation based on classical mechanics may be visualised in physical terms. A system of N interacting point-masses represents a molecule or ion containing N atoms, and the force on one particle depends, to a first approximation, only on the linear displacements of all the particles. The components of the forces on the particle are given by a set of $3N$ linear equations:

$$\begin{aligned} F_x^1 &= -k_{xx}^{11} \cdot x_1 - k_{xy}^{11} \cdot y_1 - k_{xz}^{11} \cdot z_1 - k_{xx}^{12} x_2 \dots k_{xz}^{1N} \cdot z_n \\ F_y^1 &= -k_{yx}^{11} \cdot x_1 - k_{yy}^{11} \cdot y_1 - k_{yz}^{11} \cdot z_1 \dots \\ F_z^1 &= -k_{zx}^{11} \cdot x_1 - k_{zy}^{11} \cdot y_1 - k_{zz}^{11} \cdot z_1 \dots \end{aligned} \quad 3.3.1$$

The displacements x_i, y_i, z_i are measured from the equilibrium position of the i^{th} particle, and the force constants k_{xy}^{ij} determine how the x -component of the force on the i^{th} particle depends on the y -component of the j^{th} particle. Similar sets of three equations describe the other particles. Solutions of these equations must be found in which all the particles have a simple harmonic motion of the same frequency, so that the displacement of the i^{th} atom is of the form

$$S_i = S_i^0 \cos(2\pi\mathcal{V}t + \phi) \quad 3.3.2$$

where $\mathcal{V}$ is the frequency and ϕ a phase angle.

Application of Newton's second law of motion to each component of the force, and substitution for S_i and S_i^0 from equation 3.3.2 yields:

$$\begin{aligned} 4\pi^2\mathcal{V}^2 m_1 x_1 &= k_{xx}^{11} x_1 + k_{xy}^{11} y_1 \dots + k_{xz}^{1N} z_N \\ 4\pi^2\mathcal{V}^2 m_1 y_1 &= \dots \\ 4\pi^2\mathcal{V}^2 m_N z_N &= k_{zx}^{N1} x_1 + \dots + k_{zz}^{NN} z_N \end{aligned} \quad 3.3.3$$

This system of linear and homogeneous equations for $x_1 y_1 \dots z_N$ cannot be solved for arbitrary values of the coefficients occurring in them, but only if the determinant of the coefficients is equal to zero. As the force constants are fixed for a given system, the only way to fulfil this condition is by a suitable choice of the frequency $\mathcal{V}$. Only for certain frequencies, therefore, is a simultaneous simple harmonic motion of all the particles possible. The determinant of the coefficients is of the order $3N$ in $\mathcal{V}$, so that in general there will be $3N$ solutions giving $3N$ normal modes with different frequencies. Three solutions will be zero, corresponding to the linear displacement of the centre of gravity of the whole system while three more solutions, corresponding to rotation of the whole system about the centre of gravity, will also be zero. In the general case there

are therefore $3N-6$ normal modes.

Any periodic motion of a molecule may be resolved into a sum of normal modes with appropriate amplitudes. In a completely unsymmetrical molecule there will always be an oscillating dipole associated with each normal mode, and there should be $3N-6$ absorption bands in the infra-red spectrum. If the molecule has elements of symmetry, the determinant is symmetrical too, and this could mean that two or more of the solutions are identical; these are called degenerate normal modes and there will, in this case, be fewer bands in the spectrum than expected. The presence of symmetry may result in there being no oscillating dipole moment associated with a particular normal mode and the band will therefore be absent from the infra-red spectrum.

The position and type of nuclei within a molecule determine its symmetry and quite generally, molecules of different symmetry have qualitatively different spectra. A plane of symmetry σ exists when the corresponding operation σ , called reflection at the plane, produces a molecule which is indistinguishable from the original one. The molecule H_2O has two planes of symmetry, one is the plane of the molecule and the other is the plane perpendicular to this which bisects the H-O-H angle.

A centre of symmetry i exists when the operation i , reflection at the centre (or inversion), produces a molecule indistinguishable from the original; a molecule can have only one centre of symmetry and there may or may not be an atom there, all other atoms will occur in pairs. A p -fold axis of symmetry C_p exists when rotation about the axis by an angle of $\frac{360}{p}$ degrees produces a configuration indistinguishable from the original. When rotation by $\frac{360}{p}$ degrees about an axis followed by a reflection at a plane perpendicular to the axis transforms a molecule into itself, then a p -fold rotation-reflection axis S_p exists. A two-fold rotation-reflection axis is always identical with a centre of symmetry, $s_2 = i$, since the same pairs of atoms are exchanged in the two operations. Any molecule having a p -fold axis C_p and a plane of symmetry σ_h perpendicular to this axis must have a p -fold rotation-reflection axis, but only when p is odd does the existence of S_p necessarily imply C_p and σ_h . The identity I is a trivial element which all molecules have, the corresponding operation is to leave the molecule unchanged, and it is included because it can now be said quite generally that if two symmetry operations are carried out in succession the result is

the same as that of one other possible symmetry operation of the molecule. A number of elements of any kind such that the product of any two is again one of them is called a group. A point group is a possible combination of symmetry operations which leaves at least one point unchanged and a limited number of such point groups exist, every molecule belonging to one of them.

Point groups having not more than one (if any) three-fold (or higher-fold) axis are called axial point groups. Cubic point groups, which form the basis of the cubic crystal system, possess more three-fold (or higher-fold) axis.

A molecule having three mutually perpendicular two-fold axes and four three-fold axes with a plane of symmetry σ_d through each pair of three-fold axes belongs to point group T_d . Such a molecule has six planes of symmetry and this implies that the two-fold axes are also four-fold rotation-reflection axes. A regular tetrahedron has this symmetry and all tetrahedral molecules are examples of this point group, orthophosphate ions of the apatite lattice are such molecules as these.

The hydrogen phosphate ion may possibly belong to two point groups. If the ion has a configuration

similar to that found for CH_3OH , then the hydrogen atom would be located in one of the planes of symmetry of the PO_4 group, and the ion would then have just one plane of symmetry, the P-O-H plane. In this case the molecule would belong to the point group C_s (the one plane of symmetry is the only symmetry element, apart from I, in the molecule). Alternatively the hydroxyl group may be considered to be free to rotate about its P-O bond, to give an average position of the OH bond along the C_3 axis, the ion would now belong to the point group C_{3v} (it has a 3-fold axis and 3 planes of symmetry σ_v passing through the axis).

The cubic point group to which orthophosphate belongs has four three-fold axes and non-degenerate vibrations can only be symmetric with respect to these axes, they may, however, be either symmetric or antisymmetric with respect to the six planes of symmetry σ_d through the C_3 axes. There are therefore two types, A_1 and A_2 , of non-degenerate vibrations. An examination¹⁸⁵ on the basis of group theory shows that there is one doubly degenerate species E and two triply degenerate species F_1 and F_2 . Their characters are as follows:

T_d	I	$8C_3$	$6C_2$	$6S_4$	$3C_2^2$	$3C_2$
A_1	+1	+1	+1	+1	+1	
A_2	+1	+1	-1	-1	+1	
E	+2	-1	0	0	0	3.3.4
F_1	+3	0	-1	+1	-1	
F_2	+3	0	+1	-1	-1	

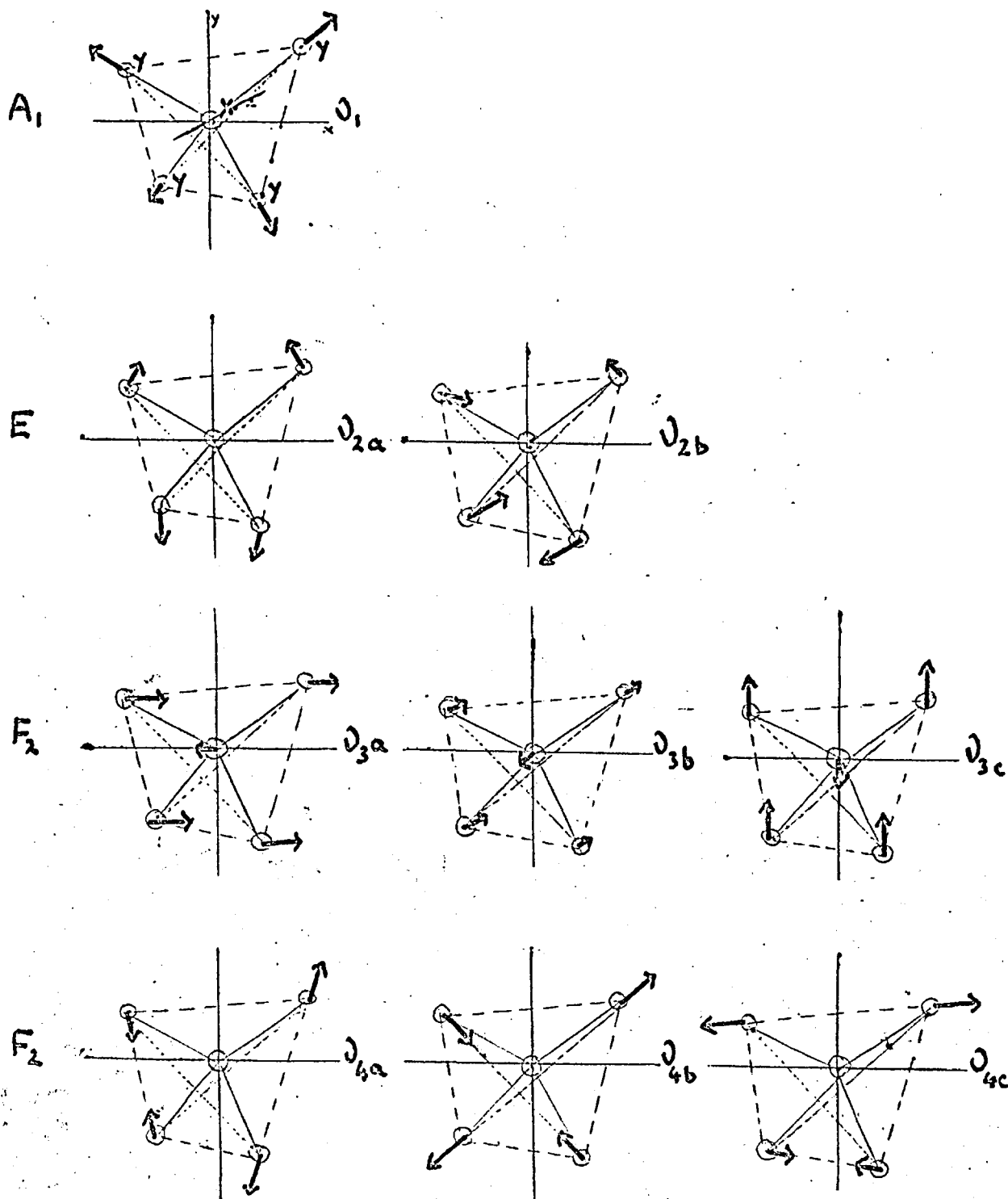
where +1 and -1 indicate symmetric and antisymmetric, and the top row shows the point group and the symmetric operations including the identity. Below are the species and the behaviour of the vibrations having these species for each operation in the top row. The normal vibrations of a tetrahedral molecule are of the species A_1 , E and F_2 . Figure 3.3.1 shows the normal vibrations of a tetrahedral molecule.

The selection rules for a five atom molecule of T_d symmetry are $A_1(R)+E(R)+2F_2(R,i.r.)$ where R means Raman and i.r. means infra-red active. Assignments of bands are well established for simple aqueous phosphate and are shown below:

Normal Mode	Degeneracy	Species	Frequency in cm^{-1} .	i.r. activity
ν_1	1	A_1	980	Inactive
ν_2	2	E	363	Inactive
ν_3	3	F_2	1082	Active
ν_4	3	F_2	515	Active

Figure 3.3.1

The normal vibrations of a tetrahedral XY_4 molecule.



The spectra of alkali metal phosphates have been found to be consistent with the C_{3v} configuration for the hydrogen phosphate ion. The characters of the species for this point group, on the basis of group theory are as follows:

C_{3v}	I	$2C_3(z)$	$3\sigma_v$
A_1	+1	+1	+1
A_2	+1	+1	-1
E	+2	-1	0

The selection rules for the ion are $4A_1 + 4E$, and the band assignments are shown below:

Normal Mode	Degeneracy	Species	Frequency in cm^{-1}	i.r. activity
ν_1	1	A_1	2900	Active
ν_2	1	A_1	988	Active
ν_3	1	A_1	862	Active
ν_4	1	A_1	537	Active
ν_5	2	E	1230	Active
ν_6	2	E	1076	Active
ν_7	2	E	537	Active
ν_8	2	E	394	Active
γ_{OH}			970	Active
δ_{OH}			766	Active

Fig. 3.3.2 shows some of the normal vibrations of an XY_4 molecule, of point group C_{3v} .

Normal vibrational modes and degeneracies of any polyatomic species in a crystal lattice will be affected by the symmetry of the crystal field. The space group of hydroxyapatite, noted in chapter 2, is $P6_3/m$ but it was also pointed out that the hydroxyl ions are not located on the mirror planes but are displaced along the hexagonal screw axis. For the space group $P6_3$, a more accurate description of the symmetry properties of hydroxyapatite, the phosphate ions are located on sites of C_1 symmetry. The ions would therefore be reduced in symmetry from T_d to C_1 and all nine internal modes of the ion would become infra-red active and of the same species, A.

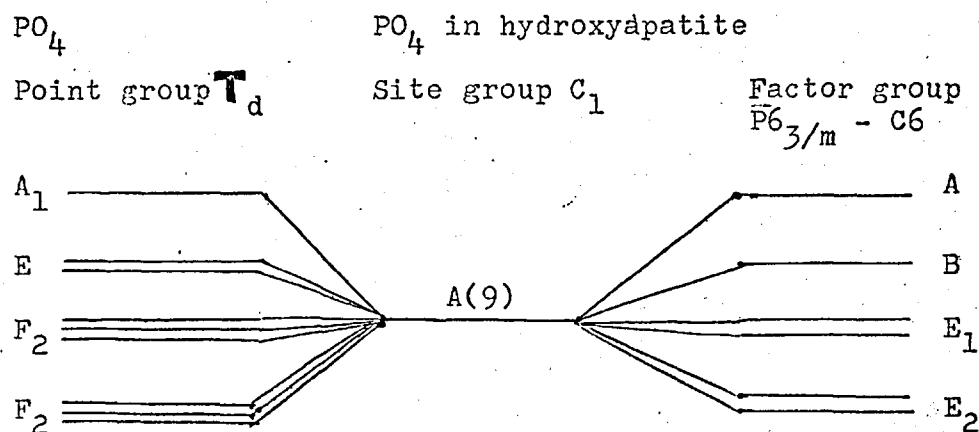
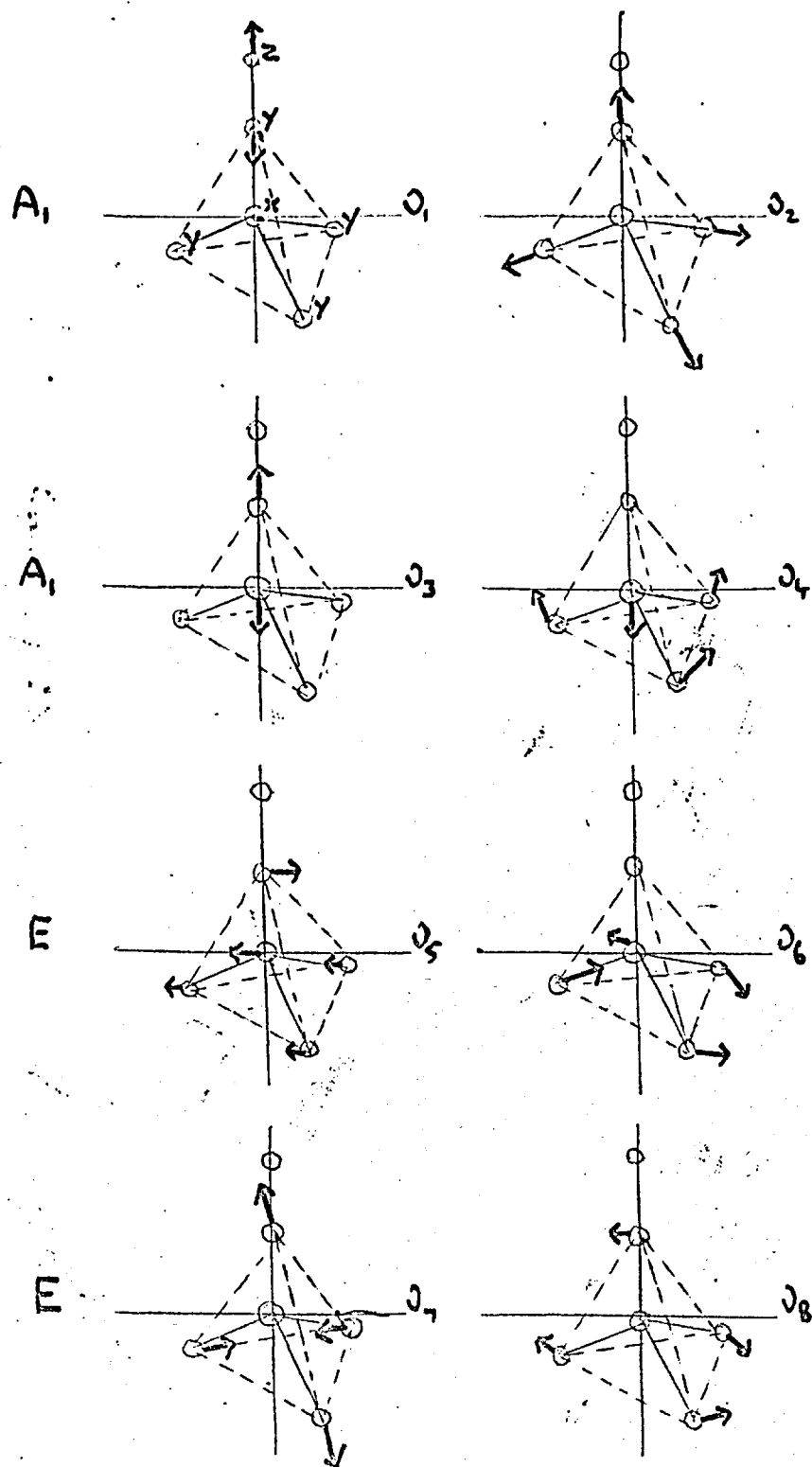
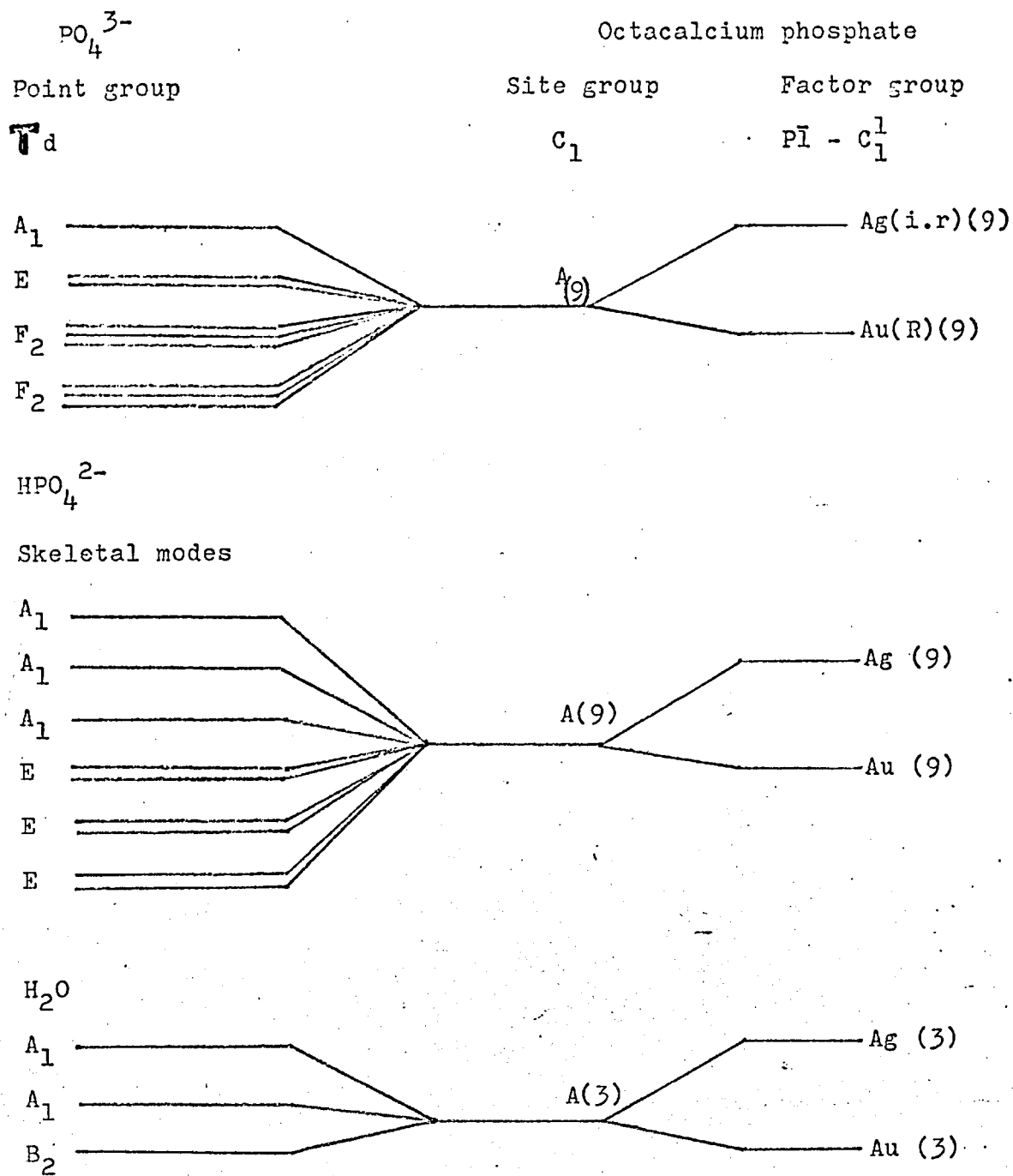


Figure 3.3.2

The normal vibration of a point group C_{3v} XY_4Z molecule.



The absence of information on the structure of calcium deficient apatites means that little can be said about the effect of lattice symmetry on the polyatomic ions. However, the structural determination of octacalcium phosphate enables a brief account to be made of the environment of the molecules orthophosphate, hydrogen orthophosphate and water in this lattice. The space group of octacalcium phosphate, as noted in chapter 2, is $P\bar{1}$ and the sites of the ions and molecules present in this lattice are therefore of C_1 symmetry. The subsequent reduction in degeneracy due to symmetry loss and coupling between molecular species may be summarised:



To obtain spectra of measurable intensity for liquid hydrocarbons, for example, it would be necessary for infra-red radiation to traverse a layer of liquid of thickness 1 to 100 microns, and assuming a molecular width of $10\text{\AA}$ this would correspond to a layer of between 1,000 and 100,000 molecules in depth. It is therefore most unlikely that a monomolecular layer of chemisorbed molecules could be detected by this means unless a large surface is exposed to the radiation. This should be the case with adsorbents used in this study.

Considerable work has been recorded¹⁸⁶ on the infra-red spectra of adsorbed species and it is generally the case that free adsorbate molecules exhibit major differences, in the stretching region of the spectrum, from chemisorbed groups. From spectra obtained for butenes adsorbed onto porous glass it was estimated that an adsorption of about 5×10^{11} carbonium ions cm^{-2} are capable of detection by such frequency shifts¹⁸⁷. The reaction of a hydrophilic silica surface with methanol, to yield a thermally stable hydrophilic surface, was studied¹⁸⁸ and the intensity of the free hydroxyl band was seen to decrease during the reaction with a corresponding increase in C-H stretching modes.

The number of Brönsted acid sites on the surface of calcium deficient apatites may be sufficient to provide enough diazo-adsorption reaction-sites for detection by infra-red spectroscopy.

3.3.2 X-ray powder diffraction

Powder diffraction photographs of apatite samples were taken as a means of crystal identification. Diffraction lines may be indexed and the distance d between successive identical planes of atoms in the crystal related to the angle θ between the X-ray beam and these atomic planes by Bragg's law¹⁸⁹ $\frac{d}{n} = \frac{\lambda}{2\sin \theta}$ where λ is the X-ray wavelength, and n any whole number. For crystals of hexagonal symmetry, such as hydroxyapatite, lattice unit-cell parameters a and c are related to d by the relation¹⁹⁰

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

A comparison of a and c for different samples may then be made.

The uses to which these techniques of adsorption-desorption under isothermal conditions, infra-red spectroscopy and X-ray powder diffraction have been put in this work are described in chapter 5. Chapter 4 will deal with the preparations of the various materials.

CHAPTER 4

PREPARATION OF MATERIALS

The three sections of this chapter will deal with the methods employed in the preparation of apatite, aliphatic diazo compounds, and surface modified apatite samples.

4.1 Preparation of apatites and related salts.

A total of twenty-eight calcium phosphate salts have been prepared for study and a further seven obtained from various sources. The various methods which have been employed in these preparations will be described but characterisation of the salts will be discussed in the next chapter.

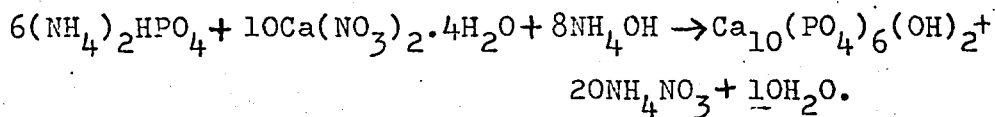
4.1.1 Hydroxyapatite

Nine attempts to prepare samples of stoichiometric hydroxyapatite (HA) have been made, all being various modifications of a single method described by Hayek and Newesley¹⁹¹. HA5 and HA6 refer to precipitations carried out according to their method, which will be described first.

Solutions of 0.33 mole of analytical grade calcium nitrate tetrahydrate in 400 ml distilled water and 0.2

mole of analytical grade diammonium hydrogen phosphate in 600 ml distilled water were made up and adjusted to pH11 by the addition of 0.880 ammonia solution. The solutions were then diluted with more distilled water to 600 ml and 800 ml respectively before the phosphate solution was added, over a period of about three hours at room temperature, to the stirred solution of calcium nitrate. A voluminous precipitate formed and gentle boiling for 15 minutes improved its filtration. The filtrand was washed with 100 ml of hot distilled water and drained at the pump before drying for five hours at 150°C. Grinding, followed by heating at 240°C for one hour, removed any ammonium nitrate which may have adhered to the hydroxyapatite crystallites.

The reaction may be represented by the equation



This procedure is limited because it allows atmospheric carbon dioxide to enter the precipitation system. To overcome this difficulty, preparations HA 7, 8 and 10 were carried out under an atmosphere of nitrogen in an enclosed system, whereas preparations HA 11, 13, 15 and 17 were precipitated in air, which had been passed through an ammonium hydroxide solution to remove any

carbon dioxide which would otherwise be precipitated in the form of carbonate ions.

A second problem inherent in this method is that there is no way of controlling the pH of the precipitating liquor. It may be readily appreciated from the equation for the reaction that ammonium hydroxide is used in the course of the precipitation in consequence of which the solution pH will be lowered. Such a lowering of pH could well result in the formation of less basic phases than stoichiometric hydroxyapatite.

Since it was noted in chapter two that the final stage of hydroxyapatite crystal growth does not commence until about seven hours⁹⁹ after the reaction is initiated it is clear that the product of the method described above may well not be a well crystallized phase. This rapid precipitation followed by drying is also inconsistent with the observation, also noted in chapter two, that the crystal-solution interface reaches equilibrium only after a considerable number of hours¹⁰³.

Heating the sample to 240°C, in air, is a particularly severe method of removing adsorbed ammonium nitrate. Such conditions as this may be expected to affect, considerably, the character of the particle surface.

For these reasons, the following general procedure

was adopted for the remaining hydroxyapatite preparations, while various adjustments for each sample are recorded in table 4.1.1. Freshly distilled water to eliminate carbon dioxide contamination as far as possible, was used to make up the solutions of phosphate and calcium. The pH values, before commencing the phosphate addition, are recorded in the table and these were maintained, throughout the mixing, by the addition of more analytical grade 0.880 ammonium hydroxide solution. The times taken for mixing the solutions were, with one exception, longer than three hours and are included in the table. Stirring, by 'Teflon' coated magnetic stirrers, was maintained throughout the solution addition stage and for a further period to aid the approach to crystal equilibrium. After filtration at the pump, precipitates were washed five times with 500 ml aliquots of an ammonium nitrate/ammonia solution at the pH of precipitation to remove any surplus calcium and finally washed five times with 500 ml aliquots of freshly distilled water. Products were dried overnight at 100°C before being ground and sieved. In all cases yields were of about 95% of the theoretical amount.

Table 4.1.1The preparation of stoichiometric hydroxyapatite samples.

Preparation Number	pH of Reaction ^a	Period of Phosphate Addition	Period allowed for crystal equilibrium, after addition.
HA 5	11.0 ^b	3 hours	0
HA 6	11.0 ^b	3 hours	0
HA 7	9.5	3 hours	9 hours
HA 8	10.5	10 minutes	0
HA10	11.0	48 hours	624 hours
HA11	12.0 ^c	48 hours	288 hours
HA13	11.0	48 hours	336 hours
HA15	9.9	48 hours	400 hours
HA17	12.0 ^c	72 hours	500 hours

Notes: a. pH values quoted are within ± 0.1 of the experimental values.

b. Original value, prior to mixing.

c. Molarity of phosphate solution reduced from 0.25M to 0.17M to avoid reprecipitation.

4.1.2 Non-stoichiometric apatites.

The procedure adopted for the precipitation of the

Table 4.1.2The preparation of non-stoichiometric apatite samples

Prep. No.	pH of Reaction ^a	Period of Phosphate addition	Period allowed for crystal equilibrium, after addition.
HA 9	5.8	10 minutes	50 minutes
HA12	5.7	48 hours	336 hours
HA14	5.5	48 hours	400 hours
HA16	5.2	72 hours	500 hours

Notes: a. pH values quoted are within ± 0.1 of the experimental values.

Table 4.1.3The preparation of octa-calcium phosphate samples.

Prep. No.	pH of Reaction ^a	Period of Solution mixing	Period allowed for crystal equilibrium, after mixing.
OCP 1	8.0 ^b	3 hours	21 hours
OCP 2	7.0 ^b	- c	2 months
OCP 3	6.6 ^b	- c	2 months

Notes: a. pH values quoted are within ± 0.1 of the experimental values.

b. Final value after period of equilibration

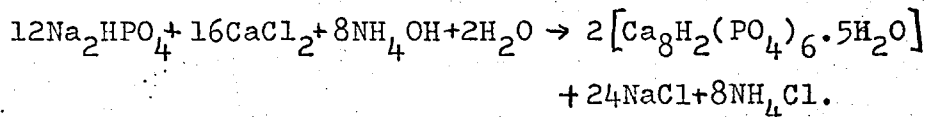
c. Method does not involve the mixing of solutions.

four calcium deficient apatite samples was a modification of the method described immediately above. The difference was in the pH of reaction alone, no other adjustments being made. Solutions and precipitating liquors were maintained at the pH values quoted in table 4.1.2 by suitable ammonium nitrate/ammonia buffers.

4.1.3 Octa-calcium phosphate

Three different methods were employed in attempts to prepare samples of octacalcium phosphate, each will be described briefly, table 4.1.3 listing some of the details of the preparations.

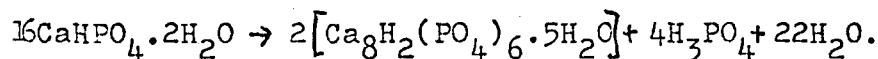
The sample referred to as OCP 1 was prepared according to an early method¹⁹² in which it was noted that although the addition of disodium phosphate to calcium chloride leads to the formation of dicalcium phosphate dihydrate, a reversal of the procedure produces a more basic solid provided the mixture remains alkaline:



A solution of 100 ml of 0.1M calcium chloride was added, with magnetic stirring, to a solution of 1200 ml

of 0.1 M of disodium phosphate over a period of three hours, pH 8 being maintained by the addition of ammonium chloride/ammonia buffer. Stirring was continued for a further 21 hours before filtering and washing in the manner described earlier for the modified preparation of apatites, with the exception that washing with buffered solution was omitted.

OCP 2 refers to a sample prepared by a more recent method⁸⁵ in which one gramme of dicalcium phosphate dihydrate was hydrolysed in 500 ml 0.5 M sodium acetate solution at a temperature of 40°C. Stirring was maintained throughout the period of two months allowed for octacalcium phosphate formation:



The hydrolysis of one gramme of dicalcium phosphate dihydrate in 0.01 M hydrochloric acid¹⁹³, in a manner similar to that described above, yielded, after a period of two months, the sample OCP 3.

4.1.4 The pyrolysis of calcium phosphate.

Samples of some of the preparations described in sections 4.1.1 to 4.1.3 have been heated, under various atmospheres in order to produce calcium phosphates having distinct characteristics.

Three types of pyrolysis reaction were carried out and table 4.1.4 indicates which samples were subjected to these treatments. Two gramme samples of preparations HA 12,13,14,15,16,17 and OCP 3 were heated at 600°C in air for a period of 120 hours and are referred to as HA 12/600 A etc. A portion of HA 12/600 A was subsequently reheated at 160°C in an atmosphere of 2 cm Hg partial pressure of water vapour for 24 hours and is termed HA 12/600A/160W. Two other materials called HA12/160V and HA12/600V were heated, under a pressure of less than 10^{-6} cm Hg for 120 hours, at 160°C and 600°C respectively.

Table 4.1.4

Pyrolysed calcium phosphate preparations.

Prep. Number	Parent Material	Temperature of treatment	Atmosphere of treatment
HA12/600A	HA12	600°C	Atmospheric
HA13/600A	HA13	600°C	Atmospheric
HA14/600A	HA14	600°C	Atmospheric
HA15/600A	HA15	600°C	Atmospheric
HA16/600A	HA16	600°C	Atmospheric
HA17/600A	HA17	600°C	Atmospheric
OCP3/600A	OCP3	600°C	Atmospheric
HA12/600A/160W	HA12/600A	160°C	Water vapour at 2cmHg partial pressure
HA12/160V	HA12	160°C	< 10^{-6} cmHg pressure
HA16/160V	HA16	160°C	< 10^{-6} cmHg pressure

Prep. Number	Parent Material	Temperature of treatment	Atmosphere of treatment
HA17/160V	HA17	160°C	< 10 ⁻⁶ cmHg pressure
HA12/600V	HA12	600°C	< 10 ⁻⁶ cmHg pressure

4.1.5 Materials obtained from other sources.

Table 4.1.5 summarises the sources of samples other than those described above.

Table 4.1.5

Materials obtained from other sources.

Sample

No.	Source	Conditions of preparation
HA4	M.D. Butler ⁴²	Precipitated hydroxyapatite ¹⁹¹
HAC	B. Coughlan ¹⁹⁴	Precipitated hydroxyapatite ¹⁹¹
PCP	Hopkin & Williams Ltd.	Commercial sample of precipitated, basic calcium phosphate.
BA	-do-	Commercial sample of Bone Ash.
ND	Speirs	Normal, ground dentine ¹⁹⁵
AD	"	Anorganic, ground dentine ¹⁹⁵
FA	Durango, Mexico	Mineral fluorapatite.

4.2 Preparation of Aliphatic Diazo-Compounds.

Since the aliphatic diazo-compounds were prepared by

five distinct types of reaction, the various procedures will be described first, table 4.2 indicating which of the four methods (4.2.1, 4.2.2, 4.2.3, 4.2.4 or 4.2.5) were used to prepare each compound.

4.2.1 Preparation of disubstituted derivatives of diazomethane^{125-132.}

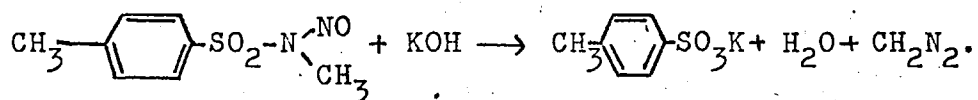
Ketohydrazone (0.025 moles) was placed in a 100 ml, ground-glass stoppered, bottle with yellow mercuric oxide (0.025 moles) and petroleum ether (25 ml) of boiling point in the range 40-60°C. The bottle was closed, wrapped in a wet towel, firmly bound with wire to keep the stopper in place and shaken mechanically at room temperature overnight. The mixture was then filtered to yield the disubstituted derivative of diazomethane in a solution of petroleum ether.

$$\begin{matrix} R \\ \diagup \\ C \\ \diagdown \\ R \end{matrix} = N-NH_2 + HgO \rightarrow \begin{matrix} R \\ \diagup \\ CN_2 \\ \diagdown \\ R \end{matrix} + Hg + H_2O.$$
 The solution was then dried over metallic sodium and the concentration evaluated (the method is described in chapter five) and adjusted as necessary.

4.2.2 Preparation of an ethereal solution of diazomethane^{118.}

2-(2-ethoxy ethoxy)-ethanol (35ml) and diethyl ether (10 ml) were added to a solution of potassium hydroxide (6 g) in water (10 ml). The whole was then

placed in a long-necked distilling flask fitted with a dropping funnel and an efficient condenser. The flask with contents was placed in a water-bath and maintained at a temperature of 70°C. The dropwise addition of a solution of N-methyl-N-nitroso-p-toluenesulphonamide (21.5 g) in diethyl ether (140 ml) was commenced as soon as the ether in the flask began to distil. The addition was continued over a period of 20 minutes and an ethereal solution of diazomethane collected in more diethyl ether (20 ml) in a receiving flask, the outlet tube of the condenser dipping below the surface of the receiving liquid, which was cooled to a temperature of 0°C. When the dropping funnel was empty, a further quantity of diethyl ether (40 ml) was added slowly and the distillation continued until the distilling ether was colourless.

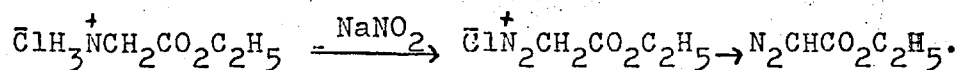


The ethereal solution was then dried and its concentration determined as in preparation 4.2.1. It could be stored, over sodium, at 0°C.

4.2.3 Preparation of an ethereal solution of ethyl diazoacetic ester¹¹⁰.

A solution of ethyl amino acetate hydrochloride (35 g)

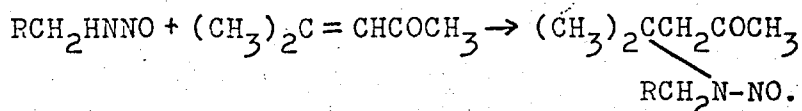
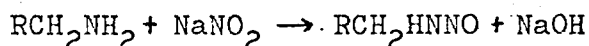
and sodium acetate (0.8 g) in water (40 ml) was added to a 250 ml Claisen flask fitted with a mechanical stirrer and cooled to 2°C with an ice-salt bath. A cold solution of sodium nitrite (20 g) in water (25 ml) was then added and the mixture stirred until the temperature had fallen to 0°C. The temperature was maintained below 2°C and stirring continued while ethanol-free diethyl ether (20 ml) and then cold 10% sulphuric acid (0.75 ml) were added. After 5 minutes the reaction mixture was blown over into a 250 ml separating funnel, through a glass tube reaching from the bottom of the reaction vessel to the top of the funnel. The lower aqueous layer was quickly blown back into the reaction flask and the ether layer removed and washed with a cold solution of 10% sodium carbonate (13 ml). Washing was repeated until the ether layer was no longer acid to moist litmus paper. The ethereal solution was dried over anhydrous sodium sulphate (3 g) and stored over metallic sodium at 0°C.



The concentration of the solution was evaluated in the manner described in chapter 5.

4.2.4 Preparation of ethereal solutions of the higher homologues of diazo-methane¹²¹⁻¹²⁴.

A solution of sodium nitrite (2 moles) in the minimum amount of water was added to the product obtained by mixing mesityl oxide (4-methyl-3-penten-2-one) (1 mole) with a primary amine (1 mole) after neutralisation with glacial acetic acid. Glacial acetic acid (1 mole) was then added, and the mixture left overnight in a water bath at 50°C, the reaction vessel having been fitted with a reflex condenser, to prevent loss of material, and a mechanical stirrer. The oily layer, containing 4-methyl-4-alkyl nitrosamino-2-pentanone, was then separated from the mixture and the aqueous layer extracted with ether (30 ml). Oily layer and ethereal extract were combined and washed twice with dilute acetic acid and then with water before being dried over anhydrous sodium sulphate.



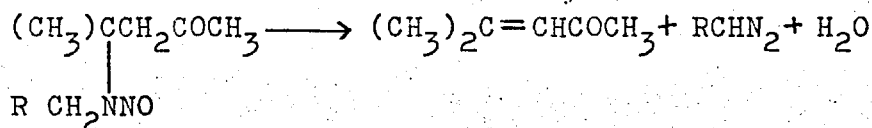
Ether could have been pumped off at room temperature and the residual nitroso derivative distilled under reduced pressure to remove any traces of olefin or

alcohol, but this was not thought to be necessary for the purpose of this work.

Two methods were employed in the preparation of diazoalkanes from this ethereal solution of nitroso-derivative.

Method 1¹²¹⁻¹²⁴.

A 20 ml Claisen flask, carrying a tap funnel, was connected to a condenser fitted with an adapter which dipped below the surface of diethyl ether (50 ml) in a receiver cooled by ice. The ethereal solution of the nitroso-derivative (30 ml) and isopropyl alcohol (3 ml) was added drop by drop to a 1% solution of sodium in isopropyl alcohol (5 ml) at 78°C, at a rate equivalent to that of distillation. As the colour of the distilling liquid faded, a further quantity of sodium isopropoxide solution (4 ml) was added. When the addition was complete, diethyl ether (25 ml) was added until the distillate was no longer coloured.



Method 2.

It was decided that for the purpose of this study, the presence of mesityl oxide in the ethereal diazoalkane

solution was of no importance. Later preparations therefore used a simplified alkaline hydrolysis reaction for obtaining diazoalkanes from the nitroso-derivative.

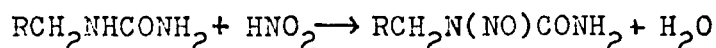
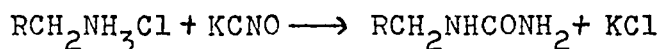
Potassium hydroxide (5 g) was first added to the ethereal nitroso-derivative solution and then water (10 ml), the mixture was gently refluxed for one hour with occasional shaking. The ethereal layer was separated, dried over potassium hydroxide pellets and stored over metallic sodium.

4.2.5 Preparation of ethereal solutions of the higher homologues of diazo-methane^{116,117,196}.

Primary amine (1 mole) was diluted with water to a volume of 500 ml and concentrated hydrochloric acid added until the solution was acid to methyl red paper.

Potassium cyanate (100 g) was then added and the mixture boiled gently for five minutes and more vigorously for a further ten minutes. The hot solution was poured into a solution of sodium nitrite (70 g) in water (100 ml) and then cooled to 0°C. A mixture of concentrated sulphuric acid (60 ml) and ice (400 g) was prepared in a 3l beaker, itself placed in a bucket containing an ice-salt mixture. The alkyl urea solution was added slowly, with constant stirring, to the sulphuric acid

solution over a period of about half an hour and gave a foaming precipitate of nitroso alkyl urea. This precipitate was immediately filtered in a Buchner funnel, and washed with water (200 ml), the process was repeated until a sample of the solid could be completely dissolved in methyl alcohol without turbidity. Nitrosoalkyl urea could be stored dry in a vacuum desiccator at a temperature below 20°C.



Diazoalkane was prepared from this nitroso-derivative by cooling a mixture of diethyl ether (150 ml) and 50% aqueous potassium hydroxide (150 ml) in a conical flask to below 0°C in an ice-salt bath and adding the nitroso-compound (1 mole) in portions with swirling, keeping the flask below 0°C. The ethereal layer became yellow with the formation of diazo-compound and was decanted into a second conical flask. A further quantity of ether (150 ml) was added in portions, with continued swirling, and the ethereal layer again decanted. The diazoalkane solution was dried by adding potassium hydroxide pellets, and stored at 0°C over sodium.

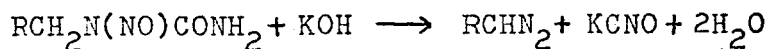


Table 4.2

Preparation of Aliphatic Diazocompounds

Prep. No.	Product	Solvent	Method of Preparation			
D1	Diazomethane	Diethyl ether	4.2.2			
D2	Ethyl diazoacetic ester	" "	4.2.3			
D3	Diphenyl diazo-methane	Petroleum ether (b.p.40-60°C)	4.2.1			
D4	Vinyl diazomethane	Diethyl ether	4.2.4 Method 1			
D5	Diazomethane	" "	4.2.4	"	1	
D6	Diazo n-octane	" "	4.2.4	"	1	
D7	Diazo n-butane	" "	4.2.4	"	1	
D8	Diazo iso-butane	" "	4.2.4	"	1	
D9	Diazo ethane	" "	4.2.4	"	2	
D10	Diethyl diazo-methane	Petroleum ether (b.p.40-60°C)	4.2.1			
D11	Diazo n-octadecane	Diethyl ether	4.2.4	"	2	
D12	Diazo n-propane	Diethyl ether	4.2.4	"	2	
D13	Diazo n-pentane	" "	4.2.4	"	2	
D14	Diazo n-octane	" "	4.2.4	"	2	
D15	Diazo n-butane	" "	4.2.4	"	2	
D16	Diazo n-octadecane	" "	4.2.5			

Prep.			Method of
No.	Product	Solvent	Preparation
D17	Diazo n-dodecane	Diethyl ether	4.2.4 Method 2
D18	Diazo n-octadecane	" "	4.2.4 " 2
D19	Diphenyl diazo- methane	Petroleum ether (b.p.40-60°C)	4.2.1
D20	Diazo n-octane	Diethyl ether	4.2.5
D21	Diphenyl diazo- methane	Petroleum ether (b.p.40-60°C)	4.2.1
D22	Diphenyl diazo- methane	- do -	4.2.1
D23	Diazo ethane	Diethyl ether	4.2.5

In all cases, diazo compounds were prepared immediately before use.

4.3 Preparation of surface modified apatites and related salts.

Two gramme samples of the calcium phosphate materials were pretreated under various conditions prior to reaction with aliphatic diazocompounds. Table 4.3 indicates the nature of these conditions, which may be generalised as follows. Some samples were taken straight from the storage bottles, kept open in a dessicator over anhydrous

silica gel, while others were further dried before contact with diazo solution. This further drying included storage in an oven at 100°C , and storage under vacuum at 100°C , each for a period exceeding 24 hours. The methods of mixing solid with solution were: standing in contact, stirring and shaking at room temperature and for periods of about 24 hours under atmospheric conditions, although some samples, after careful drying under vacuum, were contacted with anhydrous diazo solution under an atmosphere of dry ether vapour. Shaking the phosphates, in contact with diazo solution, was the most simple procedure (other than merely standing) as no extra apparatus was then required in the reaction vessel. Standing in contact was little used as it did not ensure adequate exposure of solid surface to the diazo-compounds.

The techniques used in the characterisation of these surface modified products will be discussed in the next chapter.

Table 4.3Preparation of samples of surface modified materials.

Prep. No.	Parent Salt	Method of drying salt	Diazocompound Preparation no. (inc. solvent recorded in table 4.2)	Method of Mixing ^a .
1	HA5	Oven ^c	D1	Standing
2	"	Dessicator ^a	D2	"
3	"	Dessicator	D3	"
4	"	Oven	D3	Stirring
5	"	Dessicator	D4	"
6	"	"	D5	"
7	"	"	D6	"
8	"	"	D7	"
9	"	"	D8	"
10	"	"	D9	"
11	"	"	D10	"
12	"	"	D11	"
13	"	"	D12	"
14	"	"	D13	"
15	"	"	D14	"
16	"	Oven	D14	"
17	"	Dessicator	D15	"

Prep. No.	Parent Salt	Method of drying salt	Diazocompound Preparation no. (inc. solvent recorded in table 4.2)	Method of Mixing ³ .
18	HA5	Oven	D15	Stirring
19	"	Dessicator	D16	"
20	"	"	D16	"
21	"	Oven	D16	"
22	TT600 ^a	"	D16	"
23	HA5	"	D16	"
24	"	Dessicator	D16	"
25	TT600 ^a	Oven	D16	"
26	HA5	Dessicator	D16	"
27	HA6	"	D17	"
28	OCP1	"	D18	"
29	HA6	"	D18	"
30	OCP1	"	D19	Shaking
31	HA6	"	D19	"
32	BA	"	D19	"
33	PCP	"	D19	"
34	OCP1	Oven	D20	"
35	HA9	"	D20	"
36	HA10	"	D20	"

Prep. No.	Parent Salt	Method of drying salt	Diazocompound Preparation no. (inc. solvent recorded in table 4.2)	Method of Mixing.
37	FA	Oven	D20	Shaking
38	PCP	"	D20	"
39	HA9	"	D21	"
40	HA11	"	D21	"
41	HA12	Under vacuum at 100°C.	D22	"
42	HA12/600A ^b	-do-	D22	"
43	HA12/600A/160W ^b	-do-	D22	"
44	HA12/160V ^b	Under vacuum at 160°C	D22	"
45	HA12/600V ^b	Under vacuum at 600°C	D22	"
46	HA16 ^b	Under vacuum at 160°C	D23	"
47	HA17 ^b	-do-	D23	"

Notes: a. TT600 is an aerosilica used to compare these surface modifications with samples prepared in earlier work⁴².

b. Samples were outgassed at the temperature stated.

CHAPTER 5

EXPERIMENTAL TECHNIQUES

The apparatus used in this investigation of apatites and their surface modified products are described in this chapter, mention is made of the various techniques involved.

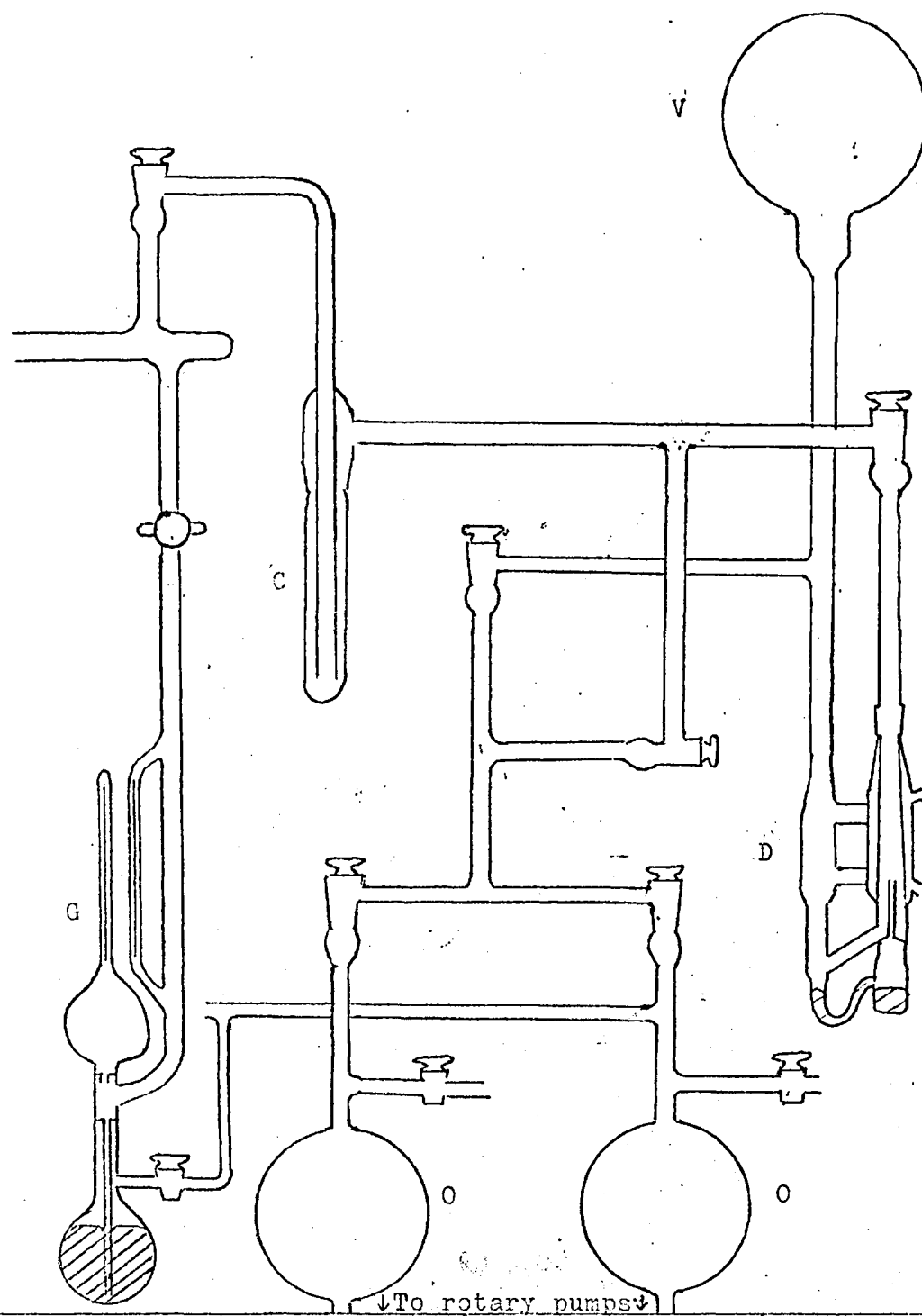
5.1 Sorption Apparatus.

A volumetric system was employed for low-temperature nitrogen sorption studies, while water sorption data were obtained from a gravimetric system. In order to outgas both the pyrex glass apparatus and the various sorbents studied, these sorption systems were connected to a high vacuum line. The method of pumping is described first.

5.1.1 Pumping system.

Figure 5.1.1 illustrates the pumping-system in which a three -stage mercury diffusion pump (D) was backed by a rotary oil-pump with a 5l buffer volume (V) and oil trap (O) situated between the pumps. The oil trap prevented any oil entering the apparatus while the buffer volume backed the diffusion pump on the occasions when the oil pump was temporarily out of use, A liquid nitrogen trap (C) prevented any condensible vapours

Figure 5.1.1

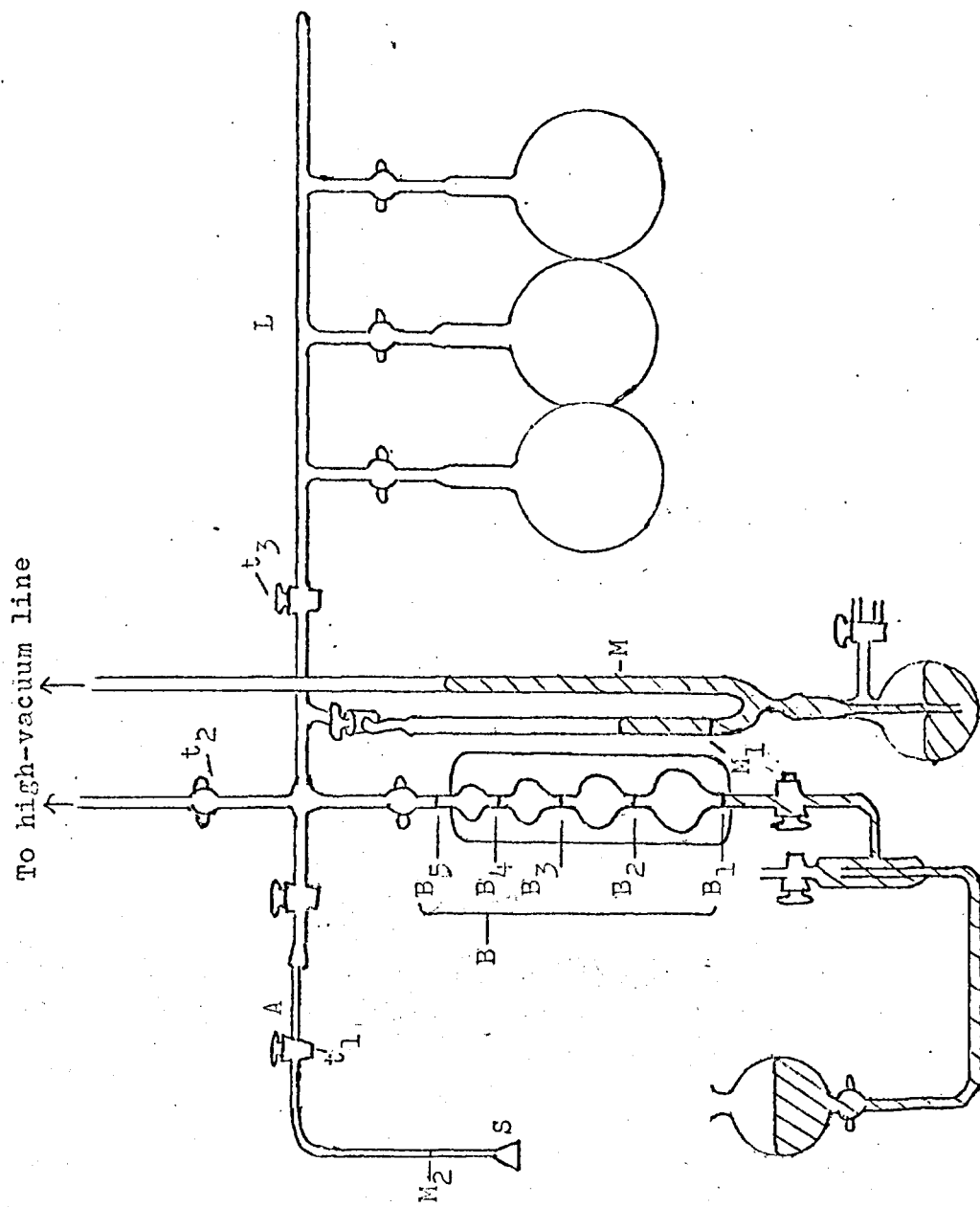
The Pumping System

passing into the pumps. A McLeod gauge (G) was used to measure the pressure of the apparatus which could be reduced to less than 10^{-6} cm Hg. All tubing and stopcocks, which were greased with Apiezon N, were of large bore to ensure a good pumping rate.

5.1.2 Volumetric Sorption Apparatus.

Two independent sorption units were connected to the high vacuum line, each one consisting of a gas burette (B), mercury manometer (M), sorption cell (S) and gas line (L). The various numbers on figure 5.1.2 indicate the extent to which each system was calibrated, the volume between marks t_1 , t_2 , t_3 , M_1 and B_5 comprised the doser volume, and its capacity, V_D , was determined as follows. The volumes of the four bulbs in the gas burette were calculated by filling the burette with mercury, whose density is well established, and weighing the latter as it was displaced, bulb by bulb, from the burette. Since the manometer limbs were constructed from 10 mm 'Veridia' precision bore tubing, the volume down to the etched mark M_1 could be established. A dose of helium was admitted to the outgassed system and the gas pressure noted as the mercury level in the burette stood at each mark from B_1 to B_5 . If the mercury level is at

Figure 5.1.2

The volumetric sorption apparatus

B_1 , the corresponding pressure of the gas P_{B1} cms H_g , and the level of the low pressure meniscus in the manometer (average value of the top and bottom of meniscus) is x_{B1} cms above M_1 , then the equation of state may be written

$$P_{B1}(V_D + V_{B1} - \pi(0.5)^2 x_{B1}) = \text{constant} \times T_R$$

where V_{B1} is the volume enclosed within the gas burette,

T_R is room temperature in degrees absolute,

and V_D , V_{B1} and $(0.5)^2 x_{B1}$ are in cm^3 ,

V_D may be evaluated by elimination of the variables in this equation.

All pressures were calculated from observation of the meniscus positions through a 1 m cathetometer, supplied by Precision Industries Ltd., allowances having been made for capillary depression, which was calculated from the meniscus height¹⁹⁷.

The sorption cell (S) was calibrated by weighing the amount of mercury it could contain. It was loaded with sorbent before being joined, at M_2 , to the tube, tap and cone assembly (A). The volume of the tube section between M_2 and t_1 , referred to as V_d , was also calibrated using mercury. The adjusted volume, V_c , of the cell (S) after being loaded with sorbent was then

calculated, after outgassing the sorbent for 24 hours at room temperature followed by a further 24 hours at 100°C , by application of the perfect gas law in the manner described previously, by the admission of a dose of helium to the whole system.

5.1.2.1 Measurement of isotherms.

The cell, containing outgassed sorbent, was surrounded with a Dewar flask containing either liquid nitrogen or liquid oxygen and allowed to reach thermal equilibrium. Temperature measurements of liquid nitrogen, T_N , was carried out with an oxygen vapour pressure thermometer while a sulphur dioxide vapour pressure thermometer was used to measure the temperature of liquid oxygen, T_O . Nitrogen gas was admitted to the doser volume and its pressure measured at room temperature, T_R , the temperature inside the burette air-jacket, T_B , was also noted. The volume of gas, in the doser volume and the gas burette, was then calculated in cm^3 at S.T.P., according to the perfect gas law. Tap t_1 was opened, the absolute temperature of the room T_R and of the burette T_B determined, and the gas pressure measured when it had reached equilibrium.

The difference between the volume of the dose

measured at S.T.P., V_1^0 and the volume, also measured at S.T.P., after equilibration with the sample V^D , represents the volume of nitrogen at S.T.P. sorbed by the outgassed sorbent. V^0 and V^D were calculated from the two equations:

$$P_{B1}^0 \left[\frac{V_D - \pi(0.5)^2 x_{B1}^0}{T_R^0} + \frac{V_{B1}}{T_B^0} \right] = \frac{P_S V^0}{T_S} \quad \text{and}$$

$$P_{B1}^1 \left[\frac{V_D + V_d - \pi(0.5)^2 x_{B1}^1}{T_R^1} + \frac{V_{B1}}{T_B^0} + \frac{V_C}{T_{N(\text{or } O)}^0} \right] = \frac{P_S V^D}{T_S},$$

where the superscripts 0 and 1 refer to measurements made before and after the opening of stopcock t_1 respectively, and P_S and T_S refer to standard pressure (76 cm Hg) and standard temperature (273°K) respectively.

All pressures were measured in cm Hg, volumes in cm^3 , and temperatures in degrees absolute.

Isotherms of the volume of gas adsorbed (in cm^3 at S.T.P.) per gramme of outgassed sorbent could be plotted from the results obtained as the mercury level in the gas burette was moved up to B_2 , B_3 and so on. When the pressure of the gas enclosed above B_5 had been measured,

the stopcock, t_1 , was closed and a new dose admitted to the doser volume, the mercury level having been lowered to B_1 . In the subsequent calculations, account had to be taken of the volume of gas enclosed above the sorbent, and adsorbed on it.

When the sorption of nitrogen had been calculated up to pressures of about 60 cm Hg, the desorption isotherms were determined, in a similar manner, from the gas volume which remained adsorbed as the pressure was lowered. The pressure was reduced by lowering the mercury level in the gas burette to successive marks until B_1 . At this point, the stopcock t_1 was closed and the doser volume outgassed through t_2 , the mercury level could then be returned to B_5 and the tap t_1 reopened for the new pressure to be measured. This procedure could be repeated until a sufficiently low pressure had been reached.

From the isothermal data of nitrogen sorption, the monolayer capacity of the sorbent, x_m , could be obtained from a plot of $\frac{P}{V(P_0 - P)}$ against $\frac{P}{P_0}$ where V is the volume of nitrogen (at S.T.P.) sorbed by one gramme of sorbent at a pressure P , and P_0 is the standard pressure.

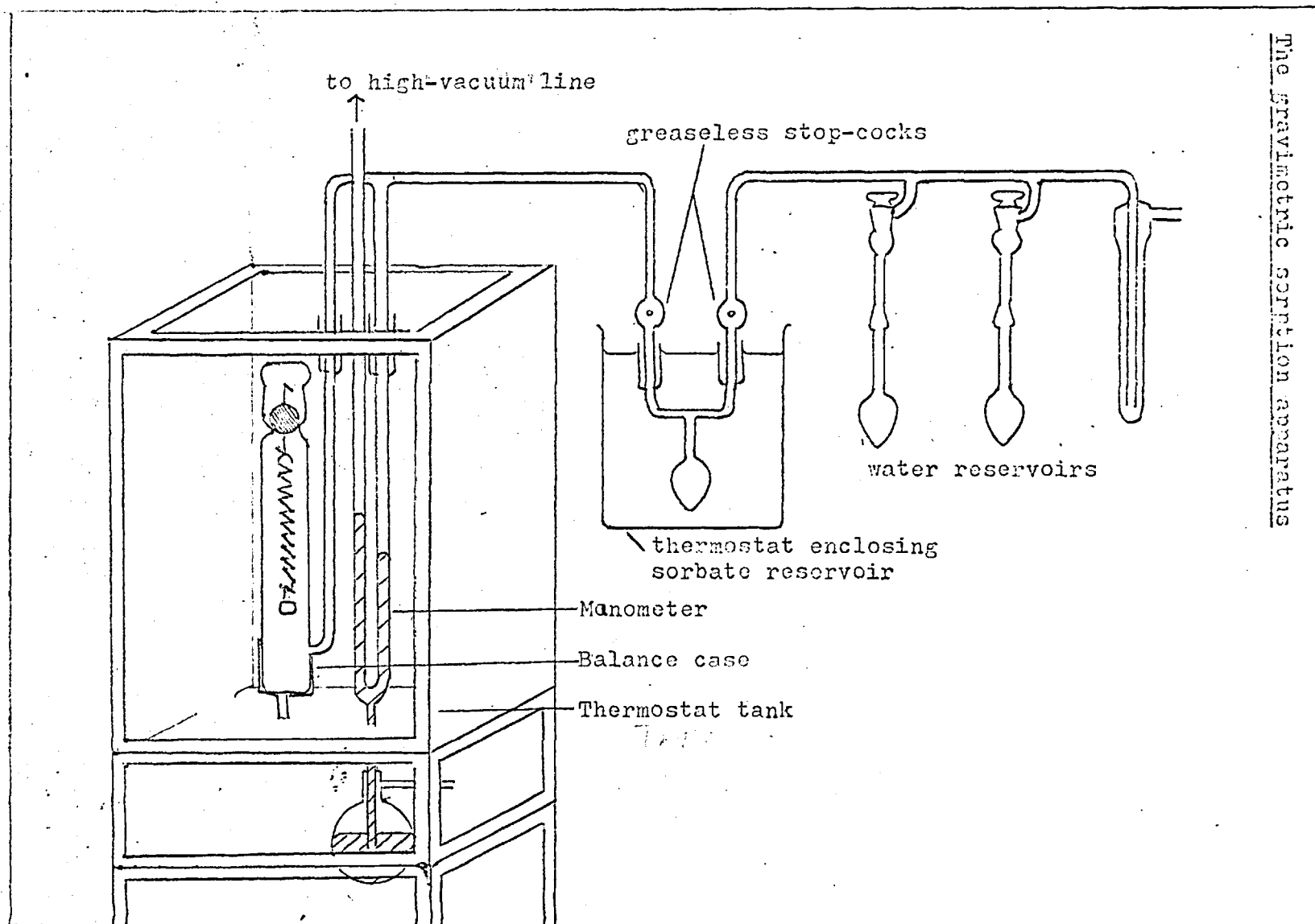
The slope and intercept of this plot were used to obtain the value of x_m in the manner described in chapter three. If the area of solid surface covered by a single molecule of nitrogen gas, at its boiling point under atmospheric pressure, is taken as $16.2 \text{ \AA}^2$ ¹⁹⁸, then the specific surface, S_{N_2} , measured from nitrogen sorption data is given by

$$S_{N_2} = \frac{x_m \times 6.023 \times 10^{20} \times 16.2 \text{ m}^2 \text{ g}^{-1}}{22.4}$$

Values of S_{N_2} were obtained for most of the apatites and surface modified apatites whose preparations were described in chapter four.

5.1.3 Gravimetric Sorption Apparatus.

Figure 5.1.3 illustrates a typical gravimetric sorption system, two independent sets of these comprised the gravimetric apparatus used in this work. Each set consisted of three 5cm bore pyrex glass balance cases connected, in parallel, to a sorbate reservoir by heated pyrex glass tubing. The B45 cone and socket assembly at the top of the balance case was greased with Edwards high vacuum silicone grease, while the 4 mm greaseless stopcocks on either side of the sorbate reservoir were supplied by G. Springham and Co. Ltd. and fitted with 'Viton A' fluorocarbon diaphragms. Pressure of sorbate was measured by observing the differences in meniscus



The gravimetric sorption apparatus

height of a mercury manometer, through a 50 cm cathetometer. The manometer was connected, through the base of a standard balance case thermostat tank⁴², to a second rotary pump which was also used to operate the McLeod guage and the manometers of the volumetric systems. In all cases pressure measurements were converted to cm Hg at 0°C, account being taken of capillary depression in the manner described in section 5.1.2. After careful double distillation of distilled water, vapour was admitted into the balance case, the pressure determined, and adsorption to the previously outgassed sorbent measured from the observed extension of the silica spring which held the sample contained in a small bucket. These springs were calibrated⁴² at the various temperatures at which isotherms were to be measured.

5.1.3.1 Measurement of isotherms.

A weighed bucket was loaded with sorbent and reweighed, it was then attached to the silica spring and carefully lowered into the balance case. After outgassing the sorbent for 24 hours at room temperature followed by 24 hours at 100°C, the tank was filled with water at the temperature of the isotherm. Temperature was controlled by a Sunvic thermostat⁴². Anhydrous

sorbent was then weighed by calculation from the spring length, measured through a 50 cm cathetometer. (From the reduction in weight of sorbent under these outgassing conditions, the reduction in the weight of samples in the volumetric system under similar conditions could also be determined.) Doses of water vapour could then be admitted in the manner described above and the sorption isotherm determined. Immersion of the sorbate reservoir in liquid nitrogen enabled vapour to be withdrawn from the system, and in this way a desorption isotherm could be determined.

Values of S_{H_2O} could be calculated from the water sorption isotherm in a manner similar to the one described for the evaluation of S_{N_2} . The area occupied by a single molecule of water on the sorbent surface at 25°C was taken as both $10.8 \text{ \AA}^2$ ¹⁸⁰ and as $14.8 \text{ \AA}^2$ ¹⁹⁹.

5.2 Other apparatus and techniques involved in this study.

Other information on the nature of the materials used in this work was obtained from chemical analysis, infra red spectroscopy and X-ray crystallography. A brief account of these methods will now be given.

5.2.1 Chemical analysis.

All the samples prepared, according to the methods described in chapter four, have been analysed by standard methods. A brief summary will be given in this section.

5.2.1.1 Calcium phosphate materials.

Calcium was determined gravimetrically as calcium carbonate²⁰⁰ and phosphorus gravimetrically as phosphomolybdate²⁰¹. Samples were tested for impurity ions, particularly sodium, chloride, sulphate and carbonate, by the usual procedures of qualitative analysis.

Pyrophosphate was determined in the heated samples by the following method⁹¹. Aliquots of sample were dissolved in 1 M perchloric acid, at room temperature, and orthophosphate determined gravimetrically as phosphomolybdate. The difference between total phosphate concentration, determined previously, and the concentration determined after pyrolysis was considered to represent the concentration of phosphate which had condensed to pyrophosphate.

5.2.1.2 Aliphatic diazocompounds.

The diazo-compounds were characterised by conversion into the corresponding p-nitrobenzoates, 3,5-dinitro-

benzoates or acetates¹²¹, and the melting points of these esters compared with published values^{202,203}.

Estimations of some of the sample concentrations in ethereal solutions were made by the following method^{117,204}. An aliquot (5 ml) of solution was pipetted into 0.2 M ethanolic benzoic acid (10 ml), excess benzoic acid was then estimated by titration against a standard 0.07 M methanolic potassium hydroxide solution.

5.2.1.3 Surface modified materials.

Modified samples were outgassed, under the conditions specified earlier in this chapter, allowed to reach equilibrium with water vapour and reoutgassed before the determination of carbon and hydrogen was carried out. These conditions were necessary to remove any excess of solvent ether or diazo-compound decomposition product. Analysis of carbon as carbon dioxide and hydrogen as water was made by the usual methods of organic micro-analysis.

5.2.2 Infra red spectroscopy

Accurate measurement of the infra red absorption spectrum of a powdered sample may be made only if the amount of radiation scattered by the sample has been

reduced to a small fraction of the incident radiation. Two methods of achieving this reduction were employed in this study. Intimate mixtures of potassium bromide containing about 2% of sample were prepared and then pressed together to form a transparent disc about 1 mm in thickness. The alternative to this involved the preparation of a mixture of sample with an oily liquid of similar refractive index, the mull was then squeezed between two plates of potassium bromide.

The alkali halide disc method has been employed by most other investigators^{24,25,94-96} of the infra red absorption spectra of apatites but it is unreliable because of the possibility of pressure induced phase changes in the sample and perhaps reaction with the halide itself may occur.

There are two difficulties associated with the use of mulling agents. Firstly the refractive index of the agent should be equal to that of the sample. This is not possible to achieve at all wavelengths, and in any case non-cubic crystals have more than one refractive index. The second problem is that the mulling agent may have absorption bands which interfere with the specimen bands.

Absorption spectra of the modified apatites were obtained by the alkali disc method, while other samples were analysed using nujol (a liquid paraffin) mulls. Measurements of infra red absorption bands were made on a Grubb-Parsons 'Spectromaster' grating spectrometer, although some preliminary work was done on a Perkin Elmer 237 grating spectrometer.

5.2.3 X-ray powder diffraction.

Powder diffraction photographs of many of the precipitated apatite materials were taken on a Guinier Camera fitted with a quartz monochromator. Copper K_{α} x-radiation was generated by means of a Hilger and Watts Microfocus x-ray set, which was operated at 40 KV and 1.5 mA. The copper target was cooled with circulating oil, itself water cooled. Four powder samples could be photographed simultaneously, each sample having been mounted in one of four rectangular apertures of a flat plate and retained by strips of tape on each side of the plate.

Calculation of the lattice constants was made from the spacings of the (410) and (004) reflections. For the determination of these spacings from the Bragg

equation¹⁸⁹, two constant factors needed to be known.

Firstly, the camera had a radius of 57.3 mm. and

secondly the wavelength of copper K_{α} radiation was

taken as 1.5418 Å. This value is a weighted mean of

the wavelengths $CuK_{\alpha 1}$ and $CuK_{\alpha 2}$, assuming that the former

is twice as intense as the latter¹⁹⁰. The use of a

weighted mean for the wavelength was required because

the two components were not resolved at the low angle

of diffraction used.

CHAPTER 6

RESULTS AND DISCUSSION

Characterisation of the materials used in this work will be dealt with in the first section of this chapter, which will list and discuss results obtained from nitrogen sorption, chemical analysis, infra-red spectroscopy and X-ray powder diffraction photography.

Extensive work has been involved in the determination of water sorption isotherms, and section 6.2 is devoted to an interpretation of the data derived from this study.

6.1 Characterisation of materials.

Results obtained from the four techniques mentioned in the opening paragraph of this chapter will be discussed in sections 6.1.1 to 6.1.4.

6.1.1 Nitrogen sorption studies.

The sorption of nitrogen by the various materials has been studied in the manner described in chapter five and some representative isotherms are shown in figure 6.1.1. A general description of these isotherms is now made while calculations involving the isotherms are left

Figure 6.1.1 (a)

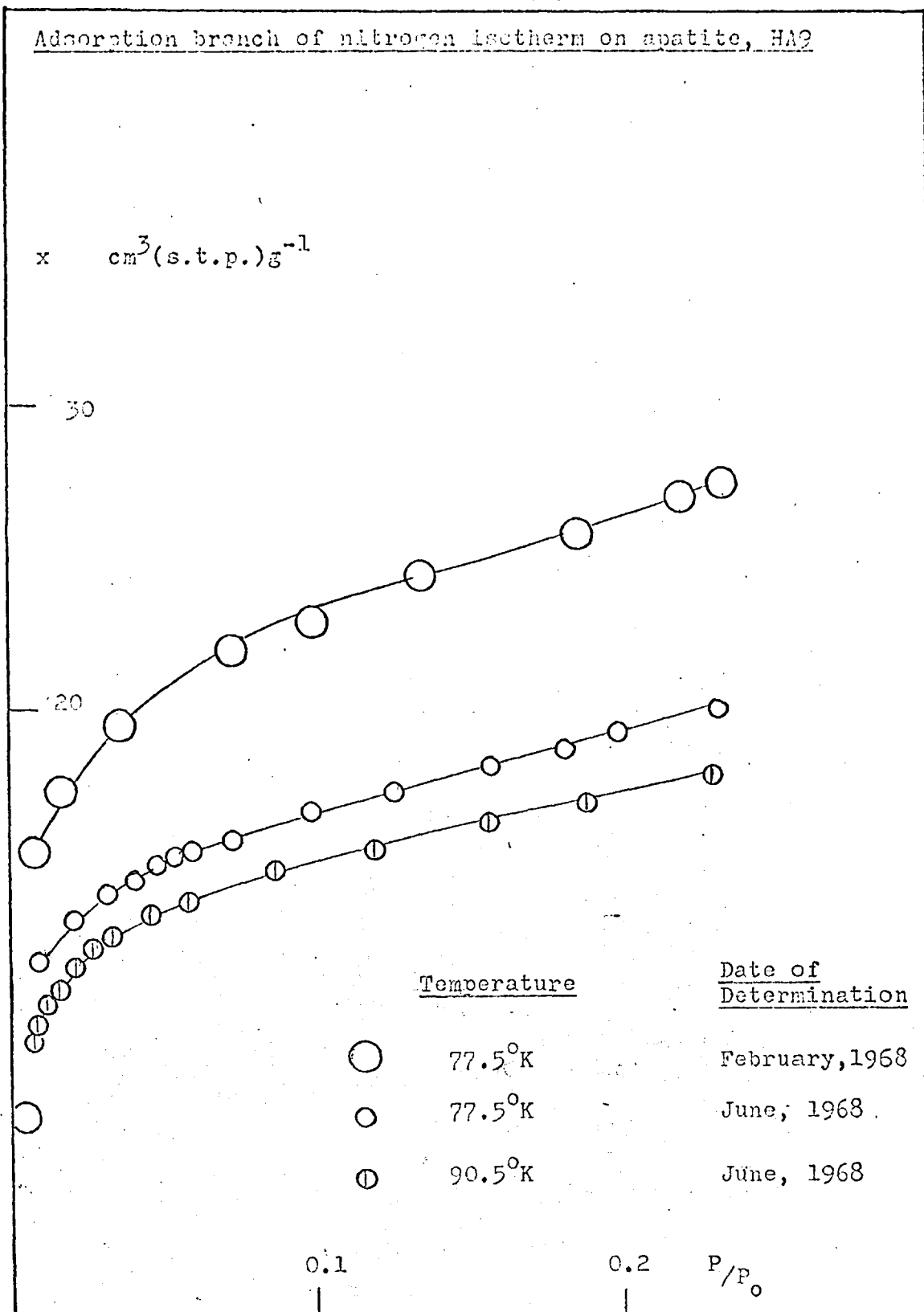


Figure 6.1.1 (b)

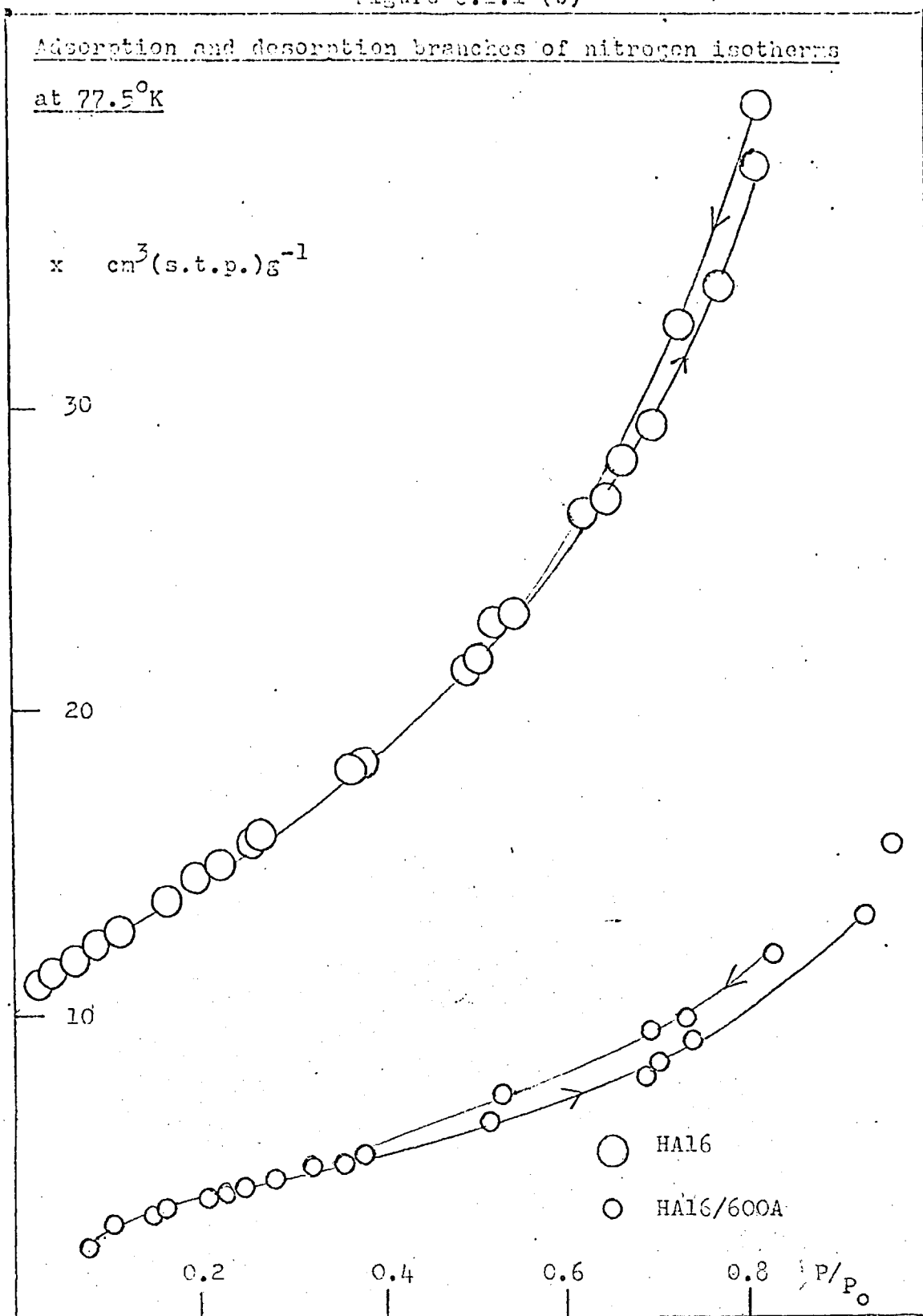
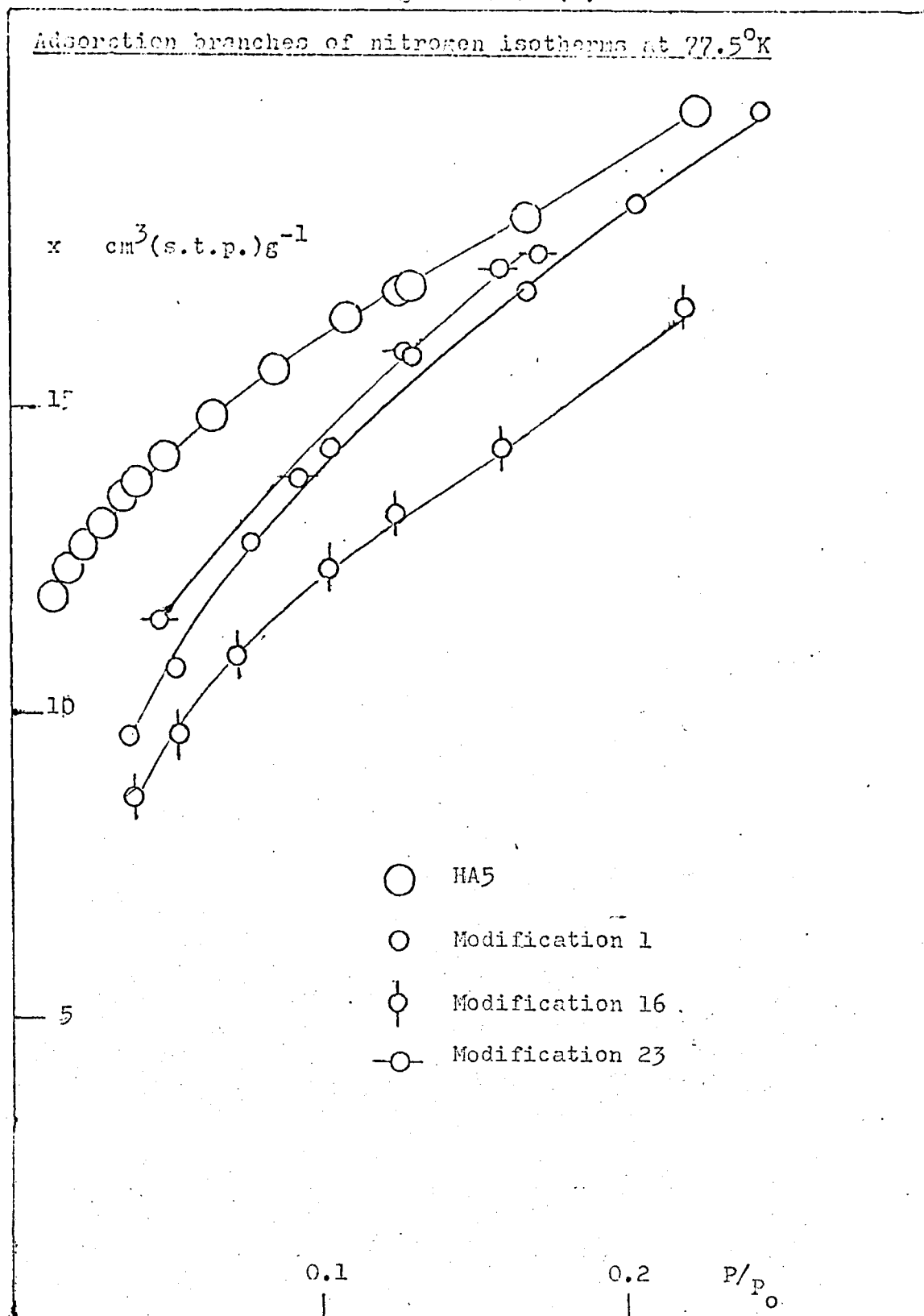


Figure 6.1.1 (c)



until later.

Direct comparison of isotherms of sorption by the same sample over a period of time and under similar conditions has been employed to ascertain the stability of sorbent surfaces. Two nitrogen sorption isotherms for HA 9 at liquid nitrogen temperature are shown in diagram (a) and the striking difference in sorption character after four months may be seen. It must be remembered that this salt was precipitated, filtered and dried rapidly and it seems highly likely that storage for these few months, in air, allowed the surface of this salt to reach a final state. Further nitrogen sorption experiments on this material confirmed its eventual stability. It was principally for this reason that all later precipitations were carried out over extended periods. Provided sufficient time was allowed for sorption to reach equilibrium, all later isotherms were reproducible within the limits of experimental error.

Physically adsorbed ether and weakly bonded polymeric materials may be removed from the apatite surface only after water sorption and outgassing. So that the more permanent nature of the surface is characterised, the modified materials were subjected to repeated nitrogen

sorption. In all cases, however, there were no measurable changes in sorption characteristics.

Under the conditions of these nitrogen experiments, all isotherms were found to be irreversible (see diagram (b)). This is in disagreement with earlier work⁴² but it should be remembered that in the present experiments sorption has been measured up to higher values of the relative pressure, and irreversibility would not have been so readily detectable from the earlier measurements. This hysteresis, which was noted in the range $0.4 < P/P_0 < 0.95$, may be due to capillary condensation of the sorbate in inter-particular pores, but no attempt was made to determine pore size distributions in the sorbents.

Figure 6.1.1 (c) illustrates the change in shape of the adsorption isotherm which occurs after modification. The sharp knee for the parent apatite becomes a gentle curve for those modifications whose isotherms are shown. This was the case for every material studied. The knee in a sorption isotherm is dependent on temperature and the nature of the interaction between sorbent and sorbate. In the BET equation, for example, the parameter c dictates the shape while x_m determines the

extent of sorption at any relative pressure. Type 2 isotherms, of the kind found in this nitrogen sorption study, require a large c value, and decreasing c implies a more gentle curve in the region of x_m . Type 3 isotherms, those which are characteristic of systems where sorbate-sorbate attraction is more important than sorbent-sorbate interaction require c values of less than unity. More will be said later on the magnitude of the c values but it may be said that, with regard to the approximation mentioned in chapter three, i.e. $c = e^{\frac{E_1-L}{RT}}$, a decrease in c implies a decrease in E_1 or more simply a less energetically adsorbing surface.

Calculations of x_m , the monolayer capacity, and S , the specific surface, of each sorbent are discussed next.

6.1.1.1 Determination of the specific surfaces of materials studied in this work.

Values of the monolayer capacity of each sorbent have been calculated, in the manner described in chapter three, from the linear segment of a B.E.T. plot. Some such plots are shown in figure 6.1.1.1, and values of x_m are listed in table 6.1.1.1 together with the

Figure 6.1.1.1

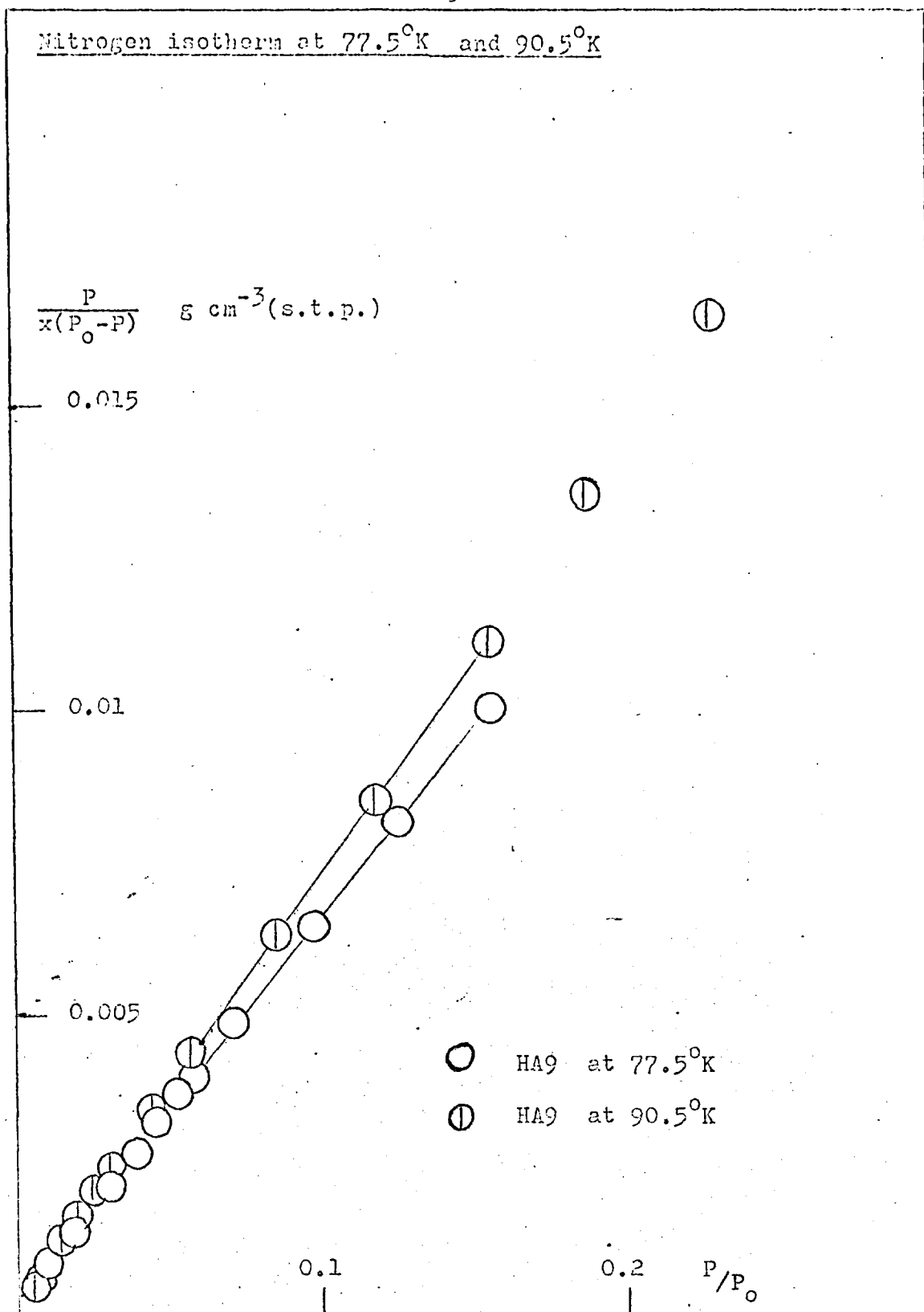


Figure 6.1.1.1

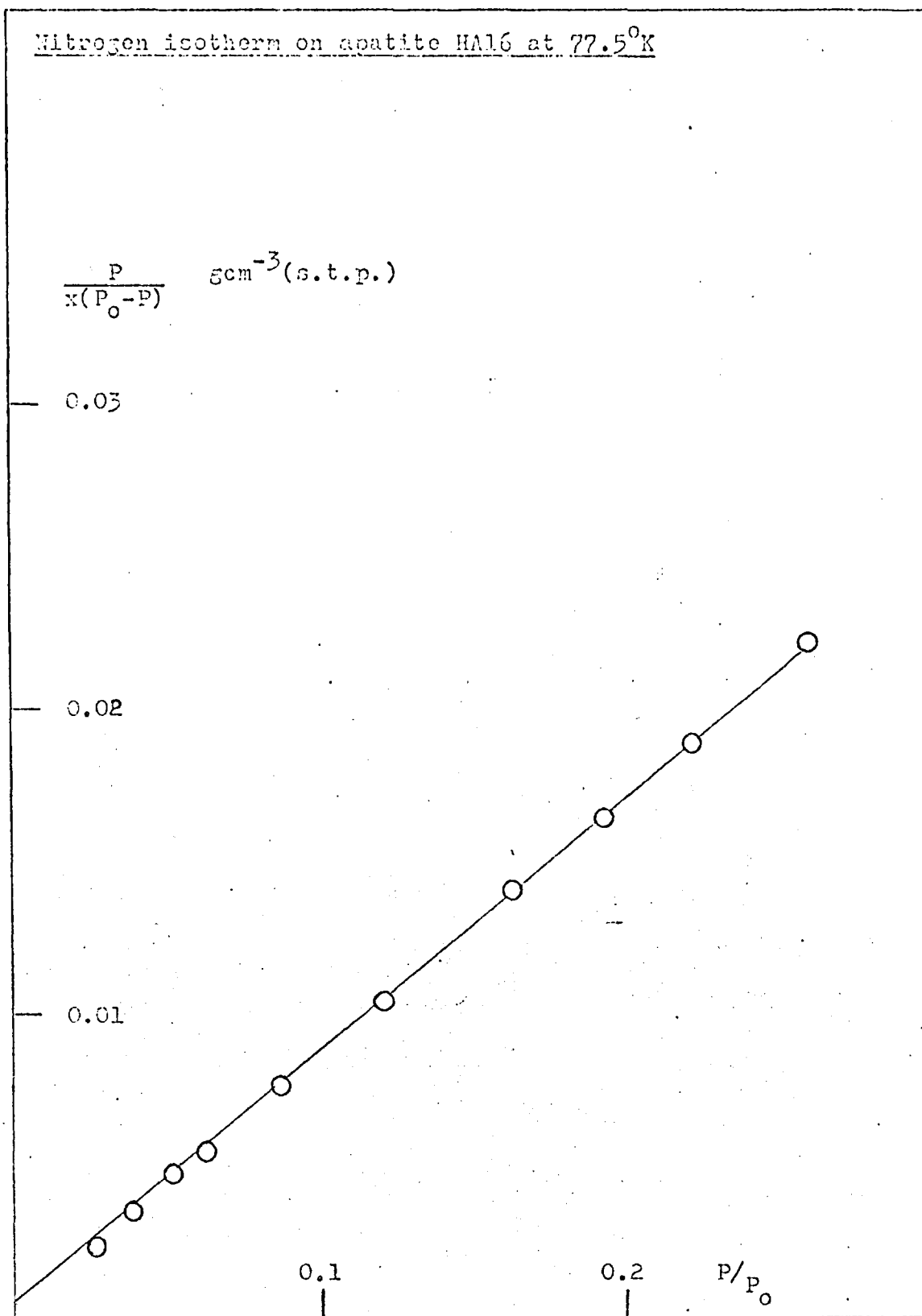


Table 6.1.1.1 (a)

Values of x_m and S determined from nitrogen sorption.

Apatite Prep. No.	Monolayer capacity x_m , $\text{cm}^3(\text{S.T.P})\text{g}^{-1}$	Specific Surface S, m^2g^{-1}
HA 5	15.7	68.2
HA 6	16.4	71.3
HA 9	15.5 (21.6)	67.3 (93.6)
HA 10	27.4	119.0
HA 11	15.7	68.0
HA 12	17.8	77.3
HA 13	13.6	59.3
HA 14	18.2	79.1
HA 15	15.2	66.4
HA 16	12.5	54.4
HA 17	23.3	101.6
OCP 1	30.0	130.8
OCP 2	9.5	41.3
HA 12/600 A	5.1	22.1
HA 13/600 A	11.9	51.7
HA 16/600 A	3.6	15.7
HA 17/600 A	11.9	51.9
HA 12/600A/160 W	5.8	25.3
HA 12/160 V	15.3	66.5

Table 6.1.1.1 (a) (contd.)Values of x_m and S determined from nitrogen sorption.

Apatite	Monolayer Capacity	Specific Surface
Prep. No.	$x_m, \text{cm}^3(\text{S.T.P.})\text{g}^{-1}$	$S, \text{m}^2\text{g}^{-1}$
HA 16/160 V	12.8	55.8
HA 17/160 V	24.4	106.3
HA 12/600 V	13.1	56.9
HA 4	18.3	79.5
HA C	20.2	87.5
PCP	5.8	25.2
BA	8.9	38.8
ND	4.8	20.9
AD	17.1	74.1

Details of these preparations were listed in the
table of section 4.1.

Table 6.1.1.1 (b)

Values of x_m and S determined from nitrogen sorption.

Modification Prep. No.	Parent Apatite	Monolayer Capacity $x_m, \text{cm}^3(\text{S.T.P})\text{g}^{-1}$	Specific surface S, m^2g^{-1}
1	HA5	15.8	68.8
2	HA5	15.6	68.0
3	HA5	15.6	68.0
4	HA5	15.8	68.8
5	HA5	15.7	68.5
7	HA5	15.6	68.0
15	HA5	15.0	65.2
16	HA5	14.1	61.5
17	HA5	15.0	65.3
18	HA5	15.8	68.8
23	HA5	18.0	78.4
24	HA5	16.0	69.6
26	HA5	15.7	68.5
27	HA6	13.0	56.6
28	OCP1	17.4	75.8
29	HA6	14.2	62.0
30	OCP1	29.0	126.2
31	HA6	15.8	68.8

Table 6.1.1.1 (b) (contd.)

Values of x_m and S determined from nitrogen sorption.

Modification	Parent	Monolayer Capacity	Specific Surface
Prep. No.	Apatite	$x_m, \text{cm}^3(\text{S.T.P.})\text{g}^{-1}$	$S, \text{m}^2\text{g}^{-1}$
39	HA9	21.1	91.9
40	HA11	15.7	68.5
41	HA12	18.5	80.7
42	HA12/600A	6.6	28.9
43	HA12/600A/160W	5.7	24.7
44	HA13/160V	14.7	64.3
45	HA12/600V	13.0	56.7
46	HA16	13.3	57.9
47	HA17	23.6	102.9

Preparation of sorbents has been dealt with in
section 4.3.

corresponding values of S . Results shown in brackets are for those salts which were precipitated rapidly and indicate non-equilibrium values.

It is apparent that most of the modified salts do not show any considerable differences from their parent apatites.

Significant changes in X_m have been induced by the various heat treatments attempted. Two calcium deficient apatites, namely HA 12 and HA 16, were maintained at 600°C for 120 hours in air, before their S values were redetermined. In the former case the area was reduced to 28.6% of its original value, while for HA 16 the reduction was to 28.9%. The closeness of these reductions may not be of any significance but it must be remembered that they were prepared under similar conditions. There is no such marked area reduction after the pyrolysis of the other, less calcium-deficient apatites. Possible causes of area reduction depend on factors which affect the size of the apatite particles, these may increase by sintering or oriented crystallites may grow in size. A distinction between these alternatives may be found from X-ray studies.

A sample of HA 12 which had been heated for 120 hours at 600°C under vacuum underwent a specific surface reduction to only 73.6% of its former value. Comparison of this result with the considerable change which occurred after pyrolysis in air (all other conditions assumed to be equal) suggests that either atmospheric water or evolved structural water is necessary for such considerable changes to occur.

Samples of these salts which were heated at 160°C for 120 hours under vacuum showed various changes in S. It is probable that this treatment would remove much of the adsorbed water and expose more surface for nitrogen sorption. Slight reductions in S could be predicted if sintering was thought to take place.

6.1.1.2 The c parameter of the B.E.T. equation.

The type 2 nitrogen sorption isotherms are close to theoretical B.E.T. isotherms only within the range $0.1 < P/P_0 < 0.3$, this accounts for the divergence from linearity of the measured points in figure 6.1.1.1.

Sorption into a monolayer is unlikely to occur on sites of equal energy, and the assumption that E_1 has a single value is not justifiable. E_1 may be assumed to be a function of the monolayer coverage, $\frac{x}{x_m}$, with

the more energetic sites being occupied at lower values of this coverage. In this case, the plot of $\frac{P/P_o}{x(1-P/P_o)}$ versus P/P_o would have a slope represented by

$$\left\{ \frac{\frac{P/P_o}{x(1-P/P_o)}}{\frac{\partial P/P_o}{\partial x_m}} \right\} = \frac{c-1}{cx'_m}, \text{ if the equation,}$$

$$\frac{P/P_o}{x(1-P/P_o)} = \frac{c-1}{cx'_m} \frac{P}{P_o} + \frac{1}{cx'_m}, \text{ refers to particular values}$$

of $\frac{x}{x_m}$. Similarly the intercept of a tangent to the curve

at $\frac{x}{x_m}$ would be at $\frac{1}{cx'_m}$. c in this $\frac{x}{x_m}$ dependent equation

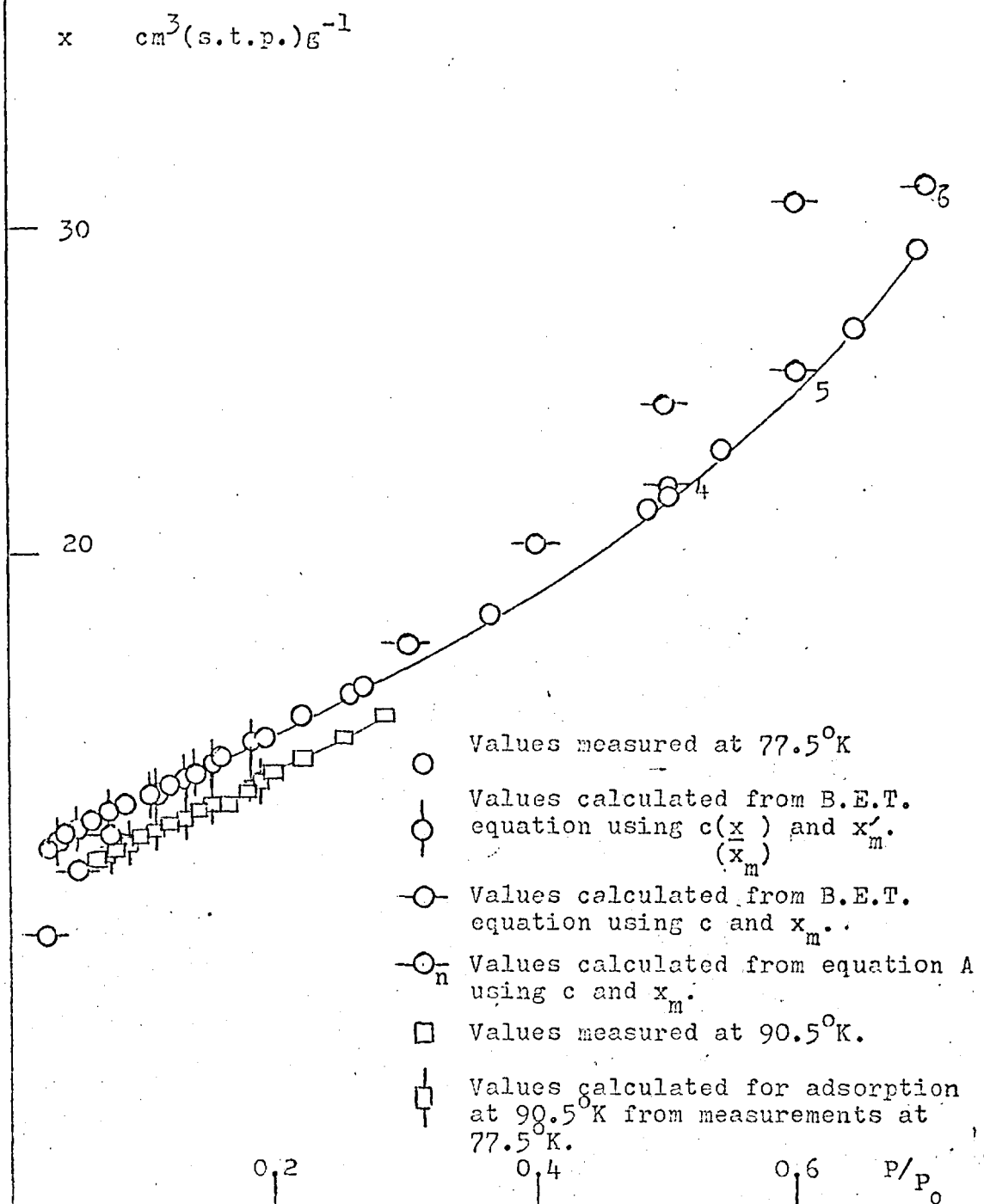
may thus be determined and will be characteristic of the value of $\frac{x}{x_m}$. It should be noted here that x'_m will be

the monolayer capacity, not of the complete surface as x_m , but of those sites with an energy greater than or equal to the limiting value, E_1 . These values of c and x'_m have been used to calculate theoretical isotherms, one of which is shown in figure 6.1.1.2 together with the curve obtained from the 'ideal' B.E.T. equation (constant c , x_m).

The lack of agreement in the region $P/P_o > 0.3$ may

Figure 6.1.1.2

Adsorption branches of nitrogen isotherms on apatite, HA16



be due to a limitation on the thickness of the adsorbed film, the B.E.T. model assumes an infinite number of molecular layers. It may be significant that this region also corresponds to the irreversible region of sorption. A finite thickness of the adsorbed layer may be quantitatively predicted if the summation of sorption in each layer is limited to n terms only. The equation then becomes

$$\frac{x}{x_m} = \frac{c \frac{P}{P_o}}{1 - \frac{P}{P_o}} \cdot \frac{1 - (n+1)(\frac{P}{P_o})^n + n(\frac{P}{P_o})^{n+1}}{1 + (c-1)\frac{P}{P_o} - c(\frac{P}{P_o})^{n+1}} \quad \text{Equation A,}$$

and n represents the number of molecular layers. This equation provides agreement with measured isotherms only if n increases with P/P_o , and figure 6.1.1.2 shows the n values necessary for reasonable agreement at each relative pressure. This equation reduces to the B.E.T. equation at low values of P/P_o , since all $(P/P_o)^n$ terms will be negligible.

These calculated isotherms may be useful in predicting the shape of isotherms at other temperatures, but this is only done at low values of P/P_o in the present work because measurement of isotherms at liquid oxygen temperatures could only be made at such values of relative pressure. In order to predict the shape of isotherms the assumption $c = \frac{E_1 - L}{RT}$ was made, i.e.

$RT \ln c = E_1 - L$, and therefore $T_1 \ln c_1 = T_2 \ln c_2$.

Knowledge of C_1 , T_1 and T_2 enables C_2 to be determined for each value of C_1 throughout the isotherm. Such a calculated isotherm is drawn in figure 6.1.1.2, together with measured values, and the good correspondence lends support to the validity of this treatment.

6.1.1.3 Heat of adsorption.

Following the determination of c described above, values of E_1 have been obtained and are shown, for one sorbent, in figure 6.1.1.3(a).

$\Delta \bar{H}$ was determined from isotherms at two temperatures by application of the Clausius-Clapeyron equation. Differential heats calculated from data at only two temperatures are of doubtful accuracy but give energy of sorption values which agree well with values of E_1 .

The gentle curve, in the region of the monolayer capacity, of isotherms for modified apatites, as noted in section 6.1.1, is reflected in the E_1 values obtained from c parameters of these isotherms. Figure 6.1.1.3(b) shows a comparison of E_1 versus X/x_m for parent and a modified apatite, values yielded from $\Delta \bar{H}$ for these systems are also included for comparison. These results suggest that the diazoreaction is occurring on sites which would otherwise have been of high nitrogen adsorption potential.

Figure 6.1.1.3(a)

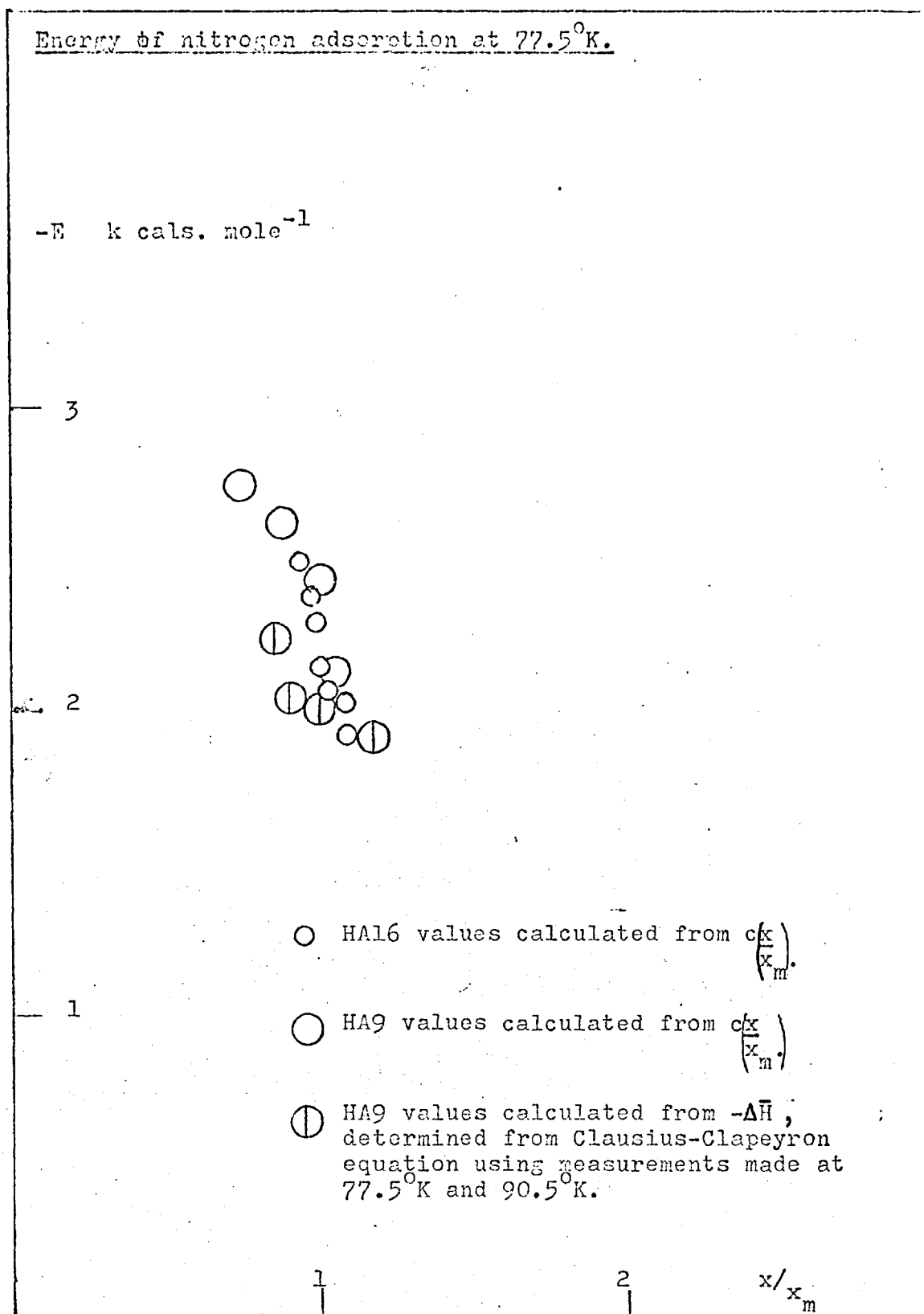


Figure 6.1.1.3(b)

Energy of nitrogen adsorption at 77.5°K

-E k cal, mole⁻¹

3

2

1

○ HA12 values calculated from $\left(\frac{x}{x_m}\right)$

⊙ HA12 values calculated from $-\Delta\bar{H}$, determined from Clausius-Clapeyron equation.

○ Modification 41 values calculated from $\left(\frac{x}{x_m}\right)$

⊙ Modification 41 values calculated from $-\Delta\bar{H}$, determined from Clausius-Clapeyron equation.

1

2

x/x_m

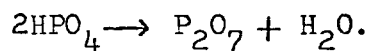
6.1.2 Chemical Analysis

Three parts of this section will deal in turn with results of the chemical analysis of the apatites, aliphatic diazocompounds, and surface modified apatites.

6.1.2.1 Chemical analysis of apatites.

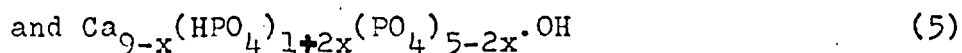
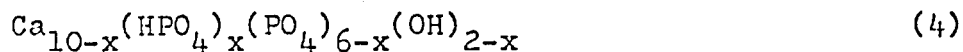
Only HA5 and HA6 of the salts precipitated in the course of this work had any detectable amounts of impurity ions and in both cases these were of carbonate. Precautions taken to prevent incorporation of carbon dioxide in subsequent systems were adequate.

Table 6.1.2.1 lists the various preparations, together with both Ca/P and $\text{P}_2\text{O}_7/\text{P}$ molar ratios where measured. Values of the pH of each precipitating system are included and it is evident that high pH corresponds with a high solid Ca/P molar ratio and a low $\text{P}_2\text{O}_7/\text{P}$ ratio. This result is in accord with expectations as a decrease in solution pH will considerably increase the concentration of HPO_4^- ions, and pyrolysis of salts precipitated in this region will produce larger proportions of pyrophosphate ions according to the equation,



When the results of $\text{P}_2\text{O}_7/\text{P}$ molar ratio determinations are plotted against Ca/P molar ratios, as in figure 6.1.2.1, they fall close to values predicted by the two unit cell

formulae,



where $0 \leq x \leq 1$.

This observation, which is in agreement with earlier work mentioned in chapter two, is helpful as it assumes that at least some of the missing calcium ions of the non-stoichiometric salts are replaced by protons closely associated with orthophosphate ions. Such a unit would exhibit Brönsted acidity and is a probable site for diazo reaction. The small amounts of pyrophosphate present in pyrolysed stoichiometric apatite may be formed from surface hydrolysed phosphate ions.

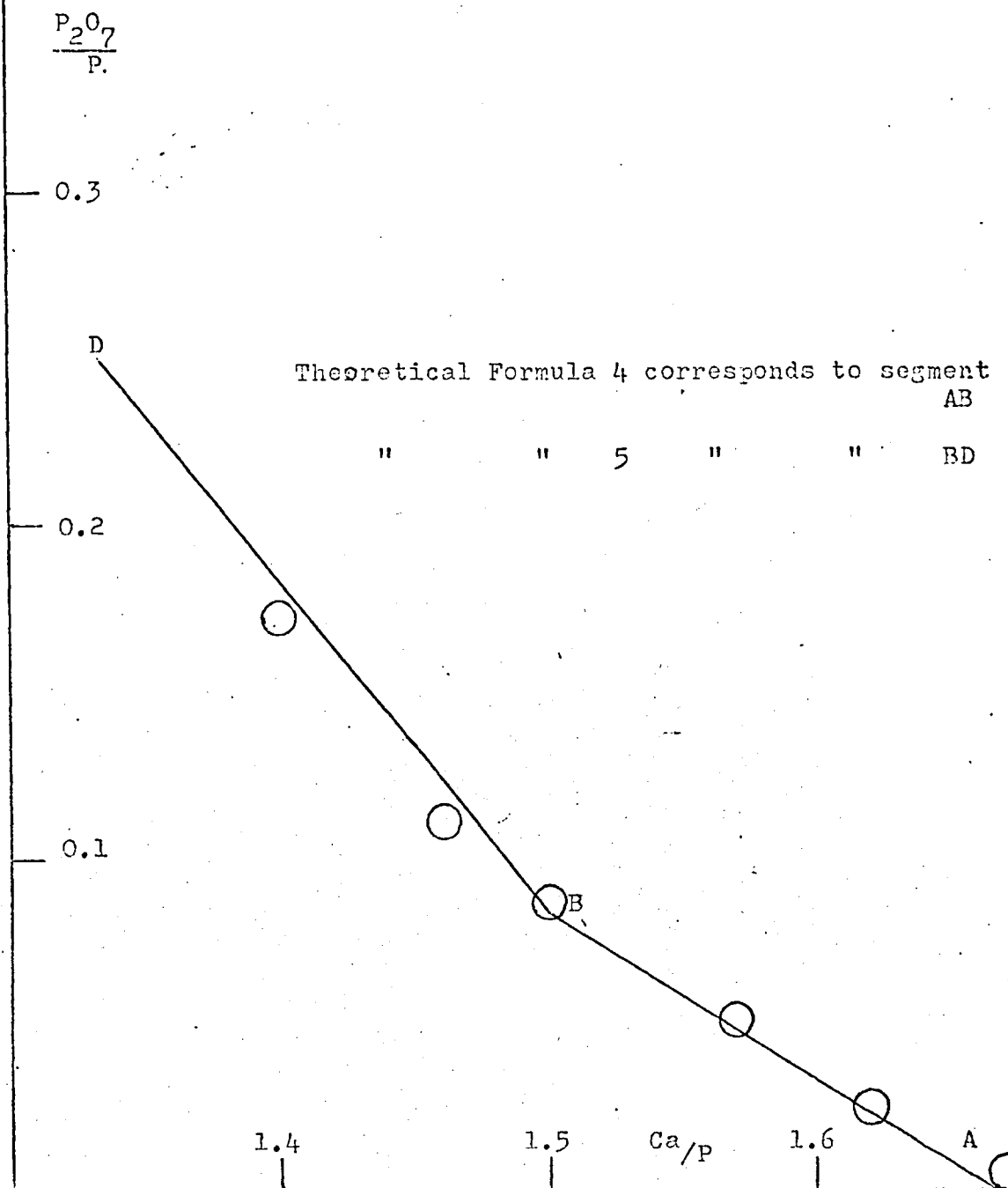
Table 6.1.2.1Chemical analysis of apatites.

Prep. No.	Ca/P molar ratio	P ₂ O ₇ /P molar ratio	pH of precipitating solution
HA 5	1.66	-	11.0
HA 6	1.66	-	11.0
HA 7	1.56	-	9.5
HA 8	1.59	-	10.5
HA 9	1.52	-	5.8
HA 10	1.63	-	11.0
HA 11	1.67	-	12.0
HA 12	1.46	0.112	5.7
HA 13	1.67	0.006	11.0
HA 14	1.40	0.173	5.5
HA 15	1.57	0.052	9.9
HA 16	1.50	0.087	5.2
HA 17	1.62	0.026	12.0
OCP 1	1.47	-	8.0
OCP 2	1.37	-	7.0
OCP 3	1.29	-	6.6

P₂O₇/P mole ratios determined from samples heated
in air at 600°C for 120 hours.

Figure 6.1.2.1

Pyrophosphate to total phosphate molar ratio after
heating apatites at 600°C for 120 hours versus calcium
to phosphorus molar ratio.



Lower than expected values of Ca/P were obtained for samples HA 7, HA 8, HA 15 and HA 17, and for the first two of these calcium may not have had time to reach an equilibrium, stoichiometric lattice concentration over the brief period allowed for precipitation. Both of the preparations to yield HA 15 and HA 17 did not involve heating of the precipitating liquor. This stage was used in the earlier preparations as an attempt to improve the filtering properties of the liquor. It is probable that the exceedingly low crystallisation rate of apatite at room temperature results in an incomplete lattice unless phosphate to calcium addition is very slow. The nature of apatite crystallisation is not clearly understood, however.

The low value of Ca/P for OCP 3 suggests that this material is not octacalcium phosphate. The values for OCP 1 and OCP 2 are, on the other hand, too high. Further comment may be made on these salts after their X-ray powder diffraction patterns have been discussed.

6.1.2.2 Chemical analysis of aliphatic diazo compounds.

The preparation of diazocompounds has followed well established methods and only a few checks were made of the composition of products. According to those routines mentioned in section 5.2.1.2, the characterisations of certain preparations have been made, and are reported in table 6.1.2.2

Table 6.1.2.2Characterisation of diazo compounds.

Compound Prep. No.	Ester	Melting Point	Published ^{202,203} Melting Point
D 1	Me p-nitrobenzoate	95°C	95.5°C, 96°C
D 23	Et p-nitrobenzoate	56°C	56°C, 57°C
D 14	n-Octyl 3,5-dinitro- benzoate	58°C	60.5°C -

The presence of a diazocompound in ethereal solution may be detected by its strong colour, and by the fact that this colour is removed by addition of dilute acid. This decolorisation is accompanied by vigorous effervescence.

Estimates of solution concentrations were made by the titration method, described in section 5.2.1.2, and concentrations of all diazo compounds used in the preparation of the modified apatites were about 0.1 M in ether.

6.1.2.3 Chemical analysis of modified apatites.

Table 6.1.2.3 (a) lists the results obtained from carbon content estimations, and also shows the number of organic groups, per hundred square Angström units, which would be necessary to accommodate each quantity of carbon on the surface.

Table 6.1.2.3 (a)Carbon content determinations on modified apatites.

Mod. No.	Modifying Organic Group	Parent Material	% Carbon	No. of groups per 100Å ² of surface.
1	-CH ₃	HA5	0.40	2.9
2	-CHCO ₂ C ₂ H ₅	"	0.60	1.1
3	-CHPh ₂	"	1.95	1.1
4	-CHPh ₂	"	1.95	1.1
15	-n-C ₈ H ₁₇	"	3.91	3.7
16	-n-C ₈ H ₁₇	"	4.26	4.3
23	-n-C ₁₈ H ₃₇	"	3.93	1.4
27	-n-C ₁₂ H ₂₅	HA6	5.11	3.8
39	-CHPh ₂	HA9	7.30	3.1
40	-CHPh ₂	HA11	2.18	1.2
41	-CHPh ₂	HA12	6.41	3.1
42	-CHPh ₂	HA12/600A	2.51	3.3
43	-CHPh ₂	HA12/600A/160W	2.48	3.9
44	-CHPh ₂	HA12/160V	6.51	3.9
45	-CHPh ₂	HA12/600V	0.76	0.5
46	-C ₂ H ₅	HA16	1.02	4.4
47	-C ₂ H ₅	HA17	0.30	0.7

These calculations of the number of organic groups per $100\text{\AA}^2$ of apatite surface may be compared with the following results calculated from measurements published elsewhere⁴². All materials have in these cases been modified by reaction with diazomethane.

Table 6.1.2.3 (b)

Parent Material	No. of groups per $100\text{\AA}^2$
Commercial Aerosil silica TT600 (see note a.)	16.44
Aerosil silica 200 (see note b.)	3.22
" " 150 (" " ")	5.20
Alumina (see note c.)	1.04
Hydroxyapatite (see note d.)	2.55

key: (a) Silica supplied by Degussa of Frankfurt, and produced by a gas-phase pyrolytic reaction between silicon tetrachloride, hydrogen and air. It has a specific surface of about $200\text{ m}^2\text{g}^{-1}$.

(b) Samples of TT600 which had been hydrothermally treated at 200°C and 150°C respectively for 18 hours. The specific surfaces of these two materials were $41.2\text{ m}^2\text{g}^{-1}$ and $43.3\text{ m}^2\text{g}^{-1}$ respectively.

(c) Alumina prepared by the ignition of Gibbsite ($\text{Al}(\text{OH})_3$) at 480°C for 24 hours. Specific surface

of this material is $196 \text{ m}^2 \text{g}^{-1}$.

- (d) Hydroxyapatite preparation HA 4 referred to in section 4.1.5.

The results listed in table 6.1.2.3 (b) have been calculated from the determination of methoxyl groups present on the surface. The density of groups present on the surface of the TT600 sample implies an area of only $6.083 \text{ \AA}^2$ contains each methoxyl group and this is too small to accommodate such groups unless they are all packed together very closely. A similar high density of groups is apparent from some of the values in table 6.1.2.3 (a).

Those materials numbered between modifications 1 and 41, inclusive, were prepared from parent materials of unknown surface condition, and hydrolysis of surface ions may contribute to a higher than predicted carbon concentration after diazo reaction. Of the other modified salts, numbers 46 and 47 were prepared from anhydrous apatites (outgassed at 160°C), under an atmosphere of ether and using anhydrous solutions of diazomethane. The number of organic groups per $100 \text{ \AA}^2$ of surface of these two materials depends on the calcium deficiency of the apatite, thus HA 16 whose Ca/P molar ratio is 1.50 can accommodate 4.4 groups per $100 \text{ \AA}^2$ while the less calcium deficient salt, HA 17 can contain only 0.7 groups on such an area.

The various heat-treated samples of HA 12 behave in different ways on alkylation and it is significant to observe that modification number 45, whose parent material had been heated under vacuum at 600°C, contained far fewer organic groups. This result is expected if it is assumed that the diazo reaction occurs at the pyrolysable hydrogen phosphate ions. The other samples of HA 12 provide a good surface for the reaction, perhaps for the following reasons. Modification 42, from HA12/600 A, was prepared after the parent material had been exposed to the atmosphere and surface P_2O_7 would have had the opportunity of rehydrolysis, liberating sites for the reaction to occur. The modification of HA12/600A/16OW, number 43, was of a carefully rehydrolysed salt and may be expected to have properties somewhat similar to numbers 41 and 42. The other sample of this salt, which had been heated at 160°C under vacuum, may be assumed to have been reasonably free of adsorbed water but unpyrolysed and would present a good surface for the diazo-reaction.

6.1.3 Infra-red spectroscopy

Spectra of apatites and modified apatites are discussed in the two parts of this section.

6.1.3.1 Infra-red spectra of apatite and related salts.

Frequencies and assignments for the infra-red absorption

bands of the apatites are shown in table 6.1.3.1. Many frequencies are observed for which assignments are difficult, and since a complete interpretation is outside the scope of this work no detailed discussion has been attempted. Some general aspects of the frequencies are described.

The low value for the hydroxyl ion stretching vibration is in agreement with the value predicted if a bifurcated type of hydrogen bonding occurs with oxygen atoms of the surrounding phosphate ions. This was discussed in chapter two. If the observed band at about 632 cm^{-1} is assigned to a librational mode of the hydroxyl ion, the case for hydrogen bonding is substantially supported.

It was notable that the observed frequency at 632 cm^{-1} was observed in all materials other than in OCP 3. While this may appear to contradict earlier investigations^{24,25} it must be pointed out that this present work employed mulls of the salts whereas the earlier study used KBr discs, some early work in this study also using KBr discs demonstrated the difficulties in obtaining reproducible results from this technique. Figure 6.1.3.1 (a) indicates this region of the spectrum for three salts, in nujol mulls, and the size of the absorption, at 632 cm^{-1} for the calcium-deficient salt may be seen.

Figure 6.1.3.1 (a) also shows the observed frequencies

of the $\nu_4(\text{PO}_4)$ mode.

The sample of OCP 2 shows no absorption at 632 cm^{-1} but the reason for this is not clear as an $\nu_s(\text{OH})$ frequency is readily detectable.

In the $1000 - 1200\text{ cm}^{-1}$ region, many absorption frequencies have been detected, particularly for the calcium deficient apatites. Figure 6.1.3.1 (b) shows the considerable change in the shape of this band which occurs between stoichiometric and calcium deficient salts. Much of this change may be due to hydrogen phosphate stretching modes of the calcium deficient apatite. The shape of this band can be used to distinguish between hydroxyapatite and its calcium deficient variants, while the detection of characteristic frequencies has proved to be unreliable.

In view of the difference between Ca/P molar ratios measured from the octacalcium phosphate preparations in this work and the theoretical value of 1.33, it is concluded that these salts are calcium deficient apatites, or in the case of OCP 3 a more acidic salt. No attempt is therefore made to compare the infra-red spectra of these salts with measurements recorded elsewhere⁹⁴⁻⁹⁶.

Table 6.1.3.1

Frequencies and assignments for infra-red absorption bands
of apatites.

(a) Stoichiometric Hydroxyapatite.

Observed frequencies (cm^{-1})						Assignment
HA5	HA6	HA7	HA11	HA15	HA17	
3571shp	3571shp	3571shp	3571shp	3571shp	3571shp	$\nu_{\text{s}}(\text{OH})$
3430bd	3430bd	3428bd	3429bd	3430bd	3425bd	(H_2O)
				1125sh	1127sh	
				1115sh	1117sh	
					1109sh	
1096sh						
1090s	1091s	1093s	1093s	1092s	1092s	$\nu_3^{\text{III}}(\text{PO}_4)$
1058sh			1068sh	1061sh	1060sh	
1042sh	1044sh	1044sh	1042sh	1042sh	1042sh	$\nu_3^{\text{II}}(\text{PO}_4)$
1029vs	1029vs	1033vs		1028vs	1028vs	$\nu_3^{\text{I}}(\text{PO}_4)$
963m	963m	962m	964m	962m	962m	$\nu_1(\text{PO}_4)$
878w	878w	876w	871w	870w	858w	
					837w	
631m	632m	632m	634m	632m	632m	$\nu_{\text{L}}(\text{OH})$
					625w	
600m	600m	603m	602m	601m	602m	$\nu_4^{\text{III}}(\text{PO}_4)$

Table 6.1.3.1 (contd.)

Observed frequencies (cm ⁻¹)						Assignment
HA5	HA6	HA7	HA11	HA15	HA17	
575sh	574sh	574sh	574sh	573sh	575sh	ν_4'' (PO ₄)
566s	566s	563s	566s	562s	563s	ν_4' (PO ₄)

Key vs very strong

s strong

m medium

w weak

shp sharp

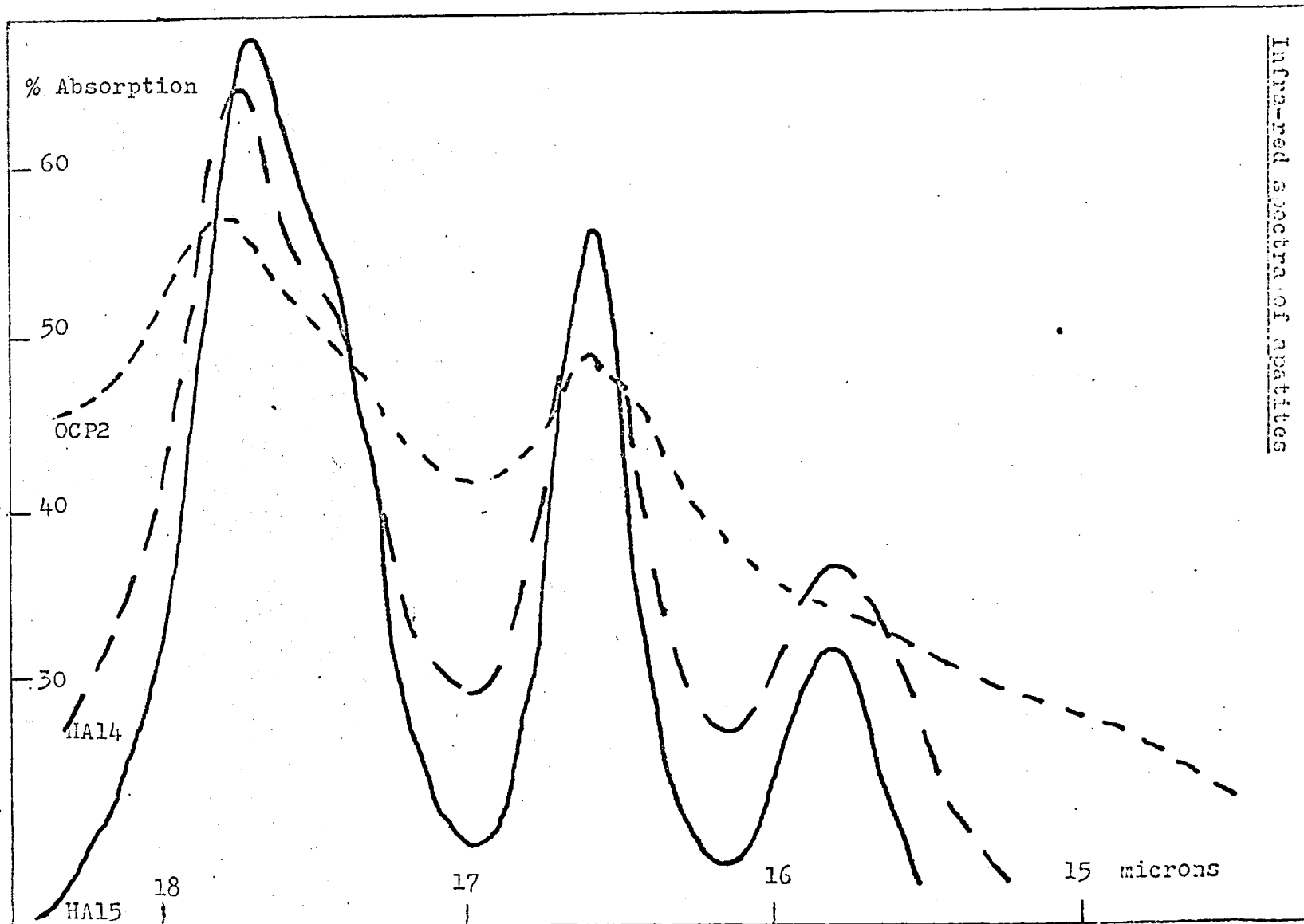
bd broad

(b) Calcium deficient apatites and octacalcium phosphate

Observed frequencies						Assignments
HA9	HA14	HA16	OCPl	OCP2	OCP3	
3570shp	3571shp	3570shp	3571shp	3570shp		$\nu_s(\text{OH})$
3428bd	3430bd		3430bd	3430bd		(H_2O)
				1256shp		
	1204w	1203w			1208shp	
	1163shp	1160shp		1185shp	1190m	
1145shp	1148shp	1149shp				
	1131shp	1134shp		1130shp		$\nu_6^{//}(\text{HPO}_4)$
1125shp	1125shp	1125shp				
1111shp	1113shp	1117shp		1110shp	1117vs	
1090s	1092s	1093s	1093s	1093s		$\nu_3^{//}(\text{PO}_4)$
1081shp	1078shp	1075shp		1080shp		$\nu_6^{//}(\text{HPO}_4)$
1060shp	1060shp	1062shp		1058shp		
	1042shp	1042shp		1042shp	1042vs	$\nu_3^{//}(\text{PO}_4)$
1032vs	1028vs	1028vs	1033s	1031vs		$\nu_3^{//}(\text{PO}_4)$
1010shp	1005shp	1005shp				
962m	963m	962m	963s	961s	980s	$\nu_1(\text{PO}_4)$
				917w		
868w	870w	870w	873w	873w		
				862w	862m	(CO_3)
		840shp			833w	

(b) contd.

Observed frequencies						Assignments
HA9	HA14	HA16	OCP1	OCP2	OCP3	
					787w	
				750bd	769shp	
631w	632m	633w	631m			$\nu_L(\text{OH})$
600m	601m	602m	600s	600s	601m	$\nu_4'''(\text{PO}_4)$
571shp	571shp	573shp	575shp	575shp	573s	$\nu_4''(\text{PO}_4)$
562s	562s	562s	562s	562s	567shp	$\nu_4'(\text{PO}_4)$



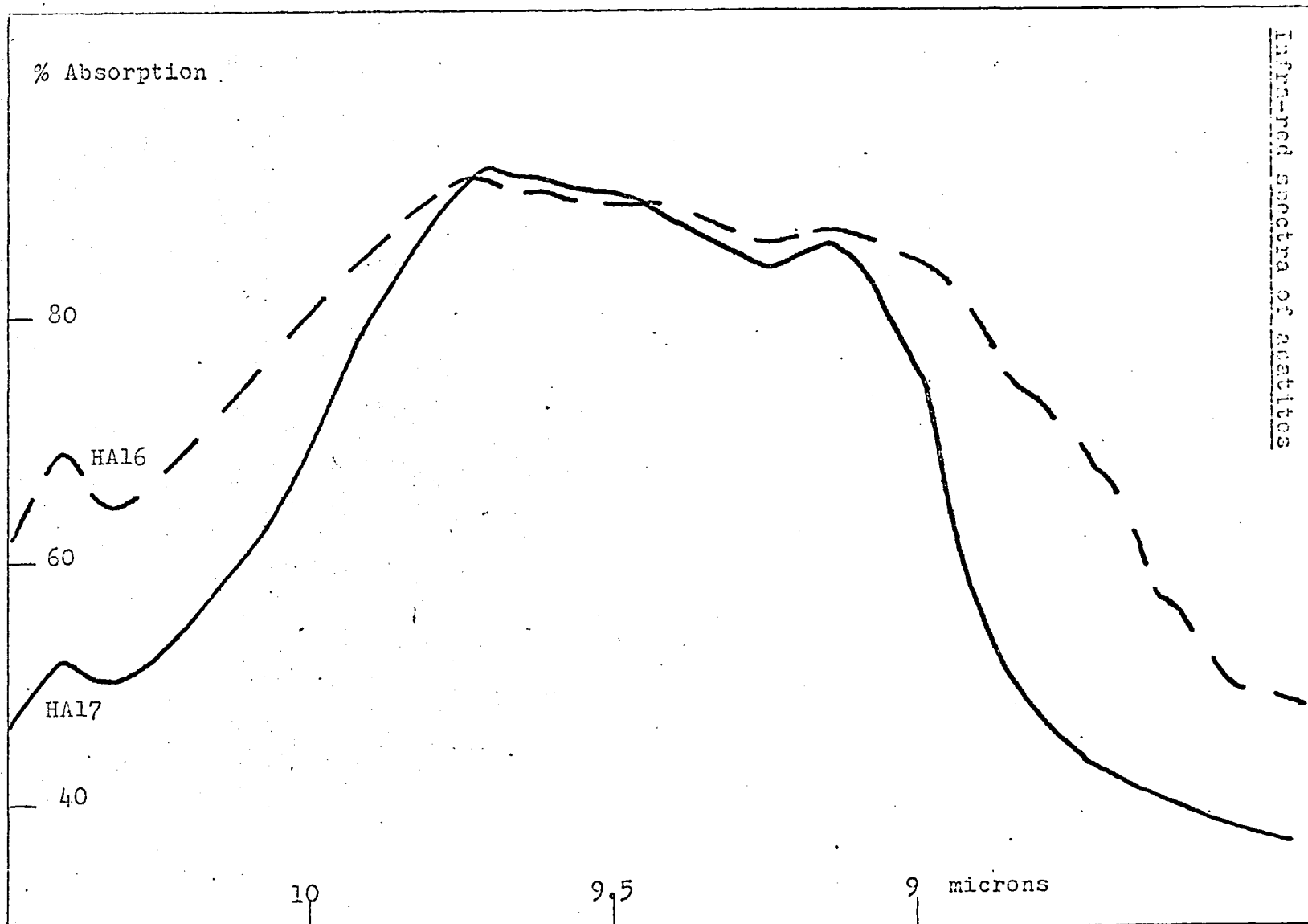


Figure 6.1.5.1(b)

6.1.3.2 Infra-red spectra of modified apatites.

Spectra of the modified apatites were obtained using KBr discs of the materials, care being taken to ensure total removal of solvent ether of the alkylation reaction. Table 6.1.3.2 shows some of the frequencies observed for modified apatites.

The results are uninformative as assignments cannot be used to prove that chemisorption of alkyl groups has occurred. It is unfortunate that the strongly absorbing phosphorus-oxygen-carbon stretching mode is coincident with the orthophosphate ν_3 mode.

Table 6.1.3.2Infra-red spectra of modified apatites.

(excluding bands listed in table 6.1.3.1.)

Observed frequencies (cm^{-1})		Assignments
Modification 16	Modification 39	
2955m		C-H stretch (CH_3)
2927m		" (CH_2)
2872m		" (CH_3)
2857m		" (CH_2)
1465w		H-C-H deformation
1449w		C- CH_3 "
1410w		
1374w		C- CH_3 "
	741w	Aromatic Out-of-plane deformation
	698w	-do-

6.1.4 X-ray Powder Diffraction

X-ray powder diffraction photographs have been used to identify most of the precipitated salts and some mention of this will first be made. Samples HA4⁴², HA5, and HA9 yielded patterns typical of apatite but contained extra lines, indicating the presence of an unidentified phase. The salt OCP 1 produced a diffuse pattern in which the stronger apatitic lines could be seen, while OCP 3, although clear, did not form a pattern due to either an apatitic or an octacalcium phosphate lattice.

The samples which were heated in air for 120 hours at 600°C produced patterns of no better resolution than those from the unpyrolysed salts. This suggests that crystal growth could not have occurred, and that the marked reduction in the specific surface noted earlier must be due to smoothing of the surface by surface sintering.

Measurements of lattice parameters for some of the materials were made, and the results are shown in figure 6.1.4. Expansion of the a-axis and contraction of the c-axis occur as calcium is removed from the lattice, a result which is in good agreement with other determinations.¹⁰²

Apatites with low calcium contents gave well resolved apatitic diffraction patterns, and no other phases were

lattice constants of apatites

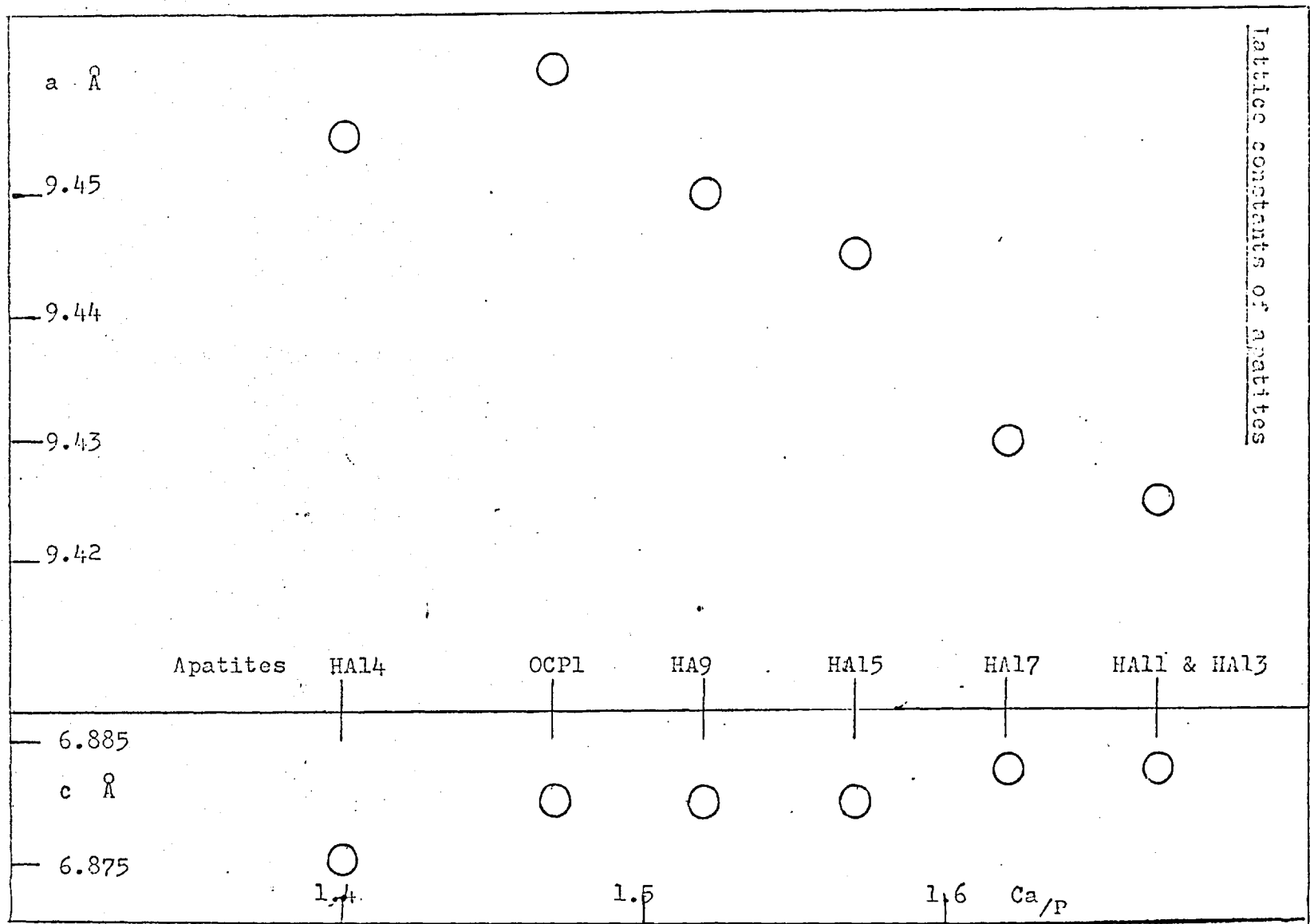
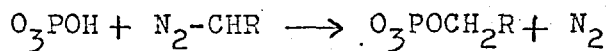


Figure 6.1.4

detected in those materials which had been stored for extended periods in their precipitating liquors. This observation, which is in agreement with those of many other authors, suggests that these calcium deficient apatites are not mixtures but are of very similar structure to stoichiometric hydroxy-apatite. The noted slight overall expansion in the lattice as calcium ions are progressively removed implies some small changes in inter ionic forces within the crystals.

6.1.5 General survey of some of the characteristics of these apatites and modified apatites.

Results of chemical analysis, infra-red spectroscopy and X-ray powder diffraction photography have supported the hypothesis of random calcium site vacancies in an apatitic lattice for the non-stoichiometric salts and it may be assumed that charge imbalance is corrected by incorporation of protons. These protons, some of which are thought to form hydrogen bonds between phosphate ions, may well react with diazo compounds to yield surface adsorbed alkyl groups:



This mechanism is supported by results of the chemical analysis of the modified apatites.

No evidence could be found for the suggestion that

hydroxyl ions are responsible for alkylation⁴². The catalysis results reported in chapter two may occur at these same sites as for diazoreaction, and reactivity in both cases increases with increase in calcium deficiency of the apatite (and therefore with increase in surface acidity or proton concentration).

The more reactive diazo compounds, such as long chain diazo alkanes, reacted very rapidly with apatites and in several cases the colour of the diazo solution was removed in a few minutes. Diphenyl diazomethane, a more stable material, was left in contact with the salts for longer times and the course of reaction could not be observed.

6.2 Water Sorption Results

6.2.1 Water sorption isotherms

Isothermal measurements of water sorption on many samples of parent and modified apatites have been carried out and a few of the results are shown in figure 6.2.1.

Before any conclusions may be drawn from sorption studies, it is of prime importance that the reproducibility of measurements is ascertained. Periodic checks of isotherms, particularly for the modified apatites, have been carried out to satisfy this requirement. Results presented here have

Figure 6.2.1(a)

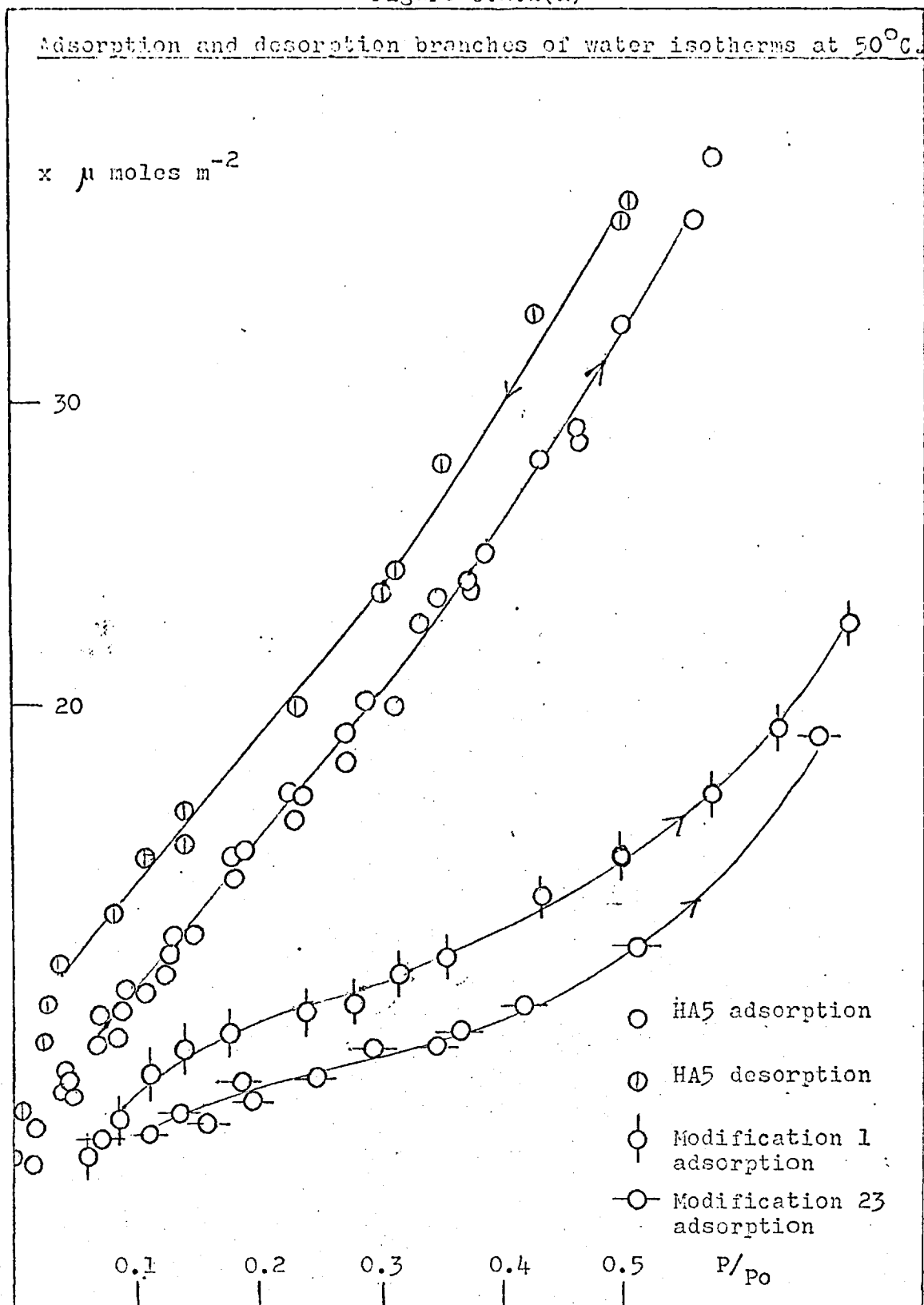


Figure 6.2.1(b)

Adsorption branches of water isotherms at 40°C.

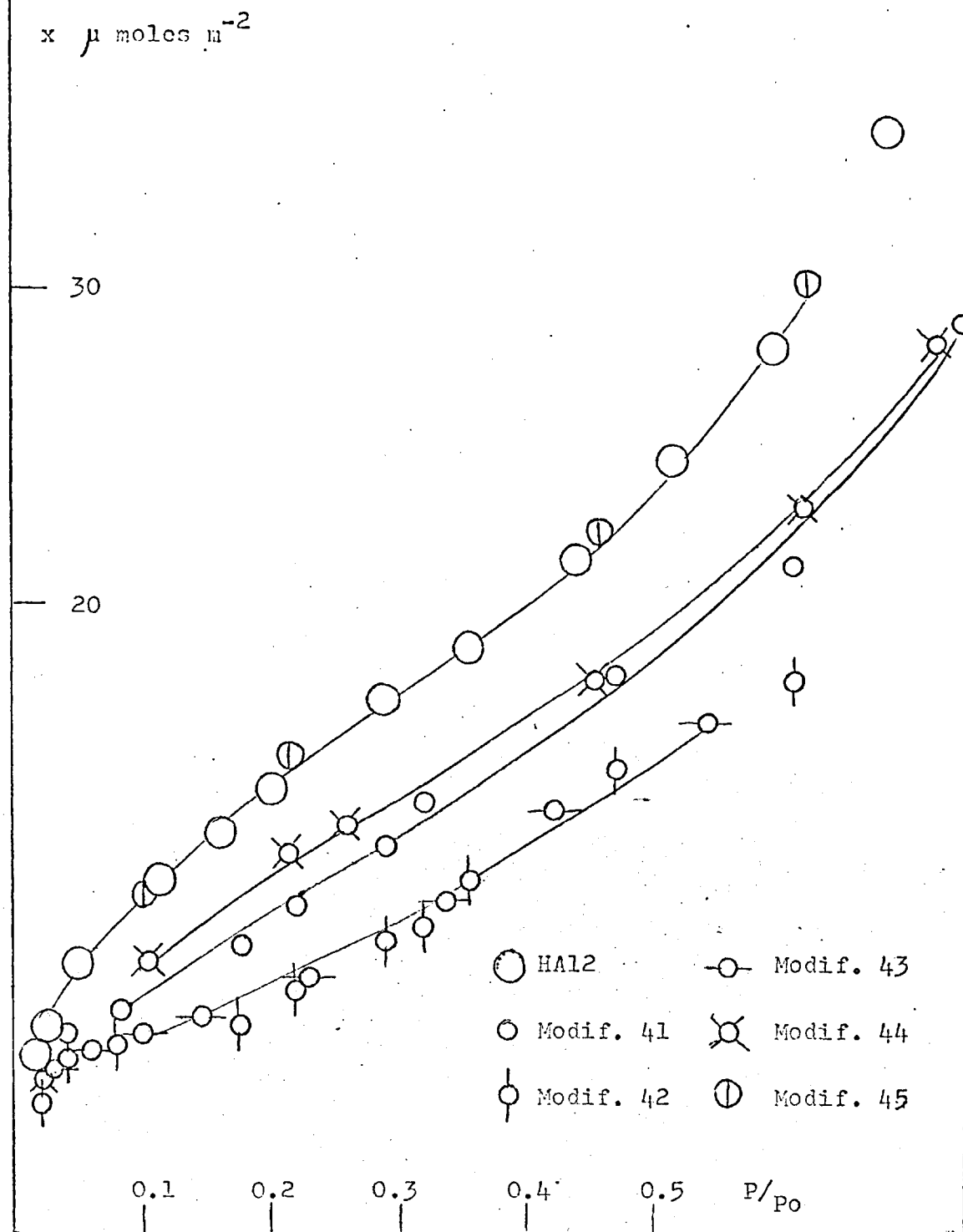
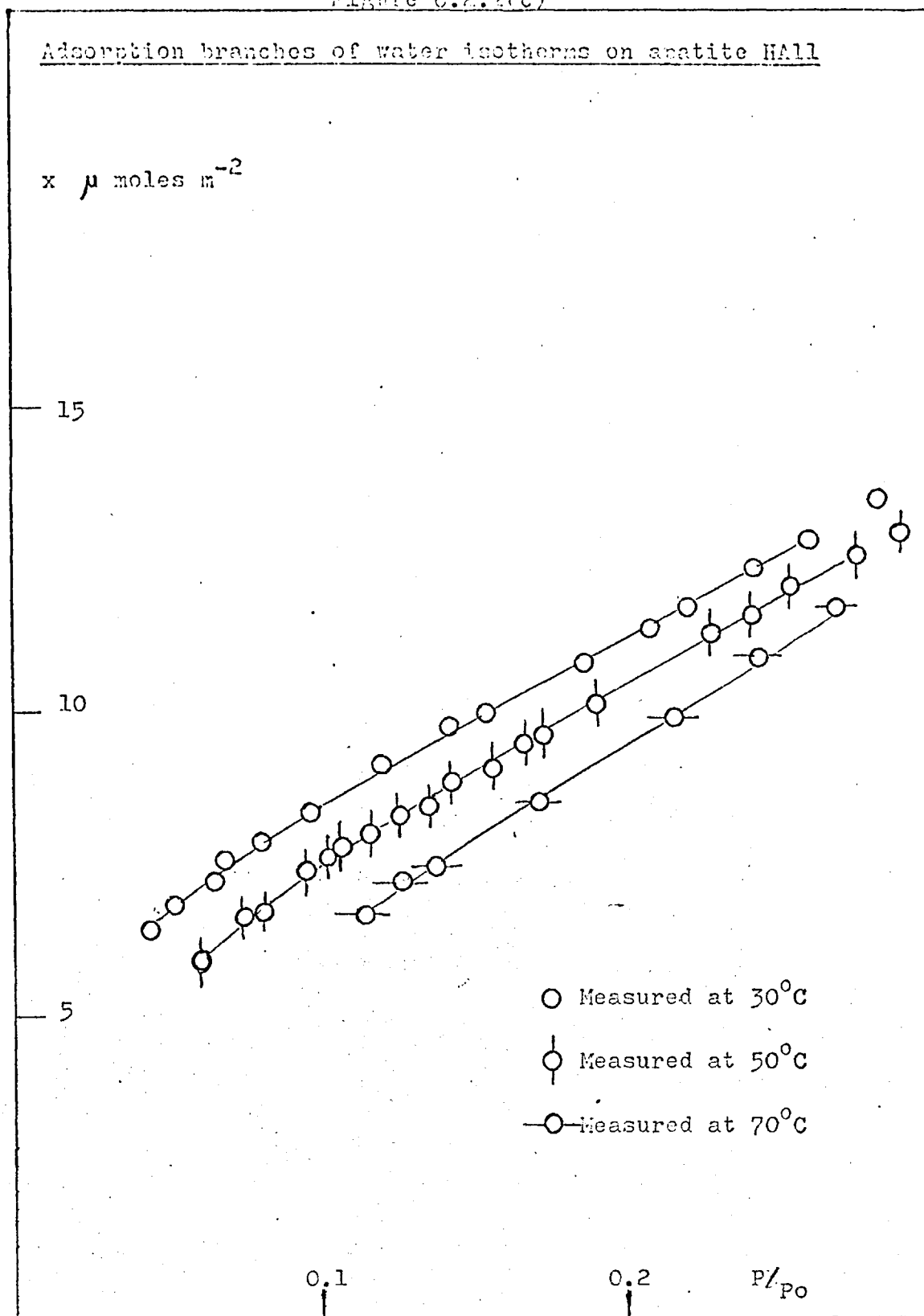


Figure 6.2.1(c)



all been found to be reproducible after at least six months.

Several hours elapsed before sorption measurements reached equilibrium, and the most satisfactory results were obtained if twenty-four hours were allowed between measurements. For this reason the adsorption-desorption isotherms took some weeks to complete. In spite of this, about eighty isotherms were determined and the results presented here, in figure 6.2.1, are typical. In order that isotherms of different sorbents may be compared, absolute units of water sorption per square metre of anhydrous sorbent are used.

Water sorption isotherms for both parent and modified apatites have been found to be irreversible in every case. Figure 6.2.1 (a) shows a typical result, although the shape of the desorption loop did change from sorbent to sorbent.

The reduction in water sorption after modification is clear from figures 6.2.1 (a) and (b), and in every case the apatite samples have been rendered less hydrophilic after diazo reaction. A comparison of the water sorption by modified and parent salts will be made in section 6.2.2, but it is clear from the isotherms presented that sorption per square metre of sorbent surface is substantially less, over the entire region of relative pressure, after modification.

Measurement of isotherms has been made at several temperatures for many sorbents and a family of adsorption runs for water by HALL, at temperatures between 30°C and 70°C is shown in figure 6.2.1 (c). The changes in hydrophilic character after modification were found to be qualitatively independent of temperature, but an accurate study of the temperature dependence of these changes was prevented by the uncertainty of results caused by experimental error.

Although no quantitative estimation of the errors involved in the determination of these water sorption isotherms was made it should be pointed out that the major contribution to the uncertainty of the results was due to random error, normally self-cancelling. The simple experimental arrangements, together with the fact that isotherms on all samples were determined under carefully controlled conditions, limited systematic error to faults caused by inaccurate specific surface determinations and incorrect measurement of the out-gassed weight of the sorbent.

6.2.2 Comparison of water sorption results

Figure 6.2.2 (a) expresses the isotherms of figure 6.2.1 (a) as the ratio of the amount sorbed by modified

Figure 6.2.2(a)

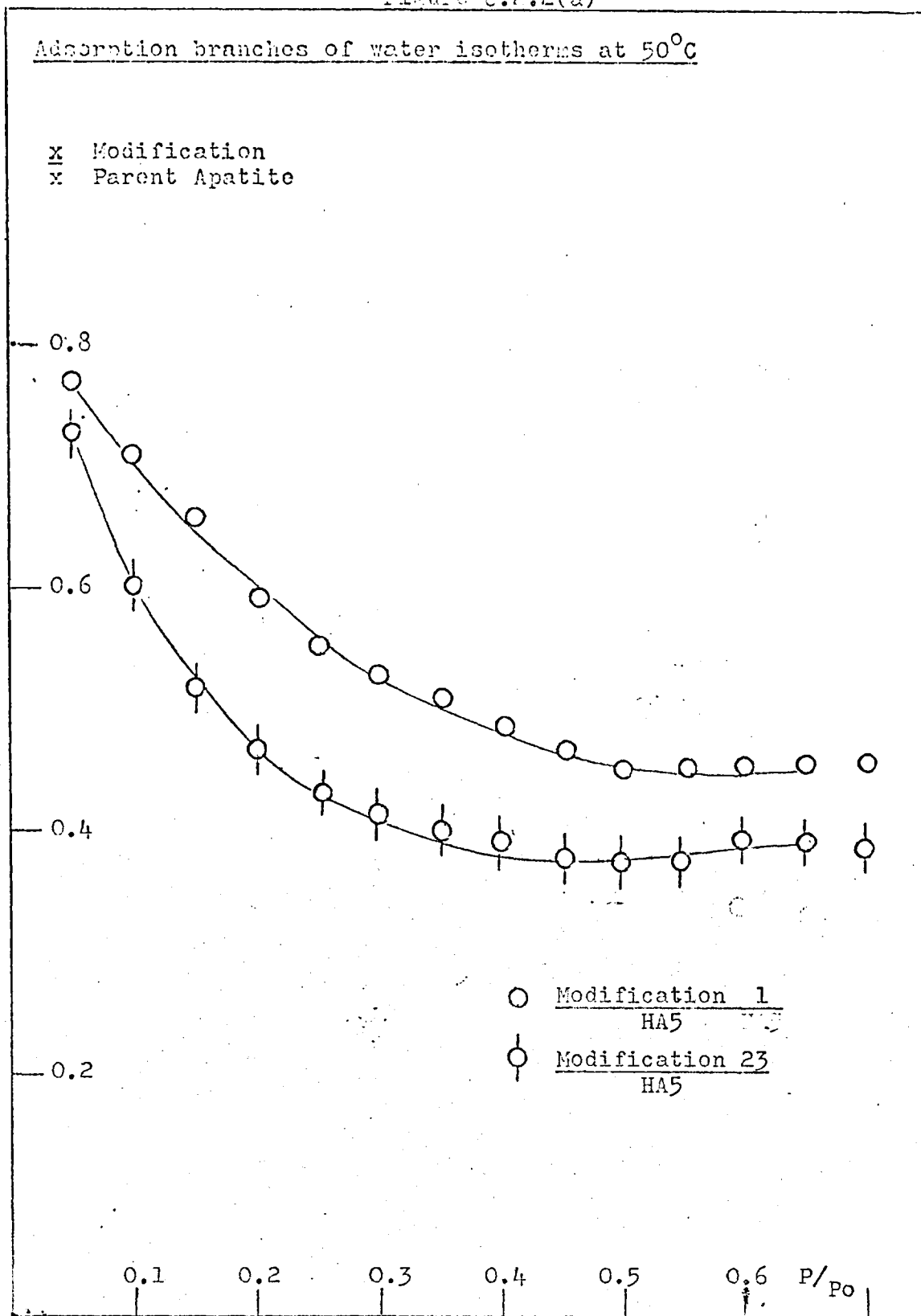


Figure 6.2.2(b)

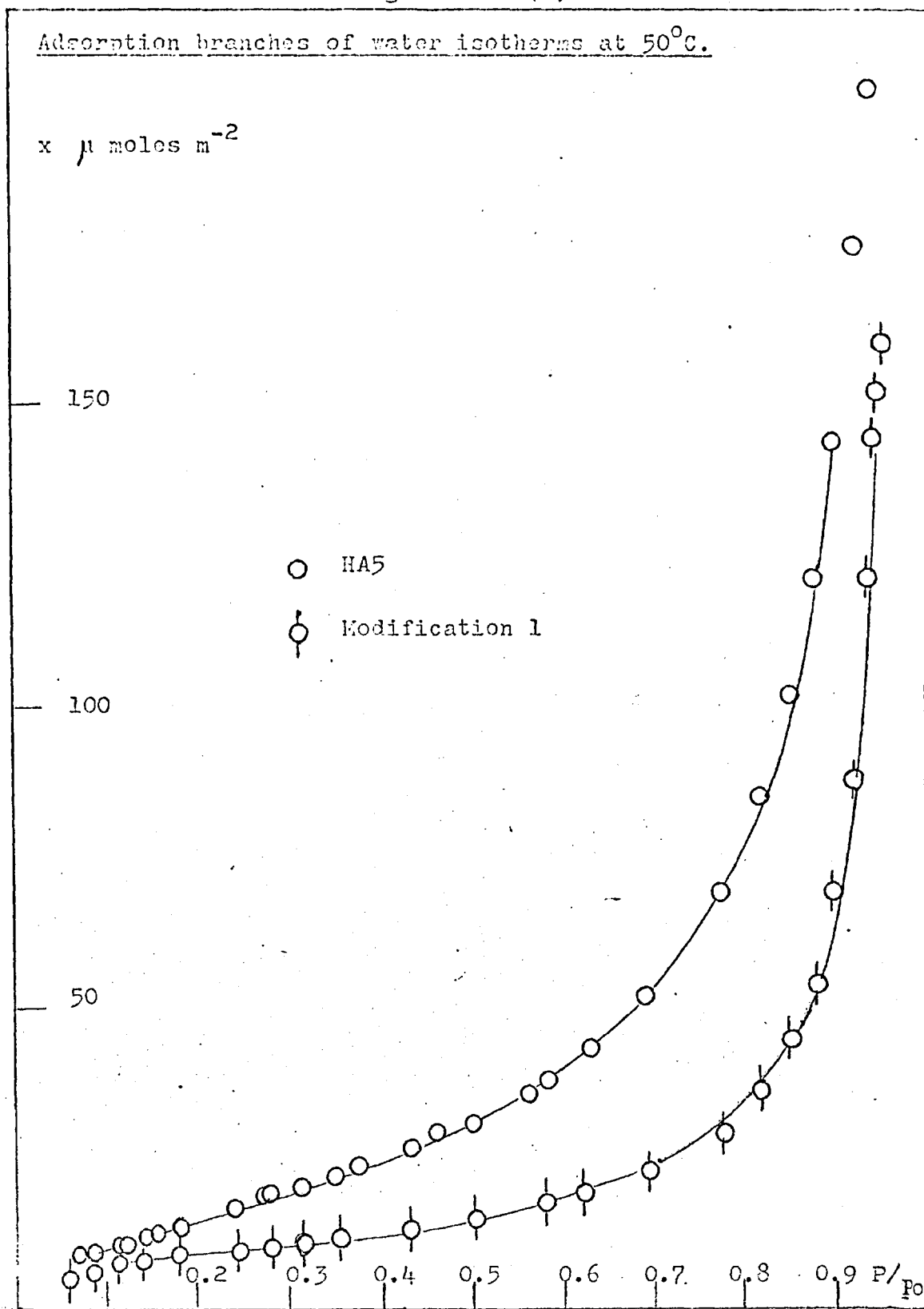


Figure 6.2.2(c)

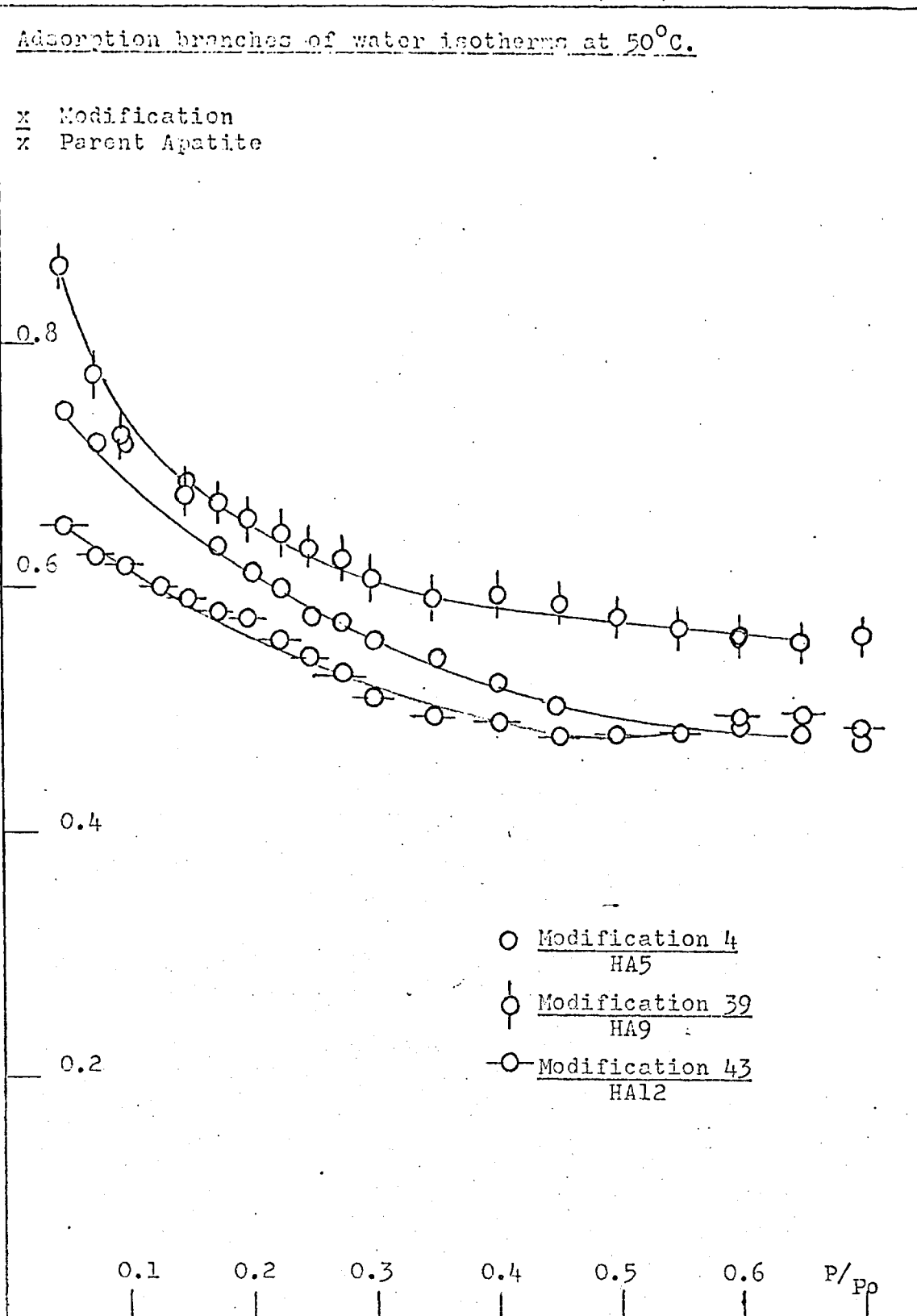


Figure 6.2.2(d)

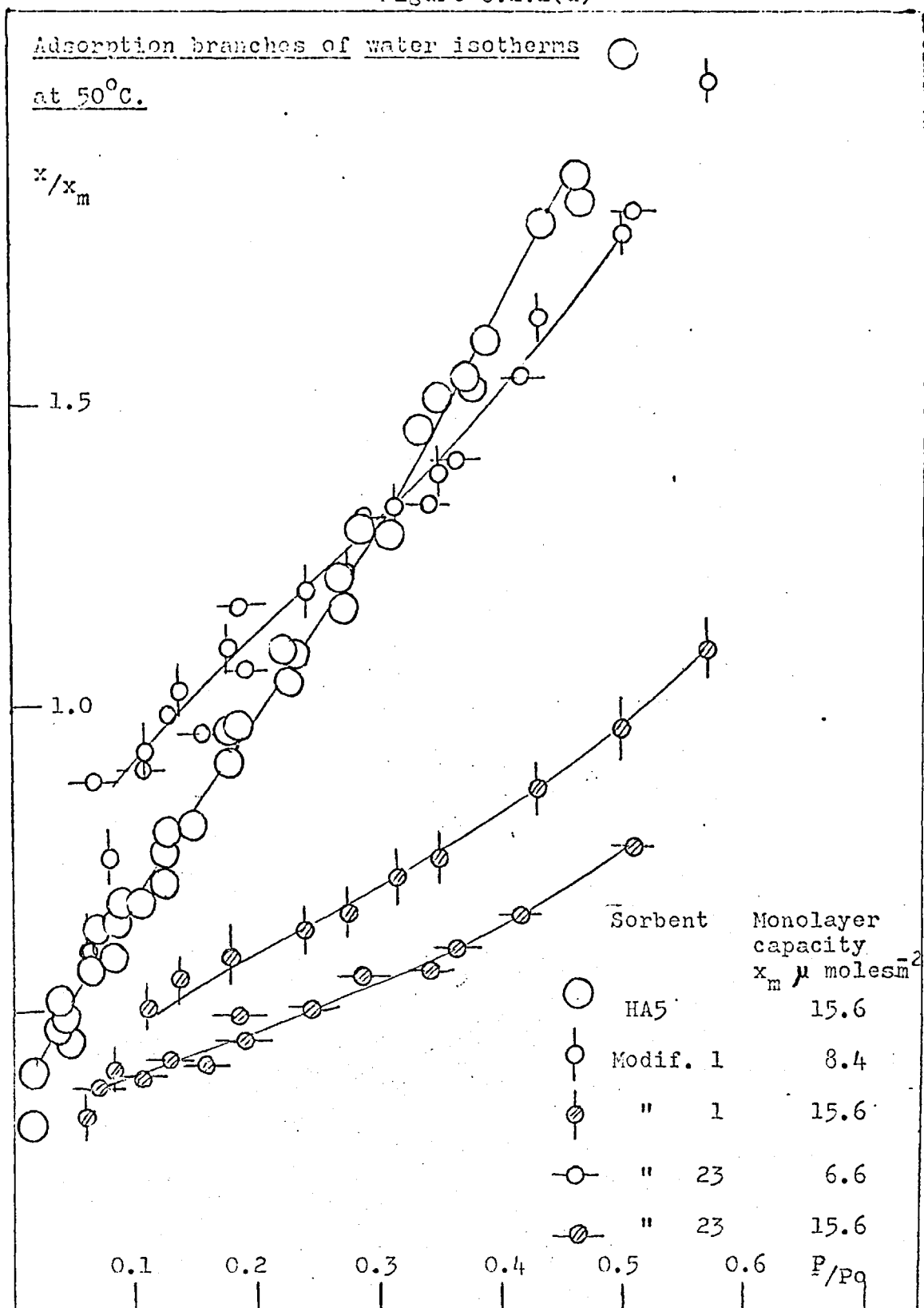
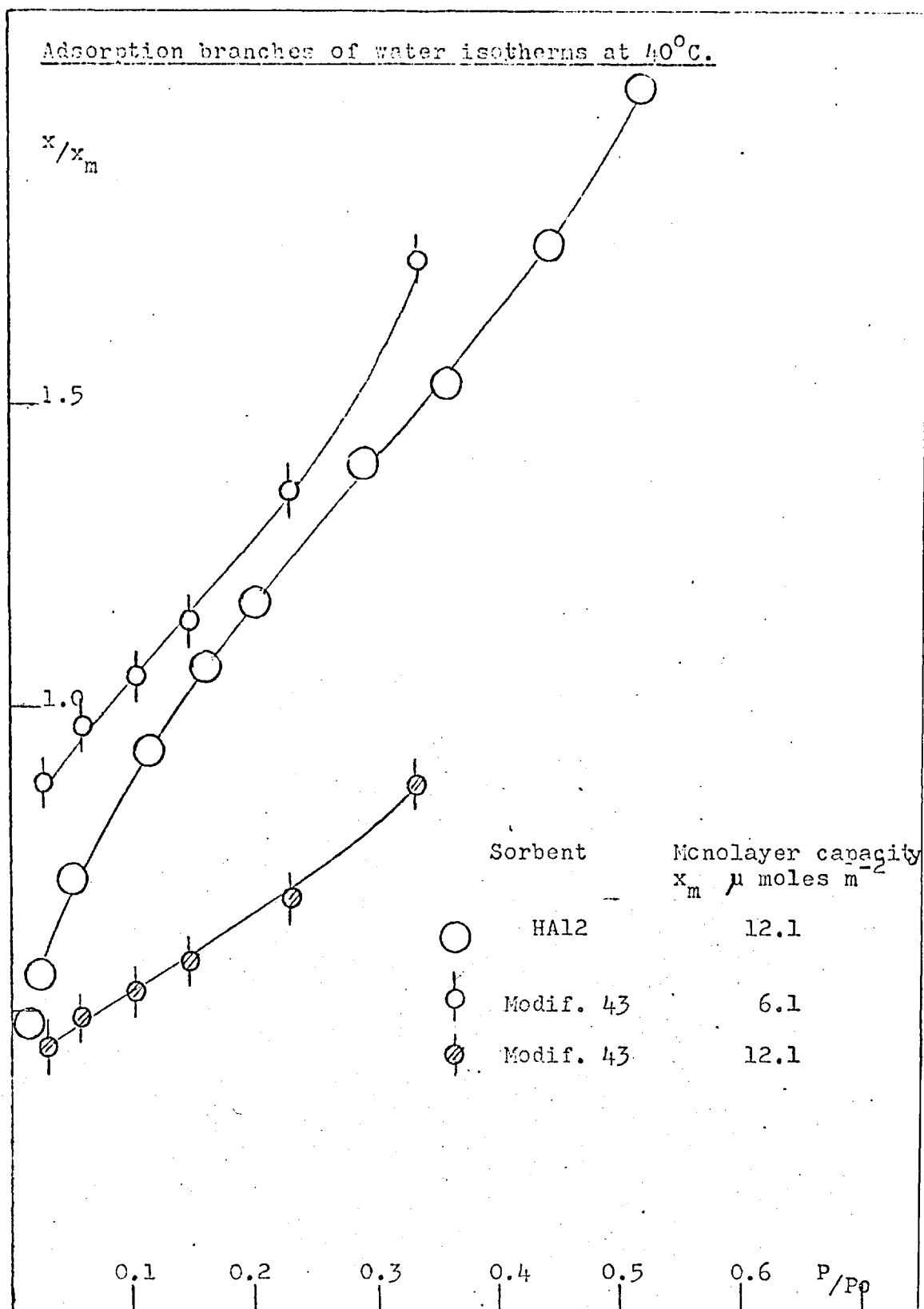


Figure 6.2.2(e)



apatite to the amount sorbed by parent material. The curves demonstrate the effectiveness, at all values of relative pressure, of diazo modification in diminishing the hydrophilic character of the apatite surface. The organic groups present on the surface of modification 23 may be seen to reduce water sorption to less than half the amount sorbed by the parent, HA5, at relative pressures in the range $0.2 < P/P_0 < 0.7$. Figure 6.2.2 (b) shows two isotherms of figure 6.2.1 (a) on a different scale, so that the effect of modification may be seen over a wider range of pressure. In general, the effect of the diazo-reaction was to decrease the water sorption of an apatite over the entire range of relative pressure.

Water sorption isotherms on three different apatites and their modifications after treatment with diphenyl diazomethane are represented in figure 6.2.2 (c). In view of the differences between their parent salts, it is notable that these isotherms are so close.

A convenient way of recording the differences between the water sorption characteristics of modified and parent apatites is shown in table 6.2.2 (a). The ratio of water sorption by modified to sorption by parent apatite at a relative pressure of 0.5 is shown for each material. The

table also includes ratios of the specific surfaces, measured from nitrogen sorption, for modified to parent salt. All water sorption results are taken from measurements made at 50°C.

The right-hand column is included so that the water sorption results may be seen to be authentic. In the case of modification 28, for example, a considerable change in the specific surface has occurred and it is therefore not realistic to consider the water sorption result as a simple change in hydrophilic character caused by surface alkylation. It is possible that a low result in the right-hand column implies a smoothing of the surface has occurred, perhaps by the formation of polymer. Most of the specific surface changes are small, however, and the large reduction in water sorption at $P/P_0 = 0.5$ gives a clear indication of the general effectiveness of the diazo-reaction for this purpose.

Calculations of the specific surface available for water sorption have been made from B.E.T. plots of the water sorption isotherms. The results of these determinations are shown in table 6.2.2 (b), together with values of the specific surface from nitrogen sorption. The assumption that an adsorbed water molecule occupies an area of $14.8\text{\AA}^2$ has been made, this being an arbitrary choice from the various

published values although its use yields values of S for the parent apatites which are close to S values calculated from nitrogen adsorption. The right-hand column of the table shows the ratio of specific surfaces determined from water sorption to those from nitrogen sorption, and it is clear from these values that there is less surface available on the modified salts for water sorption than on the parent apatites. Those materials which had been treated with diphenyl diazomethane all gave $S(H_2O)/S(N_2)$ values of less than 0.75, as did the materials numbered modifications 1, 16, 23, 27 and 46 which had been treated with normal diazo alkanes.

The two parts of table 6.2.2 will show that the surfaces of the modified apatites contain sites which are available for nitrogen sorption at $77.5^\circ A$ but which are not available for water sorption at temperatures between $30^\circ C$ and $70^\circ C$. These hydrophobic sites affect the sorption of water at all values of the relative pressure.

Table 6.2.2 (a)

Water sorption by modified apatites at 50°C and $P/P_0 = 0.5$

Modif. No.	Parent Apatite	Modifying Group	Ratio of Water Sorption at $P/P_0 = 0.5$	Ratio of Specific Surface from Nitrogen Sorption
				$\frac{X(H_2O)_{\text{Modified}}}{X(H_2O)_{\text{Parent}}}$ $\frac{S(N_2)_{\text{Modified}}}{S(N_2)_{\text{Parent}}}$
1	HA5	-CH ₃	0.45	1.01
2	"	-CHCO ₂ C ₂ H ₅	0.71	1.00
3	"	-CH(Ph) ₂	0.66	1.00
4	"	"	0.48	1.01
5	"	-CHC ₂ H ₃	0.68	1.00
7	"	-n-C ₈ H ₁₇	0.85	1.00
15	"	-n-C ₈ H ₁₇	0.51	0.96
16	"	-n-C ₈ H ₁₇	0.42	0.90
18	"	-n-C ₄ H ₉	0.65	1.01
23	"	-n-C ₁₈ H ₃₇	0.38	1.15
26	"	-n-C ₁₈ H ₃₇	0.61	1.00
27	HA6	-n-C ₁₂ H ₂₅	0.57	0.79
28	OCP1	-n-C ₁₈ H ₃₇	0.94	0.58
29	HA6	-n-C ₁₈ H ₃₇	0.97	0.87
30	OCP1	-CH(Ph) ₂	0.78	0.96
31	HA6	-CH(Ph) ₂	0.66	0.96

Table 6.2.2 (a) (contd.)

Modif. No.	Parent Apatite	Modifying Group	Ratio of Water Sorption at $P/P_0 = 0.5$ $\frac{X(H_2O)_{Modified}}{X(H_2O)_{Parent}}$	Ratio of Specific Surface from Nitrogen Sorption $\frac{S(N_2)_{Modified}}{S(N_2)_{Parent}}$
39	HA9	$-CH(Ph)_2$	0.58	1.28
40	HA11	"	0.82	0.89
41	HA12	"	0.76	1.04
42	HA12/600A	"	0.48	1.31
43	HA12/600A/160W	"	0.48	0.98
44	HA12/160V	"	0.77	0.97
45	HA12/600V	"	1.00	1.00
46	HA16	$-C_2H_5$	0.45	1.07

Table 6.2.2 (b)Specific surface of materials calculated from water sorptiondata at 50°C.

Material		$S(H_2O)$ in $m^2 g^{-1}$	$S(N_2)$ in $m^2 g^{-1}$	$S(H_2O)/S(N_2)$
HA5		94.8	68.2	1.39
HA6		76.3	71.3	1.07
HA9		72.0	67.3	1.07
HA12		82.7	77.3	1.07
HA16		58.2	54.4	1.07
Modification 1		51.5	68.8	0.75
"	2	59.4	68.0	0.87
"	3	58.8	68.0	0.86
"	4	47.2	68.0	0.69
"	16	43.9	61.5	0.71
"	23	46.1	78.4	0.59
"	27	23.2	56.6	0.41
"	39	45.0	91.9	0.49
"	40	48.8	68.5	0.71
"	41	57.6	80.7	0.71
"	42	15.7	28.9	0.54
"	43	13.5	24.7	0.55
"	44	51.6	64.3	0.80
"	45	60.6	56.7	1.07
"	46	34.6	57.9	0.60

The overall effect of hydrophobic sites, in the modified apatite surface, on water sorption, is readily seen in figures 6.2.2 (d) and (e). In these figures, sorption is expressed relative to the monolayer capacity (of water sorption). Open symbols represent values calculated on the basis of x_m determinations from measurements on each sorbent, while hatched symbols represent values calculated using the x_m value of the parent apatite only. From these curves it may be seen that water sorption per unit area of hydrophilic sites does not vary much for modified and unmodified samples while the sorption per unit of total sorbent area is considerably different after modification.

6.2.3 The parameter c of the B.E.T. equation.

Irreversibility of these water sorption isotherms prevents any detailed thermodynamic study from being made, but a brief description of some aspects of the adsorption isotherms is of interest.

After the methods described in section 6.1.1.2, B.E.T. plots of many adsorption isotherms have been used to find the variation of the c parameter with the amount adsorbed. In common with the nitrogen sorption results, c was found to decrease rapidly as water was adsorbed to complete the monolayer. The B.E.T. assumption that $c = e^{(E_1 - L)/RT}$ cannot

be considered in this irreversible system, but plots of $RT \ln c$ versus X/x_m are shown in figure 6.2.3 (a) for adsorption at several temperatures on the same sorbent. The closeness of these values suggests that this method would be useful for predicting isothermal values at temperatures other than those of measured values.

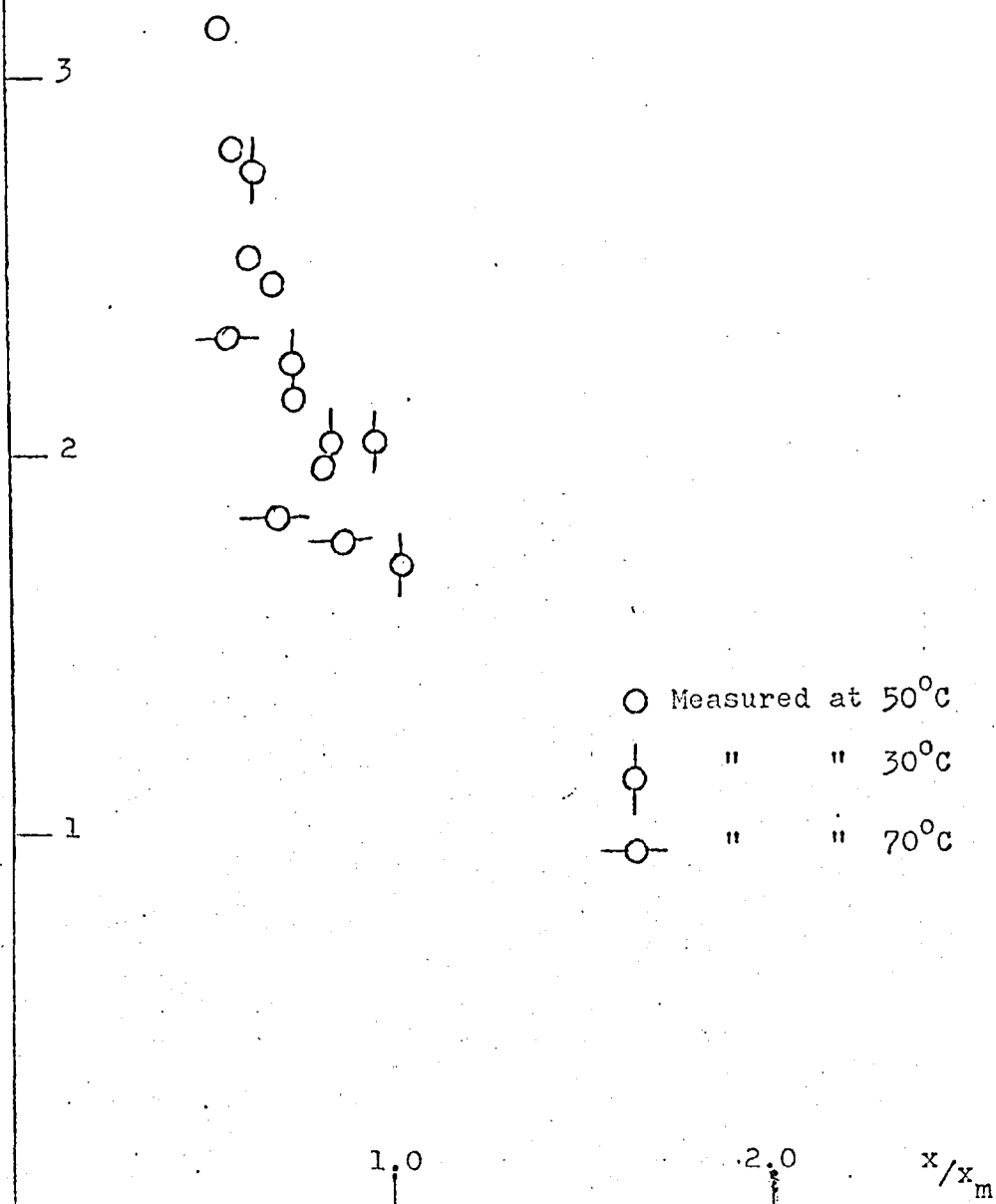
Although such a procedure has no theoretical justification, values of energies of sorption calculated from the c parameter are shown in figure 6.2.3 (b) together with values determined from apparent differential heats of adsorption calculated from the Clausius-Clapeyron equation and the adsorption branches of isotherms. The results are in good agreement but no conclusions can be drawn from them.

Figure 6.2.3 (c) shows the result of plotting $RT \ln c$ against x/x_m for parent and modified apatites. The open symbols represent the values obtained if the value of x_m was taken as 6.1 moles m^{-2} , the value derived from a B.E.T. analysis of water sorption on modification 43. These values are not close to those for the parent salt, HA12. Hatched symbols represent values if x_m for the modified material is taken as $12.1 \text{ moles m}^{-2}$, which would be the monolayer capacity if the sorbent contained no hydrophobic sites. This result supports the conclusion, made in section 6.2.2,

Figure 6.2.3(a)

RT ln c values calculated from adsorption branches of
water isotherms on apatite HAll.

RT ln c k cal. mole⁻¹



$(RT \ln c + L)$ and $(-\Delta\bar{H} - RT)$ values calculated from
adsorption branches of water isotherms on apatite HALL.

$(RT \ln c + L)$

and

$(-\Delta\bar{H} - RT)$ in k cal. mole⁻¹

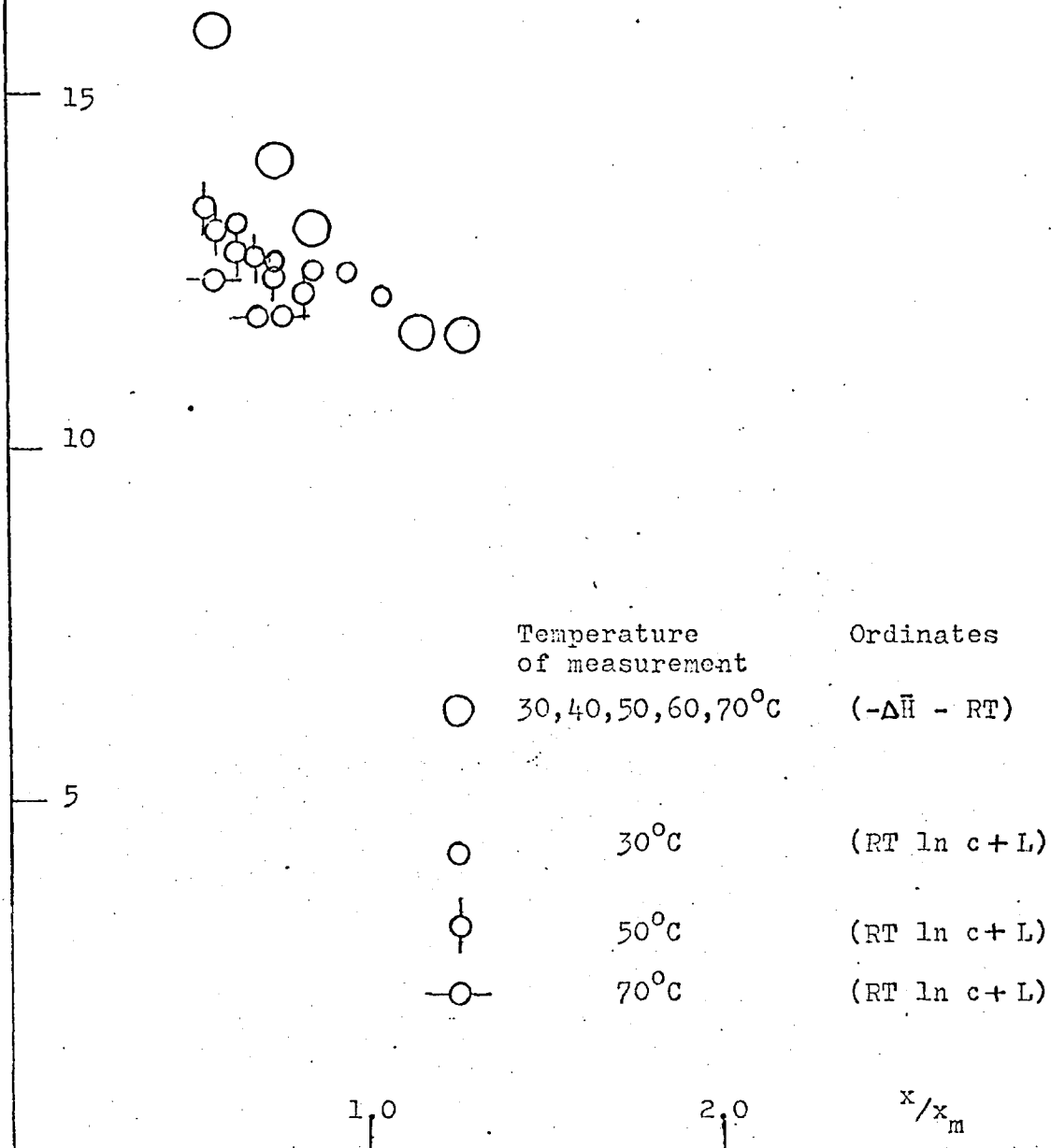
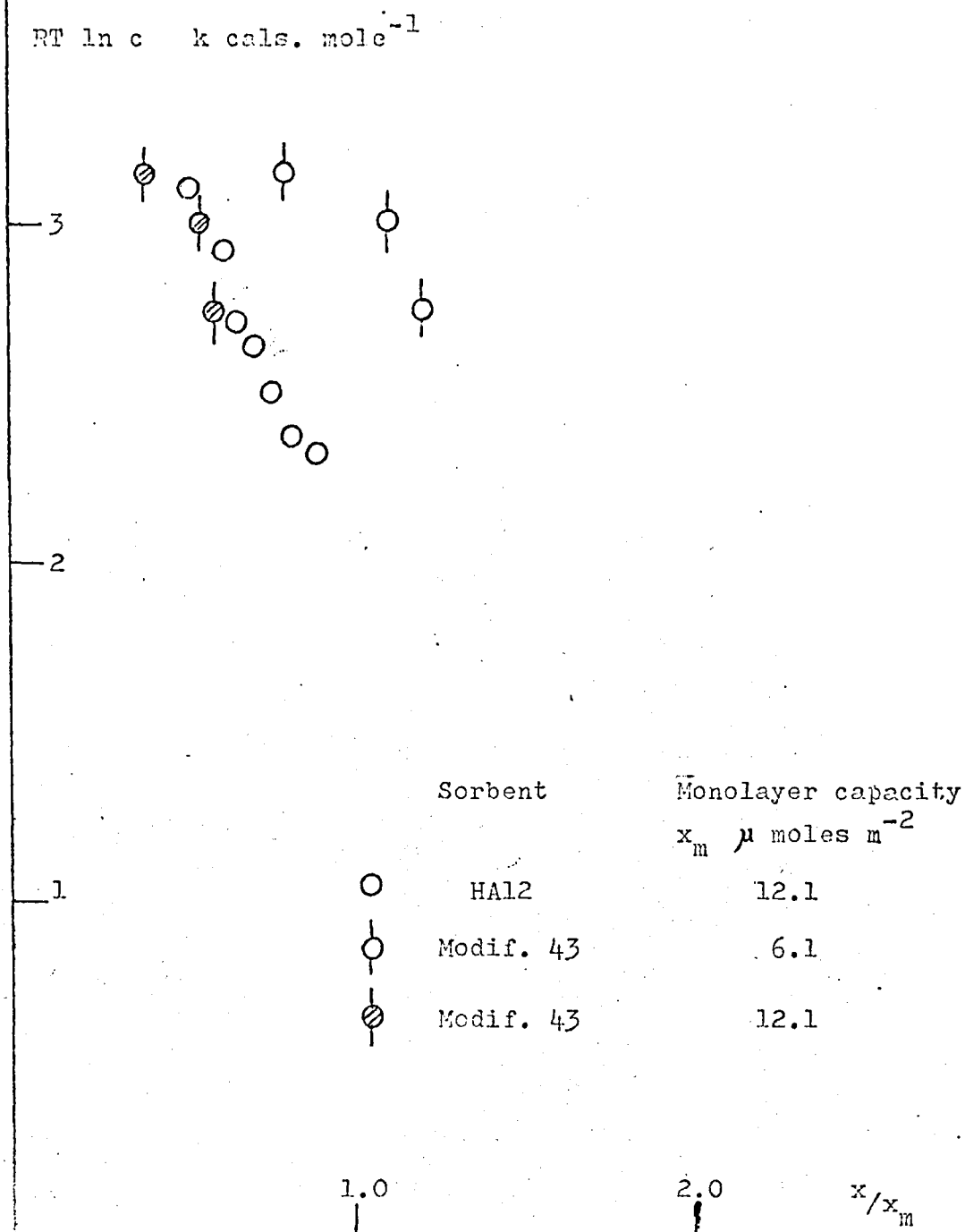


Figure 6.2.3(c)

RT ln c values calculated from adsorption branches of
water isotherms on apatite HA12 and modification. 43 at 40°C.



that the diazo-reaction yields a surface containing sites which are not available for water sorption.

6.2.4 Kinetics of adsorption.

The observation that water adsorption occurred at a finite rate suggests that uptake may include an activated process. If the energy of activation for adsorption is large, it could be estimated by measuring the rates of adsorption at neighbouring temperatures. It must, once again, be pointed out that the irreproducibility of water sorption makes energy determinations difficult.

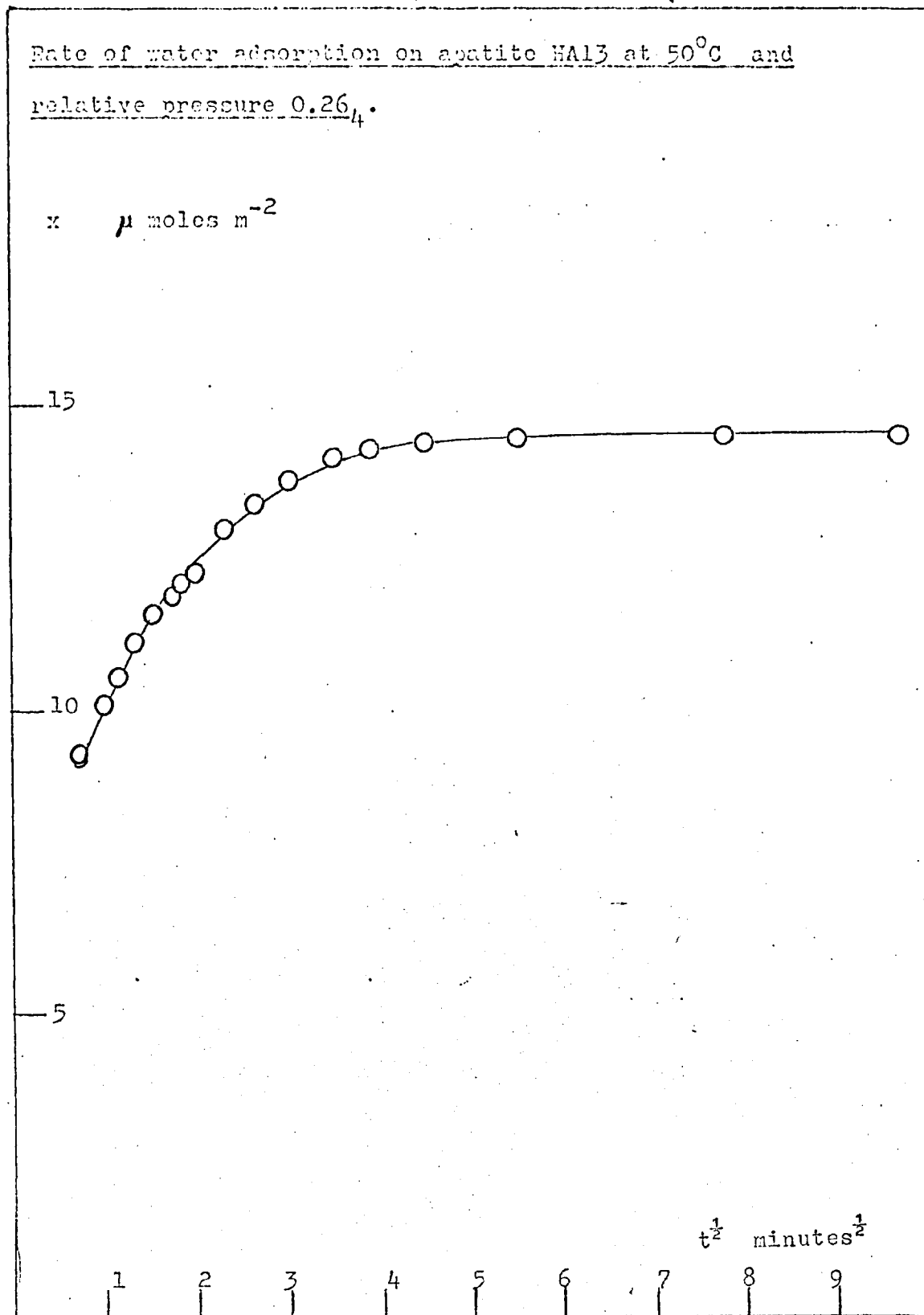
Figure 6.2.4 shows the results of plotting the amount sorbed against square root of time for one sample.

Although many other such determinations were made, no conclusions could be drawn from them. All results were found to be dependent on how the sorbents were packed in the buckets.

6.2.5 General discussion of the water sorption results.

The effect of the diazo-reaction on nearly all of the apatites studied in this work has been to confer a less hydrophilic character on each material. The extent of these changes in water sorption has been seen to depend on both the parent apatite and on the diazo compound used in the modification

Figure 6.2.4



reaction.

Water-sorption results for the modifications of the calcium deficient apatite, HAL2, and its various heat-treated forms are of particular interest. Reference to table 6.2.2 (a) will indicate the effect of each heat-treatment on the water sorption after modification, and it is clear that the sample 45 which had been treated by heating at 600°C for 120 hours under vacuum before modification was not changed by treatment with diphenyl diazomethane. This result may be compared with the number of organic groups present on the surface of this material, and table 6.1.2.3 shows that this is low. The pyrolysed samples of HAL2 contain pyrophosphate ions, and it may be assumed that the material now under discussion would have little opportunity to hydrolyse at the surface. Modification of this apatite, which contains so few surface hydrolysed ions, is minimal and it may be concluded that hydrolysed ions are necessary for modification to occur.

One sample of HAL2 which had been heated in air for 120 hours at 600°C provided a very reactive surface for alkylation and this in turn caused a considerable decrease in the hydrophilic nature of the surface. It is clear that an apatite, heated in this way, would hydrolyse at the surface

on cooling and sites for alkylation would be formed. The difference between water sorption characteristics of this material, modification 42, and modification 41 which was formed from oven-dried HAL2, may be due to the inadequacy of oven drying to remove enough adsorbed water from the surface. Water, if present in sufficient amount on a surface, could prevent alkylation by shielding reaction sites from diazo molecules.

In general terms, samples of calcium deficient apatites presented more hydrophobic surfaces after modification than did stoichiometric apatites. It is difficult to relate the hydrophobic character of modified salts specifically to the calcium deficiency of parent apatites because not enough carefully controlled experiments were performed. Nevertheless, it may be mentioned that of eight modified materials prepared from carefully dried apatites (modifications 39 to 46), four sorbed less than 60% of the amount of water adsorbed by the Parent at a relative pressure of 0.5, and these four were all calcium deficient salts with a calcium to phosphorus molar ratio near to 1.5.

The assumption that calcium deficient apatites contain acid phosphate groups, discussed in section 6.1, and the probability that all apatites will contain surface acid phosphate groups after exposure to the atmosphere may be

essential to an understanding of the reaction with diazo compounds. The only salt treated in such a way as to ensure the absence of acid phosphate groups, both internally and on the surface, was unreactive with diphenyl diazomethane. It has therefore been assumed that the alkylation of apatites involves an elimination reaction between diazo compound and hydrogen phosphate ions:

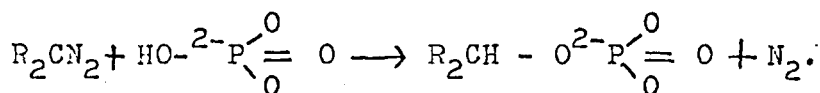
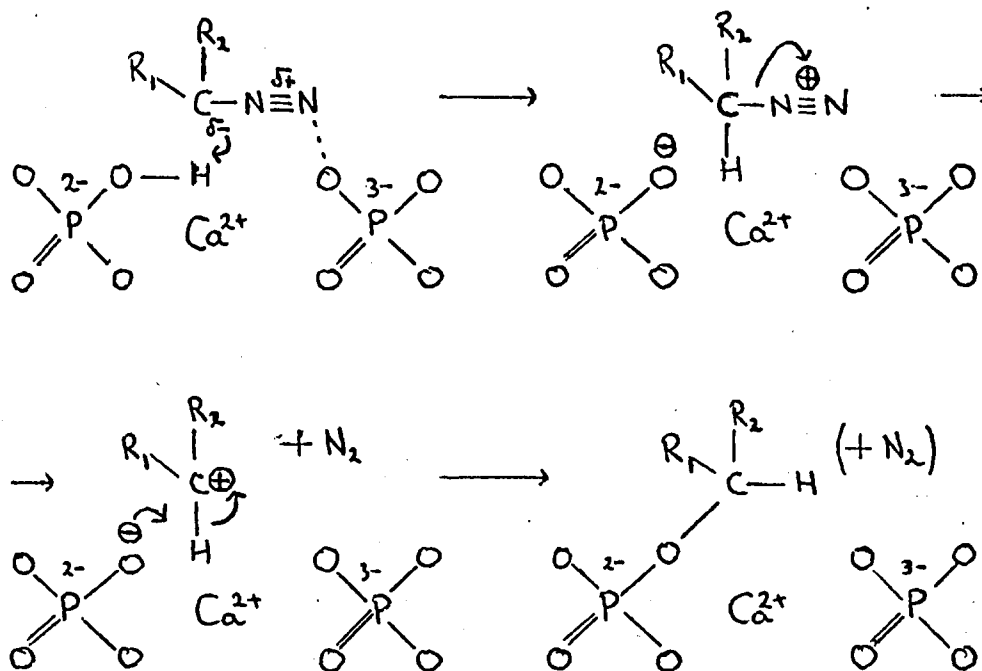


Table 6.2.2 (a) reveals that, for the modified samples of the apatite HA5, the order of effectiveness in conferring a hydrophobic surface on the salt is Modification 23 > Modification 16 > Modification 1. The organic group present on each surface is $nC_{18}H_{37}$, $nC_{8}H_{17}$ and CH_3 respectively. Modification 4, which was a sample of HA5 treated with diphenyl diazomethane, presents a surface which is only slightly less hydrophobic than the surface of modification 1. The 48% reduction in water sorption at $P/P_0 = 0.5$ of modification 4 compared with its parent salt is identical with the similar reduction for modifications 42 and 43. These were also materials modified by diphenyl diazomethane.

A model which is consistent with the surface chemistry and geometry of apatite and with the sorption and analysis results presented in this chapter is suggested for the diazo

reaction:



This mechanism is consistent with the nature of aliphatic diazo compound reactions, as described in chapter two.

CHAPTER 7

CONCLUSIONS

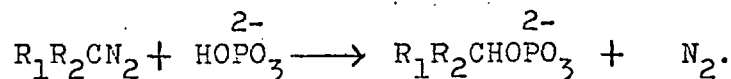
More than forty samples of apatites have been treated with ethereal solutions of aliphatic diazo compounds, and nitrogen sorption measurements have shown that this treatment did not significantly alter the specific surface of these salts. Modified samples were found, in almost every case, and at all relative pressures, to sorb less water per unit sorbent surface area (determined from nitrogen adsorption) than the parent apatites.

The adsorption branches of some water sorption isotherms were plotted with x/x_m as ordinate, where x refers to the amount of water sorbed by each sorbent and x_m refers to the water sorption monolayer capacity of the parent apatite, and P/P_0 as abscissa. This presentation showed the considerable reduction in the amount of water adsorbed, at any relative pressure, which was effected by modification. The same isothermal measurements were also plotted with x and x_m referring to the amount of water sorbed and the water sorption monolayer capacity, respectively, of each sorbent. Here the fractional monolayer coverage at each relative pressure is little changed, a result which suggests that part of the surface of the modified apatite is unaffected by modification and has a similar water sorption character to that of the

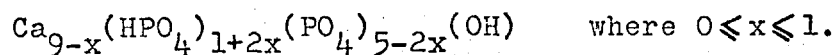
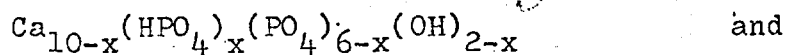
parent material. If this is the case, then it is implied that the remainder of the surface is hydrophobic, and has no effect on the adsorption branch of the water isotherm.

Although it was noted that those sorbents which had been treated with long aliphatic group diazo-n-alkanes were less hydrophilic than those treated with other diazo compounds, no attempt has been made to compare quantitatively the surface concentrations of organic groups with changes in the hydrophilic character of sorbents.

It was shown that the diazo reaction occurs only on apatites containing surface acid phosphate groups, and modification is thought to occur by the alkylation of these ions:



Calcium deficient apatites have been examined and it was found that their compositions were according to the formulae:



No conclusions were drawn regarding the content of lattice water molecules in those salts.

It is thought probable that the non-stoichiometric

apatites prepared later in this work were of similar structure to hydroxyapatite. Charge imbalance caused by the missing calcium ions is compensated for by inclusion of protons in the lattice. These protons may form hydrogen phosphate ions or form water molecules with hydroxyl ions. The unit cell parameters were found to be dependent on the calcium content of each apatite.

Identification of infra-red absorption bands, characteristic of the calcium deficient apatites, was difficult but bands in the region of the orthophosphate ν_3 mode are modified in shape by certain "shoulders" which may be due to hydrogen phosphate modes. No information on the nature of the binding of alkyl groups to apatite could be obtained from infra-red spectroscopy.

REFERENCES

1. Cornell, J., "Adhesive Restorative Dental Materials", proceedings of a workshop held in Indiana University Medical Centre, Indianapolis, U.S.A., September, 1961. Published by The Owen Litho Service, Spencer, Indiana.
2. Rose E.E. et al, "Adhesive Restorative Dental Materials".
3. Buonocore M.G., "Adhesive Restorative Dental Materials".
4. Bowen R.L., "Adhesive Restorative Dental Materials".
5. Tsou K.C., "Adhesive Restorative Dental Materials".
6. Orban B.J., "Oral Histology and Embryology", 4th Edition, 1957. Published by the C.V. Mosby Co., St. Louis, U.S.A.
7. McConnell D., Biochim. et biophys. acta, 17,450, 1955.
8. Bassett H.J., J. Chem. Soc. 111,620, 1917.
9. Neuman W.F. and Neuman M.W., Chem. Rev. 53,1, 1953.
10. Carlstrom D., Acta Radiol., Suppl., 121, 1955.
11. Trautz O.R., Ann. N.Y. Acad. Sci., 85, 145, 1960.
12. Elliott J.C., Ph.D. Thesis, London, 1964.
13. Posner A.S., Phosphorus and Its Compounds, edited by van Wazer J.R., Vol. 2, 1429, 1958. Published by Interscience, N.Y..
14. Cameron F.K. and Bell J.M., J. Am. Chem. Soc., 27,1512,1905.
15. Hendricks S.B. and Hill W.L., Proc. Natl. Acad. Sci., Wash., 36, 731, 1950.

16. Posner A.S. and Stephenson S.R., J.dent. Res., 31, 371, 1952.
17. Rowles S.L., J. Dent. Res., 42, 1101, 1963.
18. McConnell D., Archs. oral Biol., 10, 421, 1965.
19. Brown W.E., Lehr J.R., Smith J.P. and Frazier A.W.,
Nature, Lond., 196, 1050, 1962.
20. Kunin R. and Elincore K.L., cited by Newman and Newman,
The Chemical Dynamics of Bone Mineral, University of
Chicago Press, 1958.
21. Winand L., Annls. Chim., 6, 941, 1961.
22. Posner A.S., Stutman J.M. and Lippincott E.R.; Nature,
Lond., 188, 486, 1960.
23. Kuhl G. and Nebergall W.H., Z. anorg. allg. Chem., 324,
313, 1963.
24. Berry, E.E., J. inorg. nucl. Chem., 29, 317, 1967.
25. Berry, E.E., J. inorg. nucl. Chem., 29, 1585, 1967.
26. Dry M.E. and Beebe R.A., J. Phys. Chem., 64, 1300, 1960.
27. Myers M.M., J. dent. Res., 39, 664, 1960.
28. Perrin D., Nature, Lond., 208, 787, 1965.
29. Bowen R.L., J. Dent. Res., 44, 895, 1965.
30. Bowen R.L., J. Dent. Res., 44, 903, 1965.
31. Buonocore M.G. et al, J. Dent. Res., 35, 846, 1956.
32. Buonocore M.G., J. Dent. Res., 34, 849, 1955.
33. Gwinnett A.J. and Buonocore M.G., Brit. dent. J., 77, 1965.
34. Snyder W.H., Wilson C.E., Newman G.V. and Semen J.,
J. appl. pol. Sci., 11, 1509, 1967.

35. Newman G.V. and Sharpe L.H., J.N.J. Dental Soc., 37, 289, 1966.
36. Brauer, G.M., Davenport R.M. and Hansen W.C., Mod. Plastics, 34, 153, 1956.
37. Dzhigit O.M., Kiselev A.V. and Mikos-Avgul N.N., Dokl. Akad. Nauk. U.S.S.R., 70, 441, 1950.
38. Lygin V.I. and Kiselev A.V., Koll. Zn., 23, 299, 1961.
39. Scherbakova D. and Slovetzkaya K.I., Dokl. Akad. Nauk., U.S.S.R., 111, 855, 1956.
40. Kiselev A.V. et al., Proc. Acad. Sci. U.S.S.R. 124, 97, 1959.
41. Kiselev A.V., Coll. J. U.S.S.R., 25, 103, 1963.
42. Butler M.D., Ph.D. Thesis, London, 1966.
43. Eyring E.M. and Wadsworth M.E., Min. Eng. 5, 531, 1956.
44. Roev L.H. and Terenin A.N., Dokl. Akad. Nauk. U.S.S.R., 124, 373, 1959.
45. Babushkin A.A. and Uvarov A.D., Dokl. Akad. Nauk. U.S.S.R., 110, 581, 1956.
46. Barrer R.M. and Marshall D.J., J. Chem. Soc., 6616, 1965.
47. Burri C., Jakob J., Parker R.L. and Struntz H., Schweiz min. petr. 15, 327, 1935.
48. Mitchel L., Faust G.T., Hendricks S.B. and Reynolds P.S., Am. Mineral., 28, 356, 1943.
49. Henry T.H., Phil. Mag., 36, 134, 1850.
50. Deans T., Miner. Mag., 25, 135, 1938.

51. Broegger W.C. and Backstroem H., cited by Elliott J.C.
in reference 12.
52. Tschirwinsky W., Zbl. Miner. Geol. Palaont, 279, 1907.
53. Schaller W.T., Z. krist., 48, 559, 1911.
54. McConnell D., Am. J. Sci., 36, 296, 1938.
55. Hentschel H., Zbl. Miner. Geol. Palaont, 609, 1923.
56. Naray-Szabo S., Z. krist., 75, 387, 1930.
57. Mehmel M., Z. krist., 75, 323, 1930.
58. Mehmel M., Z. phys. Chem. Abt. B., 15, 223, 1931.
59. Hendricks S.B., Jefferson M.E. and Mosely V.H.,
Z. kristallogr., 81, 352, 1932.
60. Beevers C.A. and McIntyre D.B., Min. Mag., 27, 254, 1946.
61. Wondratschek M., Neues. Jb. Miner. Abh., 99, 113, 1963.
62. Bauer H., Angew. Chem., 71, 374, 1959.
63. Young R.A. and Elliott J.C., Arch. oral Biol. 11(7),
699, 1966.
64. Posner A.S., Perloff A. and Diorio A.F., Acta Cryst.,
11, 308, 1958.
65. Kay M.I., Young R.A. and Posner A.S., Nature 204, 1040, 1964.
66. van der Lugt W., Knothnerus D.I. and Young R.A., paper
presented at the 2nd International Conference on Tooth
Enamel, London, 1969.
67. Posner A.S. and Eanes E.D., Norelco Reporter, 10, 71, 1963.
68. Posner A.S., Eanes E.D., Harper R.A. and Zipkin I.,

- Arch. oral Biol., 8, 549, 1963.
69. Elliott J.C., J. dent. Res., 43, 959, 1964.
 70. Fowler B.O., cited by Brown W.E. et al in reference 19.
 71. Nakamoto K., Margoshes M. and Rundle R.E., J. Am. Chem. Soc., 77, 6480, 1955.
 72. Baddiel C.B. and Berry E.E., Spectrochim. Acta, 22, 1407, 1966.
 73. Bellamy L.J., The Infra-Red Spectra of Complex Molecules, published by R. Clay and Co., Bungay, Suffolk, 1958.
 74. Busing W.R. and Morgan H.W., J. Chem. Phys. 28, 998, 1958.
 75. Benes H.A., J. Chem. Phys., 30, 852, 1959.
 76. Hexter R.N., J. Chem. Phys., 34, 941, 1961.
 77. Mitra S.S., Solid State Physics, 13, 1, 1962.
 78. Busing W.R. and Levy H.A., J. Chem. Phys., 26, 503, 1957.
 79. Coogan C.K., J. Chem. Phys., 43, 823, 1965.
 80. Arnold P.W., Trans. Farad. Soc., 46, 1061, 1950.
 81. Tovborg Jensen A. and Hansen K.G., Experientia, 13, 311, 1957.
 82. Hayek E., Newesley H., Hassenteufel W., and Krismer B., Monatsh. Chem., 91, 249, 1960.
 83. Bierrum N., Selected Papers, published by Einar Munksgaard, Copenhagen, 1949.
 84. Neuman W.F. and Neuman M.W., The Chemical Dynamics of Bone Mineral, University of Chicago Press, 1958.
 85. Brown W.E., Lehr J.R., Smith J.P. and Frazier A.W., J. Am. Chem. Soc., 79, 5318, 1957.

86. Bjerrum N., Kgl. Danske Videnskab. Selskab. Mat.-fys. Medd., 31(7), 1, 1958.
87. Brown W.E., Nature, Lond., 196, 1048, 1962.
88. Hodge H.C., Le Fevre M. and Bale W.F., Ind. Eng. Chem., Anal. Ed., 10, 156, 1938.
89. van Wazer J.R., J. Am. Chem. Soc., 72, 647, 1950.
90. Bouille A., Compt. rend., 226, 1617, 1948.
91. Gee A. and Deitz V.R., J. Am. Chem. Soc., 77, 2961, 1955.
92. Bett J.A.S., Christner L.G. and Hall W.K., J. Am. Chem. Soc., 89, 5535, 1967.
93. Berry E.E., Bull. Soc. Chim. France, Special No., 1765, 1968.
94. Winand L. and Duyckaerts G., Bull. Soc. Chim. Belge, 71, 142, 1962.
95. Berry E.E. and Baddiel C.B., Spectrochim. acta, 23A, 1781, 1967.
96. Fowler B.O., Moreno E.C. and Brown W.E., Arch. Oral. Biol., 11, 477, 1966.
97. Stutman J.J., Termine J.D. and Posner A.S., Trans. N.Y. Acad. Sci., 27, 669, 1965.
98. Bhatnagar V.M., Bull. Soc. Chim. France, Special No., 1771, 1968.
99. Eanes E.D., Gillesen I.H. and Posner A.S., Nature 208, 365, 1965.
100. Wagner C., Z. Elektrochem., 45, 58, 1961.
101. Le Geros M.R., Discussion of reference 93, Bull. Soc. Chim. France, Special No., 1765, 1968.
102. Trautz O.R., Ann. N.Y. Acad. Sci., 60, 696, 1955.

103. Nicol S.K. and Clarke A.J., paper presented at the
2nd International Conference on Tooth Enamel, London,
1969.
104. de Bruyn, cited in reference 103.
105. Rootare H.M., Deitz V.R. and Carpenter F.G., J. Colloid
Sci., 17, 179, 1962.
106. Leftin H.P. and Hall W.K., 2nd International Congress
on Catalysis, Paris, Volume 1, 1353, 1960.
107. Bowman R.S. and Piasecky C.J., U.S. Patent 3,149,082, 1964.
108. Bett J.A.S. and Hall W.K., J. Catalysis, 10, 105, 1968.
109. Griess P., Ann., 113, 207, 1860.
110. Curtius T., Ber., 16, 2230, 1883.
111. Franchimont A.P.N., Rec. trav. chim., 9, 146, 1890.
112. von Peckmann H., Ber., 27, 1888, 1894.
113. von Peckmann H., Ber., 28, 855, 1895.
114. Eistert B., Angew Chem., 54, 99, 1941.
115. Eistert B., Angew Chem., 54, 124, 1941.
116. Werner E.A., J. Chem. Soc., 115, 1093, 1919.
117. Arndt F., Org. Syntheses, Coll. Vol. 2, 165, 1943.
118. de Boer T.J. and Backer H.J., Org. Syntheses 36, 16, 1956.
119. E.I. du Pont de Nemours and Co. Inc., Wilmington, Del.,
U.S.A., U.S. Patent 2,675,378.
120. Muller E., Ludsteck D. and Rundel W., Angew Chem.,
67, 617, 1955.

121. Adamson D.W. and Kenner J., J. Chem. Soc., 286, 1935.
122. Adamson D.W. and Kenner J., J. Chem. Soc., 1551, 1937.
123. Adamson D.W. and Kenner J., J. Chem. Soc., 181, 1939.
124. Redemann C.E., Rice F.O., Roberts R. and Ward H.P.,
Org. Syntheses, Coll. Vol. 3., 244, 1955.
125. Curtius T. and Lang H., J. prakt. chem., 44, 544, 1891.
126. Curtius T. and Rauterberg F., J. prakt. chem., 44, 192, 1891.
127. Curtius T. and Thun K., J. prakt. chem., 44, 161, 1891.
128. Staudinger H., Anthes E. and Pfenniger F., Ber., 49,
1928, 1916.
129. Staudinger H. and Gaule A., Ber., 49, 1897, 1916.
130. Staudinger H. and Gaule A., Ber., 49, 1951, 1916.
131. Staudinger H. and Goldstein J., Ber., 49, 1923, 1916.
132. Staudinger H. and Kupfer O., Ber., 44, 2197, 1911.
133. Curtius J., J. prakt. chem., 39, 107, 1889.
134. Angeli A., Atti. R. Accad. Lincei, 16(2), 790, 1907.
135. Angeli A., Atti. R. Accad. Lincei, 20(1), 626, 1911.
136. Thiele J., Ber., 44, 2522, 1911.
137. Langmuir I., J. Am. Chem. Soc., 41, 1546, 1919.
138. Langmuir I., J. Am. Chem. Soc., 42, 285, 1920.
139. Weissberger A. and Bach H., Ber., 65, 265, 1932.
140. Weissberger A. and Haase R., Ber., 64, 2896, 1931.
141. Boersch H., Monatsh., 65, 331, 1935.

142. Cox A.P., Thomas C.F. and Sheridan J., Nature, 181, 1000, 1958.
143. Clusius K. and Lüthi U., Helv. Chim. Acta., 40, 445, 1957.
144. Crawford B.L., Fletcher W.H. and Ramsay D.A., J. Chem. Phys., 19, 406, 1951.
145. Fletcher W.H. and Garrett T.P., J. Chem. Phys., 25, 50, 1956.
146. Mills I.M. and Thompson H.W., Trans. Farad. Soc. 50, 1270, 1954.
147. Ramsay D.A., J. Chem. Phys., 17, 666, 1949.
148. Yates P., Shapiro B.L., Yoda N. and Fugger J., J. Am. Chem. Soc., 79, 5756, 1957.
149. Zollinger H., Azo and Diazo Chemistry, Aliphatic and Aromatic Compounds. Published by Interscience, New York, 1961.
150. Gutsche C.D., Organic Reactions, 8, 364, 1954.
151. Watrous R.M., Brit. J. Ind. Med., 4, 111, 1947.
152. Sax N.I., Dangerous Properties of Industrial Materials. Published by Reinhold, New York, 1957.
153. Meerwein H. and Bersin T., Ber., 62, 1006, 1929.
154. Meerwein H. and Hinz G., Ann., 484, 1, 1930.
155. Biltz H. and Paetzold H., Ber. 55, 1069, 1922.
156. Kuhn R. and Baer H.H., Ber., 86, 724, 1953.
157. Newman M.S. and Beal P., J. Am. Chem. Soc., 72, 5161, 1950.
158. Müller E. and Rundel W., Angew Chem., 70, 105, 1958.

159. Müller E., Huber-Emden H. and Rundel W., Ann., 623, 34, 1959.
160. Prix-Werke A.G., Hamburg. Ger. Pat. 1,051,272.
161. Huisgen R., Angew Chem., 67, 439, 1955.
162. Brönsted J.N., and Bell R.P., J. Am. Chem. Soc., 53, 2478, 1931.
163. Norris J.F. and Strain W.H., J. Am. Chem. Soc., 57, 187, 1935.
164. Roberts J.D., McElhill E.A. and Armstrong R., J. Am. Chem. Soc., 71, 2923, 1949.
165. Roberts J.D. and Moreland W.T., J. Am. Chem. Soc., 75, 3165, 1953.
166. Taft R.W. and Smith D.J., J. Am. Chem. Soc., 76, 305, 1954.
167. Bredig G. and Fraenkel W., Z. Elektrochem., 11, 525, 1905.
168. Bredig G. and Ripley P.F., Ber., 40, 4015, 1907.
169. Fraenkel W., Z. physik. Chem., 60, 202, 1907.
170. Roberts J.D., Watanabe W. and McMahon R.E., J. Am. Chem. Soc., 73, 760, 1951.
171. Brunauer S., Deming L.S., Deming W.S. and Teller E., J. Am. Chem. Soc., 62, 1723, 1940.
172. Brunauer S., Emmett P.H. and Teller E., J. Am. Chem. Soc., 60, 309, 1938.
173. Brunauer S., Physical Adsorption of Gases. Published by Oxford University Press, 1944. Page 149.

174. Gregg S.J., The Surface Chemistry of Solids, 2nd Edition. Published by Chapman and Hall Ltd., London, 1961.
175. Hirst W., Disc. Farad. Soc., 3, 100, 1948.
176. Cook M.A., J. Am. Chem. Soc., 70, 2925, 1948.
177. Halsey G., J. Chem. Phys., 16, 931, 1948.
178. Gregg S.J. and Jacobs J., Trans. Farad. Soc., 44, 574, 1948.
179. Emmett P.H., and Brunauer S., J. Amer. Chem. Soc., 59, 1553, 1937.
180. Livingston H.K., J. Colloid Sci., 4, 447, 1949.
181. McDermott and Lowton, Canad. J. Chem., 34, 769, 1956.
182. Bangham and Razouk, Proc. Roy. Soc. A, 166, 572, 1938.
183. Haines and McIntosh, J. Chem. Phys., 15, 28, 1947.
184. Amberg and McIntosh, Canad. J. Chem., 30, 1012, 1952.
185. Herzberg, Infra-red and Raman Spectra of Polyatomic Molecules, 2nd Edition. Published by Van Nostrand, N.Y., 1964.
186. Little L.H., Infra-red spectra of Adsorbed Species. Published by Academic Press, London, 1966.
187. Little L.H., Canad. J. Chem., 39, 42, 1961.
188. Sidorov, Zh. fiz. Khim., 30, 995, 1956.
189. Bragg W.L., Proc. Camb. Phil. Soc., 17, 43, 1913.
190. Bunn C.W., Chemical Crystallography, 2nd Edition. Published by Oxford University Press, 1961.

191. Hayek E. and Newesley H., Inorg. Syntheses, 2, 63, 1963.
192. Warrington, J. Chem. Soc., 19, 296, 1866.
193. Rowles S.L., The University of Birmingham, Dental School. Private communication, 1969.
194. Coughlan B., Imperial College. Private communication, 1968.
195. Speirs, The London Hospital Medical College. Private communication, 1968.
196. Arndt F., Org. Syntheses, Coll. Vol. 2, 461, 1943.
197. Gould and Vickers, J. Sci., Inst., 29, 85, 1952.
198. Harkins W.D. and Jura G., J. Am. Chem. Soc., 66, 1362, 1944.
199. Hackermann N. and Hall A.C., J. Phys. Chem., 62, 1212, 1958.
200. Vogel A.I., A Textbook of Quantitative Inorganic Analysis, 2nd Edition. Published by Longmans, London, 1951.
201. Perrin C.H., J. Ass. off. agric. Chem., 41, 758, 1958.
202. Buchner E. and Meisenheimer, Ber. 38, 624, 1905.
203. Henstock, J. Chem. Soc., 216, 1933.
204. Marshall E.K. and Acree S.F., Ber., 43B, 2323, 1910.
205. Holmes J.M., Davies D.H., Meath W.J. and Beebe R.A., Biochem., 3(12), 2019, 1964.
206. Beebe R.A., "Adhesive Restorative Dental Materials."