STUDIES ON PREPARATION AND SOME PHYSICO-CHEMICAL ASPECTS OF SOLID SOLUTIONS OF PHOSPHATE AND VANADATE APATITES OF LEAD

Abstract

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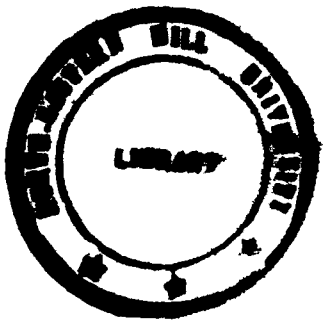
A THESIS
SUBMITTED IN FULFILMENT OF
THE REQUIREMENTS OF
THE DEGREE OF
DOCTOR OF PHILOSOPHY



To

THE NORTH-EASTERN HILL UNIVERSITY
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Calcium hydroxylapatite, $Ca_{10}(PO_4)_6(OH)_2$, the principal inorganic constituent of human bones and teeth, belongs to an isomorphous series of subatances known as apatites. It has been the subject of extensive investigations because of its biological significance and its remarkable ability to undergo a series of cationic and anionic exchange reactions, the criteria for such an exchange being the identity of charge and the proximity of ionic radii of the pairs of ions involved. Among such diverse exchange reactions a few have attained significance during the recent past consequent upon the toxicity of the elements involved, such an exchange being the mechanism for their incorporation into human skeletal system. Based on the contemporary importance given to the toxicity caused by lead and vanadium to the human system, studies on the replacement of calcium by lead (ionic radii 0.99 and 1.20 Å respectively) and of phosphorus by vanadium (Covalent radii 1.10 and 1.22 Å respectively) have been chosen for the present investigations. It is evident that a complete replacement of Ca^{2+} ions by Pb^{2+} ions leads to lead phosphate apatite, $Pb_{10}(PO_4)_6(OH)_2$, while that of PO_4^{3-} by VO_4^{3-} leads to lead vanadate apatite, $Pb_{10}(VO_4)_6(OH)_2$, both being isomorphs of calcium hydroxyl apatite. A partial replacement in either case leads to formation of solid solutions of the concerned end-members.

It has been established that inhalation of lead in the form of dust or fumes or its absorption through the skin leads to "lead poisoning" (Plumbism) which is, in general, an occupational disease. It is well known that lead salts are extensively used in petrol to improve its quality and in pottery and paints resulting in contamination leading thereby to a possibility of incorporation of this element into the human skeletal system. As in the case of lead the toxic effect of vanadium to human system has been confirmed. In addition, it could be proved that a few species coming under the marine organisms are also vulnerable to such a toxicity. It could be shown that the principal polluting sources of vanadium are its presence in certain varieties of steel as well as the industrial establishments involving the element and its salts as catalysts.

It could be unambiguously established that ions incorporated in the human skeletal system through exchange reactions on calcium hydroxylapatite of bones play a significant role in two principal bone processes, namely, calcification and resorption, the deposition and dissolution respectively of calcium hydroxylapatite at the interface of bone and body fluids. Consequently, any attempt in the direction of elimination or minimization of such a toxicity is associated with a study of the solubility of calcium hydroxylapatite as well as of the products of the exchange

reactions mentioned above under simulated biological conditions.

Prompted by such a consideration the present work which deals with the preparation, characterization and solubility equilibria of lead phosphate apatite, lead vanadate apatite and a series of eight of their solid solutions spread over the entire compositional range, was undertaken. Adopting coprecipitation of the end-members in aqueous media through a judicious modification of the existing methods, the samples were prepared at 37°C to simulate biological conditions.

Characterization of these samples was brought about through sophisticated instrumental techniques such as X-ray diffraction, electronmicroscopy, i.r. spectral studies and thermogravimetry in addition to the conventional chemical analyses. Vegard's law demands that the unit cell volume of a series of solid solutions varies linearly with the composition and offers a convenient method of scrutinizing their homogeneity. As is to be expected from the bigger size of vanadate ion, a replacement of phosphate ion by it brings about a dilation of the unit cell. A systematic linear dependence of the unit cell volumes with the proportion of vanadate ion replacing phosphate ion observed in the present

series of solid solutions confirmed their homogeneity. The electronmicrographs of a few representative samples revealed the hexagonal pattern of the crystals confirming the absence of extraneous phases and enabling approximate calculations of the specific surface areas and average dimensions of the individual crystals. The i.r. absorption spectra could confirm the identity of the samples. The predominant absorption peaks recorded in the traces of the samples were found to be due to the orthophosphate and orthovanadate ions. In addition, the absorption peaks due to carbonate and pyrophosphate ions, the two likely impurities, were found to be absent. The absence of carbonate ion eliminates the possibility of atmospheric interaction leading to the formation of carbonate apatite. Thermogravimetric analysis indicated that a temperature of 300°C chosen for driving out volatile impurities from the samples, did not inflict a chemical decomposition on them.

Studies on the solubility of the samples were undertaken at 37°C in order to investigate its dependence on the replacement of PO_4^{3-} ion by VO_4^{3-} ion on lead phosphate apatite. Since it was intended to determine the solubility product of each sample from data resulting from the chemical analyses of the saturated solution, a buffered dissolving medium was used to maintain constancy of the activity of OH^- ions

involved in such calculations. In order to investigate the reproducibility of the solubility products so determined, the studies in each case were extended to a few chosen p^H values, the range being restricted only from 2.0 to 2.7, since there was a marked fall in the solubility of all the samples at p^H value higher than 2.7. In addition, all such buffered dissolving media were maintained at a molarity of 0.165 with respect to sodium chloride to simulate biological conditions. By adopting such a medium of dissolution the complicated process of evaluating accurately the activity coefficients of polyvalent ions could be avoided by assuming all of them to be unity without foregoing accuracy. It is evident that such calculations make the solubility product, K_{sp}, and the ionic product, K_{ip}, synonymous.

Each one of the powdered samples was equilibrated with the chosen buffer combination as the medium of dissolution at a controlled rate of shaking using a constant temperature shaker-bath. The colloidal component of the solute present in its saturated solution due to its low solubility was separated by filtration at 37°C through a 1G4 sintered glass crucible before the solutions were analysed for the products of dissolution. A separate expdriment could prove the suitability of such crucibles for colloidal separation.

While phosphorus and vanadium were determined

colorimetrically, complexometry was adopted for the determination of lead, the attainable accuracy in all the cases being scrutinized by analysis of solutions of known compositions.

A scrutiny of attainment of saturation and the minimum period of equilibration required for the purpose were determined through dissolution Kinetics of a couple of representative samples. From among the concentrations of the products of dissolution, the measured total dissolved phosphorus was subdivided into the proportions of orthophosphoric acid and its three dissociation products, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} using the three dissociation constants of the acid and the equilibrium p^H of the system, the latter being required also for evaluating OH^- ion concentration needed for the calculation of solubility product.

There exists an ambiguity in the earlier literature regarding the solute phase likely to control the solubility of apatite systems since the dissolution involved is hydrolytic. That the apatites exhibit stoichiometric dissolution could not unambiguously be established by the earlier workers. In order to investigate this significant aspect of dissolution of apatites, the solubility data of the present investigations were subjected to calculations to establish which among the

possible phases exhibited a constancy for the activity product of its ions. It is evident that for the phosphate containing apatites such phases are the primary and secondary phosphates of the metal concerned in addition to the apatite. By analogy with a double salt, $Ca_2(HPO_4)(OH)_2$, a phase reported to control the solubility product of calcium hydroxylapatite by functioning as a surface coating, the ionic product of its lead counterpart, $Pb_2(HPO_4)(OH)_2$, was also calculated for the present system. Examination of the data on solubility of all the phases mentioned above reveals that the ionic product of apatite showed a constancy over the entire p^H range investigated and the calculated set of values were found to lie within the error limits. It is evident that the corresponding vanadate phases are relevant for lead vanadate apatite while the phases of both phosphate and vanadate are to be considered for the systems involving the solid solutions. Such calculations were done on the data of solubility of all these samples. That the apatite phase controlled the solubility was further supplemented by the fact that the g atom ratio, Pb/(P+V), of the saturated solutions of all the samples was in the proximity of the theoretical value (1.67) confirming unambiguously stoichiometric dissolution of apatites. An additional substantiation of this fact was that the $p^K ip$ values of the samples were found to be unaffected by the addition of common ions.

It could be established further that the solubility product of each sample of the series while remaining constant at all the p^H values investigated, decreased systematically with an increase in the extent of replacement of PO_4^{3-} by VO_4^{3} . An interpretation of these results could be provided by the concept of alterations in lattice and hydration energies of ionic crystals consequent upon isomorphous substitution.

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To

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SHILLONG-793001

JULY, 1984

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I certify that the thesis entitled "Studies on Preparation and some Physico-chemical Aspects of Solid Solutions of Phosphate and Vanadate Apatites of Lead" submitted by Mr. P.V. Ramana Rao for the degree of Doctor of Philosophy of the North-Eastern Hill University, Shillong, embodies the record of original investigation carried out by him under my supervision. He has been duly registered and the thesis presented is worthy of being considered for the Award of the Ph.D. Degree. This work has not been submitted for any Degree of any other University.

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PREFACE

Calcium hydroxylapatite, $Ca_{10}(PO_4)_6(OH)_2$, the principal inorganic constituent of human bones and teeth, belongs to a large family of isomorphous substances known as 'Apatites'. It is capable of undergoing several cationic and anionic substitutions without disrupting the crystal structure. Such substitutions are of significance both from biological and physico-chemical points of view and constitute the basis for formation of solid solutions among these isomorphs leading to the incorporation of several toxic ions into human skeletal system. Two among such incorporations are replacement of calcium by lead and of phosphate by vanadate, both the replacing elements being toxic. The present work was therefore intended to investigate the physico-chemical aspects of these substitutions.

A prerequisite for such a series of investigations was to arrive at an optimum set of experimental conditions to prepare samples of phosphate and vanadate apatites and a series of their solid solutions spread over the entire compositional range and to characterize them through sophisticated physico-chemical techniques. In spite of the fact that phosphate and vanadate apatites of lead were prepared by earlier investigators the availability of an identical set of experimental conditions for the preparation of both these samples has been lacking. It is evident that

such a set of conditions suitable for the end-members can be extended to the preparation of their solid solutions.

The physiology of bone and tooth is governed by calcification and resorption which are respectively the dissolution and deposition of calcium hydroxylapatite at the bone / body fluid and tooth / saliva interfaces. It is evident that any attempt in the direction of removal of the incorporated toxic ions is based on a knowledge of the solubility phenomena of the samples under simulated biological conditions. While the solubility of lead phosphate apatite has earlier been investigated that of lead vanadate apatite and its solid solutions with the former was not undertaken and therefore motivated the present investigations. In spite of the fact that studies on apatites are scattered over several disciplines, a physical chemist is considered to be better suited for investigating the aspects mentioned above providing thereby an additional justification for undertaking the present studies.

The thesis has been divided into three Sections. Section 1 has been an attempt at a judicious compilation of information about calcium hydroxylapatite based on the earlier investigations carried out in diverse branches of research, the physico-chemical aspects being naturally given more emphasis. The experimental work carried out by the author has been included in Sections 2 and 3. Each

Section has been presented in the conventional pattern of a research publication. The preparation of lead phosphate apatite, lead vanadate apatite and their solid solutions along with the confirmation of their homogeneity through chemical, X-ray, electronmicrographic, infrared and thermogravimetric analyses have been included in Section 2. Section 3 is constituted by the details of investigations on the solubility equilibria of samples.

A consolidated list of books and journals consulted has been given at the end of the thesis to facilitate easy reference. References pertaining to each Section have not been separately listed to avoid duplication. For such of the references, the originals of which could not be consulted due to non-availability, the particulars about their 'Chemical Abstracts' have also been given. The journals have been abbreviated based on the pattern followed in 'Chemical Titles' published by the American Chemical Society.

I express my gratitude and indebtedness to Dr.T.S.B. Narasaraju, M.Sc., Ph.D. (Hamburg), Professor of Chemistry and Head of the Department of Chemistry, North-Eastern Hill University, Shillong, for suggesting the problem and for guidance. I am grateful to Dr. Y.S.T. Rao, Reader, Department of Physics, North-Eastern Hill University,

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LIST OF ABBREVIATIONS

CaHA : $Ca_{10}(PO_4)_6(OH)_2$, Calcium Hydroxylapatite
or
Calcium Phosphate apatite

LPA : $Pb_{10}(PO_4)_6(OH)_2$, Lead phosphate apatite

LVA : $Pb_{10}(VO_4)_6(OH)_2$, Lead vanadate apatite

LPVA: $Pb_{10}(PO_4)_x(VO_4)_{6-x}(OH)_2$ Solid solution of Lead phosphate apatite and Lead vanadate apatite. $(6 > x > 0)$

K_{ip} : Ionic product of samples in their saturated solutions.

K_{sp} : Activity solubility product.

N : Avogadro's Number (6.023×10^{23}).

pK_{ip} : $- \log K_{ip}$

pK_{sp} : $- \log K_{sp}$

pK_w : $pH + pOH$

Slurry density : Weight of solute per unit volume of the medium of dissolution (g/ml).

V_{uc} : Unit cell volume ($\AA^3$).

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SECTION I

GENERAL INTRODUCTION

GENERAL INTRODUCTION

1.1 Classification of Apatites

Calcium and phosphorus exist in human and animal bones and teeth[1]. They also occur in nature principally as fluorapatite, $Ca_{10}(PO_4)_6F_2$, which is a member of an isomorphous series of minerals named by Werner[2] as "Apatites" ("Deceivers" in Greek). This name is justified because of the difficulties involved in their identification due to their non-stoichiometric existence. Some of the important members of the series[3-11] and their lattice constants are given in Table 1-1.

Table 1-1

Name, molecular formula and lattice constants of a few principal members of Apatite series:

S. No.	Name	Molecular formula	Lattice constants (Å) a	c
1	Barium hydroxyl-apatite	$Ba_{10}(PO_4)_6(OH)_2$	10.19	7.70
2	Cadmium " "	$Cd_{10}(PO_4)_6(OH)_2$	9.01	6.61
3	Calcium " "	$Ca_{10}(PO_4)_6(OH)_2$	9.42	6.88
4	Chlorapatite	$Ca_{10}(PO_4)_6\ Cl_2$	9.63	6.78
5	Fermorite	$Ca_{10}(AsO_4)_6\ F_2$	9.75	6.92
6	Fluorapatite	$Ca_{10}(PO_4)_6\ F_2$	9.37	6.88
7	Hydroxyl-vanadinite	$Ca_{10}(VO_4)_6\ (OH)_2$	9.82	6.98
8	Lead hydroxyl-apatite	$Pb_{10}(PO_4)_6(OH)_2$	9.90	7.29
9	Mimetite*	$Pb_{10}(AsO_4)_6\ Cl_2$	10.36	7.52
10	Pyromorphite*	$Pb_{10}(PO_4)_6\ Cl_2$	9.95	7.32
11	Strontium hydroxylapatite	$Sr_{10}(PO_4)_6(OH)_2$	9.76	7.28
12	Vanadinite	$Pb_{10}(VO_4)_6\ Cl_2$	10.47	7.43
13	Cadmium Chlorapatite	$Cd_{10}(PO_4)_6\ Cl_2$	9.62	6.49
14	Calcium arsenic chlorapatite	$Ca_{10}(AsO_4)_6\ Cl_2$	10.07	7.26
15	Magnesium Apatite	$Mg_{10}(PO_4)_6(OH)_2$	9.30	6.89

* Also reported as members of Pyromorphite series.

Each member of the series can undergo a series of cationic and anionic isomorphous substitutions leading to the formation of the corresponding isomorphs. A biologically important example of such a substitution is provided by the replacement of F^- by OH^- on fluorapatite resulting in the formation of hydroxylapatite, $Ca_{10}(PO_4)_6(OH)_2$. This compound is shown[1,12] to be the principal inorganic constituent of both human and animal bones and teeth and has, therefore, been the subject of extensive physico-chemical and biological investigations. Consequently a knowledge of its location and its role played in bones and teeth described below, is a pre requisite for undertaking a meaningful series of investigations on it.

1.2 Location and Role Played in Bones and Teeth:

Bone is a dense, hard and highly specialised tissue consisting of organic and inorganic constituents. The former, amounting to about 30 per cent by weight, is made up of collagen, a cement substance and a cellular component. Collagen is a complex interwoven net-work of a fibrous protein and constitutes an extra cellular matrix of bone, while the cement substance consists of a few hexoses linked with the protein. The cellular component, in turn, consists of cells designated as osteoblasts, osteoclasts and osteocytes

which are concerned respectively with dissolution, deposition and nourishment of bone. The inorganic part of the bone consists of an amorphous and a crystalline phase, the former being tricalcium phosphate while the latter is hydroxylapatite. The amorphous phase is predominant[13] in younger bone and gets partially transformed into the crystalline phase with age. About 40 per cent by weight of an adult human bone was found to be hydroxylapatite the crystals of which are oriented in the collagen fibres with their long axes parallel to the fibre direction. This view has been confirmed recently by Ascenzi.A, Bonucci.E. et.al[14] through x-ray diffraction studies contrary to an earlier finding[13] showing their presence in cement. Intimate morphological and chemical relationships exist between collagen and these crystals, the former being a nucleating agent for the precipitation of the latter.[15] The low angle X-ray scattering studies by Engström and Finean[16] suggested the average length and breadth of these crystals to be about 200 and 65 Å respectively. In addition to the constituting elements of hydroxylapatite, sodium, Potassium, magnesium, chloride, carbonate, fluoride and trace amounts of iron, copper, manganese and zinc are the usual inorganic ions present in the above and were shown[17] to be located in the hydration layer at the bone-body fluid interface. In addition, bone contains about 20 per cent of water by weight[13], present mostly in the organic matrix and in traces in hydroxylapatite crystals.

Bone plays a significant role in the metabolism and storage of calcium, phosphorus and other inorganic ions present in the human system. In addition, its mineral phase was shown[13] to be the seat of action for the removal of several toxic ions such as lead, cadmium, barium and arsenic from the body fluids. The strength and rigidity of all higher forms of life can be attributed to the individual bones and their joints which together constitute the skeletal system.

Tooth consists of an outer part known as crown, a neck which is surrounded by gum and one or more roots or fangs fitting into the sockets of the Jaw-bone. The main dental tissues are enamel, dentine and cementum. The crown is coated by enamel which rests on dentine and the latter occupies the bulk portion of tooth. Cementum helps in the fixation of tooth in the socket of the jaw-bone. As in the case of bone, the dental tissues are made up of inorganic and organic constituents. Hydroxylapatite admixed principally with ions such as magnesium and carbonate was shown[1] to be the inorganic constituent. The weight per cents. of it in enamel, dentine and cementum were found to be about 95, 75 and 35 respectively. The crystals of hydroxylapatite of bone, dentine and cementum were found to be similar in size according to their morphological similarities, while those of enamel were found to be bigger and arranged at right angles to the tooth surface. Recent X-ray diffraction studies[18] on powdered enamel samples

indicated that the formation of crystals of hydroxylapatite of enamel located on human deciduous teeth was less perfect than that of the permanent teeth. Unlike other calcified tissues which are in equilibrium with the internal fluids, enamel equilibrates with saliva and is thus a seat of action of locally administered prophylactic agents of dental caries,[19,20] a tooth decay caused by acidogenic bacteria.

1.3 Stability ranges of calcium salts of ortho phosphoric acid - Cao-P_2O_5- H_2O Phase Diagram

Studies on (i) inorganic constituents of human bones,[21] (ii) utilisation of phosphatic minerals by plant kingdom[22] and (iii) geological aspects[23] of several naturally occurring phosphates contributed to our present knowledge of the phosphates of calcium. Preliminary studies intended to establish[24-26] the conditions of existence of phosphates of calcium were restricted to the solid phase reactions of the binary system, Cao-P_2O_5. It was not, however, recognised that an imperceptible inclusion of traces of water elevates this binary system to a ternary one, Cao-P_2O_5-H_2O. Earlier investigations on this ternary system were restricted exclusively to chemical analysis, the results being unreliable due to absence of a proof of homogeneity of the phases. The amorphous nature of the

constituent phases further complicated their identification. These considerations necessitated the application of phase rule to the system and exposed the limitations of the exclusive use of chemical analysis[27] for the purpose. It is well known that important prerequisites for the validity of phase rule are the attainment of equilibrium and the existence of homogeneous phases separated by sharp boundaries. Fulfilment of these conditions in the Cao-P_2O_5-H_2O system were found to be complicated due to the slow attainment of equilibrium[28,29] and the amorphous nature of the precipitates formed.

A criterion of attainment of equilibrium in a precipitation reaction is the availability of identical results both from the sides of supersaturation and undersaturation. In addition, solid phases are characterised by a high degree of reactivity due to their large surface areas. Further, they exist as colloidal suspensions causing additional complication in their filtration. The preliminary experimental data on the conditions of existence of calcium phosphates became repetitive, disorganised and contradictory since the factors mentioned above were not given proper considerations. Cameron[30] and Bassett[31] independently carried out investigations on the applicability of Phase Rule to Cao-P_2O_5- H_2O system and the results obtained at 25°C are incorporated in the phase

diagram[32] given in Fig.1.1 The abscissa and the ordinate of a given point on the phase diagram represent the weight per cents. of phosphorus pentoxide and calcium oxide respectively, the rest being water. The possible solid phases of the system are:-

(i) anhydrous monocalcium phosphate, $Ca(H_2PO_4)_2$

(ii) monocalcium phosphate monohydrate, $Ca(H_2PO_4)_2 \cdot H_2O$

(iii) anhydrous dicalcium phosphate, $CaHPO_4$

(iv) dicalcium phosphate dihydrate, $CaHPO_4 \cdot 2H_2O$ and

(v) a crystalline precipitate of variable composition with an X-ray diffraction pattern similar to that of an apatite.

All these phases could be identified through their distinct X-ray diffraction patterns supplemented by their chemical analyses. The blank regions of the phase diagram represent the solution phase while the solid phases are indicated by areas marked by convergent lines. Anhydrous monocalcium phosphate and its monohydrate exist as well-defined crystals in acidic regions of the phase diagram which correspond evidently to the compositional ranges having a high proportion of phosphorus pentoxide; they can thus be obtained[33] by cooling solutions of such compositions. The acidic region is also found to be favourable for the formation of dicalcium phosphate.[33] The aqueous acidic

Fig. 1.1 Phase Diagram of $CaO-P_2O_5-H_2O$ System at 25^oC.

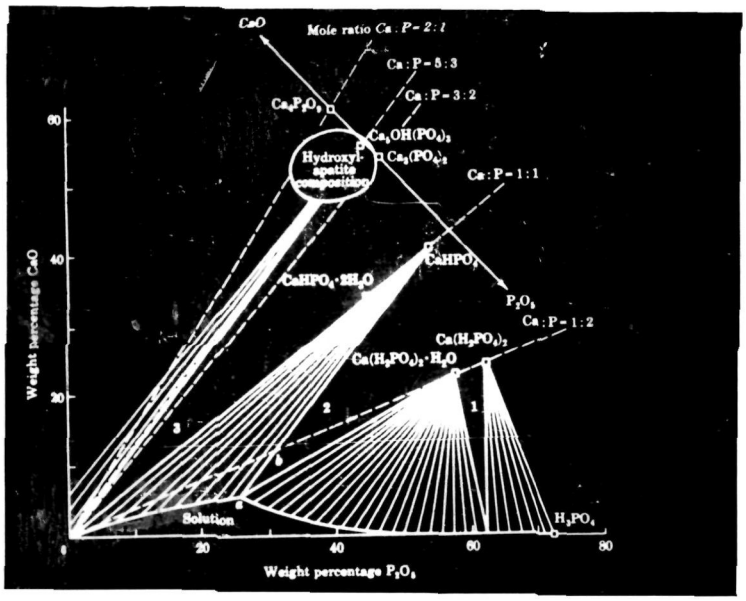

CaO
Mole ratio Ca : P = 2 : 1
Ca : P = 5 : 3
Ca : P = 3 : 2
Ca : P = 1 : 1
Ca : P = 1 : 2
Hydroxyl-apatite composition
CaHPO4·2H2O
CaHPO4
P2O5
Ca(H2PO4)2
Ca(H2PO4)2·H2O
H3PO4
Solution
1
2
3
Weight Percentage CaO
Weight percentage P2O5
0
20
40
60
80

FIG. 1.1

solutions are to be heated to an optimum temperature for the precipitation of dicalcium phosphate as it follows a retrograde solubility. Dicalcium phosphate dihydrate exists over a limited range of experimental conditions making its isolation difficult. Since a crystalline precipitate of variable composition exhibiting the X-ray diffraction pattern of naturally occurring apatites constitutes one of the phases of the diagram the region of its existence is indicated by an elliptical area. This phase is given the formula, $Ca_{10}(PO_4)_6(OH)_2$, and represented in Fig. 1-1 as $Ca_5(PO_4)_3OH$, neglecting its variable composition and water content.

Most of the investigations done on the calcium phosphates deal with the hydroxylapatite phase which is characterised by a variable composition and constitutes phosphates of calcium having a g atom ratio[21] ranging from 3/2 to 4/2; the limiting ratios correspond respectively to tricalcium phosphate (TCP), $Ca_3(PO_4)_2$, and tetracalcium phosphate, $Ca_3(PO_4)_2.CaO$, as shown in the phase diagram. It is evident from the diagram that in the alkaline region which is characterised by a higher proportion of calcium oxide, the only solid phase capable of existence is that of hydroxylapatite. The phases stable in the acidic region get transformed into hydroxylapatite for compositional

ranges indicated by an upward arrow in the diagram. Some of these conclusions could be confirmed by Seuter[34] on the basis of studies on this phase diagram at temperatures higher than 800°C.

The existence of an additional solid phase called octacalcium phosphate (OCP), $Ca_3(PO_4)_2 \cdot CaHPO_4$, in the neutral region of the ternary system was suggested by Hayek et.al.[35] OCP could be demarcated from hydroxylapatite through its X-ray diffraction pattern and electron micrographs. However, OCP has not been indicated in the phase diagram as a separate phase. Formation of OCP could be substantiated by Chaikina[36] et.al; on the basis of recent studies on this phase diagram at 25°C.

1.4 Preparative Techniques Based on Conditions of Formation

It was shown in the phase diagram of $CaO-P_2O_5-H_2O$ system that for a wide range of compositions calcium phosphates can be shown to be hydroxylapatites based on X-ray diffraction patterns which are similar to those of naturally occurring apatites. Since such a phase is shown to be stable over a wide area in the phase diagram, the corresponding g atom ratio, Ca/P was found to range from 1.5 to 2.0. These results facilitate the establishment

of experimental parameters optimum for the formation of hydroxylapatite. It is evident[37] that hydroxylapatite is the stablest of the different calcium phosphates in weakly acidic, neutral and basic media. Consequently, hydrolysis of other calcium phosphates leads to the formation of hydroxylapatite.

Basset[28] reported the precipitation of hydroxylapatite from solutions of calcium oxide and phosphorus pentoxide of appropriate concentrations which is in accordance with the suggestion offered by the phase diagram. Lorah et.al.[38] investigated the time-dependence of g atom ratio, Ca/P, of the compounds, calcium monophosphate, $Ca(H_2PO_4)_2$, calcium diphosphate, $CaHPO_4$, calcium pyrophosphate, $Ca_2P_2O_7$, and TCP, $Ca_3(PO_4)_2$, when treated with sodium hydroxide solution. They found that the ratio attained constancy equal to that of naturally occurring apatite within about 50 hours substantiating the statement that hydrolysis of calcium phosphates leads to the formation of hydroxylapatite. Schleede et.al.[26] obtained similar results by refluxing TCP with a dilute solution of Potassium hydroxide for about 7 hours.

Isolation of hydroxylapatite from bones and teeth is found to be complicated, the techniques adopted inflicting a change on the sample. Synthetic samples which

can be prepared with a high degree of purity are better suited for purposes of physicochemical investigations. A survey of different methods of formation of hydroxylapatite indicates that very few of them are suited for its preparation. Synthesis of apatites can be brought about by wet, dry and hydrothermal methods.

1.4.1 Wet Methods

Among the available methods those based on precipitation from aqueous solutions are the most suited for preparation of appreciable quantities of apatites. A method suggested by Hayek and Stadlmann[39] is widely used for the purpose because of the simplicity of experimental operations, the accompanying high yield and purity of the samples. This method is based on the following equation:-

$$10Ca(NO_3)_2 + 6(NH_4)_2HPO_4 + 8NH_4OH = Ca_{10}(PO_4)_6(OH)_2 + 6\ H_2O + 20\ NH_4NO_3 \quad \ldots\ldots\ (1\text{-}1).$$

1600 ml of a solution containing 79 g of diammonium hydrogen phosphate maintained at pH greater than 12 by the addition of ammonium hydroxide were dropped under constant stirring into 1200 ml of a solution containing 230 g of calcium nitrate, $Ca(NO_3)_2.4H_2O$, also maintained

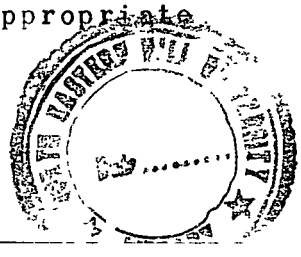
like-wise at the same pH. The amounts of the reactants taken were intended to give an yield of about 100 g of the sample on the basis of the above equation. Based on the dissociation[40-42] of phosphoric acid, it can be shown that only the orthophosphate ions are predominant at the pH maintained and thus likely complications due to co-precipitation of acid phosphates can be avoided. The accompanying volatile ammonium salts were sublimed off by heating the filtered product to about 250°C. Introducing minor alterations O' Shea et.al.[43] made use of this method to prepare samples of hydroxylapatite desired for X-ray diffraction and spectral studies. With appropriate modifications, this method could be extended to the preparation of a few more isomorphs of hydroxyl-apatite[44], the principal modification being the complexing[45] the metal ions with appropriate ligands. This method was subsequently modified by Collin[46] and Narasaraju[44], important among the modifications being the replacement of ammonium hydroxide by ethylene-diamine. The consumption of a large volume of ammonium hydroxide to attain a high alkalinity desired for the precipitation as well as its unpleasant smell may thus be avoided. A mention may be made of another wet method proposed by Rathje[37,47] known as "acidimetric precipitation" which is based on the following

equation:-

$$10Ca(NO_3)_2 + 6KH_2PO_4 + 14NaOH = Ca_{10}(PO_4)_6(OH)_2 + 6\ KNO_3 + 14NaNO_3 + 12H_2O \quad \ldots\ldots(1\text{-}2).$$

Convenient volumes of solutions of calcium nitrate and potassium dihydrogen phosphate containing the reactants in the proportions suggested by the above equation were simultaneously dropped into boiling water. The medium was maintained pink to phenolphthalein by the addition of a solution of sodium hydroxide. By a judicious selection of appropriate dilutions and rates of mixing of the solutions, crystals upto about 50 μ in length could be obtained.

By another wet method hydroxylapatite of high order of purity could be obtained by Arnold[48] involving a simultaneous addition of ammoniacal solutions of calcium acetate and of ammonium phosphate to about 10 litres of a mechanically stirred ammonium acetate solution also maintained alkaline. These methods which involve the precipitation of hydroxylapatite at high dilutions have low yields and hence are unsuitable for a rapid preparation of appreciable quantities of the sample. Kani et.al.[49] could prepare samples of hydroxylapatite similar to human dental enamel in crystallinity and g atom ratio, Ca/P, through appropriate modification of the above methods.



Narasaraju and Rai[50] obtained hydroxylapatites of phosphorus and arsenate and a series of their solid solutions over the entire compositional range by precipitation from aqueous media at 37°C introducing appropriate modifications of the method suggested by Hayek and Stadlemann.[37] During the recent past several investigators[51,52] adopted the wet methods mentioned above with minor alterations to prepare samples of hydroxylapatites intended for specific purposes. An interesting recent wet method suggested by Mayer et.al.[53] was based on the use of a reaction between solid calcium sulphate and highly alkaline solutions of sodium phosphate. This method could be extended[54] recently for the preparation of calcium vanadateapatite and of its solid solutions with hydroxyl-apatite.

1.4.2 Dry Methods

It is an established fact that an intimate heterogeneous mixture of appropriate solid ingredients when heated to an optimum temperature can lead to the formation of a desired lattice through solid state diffusion of the constituent ions. Trömel[55,56] investigated the optimum conditions for the formation of hydroxylapatite through a solid state reaction between TCP and tetracalcium phosphate, $Ca_3(PO_4)_2CaO$, or calcium oxide solid mixtures of

these ingredients in appropriate compositions with a g atom ratio, Ca/P, equal to 5/3 gave hydroxylapatite on heating for a few hours at 1050°C in a current of moist air as represented by the following equation:-

$$2Ca_3(PO_4)_2 + Ca_4P_2O_9 + H_2O = Ca_{10}(PO_4)_6(OH)_2 \quad \ldots\ldots (1\text{-}3)$$

or

$$3Ca_3(PO_4)_2 + CaO + H_2O = Ca_{10}(PO_4)_6(OH)_2 \quad \ldots\ldots (1\text{-}4)$$

Narasaraju et.al.[57] confirmed the utility of this method for preparing samples of hydroxylapatite of a high order of purity as investigated through X-ray, i.r., electron microscopic and chemical analyses. In addition, fusion of a sample of dicalcium phosphate, $CaHPO_4$, and calcium carbonate or alternatively heating of a sample of finely divided naturally occurring fluorapatite[58] at about 1400°C under a stream of moist air resulted in the formation of hydroxylapatite:-

$$12\ CaHPO_4 + 8\ CaCO_3 = 2\ Ca_{10}(PO_4)_6(OH)_2 + 8CO_2 + 4H_2O \ldots (1\text{-}5)$$

$$Ca_{10}(PO_4)_6F_2 + 2H_2O = Ca_{10}(PO_4)_6(OH)_2 + 2HF \quad \ldots\ldots (1\text{-}6)$$

An extension of the above methods to prepare chlorapatite and a series of its solid solutions with hydroxylapatite was brought about by Narasaraju and Rao[59] as shown below:-

$$3Ca_3(PO_4)_2 + 3CaCl_2 \xrightarrow{770\text{-}1040^{\circ}C} 3Ca_3(PO_4)_2 \cdot CaCl_2$$

$$\longrightarrow \underset{\text{spodiosite}}{Ca_{10}(PO_4)_6Cl_2} + 2CaCl_2 \qquad .....(1\text{-}7).$$

$$2Ca_{10}(PO_4)_6(OH)_2 + n\,CaCl_2 \longrightarrow 2Ca_{10}(PO_4)_6(OH_{2-n}, Cl_n) +$$

$$+ nCa(OH)_2 ..... \quad (1\text{-}8)$$

where n ranges from 0 to 2.

$$Ca(OH)_2 \longrightarrow CaO + H_2O \text{ (Vapour)} ..... \quad (1\text{-}9)$$

1.4.3 Hydrothermal Methods

Hydrothermal methods[60], as the name implies, deal with the application of high temperatures to aqueous solutions to facilitate the precipitation of crystals of dimensions bigger than those attainable using ordinary wet methods. Since an aqueous precipitating medium at atmospheric pressure has its boiling point as the upper limiting temperature, heating under high pressure enables this limit to be exceeded. In an autoclave the desired high pressure is produced by the vapour of the solvent of the precipitating medium since the system is subjected to a high temperature in a sealed enclosure. The principal advantage of such methods has been to enhance considerably the crystallinity and purity of the product. Such sets of results were achieved by Hayek et.al.[61] and by Perloff and Posner[62] as substantiated by formation of Homogeneous

crystals of about 0.1 mm in length in the form of hexagonal prisms. For this purpose 2 g of precipitated hydroxylapatite were heated at 380°C in an autoclave for 24 hours with 15 ml of 2M sodium hydroxide solution. The X-ray diffraction pattern of the sample was characterised by sharp peaks as expected from its crystal dimensions. Young and Sudarsanan[63] adopted a similar method to prepare a sample of strontium hydroxylapatite for crystallographic studies. Perloff and Posner[62] obtained hydroxylapatite by the hydrolysis of dicalcium phosphate and the probable reactions involved are the following:-

$$10CaHPO_4 + 2H_2O = Ca_{10}(PO_4)_6(OH)_2 + 4H^+ + 4H_2PO_4^- \quad \ldots\ldots(1\text{-}10)$$

$$14CaHPO_4 + 2H_2O = Ca_{10}(PO_4)_6(OH)_2 + 4Ca^{2+} + 8H_2PO_4^- \quad \ldots(1\text{-}11)$$

This process was brought about by heating 0.1g of dicalcium phosphate with 10 ml of water at 300°C for 10 days in a platinum-lined hydrothermal bomb and the product was found to be in the form of prismatic crystals.

Another suitable method for the preparation of single crystals of hydroxylapatite for purposes of X-ray, neutron diffraction and thermodynamic investigations was suggested by Elliot and Young[64]. A crystal sphere of 0.1 mm in diameter of synthetic chlorapatite when heated electrically on a piece of platinum foil at about 1300°C under steam at

atmospheric pressure for 2 weeks formed a single crystal of hydroxylapatite of a high order of purity. A further extension of hydrothermal methods for preparation of hydroxylapatite was brought about independently by Aoki and Hideki[65] and Kazov et.al.[66]

1.5 Chemical Analysis

Quantitative separation of calcium and phosphate, which is a prerequisite for an accurate chemical analysis of hydroxylapatite needs special analytical procedures, the details of which have been worked out by Washburn and Shear[67].

Gravimetric[67], complexometric[68] and spectrophotometric[69] techniques are usually employed for the accompanying determinations of these separated ions. Applications of atomic absorption spectroscopy to determine the metal ion concentration in apatites without a quantitative separation was brought about by Hivo et.al.[70]

1.6 Structural Aspects

That animal bones and teeth contain hydroxylapatite as an ingredient was proved[71] by the identity of X-ray diffraction patterns of the former with those of the naturally occurring hydroxylapatites as shown in Fig. 1-2(a). In addition,

Fig. 1.2 (a) X-ray Diffraction Patterns of

(i) Crystalline Synthetic Hydroxylapatite

(ii) Amorphous Synthetic Hydroxylapatite

(iii) Hydroxylapatite Obtained from Bone

1.2 (b) A Representative Debye-Scherrer Powder Pattern of Crystalline Synthetic Hydroxylapatite.

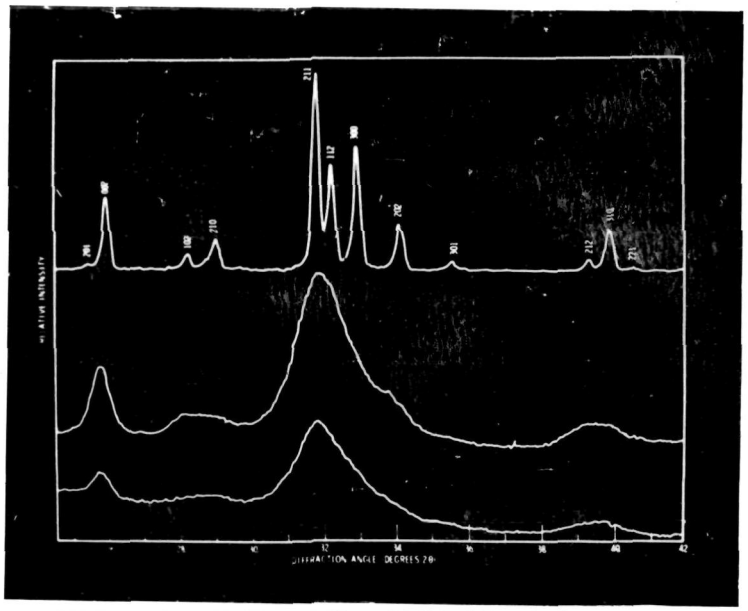


FIG. 1.2 (a)

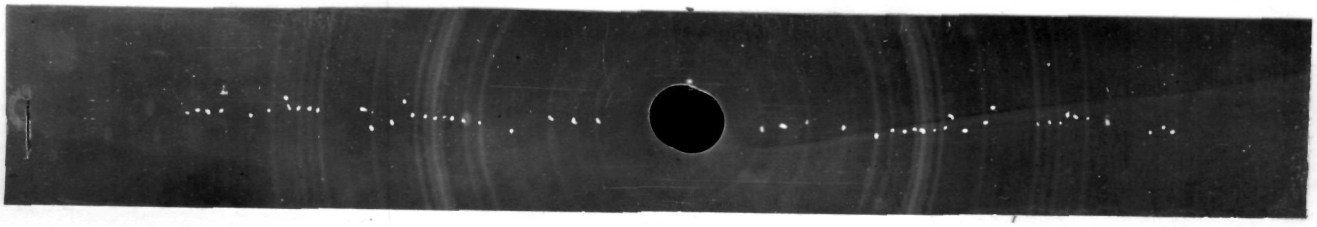


FIG. 1.2 (b)

a representative Debye-Scherrer powder pattern of synthetic hydroxylapatite is given in Fig. 1-2(b), since it serves as a reliable means of characterizing the synthetic samples.

Hydroxylapatites, both of biological and synthetic origin, crystallise in hexagonal $P6_3/m$ space group with lattice constants, 'a' and 'c', equal to 9.42 Å and 6.88 Å respectively. Nary-Szabo[72] and Mehmel[73] studied independently the details of the crystal structure of apatites and their findings were subsequently confirmed by Hendricks et.al.[24] Later Beevers and Mc Intyre[74] modified the structure proposed earlier and a few more refinements were subsequently made by Posner et.al.[75]

The ions, Ca^{2+}, PO_4^{3-} and OH^- (also sometimes referred to as the corresponding atoms or group of atoms) constitute the lattice of hydroxylapatite, their spacing[13] in the unit cell being indicated in Fig. 1-3. The ions are distributed in two planes, one over the other, such that each half is a mirror image of the other. It is evident that the whole volume of the unit cell is closely packed with the constituent ions and only for purposes of clarification of their relative positions, they are represented wide apart from one another in the figure. Out of a total of fourteen calcium ions, six are located within the unit cell and thus belong to it entirely and the remaining eight peripheral

Fig. 1.3 The Unit Cell Perspective of Hydroxylapatite.

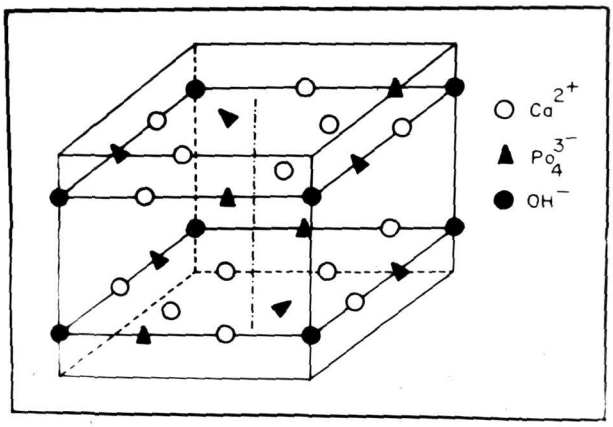


FIG. 1.3

ions are shared by adjacent unit cells such that there is an allocation of four per each. Similarly, it can be shown that out of ten phosphate groups, two situated inside and eight at the periphery, only six belong to each unit cell, these being the two situated inside and the four out of the eight peripheral ions. Likewise two out of eight hydroxyl groups represented in the figure belong to the unit cell. The number of ions present per unit cell of hydroxylapatite can thus be correlated with its molecular formula accounting thereby for the basic chemical repeat unit in the three dimensional symmetry pattern.

Fig. 1-4(A) and (B) represent cross-sections of hydroxylapatite lattice parallel to the c-axis and provide a further clarification[24] of the relative lattice-positions of the atoms. It can be shown from the figure that O-Ca-O chains exist running parallel to the c-axis. The chains are joined by phosphorus atoms constituting the inner lining of an elongated cavity which runs parallel to the c-axis and accommodates the F^-/OH^- ions. It is evident that depending upon ionic size and charge, other ions can replace F^- ions. In addition, every phosphorus atom is surrounded by four oxygen atoms forming a tetrahedron. The existence of cavities in the crystal structure accounts for the porosity and hence the surface activity of apatites. X-ray line-broadening experiments[14] using low angle scattering revealed

Fig. 1.4(a) A Cross-Section of the Apatite Lattice Parallel to the c-axis.

Fig. 1.4(b) Apatite Lattice Viewed from the Plane 001 as Reported by Beevers and Mc Intyre.

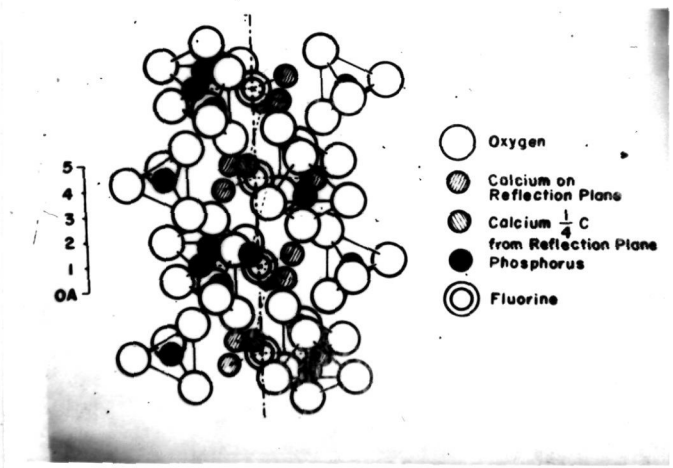


FIG. 1.4 (a)

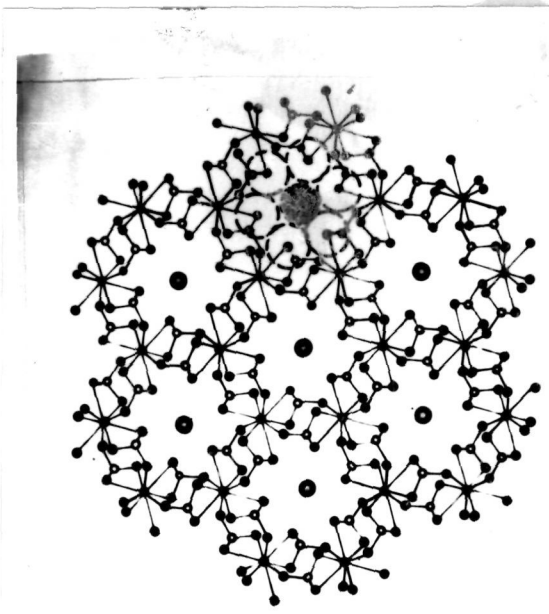


FIG. 1.4 (b)

the apatites to be thin tabular hexagons elongated in the direction of the c-axis.

As mentioned earlier, Posner et.al.[75] suggested a refinement of the crystal structure of hydroxylapatite based on three dimensional X-ray diffraction studies on single-crystals. In addition, determination of the bond-lengths and the atomic positions was made with an accuracy higher than that attained earlier. It was shown that the phosphate-tetrahedra have P-O distances shorter than those reported earlier. Further, the calcium atoms situated around the hexagonal screw-axis were shown to be co-ordinated to the hydroxyl ions and oxygen atoms of the phosphate-tetrahedra. The calcium atoms among themselves were found to constitute triangles, one over the other, in the direction of the c-axis. On the basis of these refinements, the arrangement of the constituent atoms of hydroxylapatite as projected upon the basal plane of its structure is shown in Fig. 1-5.

Kay et.al.[76] used neutron and X-ray diffraction techniques to determine the orientation of hydroxyl groups in the crystal structure of hydroxylapatite. Their studies revealed that the hydroxylgroups occur in columns parallel to the c-axis as reported by earlier workers[72,74,75] and that these columns pass through the centres of the calcium triangles. The x, y and z co-ordinates of the constituents

Fig. 1.5 Arrangement of the Constituent Atoms of Hydroxylapatite as Projected upon the Basal Plane of its Structure.(The Number in each circle represents the c-axis parameter perpendicular to the basal plane).

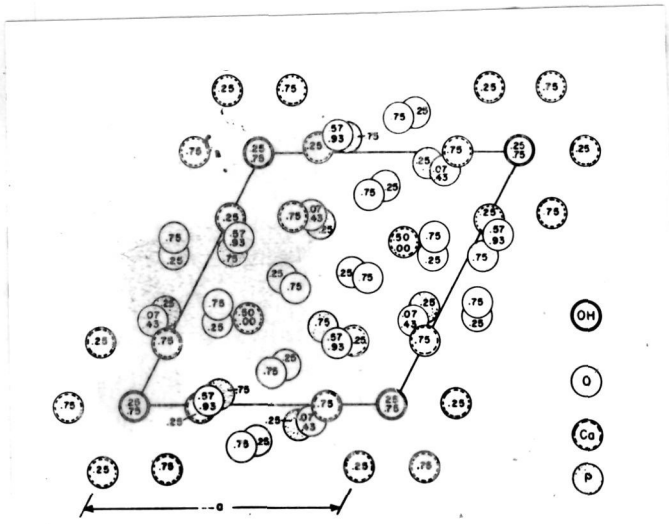


FIG. 1.5

of the hydroxylapatite lattice are given in Table 1-2. On the basis of their relative positions in the unit cell of hydroxylapatite, the calcium and oxygen atoms are designated through the subscripts given to their symbols.

Table 1-2.

Listing of Position-Parameters for the Constituent Atoms of Hydroxylapatite.[76]

Atom	No. of atoms per unit cell	Position Parameters		
		x	y	z
Ca_i	4	0.333	0.667	0.001
Ca_{ii}	6	0.246	0.993	0.250
P	6	0.400	0.369	0.250
O_i	6	0.329	0.484	0.250
O_{ii}	6	0.589	0.466	0.250
O_{iii}	12	0.348	0.259	0.073
OH	2	0.000	0.000	0.250

Young and his co-workers[77-80] carried out extensive work on the crystal structure of apatites during the recent past, the samples used being obtained exclusively by thermal methods. As mentioned earlier, apatites are normally expected

to be hexagonal belonging to the space group $P6_3/m$. They could establish that a synthetic sample of chlorapatite was pseudohexagonal belonging to the monoclinic space group, $P2_1/b$ with 'a' and 'c' being respectively 9.628 Å and 6.764 Å . It is evident that for a monoclinic system lattice parameter 'b' is equal to 2a. While the monoclinic and hexagonal structures are very similar, the former is characterised by an ordered arrangement of the Cl^- ions in chlorapatite resulting in the transformation of the mirror plane of the hexagonal structure to a glide plane in the monoclinic structure with an accompanying doubling of one of the cell dimensions. Subsequent structural analysis of single-crystals of hydroxylapatite by these workers confirmed the analogy between this compound and chlorapatite regarding the monoclinic structure, the corresponding lattice parameters being 9.4214 Å and 6.8814 Å . The single-crystal of hydroxylapatite used for these investigations was obtained by the conversion of that of chlorapatite by heating in steam at 1200°C. However, the significance of the monoclinic space group for biological considerations is yet to be proved. In addition, the optimum range of temperatures required for the phase transformation from monoclinic to hexagonal form is yet to be investigated to know whether the

monoclinic form exists under in vivo conditions. It will be of interest to investigate the role of trace-impurities like F^-, Cl^-, CO_3^{2-} and Mg^{2+} ions in bringing about such a phase transformation. Recently Elliot, Bonel and Trömbe[81] substantiated the findings of Young by reporting that a sample, $Ca_{10}(PO_4)_6\ Co_3$, termed as carbonateapatite, exhibits a pseudohexagonal symmetry with monoclinic space group, P_b, with lattice parameters 'a' and 'c' being equal 9.557 Å and 6.872 Å and b approximately equal to 2a.

For purposes of characterisation of samples of synthetic apatites such refinements in the structure brought about by precise X-ray diffraction studies may not be of great relevance. In addition, as these structural refinements were carried out using samples obtained by dry methods, the divergence, if any, shown by precipitated samples of apatites from the hexagonal structure is not yet established.

The conclusions drawn from X-ray diffraction studies on the structural aspects of apatites can be supplemented by its electronmicroscopic patterns which can confirm the homogeneity of the samples by proving the absence of extraneous phases. In addition, they provide information regarding the geometry and dimensions of its individual crystals. Though X-ray diffraction patterns of bone help in

proving the presence of hydroxylapatite and determining its lattice constants, they do not permit one to see the shape of bone crystals or to visualise directly the relationship these crystals hold to the other ingredients of bone. These aspects can be fulfilled by electron microscopic investigations of bone, the corresponding *in vitro* studies being carried out by Hayek et.al.[35] Extensive *in vivo* electron microscopic studies carried out by Robinson[13] could throw light on the uniformity in size of the inorganic crystalline component and the spatial relationship existing between the Collagen fibres, cement substance and calcium hydroxylapatite in bone.

1.7 Isomorphus Substitution of Biological Significance

By the term isomorphous substitution is meant a replacement of one ion by another in a crystal lattice without disrupting the geometry of the crystal. This can be classified as isoionic and heteroionic substitutions. While isoionic substitution is defined as a process by which ions from a solution phase exchange with identical ions of a solid phase in contact with it, the composition of the two phases being unaltered, heteroionic substitution involves a replacement by a different ion present in a solution in contact with the solid phase, changing thereby

the composition of both the phases. Hydroxylapatite is unique in that it can undergo a series of iso-and heteroionic substitutions[82] involving both cations and anions, the criteria being similarity in charge and size of the ions concerned. Klement and Zureda[83] showed that metal ions with ionic radii of about 1.0 Å can form apatites, the most important among them being Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} and Cd^{2+} with ionic radii 0.99, 1.13, 1.35, 1.20 and 0.97 Å respectively.

1.7.1 Isoionic Substitutions

Isoionic substitutions of calcium and phosphate have been investigated extensively on synthetic hydroxylapatite, human bones and teeth[84,85] , Such studies are not only significant in providing an explanation for the skeletal fixation of calcium and phosphorus but also throw light on the phenomenon of resorption, a process by which portions of bone during growth are dissolved and returned to blood stream. Such substitutions were investigated by tracer technique[1] in which a slice of the labelled tissue is placed in contact with a photographic film which functions as a radiation detector.

1.7.2 Heteroionic Substitutions

Among heteroionic substitutions the following are considered relevant by virtue of extensive biological significance associated with them:-

(a) $Ca^{2+} \rightleftarrows Sr^{2+}$, (b) $Ca^{2+} \rightleftarrows Ba^{2+}$

(c) $Ca^{2+} \rightleftarrows Pb^{2+}$ (d) $Ca^{2+} \rightleftarrows Zn^{2+}$

(e) $F^- \rightleftarrows OH^-$ and (f) $PO_4^{3-} \rightleftarrows AsO_4^{3-}$

and merit a mention in the present context.

(a) Ca^{2+} - Sr^{2+} Substitution.

Ca^{2+} - Sr^{2+} substitution on hydroxylapatite is one of the most important heteroionic substitutions since it explains the mechanism of incorporation in the human skeletal system of β-active Sr-90 produced in atomic explosions. This can be represented as follows:-

$$Ca_{10}(PO_4)_6(OH)_2 + nSr^{2+} \rightleftarrows Sr_n\,Ca_{10-n}(PO_4)_6(OH)_2 + nCa^{2+} \quad \ldots(1\text{-}12)$$

Solid solution of hydroxylapatite of calcium and strontium

In-corporation of Sr-90 can prove fatal, because of its long half-life period (about 20 years), even when it is present in traces. Hence studies on this substitution reaction are supposed to be helpful in suggesting a possibility of removal of the incorporated strontium. Knappwost and Ehret[86] investigated the kinetics of this substitution using β-active Sr-89 as a tracer. Synthetic samples of hydroxylapatite of different surface areas were equilibrated with solutions of strontium nitrate labelled with Sr-89. Adsorption of strontium

ions and their subsequent diffusion into the crystal interior accompanied by a simultaneous recrystallisation of the equilibrated hydroxylapatite were shown to be the factors governing such a substitution.

Collin[87] showed through coprecipitation that a series of homogeneous solid solutions of hydroxylapatite of calcium and strontium over the entire compositional range could be formed confirming thereby the occurrence of isomorphous substitution between these ions. These results were subsequently confirmed by Narasaraju et.al.[88,89]

X-ray diffraction studies by Khudolozhkin et.al.[90] could prove that for replacement of calcium by strontium or barium on the apatite lattice, sites of Ca(II) are preferred to those of Ca (I). A substantiation of these results was provided by Trombe et al.[91-93] using i.r. spectroscopy and thermoanalytical studies. Based on <u>in vivo</u> studies on isomorphous substitutions on apatite crystals, Baud[94] could show that the dimensions of the unit-cell were dependent on the chemical composition; the alteration in the former offers an evidence for the occurrence of substitution.

(b) Ca^{2+} - Ba^{2+} Substitution

Because of the toxic effects of elemental barium

and its soluble salts, replacement of Ca^{2+} by Ba^{2+} on hydroxylapatite is another heteroionic substitution[57] of importance. As in the case of strontium, β-active Ba-140 (half-life, 12.8 days), a product of atomic explosions, gets incorporated in the human skeletal system based on the following equation:-

$$Ca_{10}(PO_4)_6(OH)_2 + nBa^{2+} \rightleftharpoons \underset{\text{Solid solution of hydroxylapatite of calcium and barium.}}{Ba_nCa_{10-n}(PO_4)_6(OH)_2} + nCa^{2+} \quad ...(1\text{-}13)$$

It is evident that radiation damage caused by Ba-140 is much less than that by Sr-90 consequent upon the relatively smaller half-life period of the former. Unlike strontium, the non-active barium is toxic and so the studies on such a substitution are of importance to explore a possibility of elimination of the incorporated barium. Narasaraju etal.[57] made investigations in detail, on the various aspects of Ca^{2+} - Ba^{2+} substitution. Samples of hydroxylapatites of calcium and barium and a series of their solid solutions were prepared by a thermal method over the entire compositional range. The samples could be characterised by chemical, i.r, X-ray diffraction and electronmicroscopic analyses. It could be shown through tracer technique by Samachson et al.[95] that there is a preferential uptake of Ba-133 over Ca-47 and Sr-85 on human bones. In addition, it was shown by Samachson

and Schmitz[96] that traces of Zn^{2+} when present in the equilibrating solution increase the uptake of Sr-85 and Ba-133. These results were explained on the basis of the supposition that Zn^{2+} distorts the surface of hydroxylapatite facilitating a replacement of Ca^{2+} by larger alkaline earth ions.

(c) Ca^{2+} - Pb^{2+} Substitution

Inhalation of lead in the form of dust or its adsorption through skin leads to "lead-poisoning"[97](also known as "plumbism"). The mechanism of this process can be attributed to isomorphous substitution of Ca^{2+} by Pb^{2+} on bone. As envisaged by Klement[98] lead-poisoning occurs due to formation of solid solutions of hydroxylapatites of calcium and lead on bones. Formation of such a series of solid solutions over the entire compositional range by coprecipitation in aqueous media was reported by Müller[6] and later substantiated by Narasaraju et al.[44] and also by Rao and Chickerur[99]. The chemical reaction involved may be represented as follows:-

$$Ca_{10}(PO_4)_6(OH)_2 + nPb^{2+} \rightleftharpoons \underbrace{Pb_nCa_{10-n}(PO_4)_6(OH)_2}_{\text{Solid solution of hydroxylapatites of calcium and lead.}} + nCa^{2+} \quad ...(1\text{-}14)$$

A famous recent example of lead-poisoning has been the toxic

effect of lead present in the coating of pottery in Mexico, the damage being termed as "Problem of lead in Mexican pottery"[100] Consequent upon the contemporary significance of this exchange a few more aspects of the latter constituted the subject matter of the investigations reported in the present work.

(d) Ca^{2+} - Zn^{2+} Substitution

Samachson et al.[101-103] made extensive investigations on the replacement of Ca^{2+} by Zn^{2+} on the hydroxylapatite of bones. Based on detailed radio-chemical studies on this exchange using solutions labelled with Zn-65 it could be confirmed that the uptake of Zn^{2+} by calcium hydroxylapatite could be 100 per cent.within five minutes. Further, this process was found to be considerably reduced by chelating agents like E.D.T.A. Proof for the occurrence of exchange was provided by estimation of the amount of extra calcium which entered the solution during equilibration resulting in an ion to ion replacement of lattice-Ca^{2+} by Zn^{2+} present in the equilibrating solution. The exchange which was found to be rapid initially was dependent on a subsequent diffusion of Zn^{2+} ions into the crystal lattice.

(e) F^- - OH^- Substitution

Through neutron - and X-ray diffraction studies,

Kay et al.[76] could confirm the earlier findings that the OH^- groups are located in the cavities running parallel to the C-axis of the apatite lattice. Based on the dimensions of these cavities, it can be shown that, among others, ions of the type F^-, OH^- and Cl^- with ionic radii 1.32, 1.68 and 1.81 Å respectively fit into them. Further, F^- ion due to its spherical symmetry is better suited for the purpose than OH^- ion. A replacement of OH^- by F^- brings about a contraction of the unit cell of hydroxylapatite as expected from such a spherical symmetry.[3,5,104] The OH^- - F^- exchange is of significance in explaining the occurrence of dental caries which involves the attack of the apatitic inorganic phase of enamel by acidogenic bacteria existing in the vicinity of the enamel surface. Various aspects of this substitution and the role of F^- ion as a prophylactic in the occurrence of dental caries have been extensively investigated by Knappwost.[19,20,105,106] He proved that the tooth surface enriched with F^- ions was more resistant to caries. Through experimental investigations he could suggest a convincing mechanism of the caries - prophylactic action of fluorine. An oral dose of 1-5 mg of fluorine taken daily was found to accelerate the deposition of fluorapatite layers on the tooth surface resulting, inter alia, in the accompanying alteration in the viscosity of saliva. Such a deposition which was found to be favoured

on the effected regions of the tooth surface could retard further corrosion by acidogenic bacteria, fluorapatite being less soluble than hydroxylapatite. These conclusions could be drawn from the kinetic studies of this substitution which can be represented as follows:-

$$Ca_{10}(PO_4)_6(OH)_2 + XF^- \rightleftharpoons \underset{\text{Solid solution of hydroxylapatite and fluorapatite.}}{Ca_{10}(PO_4)_6(OH_{2-x}F_x)} + XOH^- \quad ....(1\text{-}15)$$

The product of this substitution is a solid solution of hydroxylapatite and fluorapatite known as fluorhydroxylapatite. Liang and Higuchi[107], Stearns and Berndt[108] and Higuchi et al.[109] investigated the interference caused by the co-precipitation of calcium fluoride during the progress of this substitution reaction. Based on the results of the kinetic studies of this substitution, the most important measure suggested for the prevention of the dental caries has been the application of F^- ions in some suitable form to the dental tissue. This process known as fluoridation[1] has been in vogue since a few decades.

1 ppm of fluoride in drinking water was found to be an optimal level for caries control; a level higher than this was found to lead to mottled enamel and also to certain toxic effects. Several mechanisms are suggested to explain the prophylactic action of fluorine in the

occurrence of dental caries, the most important among which is based on the exchange of OH^- ion of hydroxylapatite of tooth by F^- ion resulting in the formation of fluorhydroxylapatite. It was shown by Narasaraju[110] that fluorhydroxylapatite is less soluble than hydroxylapatite accounting thereby for the caries - resistance imparted to the dental tissues by fluoridation. These conclusions could be substanciated by results of recent investigations[111-116] on F^- - OH^- exchange. Narasaraju et al.[117] could establish the conditions favourable for the occurrence of OH^- - F^- exchange on hydroxylapatite, the principal among them being (i) an increase in the concentration of F^- ion, (ii) a decrease in pH of the medium of exchange and (iii) a reduction in the grain size of the sample of hydroxylapatite. Through NMR studies, Young et al.[118] could investigate the location of F^- ions present in traces in hydroxylapatite and a mechanism was suggested to explain the prophylactic action of fluorine in the occurrence of dental caries. Vander Lugt et al.[119] carried out similar studies and established the role played by internuclear distances in the formation of hydrogen bonding between OH^- and F^- in the apatite lattice. Subsequent NMR studies on F^- - OH^- exchange on hydroxylapatite were carried out by Lundin et al.[120] and Knubovets et al.[121] That a halide substitution of OH^- on apatite lattice is possible was

proved by O'Shea et al.[43] Based on Laser-Raman spectral studies, attaining an accuracy as low as five per cent. Further studies on the prophylactic action of fluorine in the occurrence of dental caries were made by Fetkowska-Mielink and Krystina,[122] Aoba, Takaaki et al.[123] and Freund et al[124] based on physico-chemical changes undergone by amorphous and apatitic calcium phosphate.

(f) PO_4^{3-} - AsO_4^{3-} Substitution

Another example of a heteroionic substitution[125] of importance is replacement of PO_4^{3-} by AsO_4^{3-} on hydroxylapatite, accounting for the toxic effects of arsenic[126] and its soluble salts.[127] The substitution reaction can be represented as follows:-

$$Ca_{10}(PO_4)_6(OH)_2 + n\ AsO_4^{3-} \rightleftharpoons \underbrace{Ca_{10}(PO_4)_{6-n}(AsO_4)_n(OH)_2}_{\text{Solid solution of phosphorus and arsenic hydroxylapatite}} + n\ PO_4^{3-} \quad \ldots\ldots \quad (1\text{-}16)$$

While the existing literature confirms the occurrence of this substitution reaction,[125,128] spread over the entire compositional range, the utility of a knowledge of the mechanism of this substitution for the removal of incorporated arsenic is yet to be investigated. Evidence for the occurrence of such a substitution reaction on lead hydroxylapatite could be provided by Rao.[129]

(g) Miscellaneous Substitutions

In addition to the detailed investigations on heteroionic substitution on hydroxylapatite described above, scattered results on some aspects of a few more miscellaneous substitutions are available.

Though the presence of CO_3^{2-} ion in human bones is established, the concept that it exists due to heteroionic substitution is still controvertial.[130,131] Studies on the possibility of a substitution reaction of hydroxylapatite involving[132,133] CO_3^{2-} ion are, therefore, of importance. Extensive X-ray studies of a mineral, francolite, $(Ca, Mg, Na,K)_{10}[(P,C)O_4]_6(F,OH)_2$ which is a carbonate-containing fluorapatite, indicated the absence of free calcium carbonate and proved the similarity of its X-ray pattern with that of fluorapatite suggesting thereby the presence of CO_3^{2-} ion in the apatite lattice. Additional evidence in favour of this observation was provided by Le Geros et al.[134] and Bonel and Montel.[135-137] However, solubility studies of francolite indicated a preferential dissolution of CO_3^{2-} ion which can be attributed to its free existence, providing thereby evidence against the CO_3^{2-} substitution.[138] Whether CO_3^{2-} ion exists as a separate submicroscopic phase or as a substituent in apatite lattice is yet to be unambiguously clarified.

Knappwost showed through radio-chemical studies,[139] that PO_4^{3-} - SiO_4^{4-} substitution was possible when it is accompanied by a compensation of the surplus negative charge through introduction of a univalent metal ion like Na^+ into the apatite lattice. Some aspects of this substitution were investigated by Azimove et al.[140,141] and by Gaude et al.[142]. Neuman showed that monovalent ions like Na^+ and H_3O^+ (ionic radii, 0.95 and 1.00 Å respectively) can displace Ca^{2+} ion (ionic radius, 0.99 Å) partially from the apatite lattice, charge compensation being brought about by appropriate depletion of some of the boundary ions.

The occurrence of Ca^{2+} - Eu^{2+} substitution on hydroxylapatite could recently be established by Mayer et al.[143] They could prepare fluor,- chlor - and hydroxylapatites of europium as well as a few solid solutions of some of these isomorphs. Gilinskaya and Shcherbakova[144] could provide evidence for the replacement of Ca^{2+} by Mn^{2+} ions, the latter being capable of occupying both Ca(I) and Ca(II) lattice positions.[76] These results were confirmed by Dubrov et al.[145] through EPR studies. Vinnikov and Gugel[146] also carried out similar exchange studies on fluor and chlorapatites. Synthesis of oxyapatites of composition, $M_4Nd_6(SiO_4)_4(EO_4)_2O_2$, where M = Ca,Sr and

E = P, As and V was accomplished by Fedorov et al.[147], the characterisation of the samples being done by X-ray diffraction studies. Mayer et al.[148] carried out similar investigations in the system $Ln_x M_{10-2x} Na_x (PO_4)_6F_2$ where Ln = La, Pr, Nd, Sm, Eu, Dy, Er, Lu, Y and M = Ca, Sr and Ba.

Evidence for Ca^{2+} - Fe^{2+} substitution on hydroxylapatite over a limited compositional range was provided, through Mössbaur studies by Khudolozhkin et al.,[149] a substantiation of these results by chemical analysis being done by Rao.[150] Through equilibration studies of hydroxylapatite with solutions containing Ni^{2+} and Cu^{2+} ions, Misra et al.[151] could provide evidence for the replacement of Ca^{2+} by Ni^{2+} and Cu^{2+} ions on the apatite lattice. Narasaraju et al.[152] investigated Ca^{2+} - Co^{2+} and Ca^{2+} - Cd^{2+} exchanges on hydroxylapatite. Band, Besse et al.[153,154] reported the existence of a series of compounds having the general formula $Ba_{10}(ReO_5)_6$ x 2 , (where x = Br,I) named by them as 'New rheniumapatites' while Schiff, Francosis, Alain et al.[155] reported the formation of a series of apatites containing S^{2-} and SO_4^{2-} ions. Berak et al.[156] could prepare strontium oxyapatite.

1.8 Studies on Solubility

1.8.1 Significance

During the recent past phenomena associated with dissolution of [21,86,157-162] hydroxylapatite have attracted considerable attention because of their significance in diverse fields. An understanding of the physiology of human bones and teeth from the point of view of calcification and resorption is possible through studies on the solubilities of hydroxylapatite. Further, such studies constitute the basis of the different aspects concerning the occurrence of dental caries and the prophylactic action of fluorine.[19,20] In addition, it is evident that the availability of phosphatic fertilizers to plant kingdom can be explained through the solubility behaviour of hydroxylapatite, the latter being the stablest phase of calcium phosphates in aqueous media.

It is, therefore, no wonder that the solubility phenomena of hydroxylapatite have attained inter disciplinary significance and have been demanding the attention of physical chemists, bone biologists, dentists, chemical engineers and geologists, to mention only a few. A survey of literature on solubility of hydroxylapatite shows that the results can be classified under (i) Non-stoichiometric and (ii) Stoichiometric dissolutions. The reported

investigations, in general, were carried out with either synthetic or natural samples obtained from bones and teeth.

1.8.2 Non-stoichiometric Dissolution

Extensive studies on solubility of hydroxylapatite carried out independently by Neuman and Co-workers[157] and Rootare et.al.[159] could provide ample evidence to show that the sample exhibits a non-stoichiometric dissolution on the basis of a divergence of Ca/P, g atom ratio, of its saturated aqueous solutions from the stoichiometric value of 1.67 . The divergence from stoichiometric behaviour was attributed to the formation of a surface coating on the solute consequent upon its hydrolytic dissolution. While Rootare et al.[159] could prove this surface coating to be a complex, $Ca_2(HPO_4)(OH)_2$,[163-165] others could provide evidence that it is either calcium monohydrogen phosphate, $CaHPO_4$, or calcium pyrophosphate, $Ca_2P_2O_7$, or octacalcium phosphate, $Ca_4H(PO_4)_3$.

In order to simulate biological conditions and to maintain a constant ionic environment in the medium of dissolution, Levinskas and Neuman[157], used 0.165M aqueous solutions of sodium chloride as solvent to study the

solubility of hydroxylapatite. They reported that for a given set of experimental conditions, (i) the g atom ratio, Ca/P, of the saturated solution was different from that of the solute and that (ii) no reproducible values for the solubility product, K_{sp}, could be obtained. It was therefore supposed that the compound deviated from the established laws of solubility.

The solubility products of a number of commercial and laboratory-made samples of hydroxylapatite were determined by Rootare et al.[159] They observed that the values obtained were divergent and dependent upon the solute to solvent ratio. Further, as shown by Lavinska and Neuman[157], the g atom ratio, Ca/P, of solutions is not constant at the stoichiometric value of 1.67 . These investigators gave a convincing explanation to account for the observed behaviour from the point of view of established physico-chemical principles. Their theoretical considerations were subsequently substantiated by La Mer.[160] Hydroxylapatite being the salt of a weak acid, undergoes hydrolysis in aqueous solutions yielding a solid surface complex, $Ca_2(HPO_4)(OH)_2$, which was found to dominate the solubility equilibria according to the following equations:-

$$Ca_{10}(PO_4)_6(OH)_2 + 6H_2O = 4Ca_2(HPO_4)(OH)_2 + 2Ca^{2+} + 2HPO_4^{2-} \quad \ldots (1.17)$$

$$4Ca_2(HPO_4)(OH)_2 = 8Ca^{2+} + 4HPO_4^{2-} + 8OH^- \quad \ldots \quad (1.18)$$

Thus, it is evident that when equation (1.17) predominates the g atom ratio, Ca/P, in the solution is unity while it becomes 2 with the establishment of equation (1.18). When both the equations contribute equally to the solution process this ratio becomes 10/6 as expected for the stoichiometric dissolution of hydroxylapatite.

The non-reproducibility of the K_{sp} of hydroxylapatite as reported by Lavinskas and Neuman[157] was attributed by La Mer[160] to the complications involved in the accurate determination of individual ion activity coefficients for the systems employed. It was pointed out by La Mer that by virtue of its biological significance an aqueous 0.165 M solution of sodium chloride which is the solvent employed by Neuman, can be considered as a standard solvent of reference in which all ion activity coefficients can be assumed to be unity. Based on that assumption the complicated problem of evaluating the individual ion activity coefficients involved in the solubility equilibria of hydroxylapatite can be avoided. It was shown by La Mer that Neuman's data, when recalculated on the basis of the foregoing considerations, indicated that the solubility of hydroxylapatite responded precisely to the principles of solubility product.

Details of similar studies carried out with natural samples were also available in the literature. Brudevold et al.[163] investigated the solubility of dental enamel with saliva as a medium of dissolution. They found that among the possible solid phases, calcium monohydrogen phosphate, $CaHPO_4$, was found to give a constant K_{sp} in the pH range, 4.5 - 7.5 . Francis[161] investigated the solubility of synthetic hydroxylapatite, dental enamel and a few more allied natural phosphatic minerals in solutions buffered to a pH range, 3.5 - 6.0 . He could show through chemical analysis the formation of a coating of $CaHPO_4$ on the surface of those equilibrated with acid buffers. He also emphasized the significance of corrections which are to be applied for the evaluation of K_{sp} of the samples taking into account the complexing of the products of dissolution in acetate, lactate and phosphate buffers. The change in the composition of the solution observed during dissolution of hydroxylapatite could be explained on the basis of deposition of $CaHPO_4$ on its surface. Based on such theoretical considerations, Francis explained the role played by the parameters such as particle size, solute to solvent ratio, type and concentration of buffers and pH in deciding the composition of hydroxylapatite solution.

Fleisch et al.[164] investigated the role of a surface coating of calcium pyrophosphate, $Ca_2P_2O_7$, in controlling the solubility of hydroxylapatite. By extending the analogy to the

bone processes a mechanism was suggested for the calcification and resorption.

Dissolution kinetic studies of synthetic samples of hydroxylapatites of calcium and strontium were investigated by Chickerur et al.[166] at 370°C using IG4 sintered glass crucible for separating the colloidal component of the solute from the saturated solutions. A non-stoichiometric dissolution was reported. The process was found to obey first order kinetics which could be explained on the basis of the surface complex theory suggested by Rootare et al.[159]

Blitz et al.[165] studied the solubility equilibria of hydroxylapatite obtained from animal bones and teeth in order to characterise the phases likely to be formed as a result of the reactions occurring on the surface of the samples and also to study the role of such phases in governing the solubility of the sample. They concluded that octacalcium phosphate, $Ca_4H(PO_4)O_3$, formed during dissolution of hydroxylapatite controlled its solubility.

1.8.3 Stoichiometric Dissolution

The credit of proving for the first time that hydroxylapatite obeys the established laws of solubility

goes to Clark.[158] He investigated the solubility equilibria of hydroxylapatite over a wide range of experimental conditions, the samples used being obtained by mixing solutions of calcium hydroxide and orthophosphoric acid. He analysed the saturated solutions obtained from the mother liquor of precipitate. In addition, the precipitate was subjected to the conventional solubility equilibria to obtain the saturated solution which was also analysed. It could be confirmed from both the sets of investigations that hydroxylapatite exhibits stoichiometric dissolution resulting in a definite K_{sp} at 25°C, the pK_{sp} reported being 115.5

Using precipitated samples of hydroxylapatite, its solubility was investigated by Bardy et al.[167] taking the solute in the form of a pellet mounted on an electrically operated stirrer fixed in a buffered dissolving medium containing excess of potassium chloride to maintain a constant ionic environment so that the activity coefficients of the dissolved species remained constant. A stoichiometric dissolution was observed by them. Another set of investigations substantiating stoichiometric dissolution of hydroxylapatite were considered by Fassbender et al.[168,169] In addition they observed that the dissolution rate was controlled by a combination of several consecutive partial reactions and was dependent on the pH and surface area of the solute and

independent of the temperature in the range 15-35°C. Zimmermann could propose a mathematical theory on the basis of the data on the solubility of enamel, thereby suggesting the pH range vulnerable for the onset of dental caries. The influence of temperature on solubility of apatites was investigated by Valyashko et al.[170] and it was found that the solubility decreased with increasing temperature.

Solubility isotherms of well-characterised samples of synthetic hydroxylapatite were investigated by Moreno et al.[171] in the pH range, 5.0 - 7.0, and a stoichiometric dissolution was reported. Chander and Fuerstenau[172] used thermodynamics to study the interfacial properties and equilibria in the apatite - aqueous solution system. They observed that electrical double layer properties play an important role in the solubility of apatite. Systematic investigations on the solubility of hydroxylapatite were carried out by Wier et al.,[162] using commercial samples subjected to a rigorous purification either by refluxing for 24 hours in contact with water or by auto-claving in presence of IN ammonium chloride solution for 50 days at 120°C under a pressure of 1.06 kg/cm^2, the wash-liquid being periodically replaced. Systematic characterization of the samples was done through X-ray, petrographic and

chemical analyses. The samples were equilibrated in media with pH values ranging from 4.3 - 6.7 and choosing 0.1, 0.5, 1.0 and 10.0 g of the solute per 100 ml of the solvent. The colloidal component of the solute present in the solutions was removed by using specially prepared cells made of plexiglas and fitted with cellulose acetate dialyzing membranes. Based on the results of chemical analyses of the saturated solutions and calculating the activities of the ionic species present, they could convincingly establish a stoichiometric dissolution of hydroxylapatite, the observed average pK_{sp} being 116.5 . Divergence observed in the results of solubility of hydroxylapatite was attributed to the presence of trace impurities which get eliminated on rigorous purification.

Narasaraju and Rao[173] undertook the dissolution kinetics and solubility studies of hydroxylapatite, chlorapatite and a series of their solid solutions spread over the entire compositional range in buffered media extending over a pH range, 4.9 - 7.5 . They could convincingly establish a stoichiometric dissolution of hydroxylapatite, chlorapatite and their solid solutions, the corresponding pK_{sp} values at 37°C being 110.6 for hydroxylapatite and 115.4 for chlorapatite.

1.8.4 Miscellaneous Aspects of solubility

While the bulk of the results on solubility of hydroxylapatite can be put under the abovementioned categories of non-stoichiometric and stoichiometric dissolutions, a few significant scattered results can be shown under the category of miscellaneous aspects of solubility of hydroxylapatite which involve both stoichiometric and non-stoichiometric dissolutions. The principal aspects coming under such a category are the dependence of solubility of hydroxylapatite on pH of the dissolving medium and on its crystal structure.

Among the earlier systematic investigations, mention may be made of the observations of Benedict and Kanthak[174]. They noticed that the pH dependence of solubility of dental enamel was similar to that of tricalcium phosphate indicating compositional similarities between the two.

Ericsson[175,176] investigated the pH dependence of the solubility of synthetic hydroxylapatite as well as of dental enamel. The solubility of hydroxylapatite and its optimum pH range could be calculated by him. According to him the increased solubility in the presence of CO_3^{2-}, serum and saliva is due to the formation of complexes

involving Ca^{2+} ions. Davies and Hoyle[177] carried out further investigations on the solubility of such complexes.

Narasaraju et al.[89] studied the pH-dependence of the solubility of hydroxylapatites of strontium and calcium and a series of their solid solutions distributed over the entire compositional range, the amount of the dissolved apatite being calculated exclusively from the phosphate concentration of the solution. An increase of solubility with a decrease in pH was reported. Paunio and Makinen[178] could establish an enhancement in solubility of tooth material and synthetic hydroxylapatite at a series of pH values by the presence of sulphate ions.

Dissolution kinetic studies were also made by Voegel and Garnier et al.[179] on the release of PO_4^{3-}, HPO_4^{2-} and CO_3^{2-} from powdered samples of human normal tooth enamel supposed to contain CO_3^{2-} ion and on the influence of F^- ion on it in buffered solutions spread over the acidic region.

The solubility of hydroxylapatite, fluorapatite and a few of their solid solutions was investigated by Narasaraju[110] in the pH range, 5.3 - 8.2 . The solubilities calculated exclusively from the experimentally determined phosphate contents of the saturated solutions were found to decrease with an increase in pH as well as with an increase

in fluoride content of the samples. The significance of these results in the context of prophylactic action of fluorine in the occurrence of dental caries was emphasized. Proof for anisotropic dissolution of a single crystal of hydroxylapatite was conclusively established by Jongebloed et al.[180], using citric and lactic acids as dissolving media. The dissolution parallel to c-axis was found to be much faster than that perpendicular to it. Scanning electronmicroscopic patterns of the solute after attainment of saturation could show that the single crystal was twisted along c-axis confirming thereby the existence of a screw dislocation parallel to it.

Daculsi, Kerbel and Kerbel[181] used high resolution transmission electronmicroscopy to study the acid dissolution of biological and synthetic apatite crystals and their dependence on the lattice pattern. According to them the dissolution starts at the regions of dislocation and is preferential across the 'c' axis due to the likely existence of dislocations.

1.8.5 Explanation for Divergence in solubility

The foregoing account shows that results on the solubility of hydroxylapatite are characterized by divergence and mutual contradictions among themselves. An exhaustive survey of the literature on the subject enables one to make

a critical assessment of the results to throw light on the factors responsible for such disparities.

Smith et al.[182] made attempts to clarify the reported divergence in the g atom ratio, Ca/P, of hydroxylapatite solutions by dissolving synthetic samples in dilute hydrochloric acid at a pH equal to 4.5 . When 500 g of the solute were equilibrated in 1 litre of the dissolving medium, the ratio was found to be higher than the stoichiometric value. However, when the solute was resuspended under identical conditions, stoichiometric disssolution could be observed. Similar results could be arrived at when the amount of the solute taken was less than 8 g per litre of the same dissolving medium. The non-stoichiometric dissolution was therefore attributed to the higher proportion of surface impurities dissolved along with hydroxylapatite when the amount of the solute taken for a given volume of the solvent was large. It was concluded by them that when the solute/solvent ratio was low the non-stoichiometric dissolution caused by surface impurities was less than the experimental errors associated with the micro-analytical determinations of calcium and phosphorus and was therefore not perceptible.

In addition, the role played by errors involved in the micro-determination of Ca^{2+} , PO_4^{3-} and other ions in

the case of solid solutions of apatite in causing divergence of the results is not to be ignored. The fact that the K_{sp} values of the supposed surface coatings such as $CaHPO_4$, $Ca_2HPO_4(OH)_2$ and $Ca_4H(PO_4)_3$ appear to remain constant is an evidence to substantiate this argument. It is evident that in all such cases, the concentrations / activities of the species such as Ca^{2+}, HPO_4^{2-}, $H_2PO_4^-$ and PO_4^{3-} are raised only to relatively lower powers for K_{sp} calculation resulting in a minimization in the errors associated with the determination of such ions. On the other hand when the calculations are extended to evaluation of K_{sp} of hydroxylapatite these errors get magnified.

1.9 Mechanism of Calcification

Calcification,[183,184] which involves an orderly precipitation of hydroxylapatite within the organic matrix of bone, governs the physiology of human bone. In the light of the fact that a knowledge of the solubility equilibria of hydroxylapatite plays an important role in understanding the mechanism of calcification, it has been considered appropriate to mention a few aspects of it in the present context.

The results of *in vitro* and *in vivo* studies on the solubility of hydroxylapatite facilitated the understanding of the mechanism of calcification. It has been established that calcification occurs only at certain regions of the body known as sites of calcification[1]. An important pre-requisite for the process to occur is the transport of the assimilated calcium and phosphorus to such sites which is brought about by the body - fluids. For the promotion of calcification, optimum environmental conditions should be prevalent at these sites. The mechanism of establishment of these conditions was suggested by Robison's scheme according to which a local increase in phosphate concentration is brought about at the sites of calcification when a substrate of phosphate ester is hydrolysed by an enzyme known as phosphatase resulting thereby in the deposition of hydroxylapatite.

It is found from a knowledge of solubility behaviour of hydroxylapatite that blood serum is supersaturated with respect to it and its spontaneous precipitation is therefore expected. Since such a precipitation is found to take place only at the sites of calcification due to local action as mentioned by the Robison's scheme, it is supposed that the prevention of calcification in the non-calcifying regions is due to a

possible chemical binding of calcium and/ or phosphate, the details of which are yet to be clarified. The theories suggested to explain the ability of only certain regions of the body to function as sites of calcification are controversial.

From physiological considerations, it can be shown, that in addition to calcium and phosphorus blood serum contains ions such as sodium, carbonate, magnesium and citrate. Further, about one-third of this calcium is shown to be bound to protein-fraction[185] through chelation while the rest of it exists in the ionised form or as soluble complexes of ions such as citrate and phosphate.[176] The phosphorus of blood serum exists mainly as HPO_4^{2-} and to some extent as $H_2PO_4^-$ and PO_4^{3-}. The composition of blood serum suggests that it is complicated to apply the principles of solubility product to account for the deposition of hydroxylapatite. Its calcium and phosphate concentrations are higher than those corresponding to the solubility product of hydroxylapatite and approximate to those of saturated solutions of dicalcium phosphate. It was therefore supposed by Neuman that precipitation of dicalcium phosphate takes place initially. Hydroxylapatite, which is the stablest among the calcium phosphates, is likely to be

formed due to a subsequent hydrolysis of dicalcium phosphate . Samachson[183,184] could provide a clear in sight into the basic requirements of calcification. While he agrees with earlier theories as far as the role of HPO_4^{2-} as a prerequisite for calcification is concerned, he considers the removal of H_3O^+ ion as a factor essential for the process as indicated by the following equation:-

$$10\ Ca^{2+} + 6\ HPO_4^{2-} + 10\ H_2O \longrightarrow Ca_{10}(PO_4)_6(OH)_2 + 8H_3O^+ \quad \text{.....(1.19)}$$

From the equation, it is evident that the deposition of hydroxylapatite is favoured when there is presence of proton-acceptors and a local increase in pH at the sites of calcification. The foregoing account shows that a plausible mechanism of calcification is possible only when a more comprehensive interpretation of factors controlling the solubility of hydroxylapatite is available.

1.10 Non-stoichiometric Apatites

Synthetic basic calcium phosphates obtained by wet methods have the x-ray diffraction patterns similar to hydroxylapatite but often depart from it in stoichiometry by exhibiting a g atom ratio, Ca/p, ranging from 1.33 to 1.67 . Such compounds, known as calcium deficient or

non-stoichiometric apatites, are of biological significance since the g atom ratio, Ca/p, of bone is lower than that corresponding to the stoichiometric value. Such a flexibility in the permissible values of Ca/p g atom ratio is responsible for the role of bone-hydroxylapatite as a buffer in controlling the composition of blood. These non-stoichiometric apatites have an additional importance by virtue of their role as catalysts in dehydration and dehydrogenation of primary alcohols, leading to the formation of aldehydes and ketones,[186] the catalytic activity being proportional[187] to the calcium deficiency of the sample. Wilson, Sundarsanam and Young[188] investigated the halogen deficient cadmium haloapatites with the structure $Cd_5(MO_4)_3X$ (where X=Cl, Br or I). Many theories[189,199,205] have been put forward to explain the structure and composition of these compounds. Cameron,[189] Hodge,[190] Schleede[191] and Trömel et al.[192] have advanced independently a theory based on the adsorption of HPO_4^{2-} ions to account for the non-stoichiometry of apatites. But Posner[193,194] rejected this theory on the basis that non-stoichiometry was not exclusively due to surface adsorption since the measured surface areas of the samples were too low to account for the expected uptake of HPO_4^{2-} ions. Instead, the calcium deficiency was accounted for by Posner on the basis of a statistical model depicting the

absence of Ca^{2+} ions from the columnar positions of the apatite lattice, the charge - balance being maintained by the introduction of two protons. Winand et al.,[195,196] could explain the maintenance of charge-balance through a *compensation of the two positive charges of each missing* Ca^{2+} ion by an addition of Proton and removal of a structural OH^- ion. The suggestion of Brown et al.,[197] that the calcium deficiency is caused by an epitaxial inter-growth of octacalcium phosphate, OCP, (Ca/p = 1.33) and stoichiometric hydroxylapatite (Ca/p = 1.67), was rejected by Berry[198] based on infrared and thermoanalytical evidence for the absence of OCP. Kuhl and Nebergall[199] tried to account for the existence of calcium deficient apatites on the basis of introduction of HPO_4^{2-} ions into the apatite lattice, accompanied by a partial removal of OH^- ions. Based on the recent literature[200-204] Young[205] suggested that occurrence of a deficiency of calcium hydroxide in hydroxylapatite is responsible for the nonstoichiometry. According to Young a cation-deficient apatite lattice attains a charge-balance by replacement of OH^- by Na^+.

The precipitation of calcium phosphates was studied recently by Feenstra and De Bruyu[206] by a method which allowed super-saturation to build up under well-defined conditions.

They investigated the stage preceding the growth of non-stoichiometric apatite crystals through a growth-study as a function of pH.

1.11 Inter-disciplinary significance

The trend of recent investigations[207-213] in the field of apatites establishes convincingly their interdisciplinary significance. In a brief review like the present one, only a few significant aspects other than those given earlier merit a mention.

Apatites find an increasing application as catalysts[207] in synthesis of organic compounds such as sugars and their phosphoric esters, as luminophosphors[208-213] and as starting materials for several phosphatic fertilizers.[214,215] The observation that kidney and prostrate[216-219] stones contain hydroxylapatite further enhances the biological and physico-chemical significance of this compound since its solubility behaviour can throw light on their possible elimination by dissolution.

Similar studies on apatites playarole in preventing diseases caused by inhalation[220] of dust containing apatites. Another significant role of apatites in biology is the utility of apatite-coated ceramics as dental prosthesis[221] and artificial bones.[222]

Though extensive work[1,21,30,31,157-162,173] was carried out during the recent past on various aspects of apatites in different disciplines, a researcher in the field suffers from the absence of an up-to-date reviews containing a consolidated and systematic account of apatites. The present review has been an attempt to compensate for this lacuna.

SECTION II

PREPARATION AND CHARACTERIZATION OF LEAD PHOSPHATE APATITE, LEAD VANADATE APATITE AND THEIR SOLID SOLUTIONS

PREPARATION AND CHARACTERIZATION OF LEAD PHOSPHATE APATITE, LEAD VANADATE APATITE AND THEIR SOLID SOLUTIONS.

2.1 Introduction

The toxicity of elemental lead and its compounds is well known. Their inhalation in the form of dust or fumes and absorption through the skin lead to "lead - poisoning"[97] (also known as "Plumbism") which is an occupational disease prevalent mostly among workers dealing with white-lead and pottery. The disease is characterised by symptoms such as anaemia, constipation, mental and visual disturbances and convulsions. Toxic effects caused by lead present in mexican pottery were discussed recently by Gerald et.al.[100] Studies to explain the ultimate site and mechanism of incorporation of lead in the human metabolism are consequently of great pathological significance. An awareness of the hazards caused by lead is indicated by the fact that in the united kingdom a legislation[223] to permit the use of automobiles run on petrol freed from lead is being contemplated.

According to Klement[83,98] the criterion facilitating the incorporation of lead in the human skeletal system is the formation of solid solutions of hydroxyl-apatites of calcium and lead, the factors contributing to

such a formation being the isomorphism existing between them and the closeness of the ionic radii of calcium and lead (0.99 and 1.20 Å respectively).

In the context of toxicity, vanadium does not lag very much behind lead, the principal toxic symptoms being paralysis, convulsions and sleepiness leading to bronchitis and bronchopneumonia.[224,225] While the selective toxicity of vanadium in mammals[226] is established its mechanism in living cells is still to be investigated. Apart from toxicity considerations, vanadium demands a detailed investigation by virtue of the role played by it in industries as a catalyst and in metallurgy as a principal ingredient in special varieties of steels.

Consequent upon the fact that tetrahedral VO_4^{3-} ion and its isostructural PO_4^{3-} ion[227] have covalent radii close to one another, (1.22 and 1.10 Å respectively);[228] the latter present in lead phosphate apatite, $Pb_{10}(PO_4)_6(OH)_2$, can be isomorphously replaced by the former leading to lead vanadate apatite (the two apatites being abbreviated hereafter as LPA and LVA respectively). While extensive work has been done on LPA, studies on its solid solution with LVA have not been undertaken. LVA being a compound containing both the potentially toxic elements, namely lead and vanadium,

investigations on such solid solutions are being considered to be extremely significant from the point of view of toxicity to human skeletal system and hence the present work was undertaken.

It was Klement[83] who could successfully prepare LPA for the first time both by wet and dry meyhods. While hydrolysis of secondary lead phosphate could form LPA by a wet method, the same could be prepared by a dry method by subjecting a stoichiometric mixture of tertiary lead phosphate and lead oxide to an optimum temperature under a stream of moist air. Another wet method for preparation of LPA ensuring the elimination of coprecipitation of acid phosphate and hydroxide of lead was suggested by Rathje[37,47] based on what is known as "acidimetric precipitation", a modification of the same being adopted by Muller. Solutions of lead nitrate and potassium dihydrogen phosphate added simultaneously to boiling water maintained highly alkaline resulted in the formation of LPA, the coprecipitation of acid phosphate and hydroxide of lead being avoided by the presence of surplus potassium hydrogen phosphate in the medium of precipitation.

An alternative method suggested by Hayek[45] to eliminate coprecipitation of lead was based on converting the latter into one of its soluble tartrate - complexes in

an ammoniacal medium to be dissociated by heating when desired for preparation of LPA. While studies on LPA are extensive many aspects concerning LVA are still to be investigated. LVA needed specifically for X-ray analysis was prepared for the first time by Engel[229] through hydrothermal synthesis.

The present investigations deal with preparation of LPA, LVA and a series of their solid solutions through a modified method of collins[46], the samples so prepared being characterised through chemical, X-ray, i.r, electron-microscopic and thermogravimetic analyses. The method adopted is the first of its kind for preparation of LVA in appreviable quantities by precipitation.

2.2 Experimental

The experimental work included in this section has been subdivided into (i) Preparation, (ii) chemical analysis, (iii) determination of lattice constants, (iv) electronmicroscopic investigations, (v) i.r studies and (vi) Thermoanalytical studies of the samples.

2.2.1 Preparation of the Samples

The preparation of the samples of LPA, LVA and their solid solutions was based on the following equation:-

$10\ Pb^{2+} + 6\ x\ O_4^{3-} + 2\ OH^- \longrightarrow Pb_{10}(XO_4)_6(OH)_2$.

where X = P or V for the end-members and (P+V) for the solid solutions, the proportion of P to V being varied as desired. The samples were precipitated at 37°C by mixing stoichiometric quantities of the reactants in the form of their aqueous solutions maintained at a pH of 12. The precipitation was done in an atmosphere freed from carbondioxide and the chemicals used were of L.R grade. All the solutions were prepared in water freed from carbondioxide. Based on the above equation, calculated amounts of lead acetate, diammonium hydrogen phosphate and sodium ortho vanadate were taken such that the yield was about 30 g of the sample. Ethylene diamine was used instead of ammonia since relatively smaller volumes of it were required to maintain the reacting solutions at the desired pH. In addition, the unpleasant smell of ammonia could be avoided. The desired solutions were prepared as described below:-

Solution A.

Approximately 1M lead Acetate solution; This was prepared by dissolving about 380 g of lead acetate, $Pb(CH_3COO)_2\ 3H_2O$, in water and making up the volume to 1 litre, its lead content being determined complexometrically.[230] A desired volume of this solution was

added dropwise under constant stirring to an appropriate volume of ethylene diamine, determined previously by a trial experiment, such that the solution maintained a pH of 12 on making up to 1000 ml. Since the addition of ethylene diamine to lead acetate solution resulted in precipitation, probably of lead Hydroxide, care was taken to see that mixing was done in the reverse way such that the surplus concentration of ethylene diamine facilitated the retention of lead in the form of a soluble complex.[231] This was taken in a 3 necked round-bottomed flask of 3 litre capacity.

Solution B.

Approximately 0.5M solution of Diammonium hydrogen phosphate:—This was prepared by dissolving approximately 70 g of diammonium hydrogen phosphate in water and making up the volume to 1 litre, its phosphorus content being determined by Washburn and Shear's method[67]

Solution C

Approximately 0.5M Sodium ortho vanadate solution:— A sample of Ammonium meta vanadate was subjected to heating at $\sim 400^{o}C$ for $\sim$ 4 hours to convert it into vanadium pentoxide. About 50 g of the resulting sample were dissolved in 2N sodium hydroxide solution such that the total volume

was 1 litre, the vanadium content of the solution being determined iodimetrically.

An appropriate volume of Solution 'B' or 'C' or a mixture of them which was in a stoichiometric proportion to that of Solution 'A' was treated with a predetermined volume of ethylene-diamine such that it maintained a pH of 12 on making up to 1 litre and taken in a dropping funnel. The funnel was closed by a hollow ground - glass stopper, connected to soda-lime towers and fitted into a quick-fit socket of a 3-necked flask of 3 litre capacity containing solution A maintained at $37^{o}C$. While the solution from the dropping funnel was drained drop by drop, CO_2-free air obtained by the use of soda-lime towers and water suction pump was bubbled through the solution 'A' to eliminate the formation of carbonate-apatite and to keep it, in addition, well stirred. The precipitate was refluxed for about two hours in contact with the mother liquor, left overnight, filtered through a 1G4 sintered glass crucible, washed till washings were neutral and air dried. A part of it was heated to $\sim 300^{o}C$ for ~ 6 hours, for purposes of X-ray diffraction studies. A schematic representation of the assembly of the apparatus used for the preparation of the samples was given in Figure 2.1

Fig. 2-1 Assembly of the apparatus used for the preparation of Lead Phosphate apatite, Lead Vanadate apatite and their solid solutions.

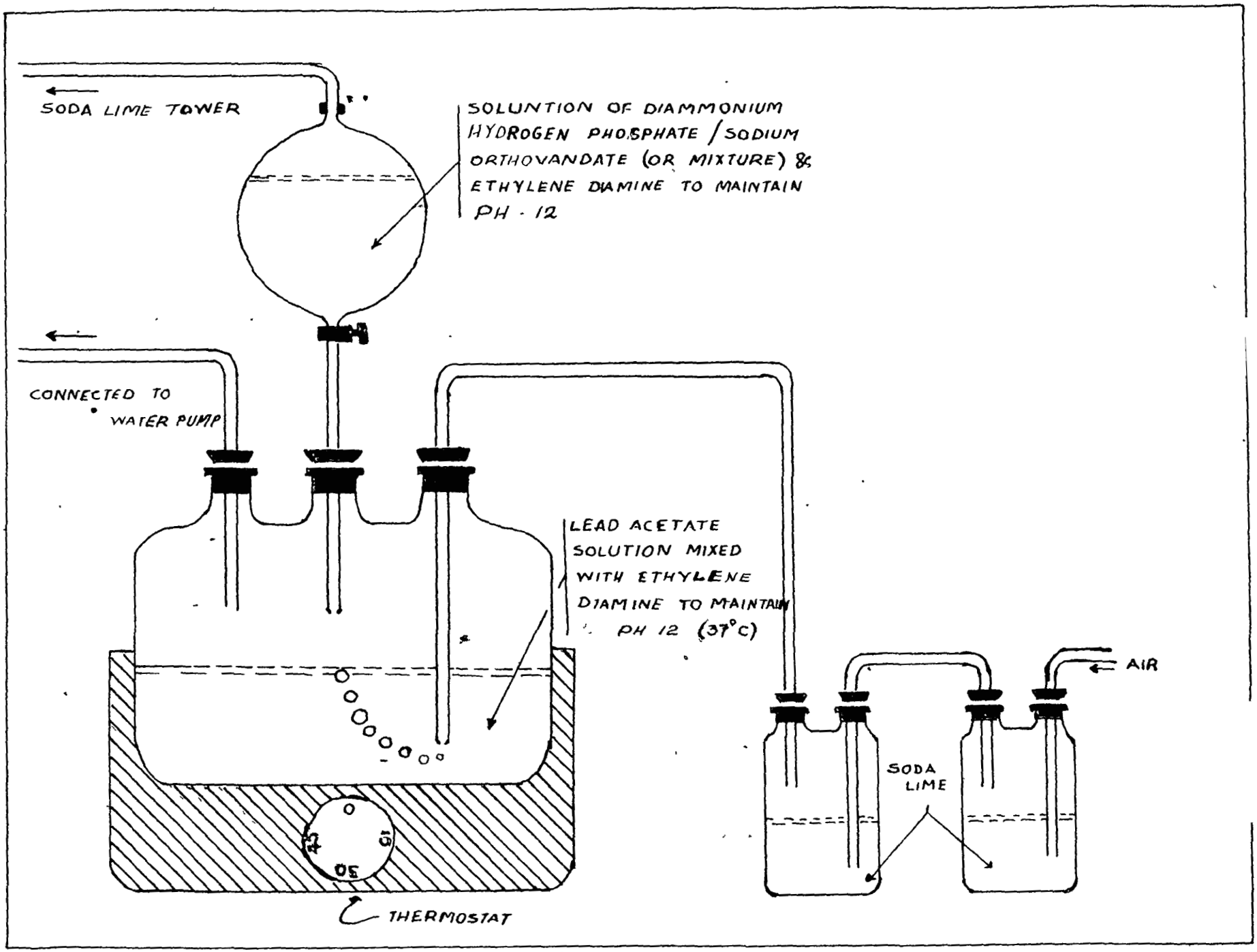

SODA LIME TOWER
SOLUNTION OF DIAMMONIUM HYDROGEN PHOSPHATE / SODIUM ORTHOVANDATE (OR MIXTURE) & ETHYLENE DIAMINE TO MAINTAIN PH - 12
CONNECTED TO WATER PUMP
LEAD ACETATE SOLUTION MIXED WITH ETHYLENE DIAMINE TO MAINTAIN PH 12 (37°C)
AIR
SODA LIME
THERMOSTAT

FIG. 2.1

2.2.2 Chemical Analyses

The chemical analysis of LPA is complicated by the mutual interference of lead and phosphate ions and consequently special analytical techniques are desired for the purpose. In presence of vanadate ions these complications become more pronounced as in the case of solid solutions of LPA and LVA. Although instrumental methods of analysis such as spectrophotometry[69], X-ray fluorescence[46] and flame photometry[232] have frequently been used for such determinations, they have a limited range of applicability. The desirability to work out special analytical techniques to bring about quantitative separation of these ions was therefore felt. When once such a separation was achieved, complexometric titrations[68] were found to be suitable for the subsequent determinations.

While for the end-embers Pb^{2+} is to be quantitatively separated from either PO_4^{3-} or VO_4^{3-} ions, for the solid solutions all the three ions are to be separated from one another. The accuracies of the procedures adopted were assessed by analysing sample solutions containing known quantities of the respective ions. The solutions used for these determinations were prepared in double-distilled water tested previously for the likely ions that

interfere in the subsequent complexometric determinations and preserved in polyethylene containers.

From an aliquot of a solution containing the three ions Pb^{2+} and PO_4^{3-} were determined gravimetrically as $Pb(IO_3)_2$ [233] and $MgNH_4PO_4.6H_2O$ [67] respectively. From another aliquot, reducing vanadium from +5 to +4 state using hydrazine hydrate, the combined amount of Pb^{2+} and VO_2^{2+} was determined complexometrically[234] from which subtraction of Pb content determined earlier gave that of vanadium.

The following solutions were prepared for the purpose

(a) Standard 0.01M EDTA Solution.

The disodium salt of EDTA (ethylene diamine tetra acetic acid) was dried for about 12 h at 80°C and cooled in a desiccated atmosphere so that the compound attained the composition of its dihydrate, $Na_2H_2C_{10}H_{12}O_8N_2.2H_2O$. 1 litre of 0.01M EDTA solution contained 3.7224 g of this dried substance.

(b) Lead Nitrate solution containing 1 mg of Pb per ml.

It was prepared by dissolving 1.0038 g of metallic lead in nitric acid (Sp. gr. 1.42) and the solution was evaporated to dryness. The mass was extracted with distilled

water and the volume made up to 1 litre. The lead content of the solution was determined complexometrically using Xylenol-orange as indicator ata pH of 5 obtained by hexamine as buffer.

(c) Potassium Dihydrogen Phosphate solution containing 1 mg of P per ml : 4.3930g of KH_2PO_4 heated previously to constant weight at 110°C were dissolved and made up to 1 litre.

(d) Sodium orthovanadate Solution containing 1 mg of 'V' per ml. Ammonium meta vanadate was heated to 400°C for 4 hr and a convenient amount of the resulting V_2O_5 was dissolved in approximately 2N sodium hydroxide solution and made up to 500 ml using the same solution. Knowing the vanadium content of the resulting solution iodimetrically[235] a required volume of it was measured accurately such that on making it up to 1 litre using 2 N sodium hydroxide the resulting solution contained 1 mg of V per ml.

In addition, (e) 0.5% solution of Xylenol orange and (f) approximately 6% solution of potassium iodate were prepared.

2.2.2.1 Quantitative Separation of Pb^{2+} and PO_4^{3-} ions.

From standard stock solutions of lead and

phosphorus (solutions 'b' and 'c' mentioned above) convenient volumes were mixed and the resulting solution was subjected to a quantitative separation of these elements by the following procedure to assess the accuracy of the method adopted.

The solution was made distinctly acidic by adding nitric acid (sp.gr. 1.42), heated to boiling, treated with ~30 ml of ~6 per cent potassium iodate solution under constant stirring and then maintained at ~70°C for ~30 minutes cooled and filtered through 1G3 sintered glass crucible. The residue was washed repeatedly using small portions of a total ~75 ml of 0.2 per cent potassium iodate solution prepared in 1 percent nitric acid. It was followed by washing successively with three 2 ml portions of ice-cold water and finally twice with a little dry acetone; the washings throughout the above operations being added to the filtrate. The crucible was dried to constant weight at 140°C and weighed as $Pb(IO_3)_2$.

From the filtrate $Mg NH_4 PO_4 \cdot 6H_2O$ was precipitated by treating it with 2 drops of methyl red indicator and an excess of 0.5M magnesium chloride solution, followed by the addition of ~9 M ammonium hydroxide till the solution

turned colourless, the presence of excess of Mg^{2+} being confirmed by the absence of further precipitation from the supernatant liquid on addition of the precipitant. It was left overnight in contact with the mother liquor, filtered through a 1G4 sintered glass crucible, washed successively with 0.4 M ammonium hydroxide, acid-free alcohol and ether till freed from the accompanying ions, dried overnight to constant weight at 37°C and weighed as $Mg\ NH_4\ PO_4.6H_2O$.

2.2.2.2 A Quantitative Separation of Pb^{2+} and VO_4^{3-} ions. From standard stock solutions of lead and vanadium (solutions 'b' and 'd' mentioned above), convenient volumes were mixed and the resulting solution was subjected to quantitative separation of the elements by the following procedure to assess the accuracy of the method adopted.

From an aliquot of this mixture lead was determined as $Pb(IO_3)_2$ as in 2.2.2.1 , while from another a combined estimation of it with vanadium was made in the following manner to get the amount of the latter. The solution was treated with ~10 ml of ~6 M hydrochloric acid and 2 ml of hydrazine hydrate, heated to boiling on a water bath to reduce vanadium from +5 to +4 state, cooled to room temperature and treated with a known volume of standard

solution of 0.01 M EDTA taking care to see that it was more than what was required, the pH being brought to ~3 by adding 2N. NaOH solution followed by the addition of 3 drops of Xylenol orange to be used as indicator. The attainment of the required pH (~ 5) was ensured by the addition of ~ 1 g of hexamine (hexamethylene tetramine). The excess EDTA was back-titrated with a standard 0.005M lead nitrate solution, the colour change being from yellow to red.

2.2.2.3 A Quantitative Separation of Pb^{2+} , PO_4^{3-} and VO_4^{3-} ions. It is evident that a combination of methods given under 2.2.2.1 and 2.2.2.2 when applied in succession to a solution containing Pb^{2+}, PO_4^{3-} and VO_4^{3-} could enable a quantitative separation of all the three ions to be made.

The above methods were applied to the chemical analyses of LPA, LVA and their solid solutions, convenient amount of each being dissolved in a minimum quantity of ~4N Nitric acid and made up to 500 ml.

2.2.3 Determination of unit-cell volumes:- The criteria for a given pair of substances to form solid solutions are that the two substances are isomorphous and the ionic radii of the corresponding pairs of ions are comparable. It is

evident that LPA and LVA fulfil these requirements. Since the replacement of PO_4^{3-} by VO_4^{3-} (covalent radii 1.10 and 1.22 Å respectively) in an apatite lattice brings about a dilation of the unit cell, a proof for the formation and homogeneity of the resulting solid solutions can be provided by the determination of the lattice constants and the accompanying calculation of the unit cell volumes. The Debye-Scherrer powder method was found to be suitable for the purpose, since the samples are microcrystalline in nature being precipitated from aqueous media. The samples subjected to these investigations were previously heated for ~6 h at ~300°C in order to increase the size of the crystals[46] so that the sharpness of the diffraction lines could be enhanced. The patterns of the samples (Nos. 1,2,3 and 8 of Table 2.5 P) were recorded using a Debye-Scherrer camera of 114.6 cm diameter with a rotating-sample exposed to Cu K_α radiation, the voltage, current strength and exposure time being 40KV, 25 mA and 5 h while those of other samples (Nos. 4,5,6 and 7 of Table 2.5 P) were recorded using Co radiation, voltage, current strength and exposure time being 20 KV, 5 mA and 40 h. The distance between each line on the pattern and the point where the transmitted beam would strike the film in the absence of diffraction was measured using a micrometer scale

from which values of 2θ and d were calculated. Using statistical methods, the lines corresponding to about 10 reflection planes were indexed for each sample.

2.2.4 Electronmicroscopic investigations

The conclusions drawn from x-ray diffraction patterns confirming the homogeneity of the samples could be supplemented by their electron micrographs which, in addition, could scrutinise the absence of extraneous phases and provide visual information about the geometry and dimensions of the individual crystals of the samples. Air-dried samples were found to be better suited for the purpose than those heated to 300°C, since the latter operation was found to lead to fusion of the individual crystals into large crystalline masses[236] preventing thereby the measurement of the dimensions of individual crystals.

A pinch of the sample was dispersed in a few ml of water and the suspension was subjected for a few minutes to ultrasonic radiation at a frequency of a few hundred kilocycles per sec. in order to break down the conglomeration of the individual crystals. A drop of the resulting slurry was taken on a copper grid, placed in the vacuum chamber of an electron microscope (Philips EM300) with carbon

as back-ground and the specimen exposed to the electron beam after evacuation, the resulting image being viewed on a small fluoroscopic screen. When the field of vision consisted of well defined individual crystals, it was photographed. From each electron micrograph, a few individual crystals, preferably of varying dimensions, were focussed at random under a calibrated eye-piece and through measurement of the length and breadth of these crystals their average dimensions were calculated. An attempt was made to calculate the specific surface areas of a few representative samples among those prepared using the measured length and breadth. The crystals of the samples which are in the form of elongated hexagonal prisms could be considered as cylinders[237] for purposes of evaluation of their approximate specific surface areas using the expression,

$\frac{(2\pi r^2 + 2\pi rh)}{\pi r^2 h \rho}$, where r = 0.5 times the average breadth, h = average length, ρ = density of the sample.

It is evident that the rates of dissolution[110] of the samples which decide the period of equilibration required for the attainment of saturation are dependent on their surface areas. In addition the utility of apatites as luminescent phosphors and ion-exchangers[117] is also

controlled by their surface areas. An evaluation of the surface areas of the samples is therefore justified.

2.2.5 Infrared Spectra

The infrared absorption spectra of the samples were recorded as nujol mulls using a Perkin Elmer Infrared Spectrophotometer, Model 297, equipped with KBr optics. The spectra were recorded within a wave-number range of 4000-650 cm^{-1}. The operation of the instrument was based on directing alternatively the i.r. radiation through the test and reference samples and bringing together the two transmitted beams on a thermo-couple. With unequal absorption in the two paths a pulsating output was generated, amplified and made to operate a variable shutter to increase or decrease the intensity of the reference beam which could then be recorded on a chart paper as a function of the wave number. In addition to the patterns recorded as nujol mulls, those using KBr pellets were also recorded in the case of the end-numbers.

2.2.6 Thermoanalytical Studies

Thermogravimetric analyses of the samples were intended to know their thermal stabilities with special reference to the removal of volatile impurities, the nature

of water associated with the samples and the decomposition temperatures. It may be mentioned that there is no earlier literature available on thermoanalytical studies of LPA and LVA. These investigations were restricted exclusively to the two end-members, LPA and LVA, and not extended to their solid solutions since the earlier investigations on allied system indicated that the solid solutions exhibited a hebaviour intermediary to that of the end-members.

A convenient weight of the sample (about 0.5g) was taken in a 10 ml capacity platinum crucible and suspended from the pan of a micro-balance, the crucible being housed in a high temperature furnace (F.C.I., Sindri, India). Starting from ambient temperature, the sample was heated at a convenient rate ($\sim 8^{\circ}C$ / min.) upto a maximum of about $900^{\circ}C$. At frequent intervals the weight of the sample and the corresponding furnace temperature were recorded so that the dependence of per cent weight loss on temperature could be represented.

2.3 Results

Table 2-1

Quantitative separation of lead and phosphorus - Assessment of Attainable accuracy

Element	Trial No. I Wt.(mg) Theo.	Exptl.	% Error	Trial No. II Wt.(mg) Theo.	Exptl.	%Error
Lead	27.47	27.33	-0.50	33.00	33.20	+0.80
Phosphorus	10.00	9.96	-0.40	70.00	70.40	+0.60

Table 2-2

Quantitative separation of lead and vanadium - Assessment of attainable accuracy

Element	Trial No. I Wt.(mg) Theo.	Exptl.	% Error	Trial No. II Wt.(mg) Theo.	Exptl.	% Error
Lead	54.70	54.80	-0.20	33.00	33.80	+0.60
Vanadium	10.00	9.90	+1.00	12.00	12.10	-0.80

Table 2-3

Quantitative separation of lead, phosphorus and vanadium - Assessment of attainable accuracy

Trial No.	Element								
	Lead			Phosphorus			Vanadium		
	Wt.(mg)		%	Wt.(mg)		%	Wt.(mg)		%
	Theo.	Exptl.	Error	Theo.	Exptl.	Error	Theo.	Exptl.	Error.
1	49.10	49.30	+0.40	10.00	10.00	0.00	10.00	9.90	-1.00
2	39.30	38.80	-1.30	12.00	11.90	-0.80	12.00	12.00	0.00
3	29.50	29.40	-0.30	14.00	14.10	+0.70	13.70	13.80	+0.70

Table 2.4

Determination of g atom ratio $\frac{Pb}{(P+V)}$, of phosphate and vanadate apatites of lead and their solid solutions

S.No.	Sample	Wt.(%)			Molecular formula*	g atom ratio, $\frac{Pb}{(P+V)}$
		Pb	P	V		
(1)	(2)	(3)	(4)	(5)	(6)	(7)
1.	Lead phosphate apatite (LPA)	77.86	6.97	-	$Pb_{10}(PO_4)_6(OH)_2$	1.67
2.	Solid Solution I	76.61	6.19	1.16	$Pb_{10}(PO_4)_{5.4}(VO_4)_{0.6}(OH)_2$	1.66
3.	" II	77.36	5.13	2.74	$Pb_{10}(PO_4)_{4.5}(VO_4)_{1.5}(OH)_2$	1.70
4.	" III	76.69	4.15	4.22	$Pb_{10}(PO_4)_{3.69}(VO_4)_{2.31}(OH)_2$	1.71
5.	" IV	75.61	3.37	5.55	$Pb_{10}(PO_4)_3(VO_4)_3(OH)_2$	1.68
6.	" V	75.46	2.99	6.40	$Pb_{10}(PO_4)_{2.6}(VO_4)_{3.4}(OH)_2$	1.64
7.	" VI	75.26	2.15	7.54	$Pb_{10}(PO_4)_{1.9}(VO_4)_{4.1}(OH)_2$	1.67
8.	" VII	75.69	1.32	8.81	$Pb_{10}(PO_4)_{1.2}(VO_4)_{4.8}(OH)_2$	1.69
9.	" VIII	75.24	0.45	10.42	$Pb_{10}(PO_4)_{0.4}(VO_4)_{5.6}(OH)_2$	1.66
10.	Lead vanadate apatite (LVA)	74.37	-	10.80	$Pb_{10}(VO_4)_6(OH)_2$	1.69

* Based exclusively on Pb, P and V contents (OH) content being assumed to be stoichiometric.

Table 2.5

Lattice Constants and Unit Cell Volumes of Phosphate and Vanadate apatites of Lead and a few of their solid solutions.

Sample No.	Molecular formula	Molecular weight	Lattice Constants A°				C/a		Unit Cell Volume $\frac{\sqrt{3}}{2} a^2 c$ (A^3)	
			a		c					
			Direct	Refined*	Direct	Refined*	Direct	Refined	Direct	Refined
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
1	$Pb_{10}(PO_4)_6(OH)_2$ (LPA)	2675.8	9.889	9.8877	7.435	7.4476	0.752	0.7532	629.7	630.6
2	$Pb_{10}(PO_4)_{5.4}(VO_4)_{0.6}(OH)_2$	2687.9	9.910	9.9172	7.460	7.4477	0.753	0.7510	634.7	634.4
3	$Pb_{10}(PO_4)_{4.5}(VO_4)_{1.5}(OH)_2$	2705.7	9.970	9.9614	7.453	7.4478	0.748	0.7477	641.7	640.0
4	$Pb_{10}(PO_4)_{3.69}(VO_4)_{2.31}(OH)_2$	2721.9	9.977	9.9997	7.458	7.4479	0.748	0.7448	642.9	645.0
5	$Pb_{10}(PO_4)_{2.6}(VO_4)_{3.4}(OH)_2$	2743.6	10.065	10.0557	7.438	7.4480	0.739	0.7407	652.5	652.2
6	$Pb_{10}(PO_4)_{1.9}(VO_4)_{4.1}(OH)_2$	2757.7	10.117	10.0911	7.417	7.4481	0.733	0.7381	657.4	656.8
7	$Pb_{10}(PO_4)_{1.2}(VO_4)_{4.8}(OH)_2$	2771.6	10.128	10.1235	7.476	7.4482	0.738	0.7357	664.1	661.1
8	$Pb_{10}(VO_4)_6(OH)_2$ LVA	2795.5	10.163	10.1825	7.447	7.4483	0.733	0.7315	666.1	668.8

*Lattice parameters were refined by the method of least squares using a micro computer and hence are given up to four places of decimal.

Table 2-6

Approximate dimensions of individual crystals and specific surface areas of phosphate and vanadate apatites of lead and of a representative solid solution.

S.No.	Sample	Density (g/ml)	Average diamensions of individual crystals (Å)		Approximate surface area (m^2/g)
			Length	Breadth	
A	Lead Phosphate apatite	6.980	2512	1012	6.8
B	Solid Solution (80% LVA)	7.081	2303	744	8.8
C	Lead vanadate apatite	7.112	2625	1062	6.4

Table 2.7 Infrared absorption bands of phosphate and vanadate apatites of lead and their solid solutions

S.No.	Molecular formula	Wave Number (cm^{-1})		
		PO_4^{3-}	VO_4^{3-}	OH^-
(1)	(2)	(3)	(4)	(5)
1	$Pb_{10}(PO_4)_6(OH)_2$	1040,975 520,570,920-1050*	-	3560,3400
2	$Pb_{10}(PO_4)_{5.4}(VO_4)_{0.6}(OH)_2$	1040,980	780	3560,3380
3	$Pb_{10}(PO_4)_{4.5}(VO_4)_{1.5}(OH)_2$	1040,980	780,760	3540,3380
4	$Pb_{10}(PO_4)_{3.69}(VO_4)_{2.31}(OH)_2$	1050,980	800,750	3420
5	$Pb_{10}(PO_4)_3(VO_4)_3(OH)_2$	1050,980	800,750	3540,3400
6	$Pb_{10}(PO_4)_{2.6}(VO_4)_{3.4}(OH)_2$	1050,980	800,750	3540,3400
7	$Pb_{10}(PO_4)_{1.9}(VO_4)_{4.1}(OH)_2$	1050,1020,980	810,750	3540,3400
8	$Pb_{10}(PO_4)_{1.2}(VO_4)_{4.8}(OH)_2$	1050,965	800,750	3540,3410
9	$Pb_{10}(PO_4)_{0.4}(VO_4)_{5.6}(OH)_2$	1025	800,735	3400
10	$Pb_{10}(VO_4)_6(OH)_2$	-	840,800,740, 320,720-810*	3515

* Determined with the sample as KBr pellet while the rest were as mujol mulls.

Fig. 2-2 Debye-Scherrer diffraction powder patterns of samples (S.Nos. 1,2,3 and 4, Table 2-5).

1. Lead phosphate apatite
2. Solid Solution No.1 (10.0 mole % Lead Vanadate apatite).
3. Solid Solution No.2 (25.0 % mole % Lead Vanadate apatite).
4. Solid Solution No.3 (38.0 mole % Lead Vanadate apatite).

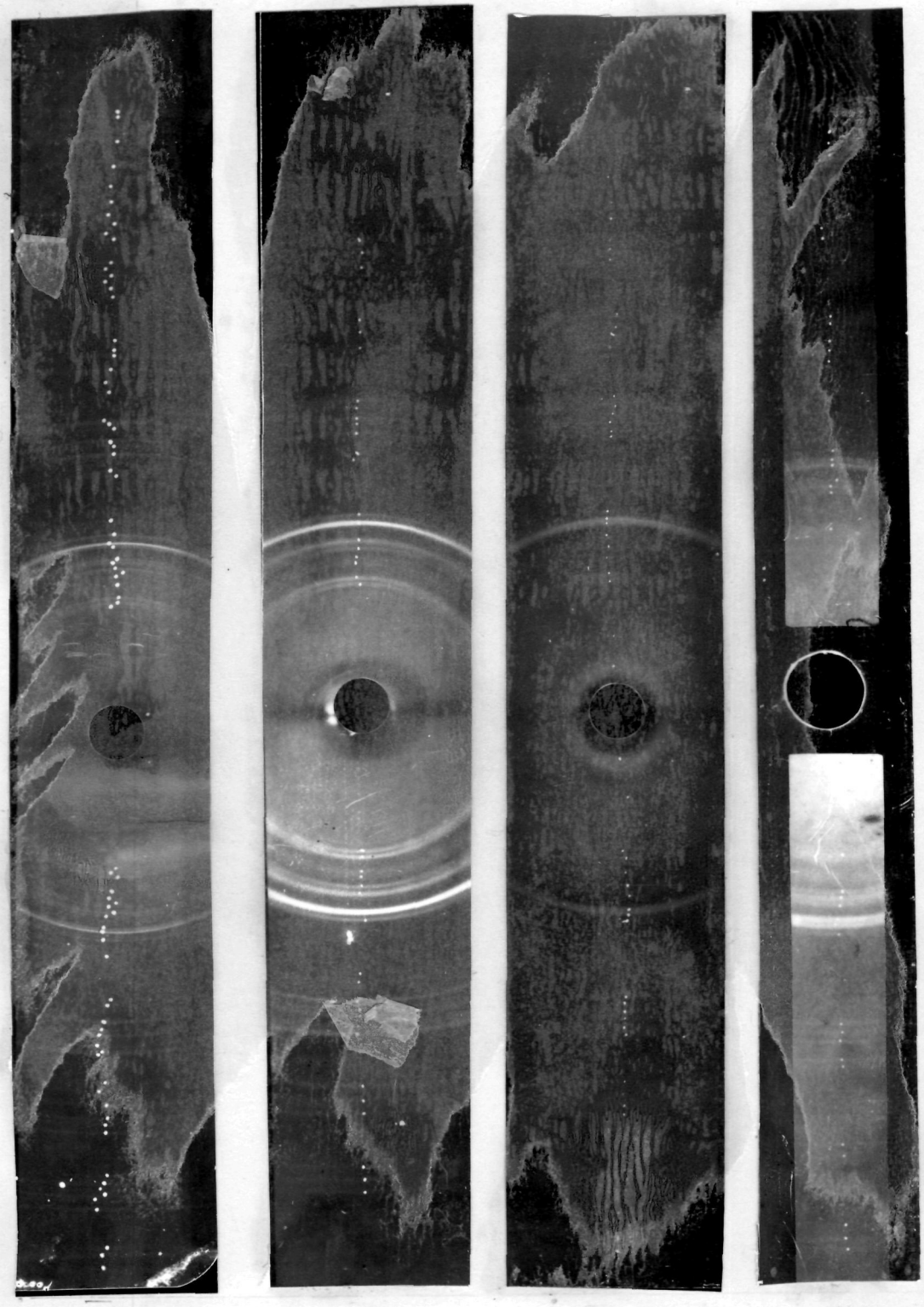


FIG. 2.2

Fig. 2-3 Debye - Scherrer diffraction powder patterns of samples (S.Nos. 5,6,7 and 8, Table 2.5).

5. Solid Solution No.4 (57.0 mole % Lead Vanadate apatite).
6. Solid Solution No. 5 (69.0 mole % Lead Vanadate apatite).
7. Solid Solution No. 6 (80.0 mole % Lead Vanadate apatite).
8. Lead Vanadate apatite.

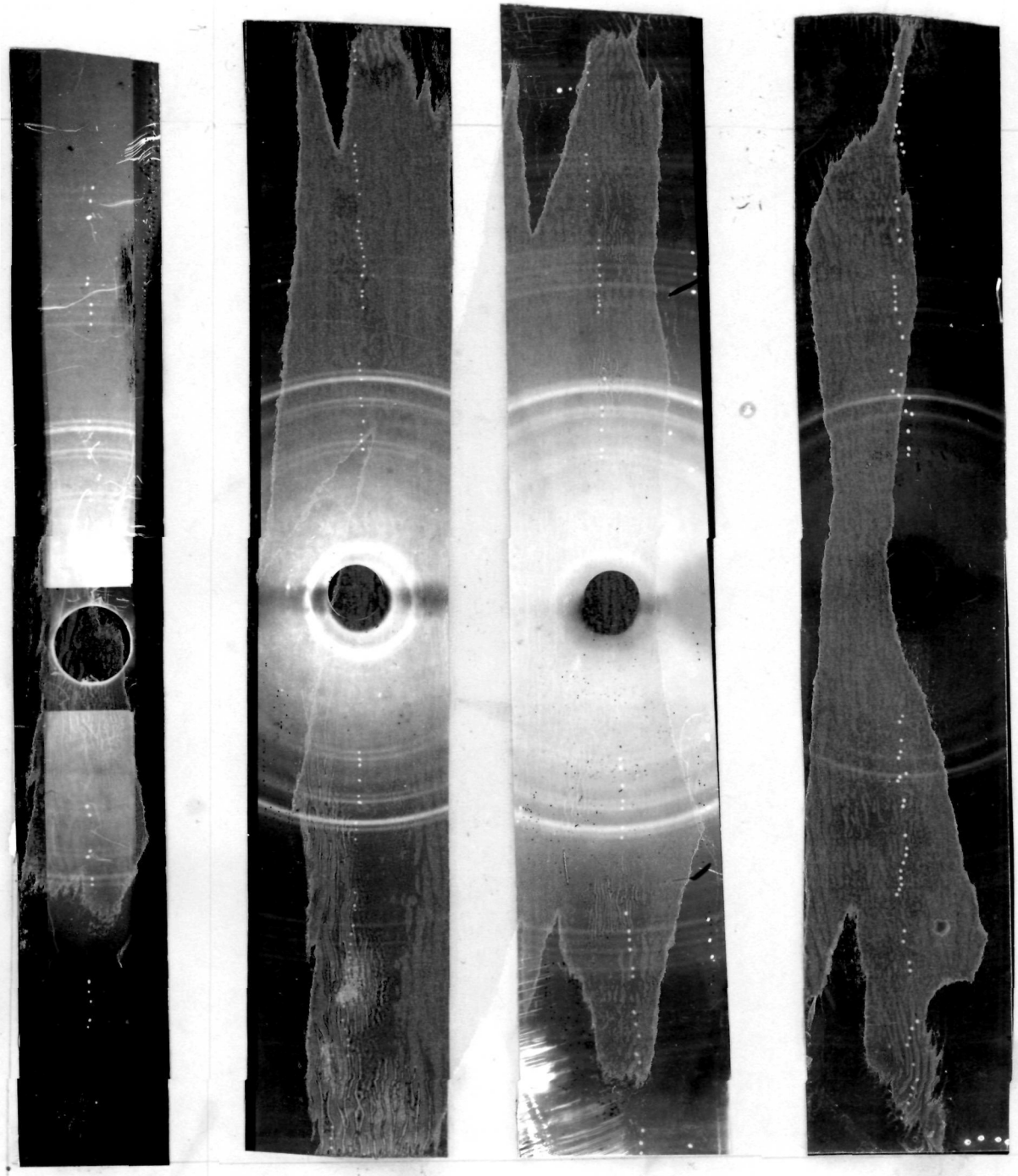


FIG. 2.3

Fig. 2.4 (I) Dependence of lattice Constants of the solid solutions of phosphate and Vanadate apatites of Lead on the mole per cent of Lead Vanadate apatite (Column 4 and 6 of Table 2.5)

(II) Dependence of the ratio of the lattice Constants (c/a) of the solid solutions on the mole per cent of Lead Vanadate apatite.(Column 8 of Table 2.5)

(III) Dependence of unit cell volumes of the solid solutions of phosphate and Vanadate apatites of Lead on the mole per cent of Lead Vanadate apatite. (Column 10 of Table 2.5)

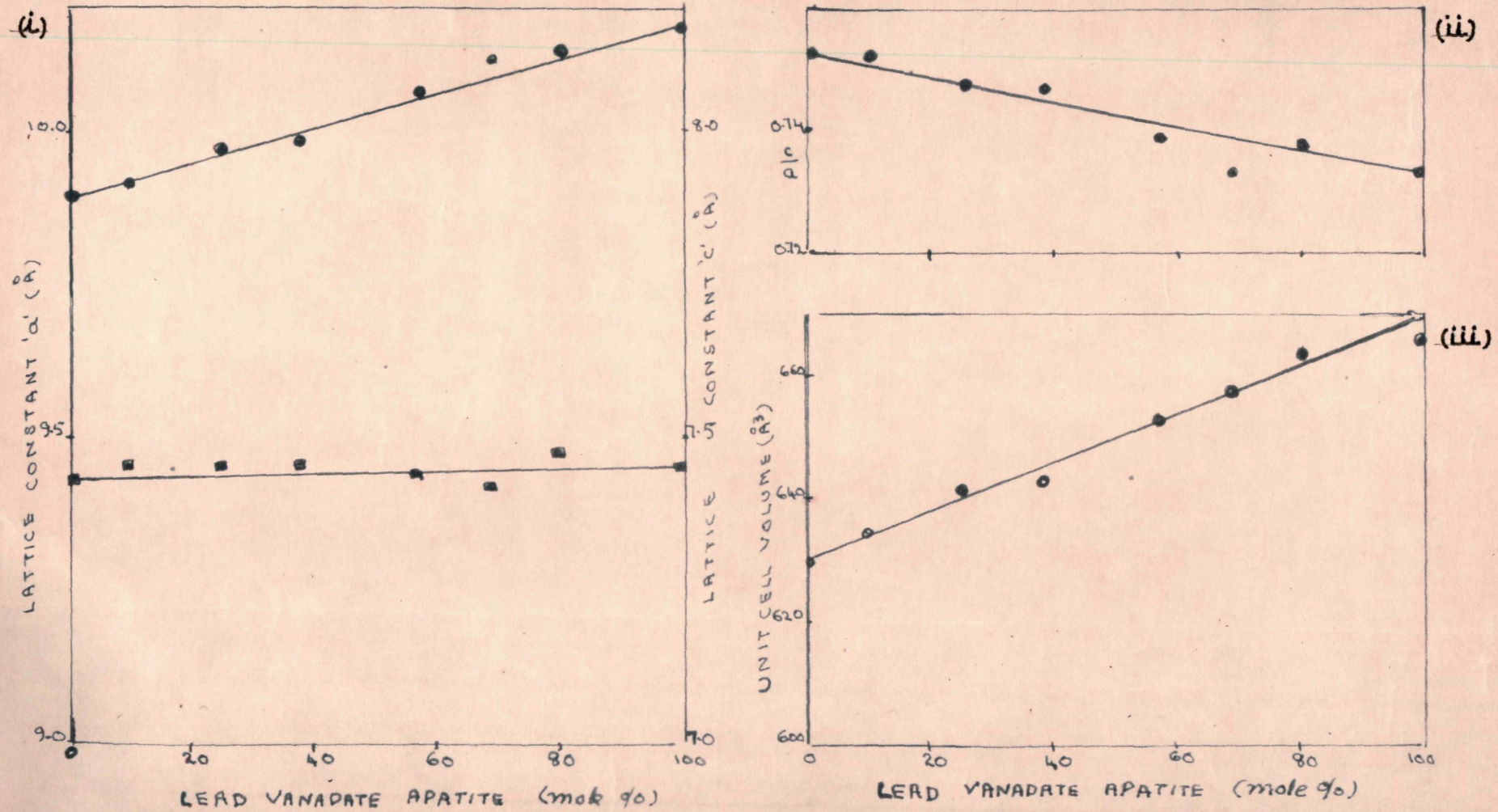

LATTICE CONSTANT 'a'
LATTICE CONSTANT 'c'
(i)
10.0
9.5
9.0
8.0
7.5
7.0
LATTICE CONSTANT 'a' (Å)
LATTICE CONSTANT 'c' (Å)
0
20
40
60
80
100
LEAD VANADATE APATITE (mole %)
(ii)
0.74
c/a
0.72
(iii.)
660
640
620
600
UNIT CELL VOLUME (Å³)
0
20
40
60
80
100
LEAD VANADATE APATITE (mole %)

Fig. 2-5 (I) Dependence of lattice constants of the solid solutions of phosphate and Vanadate apatites of Lead on the mole per cent. of Lead Vanadate apatite.
(Taken from Column 5 and 7 of Table 2.5)

(II) Dependence of the ratio of lattice constants (c/a) of the solid solutions on the mole per cent. of Lead Vanadate apatite.
(Taken from column 9 of Table 2.5)

Fig. 2.6 Dependence of unit cell volumes of the solid Solutions of phosphate and Vanadate apatites of Lead on the mole per cent. of Lead Vanadate apatite.
(Taken from column 11 of Table 2.5)

FIG. 2.6

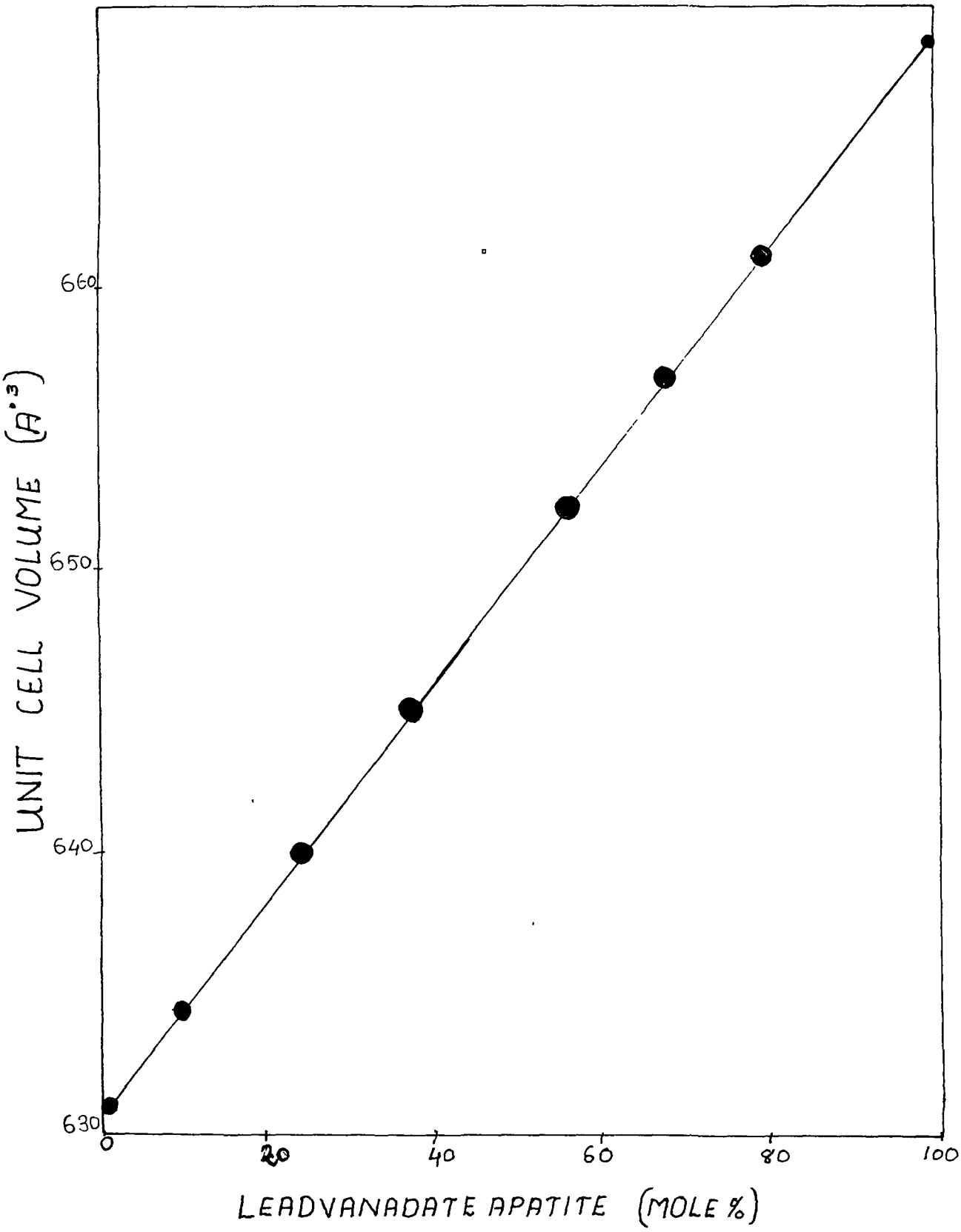

UNIT CELL VOLUME (A°3)
660
650
640
630
0
20
40
60
80
100
LEADVANADATE APATITE (MOLE %)

Fig. 2-7 Electronmicrographs of the samples
(S.Nos. A,B and C, Table 2.6)

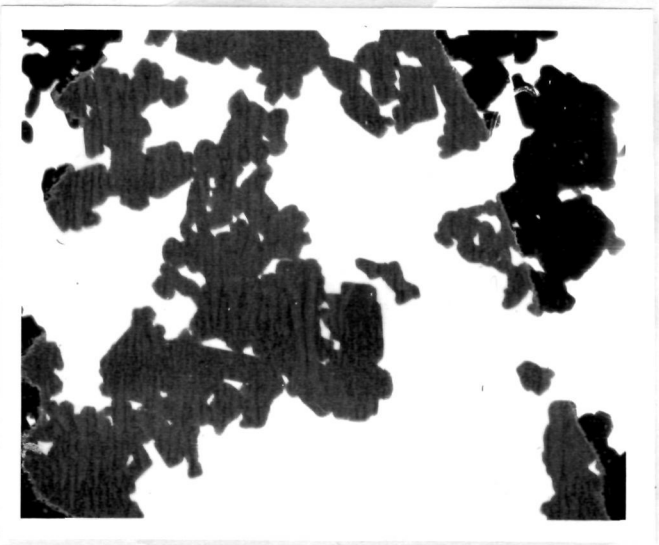
(A) Electronmicrograph of Lead Phosphate apatite.

(B) Electronmicrograph of solid solution No. 6
(80.0 mole per cent. of Lead Vanadate apatite).

(C) Electronmicrograph of Lead Vanadate apatite.

(magnification in all cases, 80,000 x).

(A)



(B)

(C)

FIG. 2.7

Fig. 2-8 I.R. traces of samples
(S.Nos.1,2 and 3, Table 2.7)

(1) Lead phosphate apatite

(2) Solid solution No.1 (10.0 mole %
Lead Vanadate apatite)

(3) Solid Solution No.2 (25.0 mole %
Lead Vanadate apatite).

FIG. 2.8

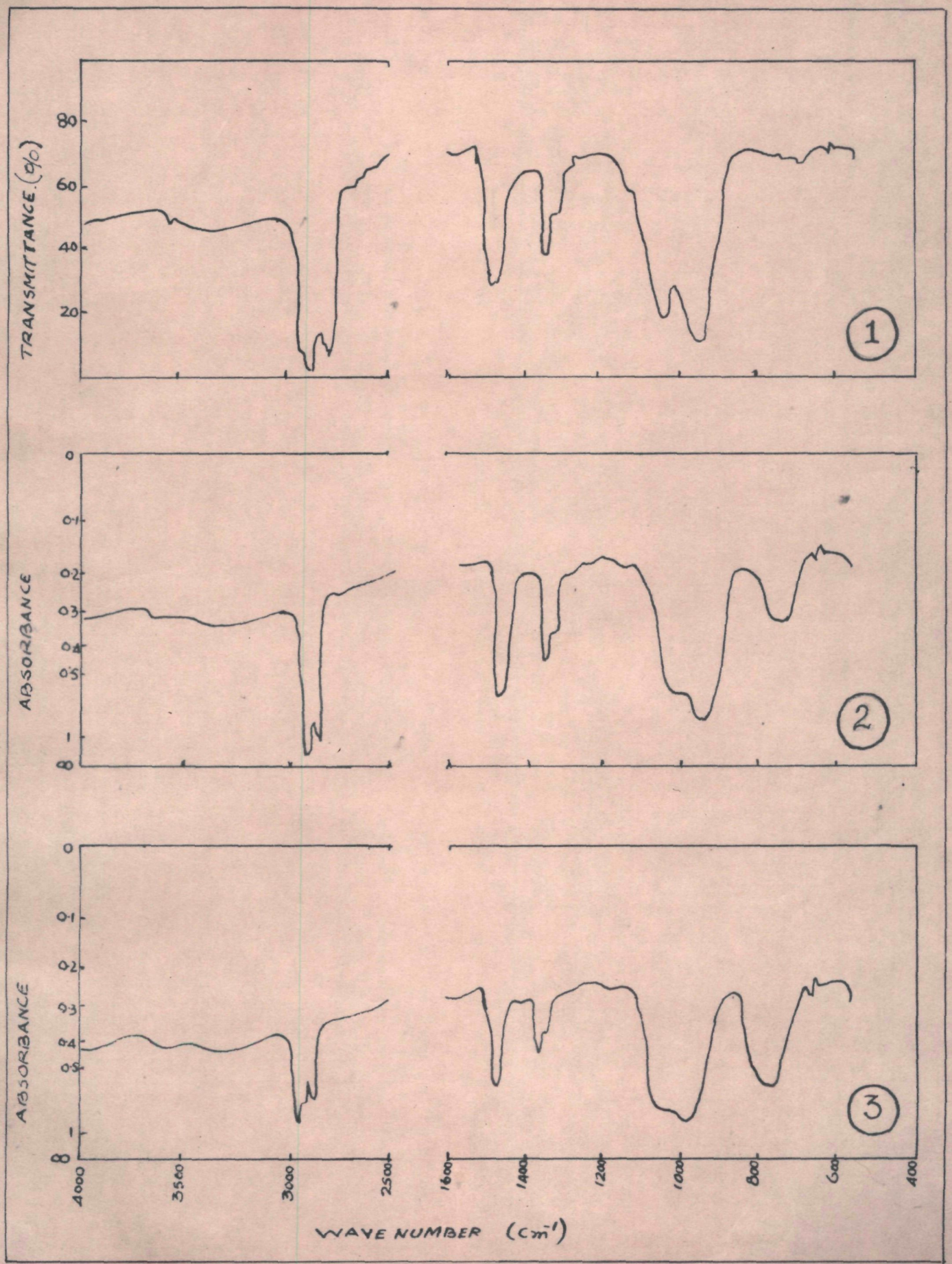

TRANSMITTANCE (%)
80
60
40
20
1
ABSORBANCE
0
0·1
0·2
0·3
0·4
0·5
1
2
ABSORBANCE
0
0·1
0·2
0·3
0·4
0·5
1
3
4000
3500
3000
2500
1600
1400
1200
1000
800
600
400
WAVE NUMBER (cm⁻¹)

Fig. 2.9 I.R. traces of samples
(S.Nos. 4,5 and 6, Table 2.7)

(4) Solid Solution No.3 (38.0 mole %
Lead Vanadate apatite)

(5) Solid Solution No.4 (50.0 mole %
Lead Vanadate apatite).

(6) Solid solution No.5 (57.0 mole %
Lead Vanadate apatite).

FIG. 2.9

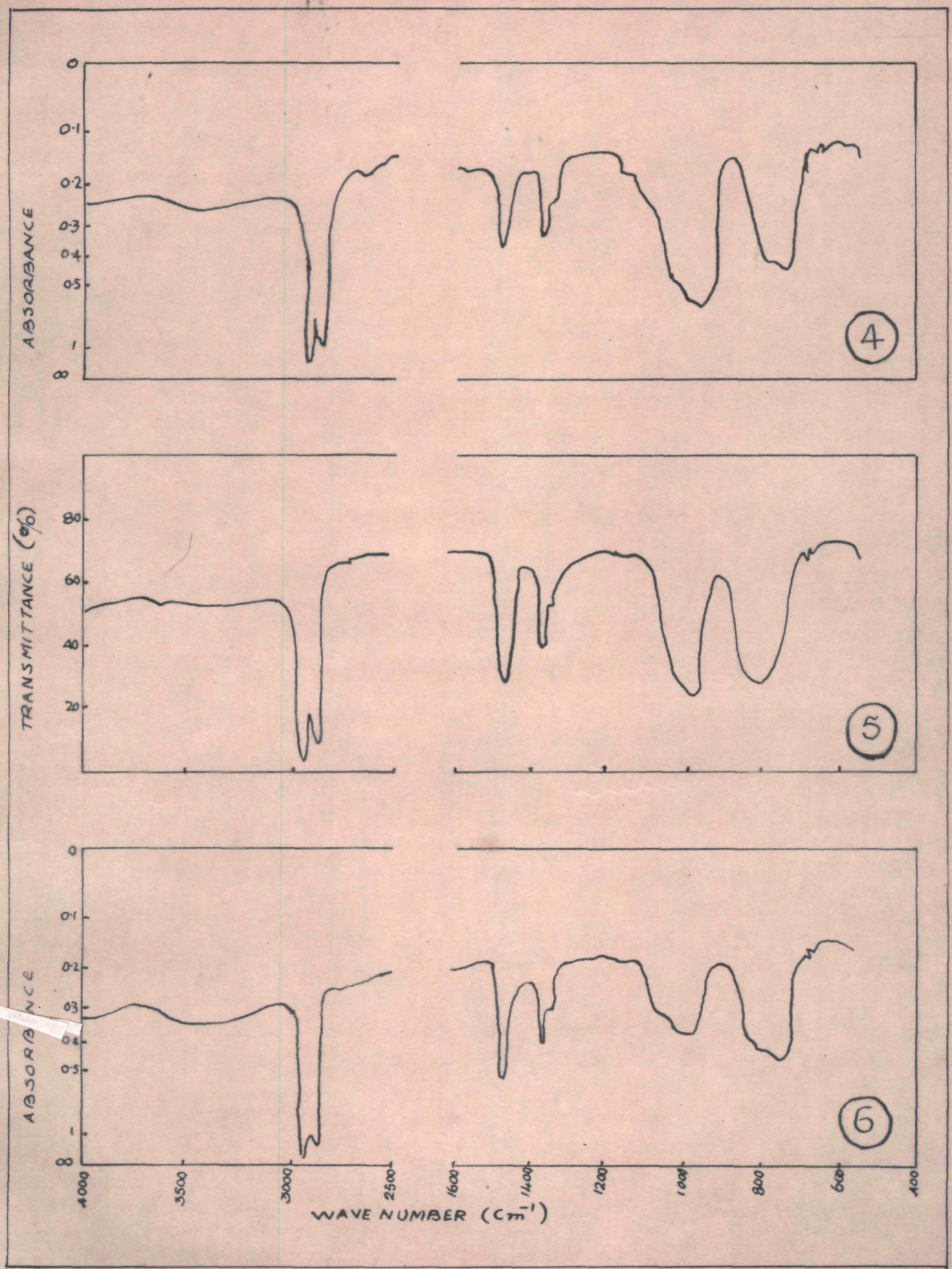

ABSORBANCE
0
0·1
0·2
0·3
0·4
0·5
1
∞
4
TRANSMITTANCE (%)
80
60
40
20
5
ABSORBANCE
0
0·1
0·2
0·3
0·4
0·5
1
∞
6
4000
3500
3000
2500
1600
1400
1200
1000
800
600
400
WAVE NUMBER (Cm⁻¹)

Fig. 2-10 I.R. traces of samples
(S.Nos. 7 and 8, Table 2.7).

(7) Solid Solution No. 6 (69.0 mole %
Lead Vanadate apatite)

(8) Solid solution No.6 (80.0 mole %
Lead Vanadate apatite)

FIG. 2.10

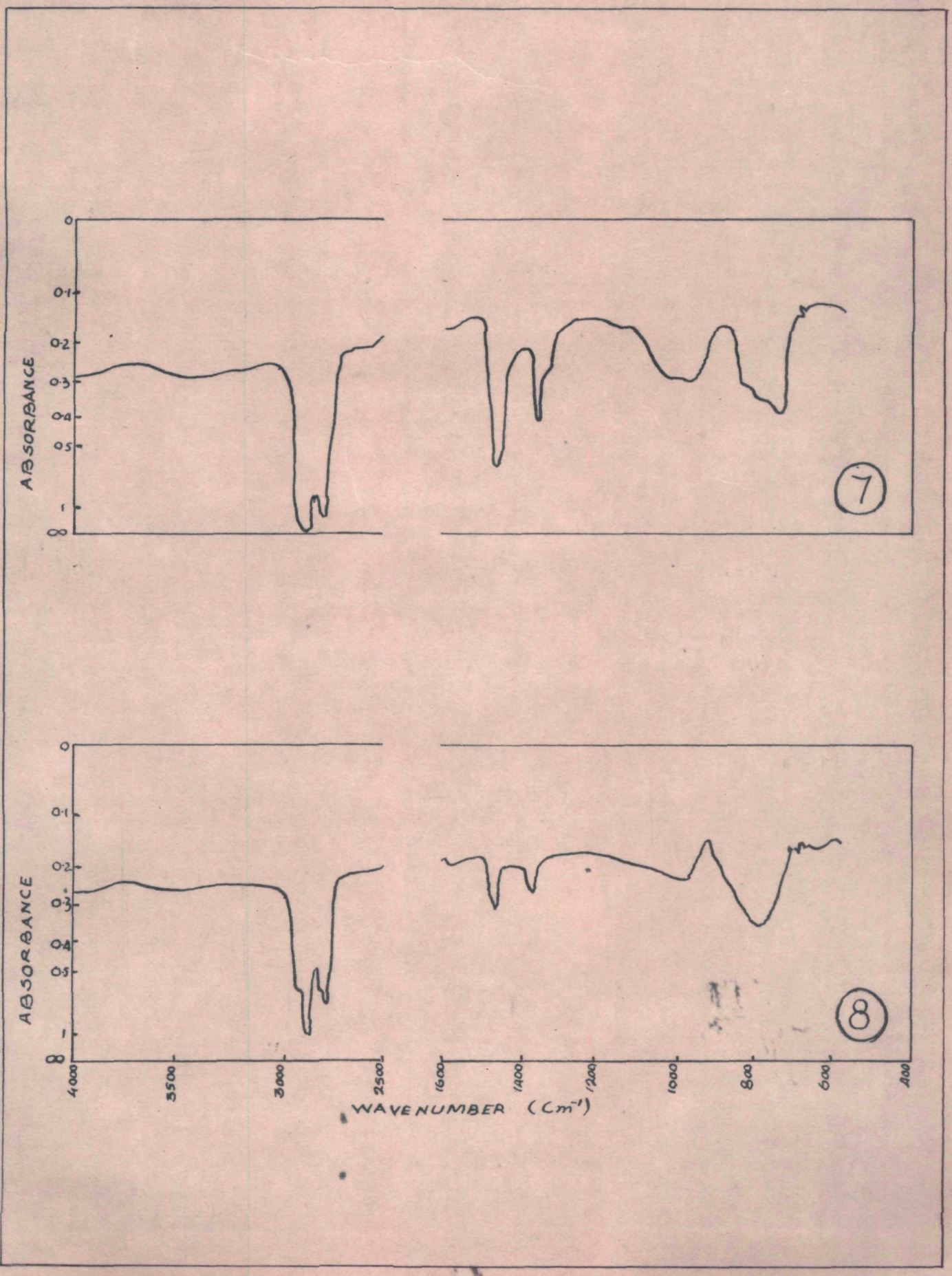

ABSORBANCE
0
0·1
0·2
0·3
0·4
0·5
1
7
ABSORBANCE
0
0·1
0·2
0·3
0·4
0·5
1
8
4000
3500
3000
2500
1600
1400
1200
1000
800
600
400
WAVENUMBER (Cm⁻¹)

Fig. 2.11 I.R. traces of samples
(S.Nos. 9 and 10, Table 2.7)

(9) Solid solution No.7 (94.0 mole %
Lead Vanadate apatite).

(10) Lead Vanadate apatite.

Fig. 2.11

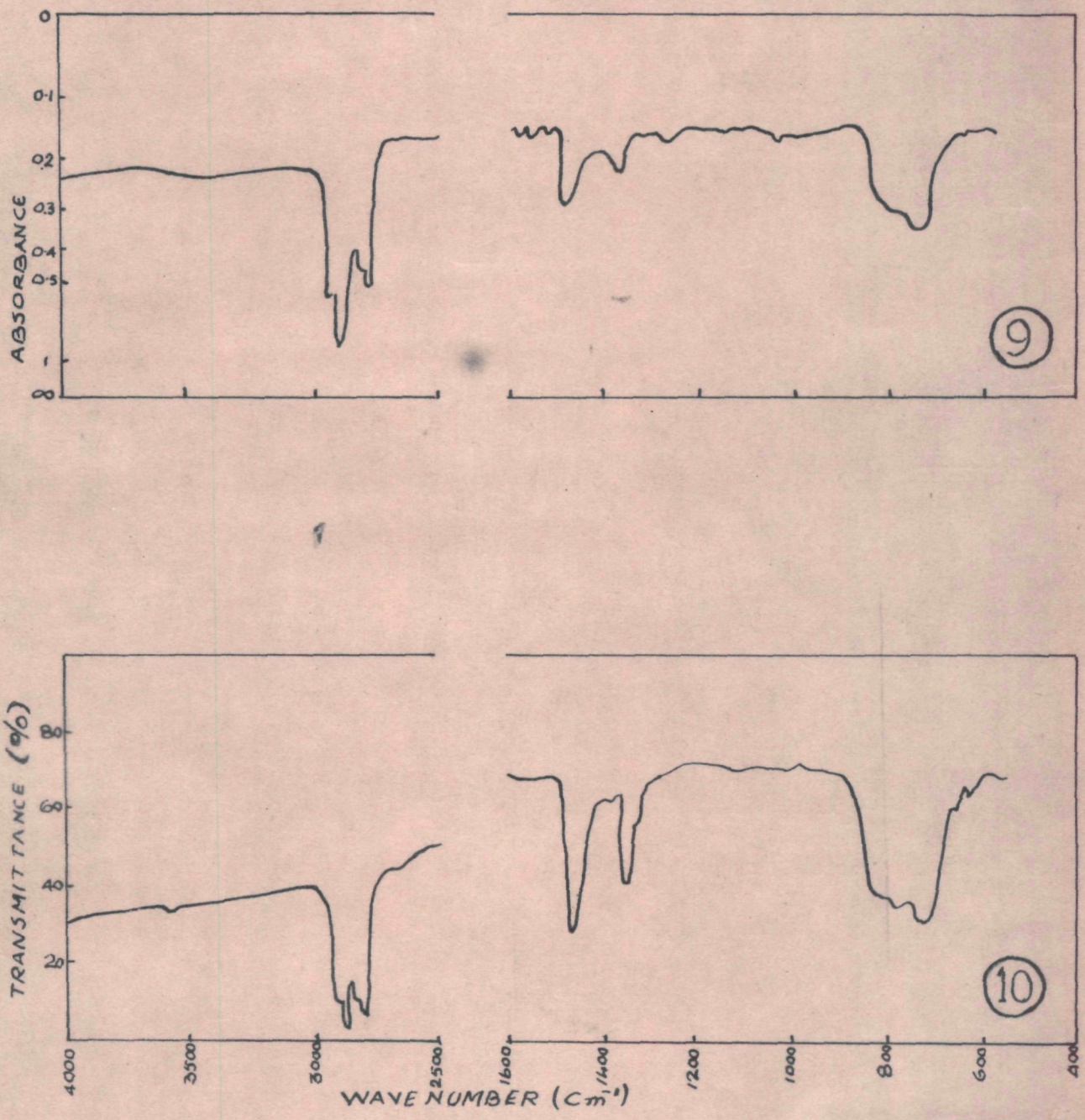

ABSORBANCE
0
0·1
0·2
0·3
0·4
0·5
9
TRANSMITTANCE (%)
80
60
40
20
10
4000
3500
3000
2500
1600
1400
1200
1000
800
600
400
WAVE NUMBER (cm⁻¹)

Fig. 2-12 I.R. traces of samples taken as KBr pellets

(1) Lead Phosphate apatite

(2) Lead Vanadate apatite.

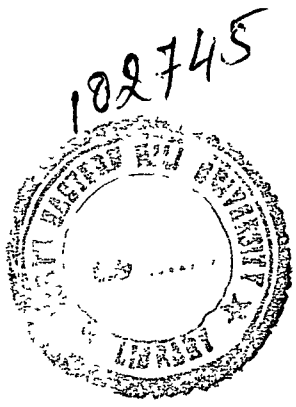
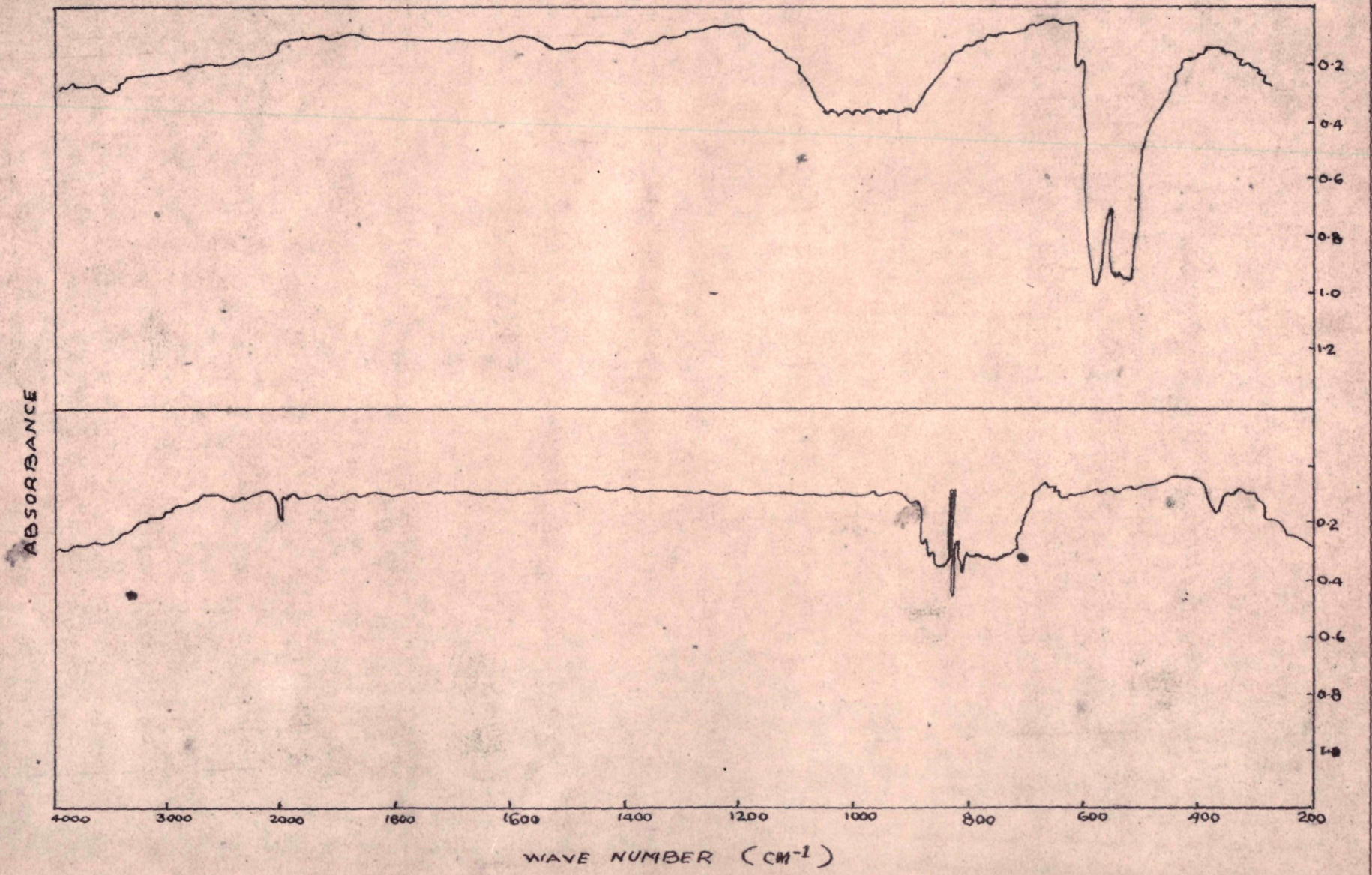


Fig. 2.12


ABSORBANCE
0·2
0·4
0·6
0·8
1·0
1·2
0·2
0·4
0·6
0·8
4000
3000
2000
1800
1600
1400
1200
1000
800
600
400
200
WAVE NUMBER (CM⁻¹)

2.3 Results

The accuracies of the methods employed for the chemical analyses of LPA, LVA and their solid solutions were scrutinised by applying these methods for analysis of sample solutions containing accurately weighed quantities of the ions concerned and the results were given in Tables 2.1 to 2.3, pp..... The analyses were conducted in each case with a set of three different concentrations. The ranges of errors expressed as weight per cents were found to be + 0.40 to - 1.30, 0.00 to - 0.80 and -1.00 to 0.73 respectively, for lead, phosphorus and vanadium when present together

Determination of the weight per cents of lead, phosphorus and vanadium of each one of the samples, arranged serially in Table 2.4 p..... in increasing order of vanadium content, was made and the results were given in columns (3), (4) and (5) of the Table. It is evident that for the samples the g atoms of phosphorus and vanadium present in 100 g of the sample can be calculated by dividing the respective percentages by the corresponding atomic weights. It is obvious that this ratio, P/V, is independent of the amount of the sample considered. Since the total number of g atoms of $(P+V)_A$ in a mole of each sample is six,

knowing this ratio, the number of g atoms of P$_2$ and V in a mole of each sample could be calculated and the molecular formulae of the samples indicated in column(6) assigned assuming the number of lead and hydroxyl ions to remain stoichiometric for the entire series of samples. In addition, the g atom ratio, $\frac{Pb}{(P+V)}$, was calculated for each sample from the corresponding weight per cents and included in column (7) of the Table; the ratio was found to vary between 1.64 and 1.71, the theoretical value being 1.67.

Figs. 2.1 and 2.2, pp..... are the Debye-Scherrer powder patterns of a few representative samples and the data obtained from them were given in Table 2.5, p..... . The patterns are distinctly similar as far as the distribution of the diffraction lines is concerned, a uniform shift in the positions of corresponding lines with increasing proportion of V-content being observed. About ten well-defined lines were chosen from each one of the patterns and their d-values were measured from which the corresponding θ values were calculated from the Bragg equation. While cards[238,239] containing hkl values corresponding to different 'd' values are available for the end-members, charts were used in the case of solid solutions. The lattice parameters in all the cases were calculated by a statistical method using the equations

given below:-

$$\alpha \Sigma x^2 + \beta \Sigma xy = \Sigma xz \quad \ldots\ldots\ldots\ldots (2.I)$$

$$\alpha \Sigma xy + \beta \Sigma y^2 = \Sigma yz \quad \ldots\ldots\ldots\ldots (2.II)$$

where

$\alpha = \frac{\lambda^2}{3a^2}$, $\beta = \frac{\lambda^2}{4c^2}$; λ = wave length of incident radiation used,

$x = h^2 + hk + k^2$, $y = l^2$ and $z = \sin^2 \theta$.

Values for 'a' and 'c' as well as for unit cell volumes were calculated by solving the above equations for α and β, and given in columns (4), (6) and (10) of the Table 2.5. A refinement of these values was brought about by the method of least squares using a microcomputer, the new set of values being given in columns (5), (7) and (11) of the Table. The assigned molecular formulae and the corresponding molecular weights of the samples were given in column (2) and (3) of the Table. A graphical representation of the dependence of 'a' and 'c' and the unit cell volume on the mole per cent composition of the samples was provided by Figs 2.3(A) and 2.3(B) pp..... .

The electronmicrographs of LPA, LVA and a representative solid solution of them were shown in Fig.2.4, P.... . It is evident from these patterns that the crystals of the samples which existed individually or in clusters were mostly tabular or ribbon like in shape

tending to look like elongated flattened hexagonal prisms. Based on the identity of the shape of the individual crystals evidence for the absence of phases other than that of apatites could be obtained confirming thereby the homogeneity of the samples. The average length and breadth and the approximate specific surface area calculated from them by assuming the hexagonals to be cylinders were given in Table 2.6 .

The infrared absorption spectra of the samples were given in Figs 2.5 to 2.8 pp . The wave number range investigated extended from 4000 - 650 cm^{-1} and the per cent transmittance or absorbance was represented as a function of the wave number of the radiation. It is evident that the absorption at 2920, 1460, 1375 cm^{-1} observed in all the patterns were of nujol. A consolidated list of absorption peaks of the samples assigned to PO_4^{3-}, VO_4^{3-} and OH^- was given in Table 2.7, P.... . The i.r patterns of the end-members were found to contain the characteristic peaks of OH^- at 3540 cm^{-1} in addition to those of either PO_4^{3-} at 1040 and 980 cm^{-1} or VO_4^{3-} at 800 - 735 cm^{-1}. The patterns of the solid solutions contained the entire set of these peaks. As expected, the intensity of the VO_4^{3-} peak increased while that of PO_4^{3-} diminished as the proportion of LVA in the samples increased. A systematic shift observed in these peaks over the entire compositional range of the solid solutions could be utilised as a criterion

for the homogeneity of the samples.

Thermogravimetric results on two representative samples, LPA and LVA, were carried out to arrive qualitatively at a suitable temperature below which alone the samples were to be heated for driving out volatile impurities. The results could show that discontinuity in the thermograms were absent up to 300^{o}C suggesting this to be the temperature desired. However, more systematic and refined studies to establish the nature of water associated with them were to be undertaken later.

2.4 DISCUSSION

2.4.1 General Aspects

A brief mention of the theoretical aspects of solid solutions[240,241] was considered relevant here since the results included in this section were mainly concerned with them. Homogeneous crystals containing variable proportions of isomorphous substances* are formed, in general, from mixture of solutions of the end-members. These are consequently known as mixed crystals or more popularly as "solid solutions". A series of solid solutions can be extended to the entire or partial miscibility of the solids concerned. Solid solutions can be classified as interstitial and substitutional types. Interstitial solid solutions are those in which atoms of one element are inserted into some of the interstices in the crystal lattice formed by the atoms of a second element resulting usually in a small increase in lattice constants of the crystal. On the other hand substitutional solid solutions are those in which the replacement of atoms of one kind in the crystal lattice by atoms of a second kind with nearly the same size takes place. The formation of substitutional solid solutions is accompanied either by an increase or a decrease in the unit cell volume depending upon the size of the substituent replaced. In general,

---

*The formation of solid solutions sometimes extends to a pair of solids belonging to dissimilar crystallographic types; the permissible range of compositions in such cases is limited and the products are known as "anomalous mixed crystals".

the ionic radii of a pair of ions competing for a given lattice position of the solid solution should not differ by more than about 15 per cent. Replacement of an ion by one or more ions of a different charge is also possible provided a charge neutrality is maintained. Such a replacement evidently results in a nonstoichiometric solid solution. A convincing proof for the formation of solid solutions can be provided by Vegard's law which states that a continuous series of solid solutions is characterised by a linear dependence of unit cell volume on the composition. Co-precipitation from solutions containing the required ions and crystallisation from molten mixtures of the end-members are the methods usually adopted for the preparation of solid solutions.

It has been established through X-ray diffraction techniques that LPA and LVA constituted a pair of isomorphous substances. The closeness of the covalent radii of P (1.10 $\mathring{A}$) and V (1.22$\mathring{A}$) suggests the possibility of formation of substitutional solid solutions between their apatites. For the preparation of these solid solutions co-precipitation from solutions containing the required ions was preferred to crystallization from fused mixtures of the end-members. A justification for such a preference is that fusion requires divergent temperatures for the apatites resulting invariably in decomposition due to inequalities in their thermal stabilities.

2.4.2 Aspects concerning precipitation of samples

It is evident that PO_4^{3-} and VO_4^{3-} ions which are required for the coprecipitation of solid solutions of LPA and LVA are the products of the third stage of dissociation of the corresponding orthoacids. Since the three stages of dissociation of these acids are pH-dependent, the selection of an optimum pH is important for such precipitations. It can be shown from a knowledge of the dissociation constants of these acids that a pH in the vicinity of 12 is the most optimum for this purpose. The particle size of the precipitates of apatites is usually in the range of colloidal dimensions resulting consequently in a pronounced surface activity. Such samples are characterised by a series of surface reactions with environmental ions of the medium of precipitation. The conditions of precipitation of LPA, LVA and their solid solutions were therefore so chosen that the environmental ions prevalent had no surface interaction with the precipitates. The temperature of precipitation of the samples was maintained at 37°C in order to simulate biological conditions since the subsequent investigations to be undertaken with the samples were intended to understand the mechanism of biological processes like calcification and resorption. The various theoretical aspects associated with the formation, properties and purity of precipitates have been incorporated in an excellent review by Salutsky.[241]

It is well known that nucleation governs the nature and purity of the precipitates formed, the phenomenon being defined as the process of generating the initial fragments of a new and more stable phase capable of further spontaneous development. When numerous nuclei are formed the precipitation will be rapid, individual crystals small, filtration and washing difficult and purity low. Nucleaction can be shown to be favoured, inter alia, by an increase in the concentration of the reacting solutions, a decrease in temperature and the presence of suspended impurities which function as seats for its occurrence. The parameters are consequently to be appropriately controlled for the formation of precipitates of desired specifications. The rate of precipitation is another important parameter deciding the crystal size of the resulting samples. A slow precipitation, as shown, results in the formation of large well-shaped crystals minimising the occurrence of crystal defects and imperfections. This can be accomplished by the addition of a very dilute solution of the precipitant accompanied by stirring to a medium in which the precipitate is sparingly soluble. Such a condition favours, in addition, recrystallisation of the precipitate on digestion, promoting thereby further growth of the individual crystals. Based on a knowledge of the various mechanisms by which impurities may be incorporated,

a few conditions such as use of dilute solutions, slow addition of precipitant, maintenance of a high temperature for precipitation, digestion and washing of the precipitate with a suitable wash liquid are considered optimum for their minimization. The various aspects of the experimental procedure adopted for the preparation of the samples in order to minimize crystal imperfection and to obtain large, well defined crystals were based on the theoretical principles of precipitation mentioned above. To supplement the chosen set of conditions of precipitation, the samples were sintered at an appropriate temperature.

While the conditions of existence and methods of preparation of tertiary phosphates and hydroxylapatites of alkaline earths were thoroughly investigated and fairly well established, studies on the corresponding salts of heavy metals were found to be of limited success.[98,242] The preparation of the tertiary phosphates of heavy metals through precipitation from aqueous media was associated with the complications due to the coprecipitation of their hydroxides and acid phosphates. In addition, the precipitates were found to be amorphous and of indefinite composition. Out of the experimental techniques suggested by Klement[98,242], Rathje and Hayek[45], for the preparation of the tertiary phosphates of heavy metals, the one suggested by Hayek with appropriate modifications was found to be suitable for the systems investigated. It involves a complexing of the heavy metal ions in an alkaline medium through a judicious selection of

an appropriate complexing agent. The complex was mixed with a solution of the desired anion and then made to dissociate by lowering of the pH of the medium. The tendency of lead to form well-defined soluble complexes with ethylenediamine and its monosubstituted derivatives as ligands was established by Keller and Eyke[231] through polarographic investigations. The complexes were found to be of the type PbL_2 where L, the ligand , was shown to be either ethylene diamine or its N-substituted derivative. Lead ions present in the solution, used as one of the precipitants for the preparation of solid solutions of LPA and LVA can thus be bound to ethylene diamine as a soluble complex. As the solutions used for the precipitation of apatites were to be maintained at pH 12, such a complexing could prevent the precipitation of lead hydroxide. Such a method of indirect availability of Pb^{2+} ions, functioning as precipitants, had the additional advantage of slowing down the rate of precipitation resulting in the formation of larger and more perfectly shaped crystals.[241]

2.4.3 Theoretical Basis for characterization of the samples:

The theoretical aspects involved in the analytical procedures adopted for characterization of the samples through chemical analyses merit no special mention in this context since routine quantitative determinations were made use of. However, a striking agreement between the experimental 'g' atom ratios, $(\frac{Pb}{P+V})$, of the samples with the stoichiometric

value justifies the suitability of the preparative as well as purification techniques adopted.

Among the techniques adopted for the characterization of the samples, X-ray diffraction happens to be the most significant since it can throw light on the homogeneity of the samples, in general, and of the solid solutions, in particular. The similarity of the patterns of LPA and LVA with those of apatites of well established[243] composition enabled their identification to be made and showed the absence of extraneous phases within the permissible limits of their detection. While fulfilment of the desired criteria justifies the formation of solid solutions of LPA and LVA over the entire compositional range, a marginal dilation in the unit cell volume consequent upon the replacement of 'P' by 'V' (Covalent radii 1.10 Å and 1.22 Å respectively) is anticipated. An examination of the patterns of the samples could reveal a systematic shift in the 2 θ values of the corresponding characteristic diffraction lines of apatites justifying such an anticipation and providing thereby a proof for the homogeneity of the samples. A more convincing evidence for such a dilation was provided by the excellent regularity with which the unit cell volumes of the samples, calculated on the basis of the experimentally determined lattice constants, increased with an increase in the proportion of LVA in the samples. A systematic replacement of P by V in the LPA lattice resulting in the

formation of solid solutions over the entire compositional range could thus be substantiated by the validity of Vegard's law which states that for a homogeneous series of solid solutions the unit cell volume varies linearly with composition. In addition, a striking sharpness of the diffraction lines in all the cases could suggest[242] the crystal dimensions of the samples to be uniformly large as supplemented by the electron-microscopic investigations.

An additional confirmation of the identity of the samples could be provided by their electronmicrographs which function as a means of visual examination of the shape of the individual crystals. Earlier studies could indicate that crystals of apatites are primarily hexagonal in shape tending to look ribbon-like, tabular or needle shaped[75,78] depending upon their dimensions. The electronmicrographs of the samples of LPA, LVA and a representative solid solution could prove the existence of such a crystal shape, confirming thereby their identity as apatites. As in the case of X-ray powder patterns, the absence of extraneous phases could be confirmed through electronmicroscopy. The approximate specific surface areas of these samples were calculated by assuming the individual hexagonal crystals to be cylindrical.

The similarity of the i.r. absorption spectra of

LPA, LVA and their solid solutions could confirm convincingly the identity of these samples supplementing thereby the evidence obtained by chemical, X-ray and electronmicroscopic analyses.

As mentioned earlier the i.r. absorption peaks characteristic of PO_4^{3-} (1040 and 980 cm^{-1}) and VO_4^{3-} (800 - 735 cm^{-1}) function as a means for the homogeneity of the solid solutions in addition to the evidence provided for the identification of the end-members. As expected, with a progressive replacement of PO_4^{3-} by VO_4^{3-} the area of the i.r. absorption peak of the latter increased at the cost of the former. Absence of extraneous peaks in the pattern could eliminate the posibility of contamination of the samples. It is evident that thermogravimetric analysis of precipitated samples provides, among others, information regarding their thermal stability. Since the precipitated samples of apatites are to be heated to appropriate temperatures to drive out volatile impurities without inflicting thermal decomposition, a knowledge of their thermal stability range is essential. Keeping this objective in view, a couple of representative samples, namely, the end-members, LPA and LVA, were subjected to such studies, as mentioned earlier. While a temperature suitable for the purpose was found to be 300°C, the studies were inconclusive to throw light on the exact decomposition temperature and the nature of water associated with the samples.

2.5 Summary

Lead phosphate apatite, lead vanadate apatite and a series of their solid solutions spread over the entire compositional range were prepared by precipitation from aqueous media at 37°C by a method specially developed for the purpose. They were characterized by the conventional chemical analyses as well as by X-ray, electronmicroscopic and i.r. studies. As was to be anticipated from the covalent radii of P and V (1.10 and 1.22 Å respectively) the X-ray studies could show a systematic increase in the lattice constants consequent upon a dilation of the unit cell, with an increase in the proportion of LVA in the solid solutions in agreement with vegard's law. The electronmicrographs of a few representative samples confirmed the absence of extraneous phases and enabled calculations of their approximate specific surface areas and the average dimensions of the individual crystals. An additional indication about the homogeneity of the samples was provided by i.r. absorption studies. As anticipated, the area under the vanadate peak increased at the cost of that under phosphate peak with a progressive increase in the proportion of VO_4^{3-} in the solid solutions. Thermogravimetric studies on a couple of representative samples established 300°C as a suitable temperature for removal of volatile impurities without causing decomposition of the samples.

SECTION III

SOLUBILITY EQUILIBRIA OF LEAD PHOSPHATE APATITE, LEAD VANADATE APATITE AND THEIR SOLID SOLUTIONS

SOLUBILITY EQUILIBRIA OF LEAD PHOSPHATE APATITE, LEAD VANADATE APATITE AND THEIR SOLID SOLUTIONS

3.1 INTRODUCTION

The fundamental physico-chemical aspects governing the dissolution of calcium hydroxylapatite in a solvent like water demand that the following equilibrium is established in its saturated solution:-

$$Ca_{10}(PO_4)_6(OH)_2 \rightleftharpoons 10\ Ca^{2+} + 6\ PO_4^{3-} + 2\ OH^- \quad \ldots \qquad (3.1)$$

It is evident that such a saturated solution is characterised by the fact that the solubility product, K_{sp}, of the solute given by $\{(a_{Ca^{2+}})^{10} \cdot (a_{PO_4^{3-}})^6 (a_{OH^-})^2$ is a constant at a given temperature, where the terms in brackets represent the activities of the respective ions. Further, the 'g' atom ratio, $\frac{Ca}{P}$, of the solution should correspond to the theoretical value of the solute, namely 1.67.

A careful survey of the existing[157-162,180,244] literature on the solubility of apatites indicates that there exist several ambiguities which need a clarification. Before such an attempt is made it is considered desirable to take

stock of the main factors leading to the existence of such uncertainties and a few such are the following:-

i) The low solubility coupled with the minute particle size of apatites leads to the existence of a colloidal component of the solutes in their aqueous solutions which is to be separated before the solution is analysed for the determination of solubility.[166]

ii) Since solutions of apatites, assumed to be saturated were either unsaturated or supersaturated, a scrutiny of attainment of saturation is to be made both from the sides of under-saturation and supersaturation.

iii) Since several solid phases are present in the Cao-P_2O_5-H_2O system as indicated by its phase diagram there is a possibility for the existence of more than one solid phase[244] functioning as solute in systems studied for the determination of solubility of apatites.

iv) By virtue of the high surface activity of apatites there is a possibility of their contamination[39,245] through adsorption and surface exchange of foreign ions which leads to divergence in the results on the solubility, the effect being accentuated when the contaminants are highly soluble.

vi) The tendency of the calcium ions to get complexed[177] with some of the ingredients of the buffer combinations causes an additional complication. A scrutiny of this aspect is to be

made before deciding the suitability of a given buffer combination.

vii) Apatites being the salts of a weak acid undergo hydrolysis in aqueous media resulting in the precipitation of insoluble phases which control the solubility equilibria.[161,259]

viii) It should not be ignored that errors involved in the evaluation of activity coefficients[160] of the products of dissolution of apatites introduce uncertainties in the calculated K_{sp} values.

It is well known that lead and its salts are highly toxic to human system. Such a toxicity leads to lead-poisoning[97] also known as plumbism. Recent investigations[223,225] could show that elemental vanadium and its compounds have also been toxic to the human system. The combined presence of these two or their compounds in the body fluids may result in the precipitation of LPA and LVA at the bone/body fluid interface causing thereby a disturbance of calcium-phosphorus metabolism through a shift in the calcification-resorption equilibrium. Investigations on the solubility of LPA,LVA and their solid solutions under a simulated set of biological conditions may provide an explanation and a means for a possible elimination of such pathological conditions. The solubility equilibria of LVA have not been studied earlier although such equilibria involving several of its isomorphs have extensively been investigated. The toxic effects of lead and vanadate and the

absence of information on the solubility equilibria of LVA in the existing literature are the motivations for undertaking the present investigations. In addition, the work was intended to eliminate the lacunae in the information available on solubility behaviour of apatites mentioned above.

3.2 EXPERIMENTAL

3.2.1 Selection of Buffers

It has been proposed to investigate the dependence of the solubility equilibria of the samples on pH of the dissolving medium at 37°C. Preliminary investigations indicated an extremely low solubility even in highly acidic media for LPA and LVA in comparison with some of their usual isomorphs. In addition, the solubilities of these samples were found to exhibit a marked decrease with an increase in pH resulting thereby in the availability of an extremely narrow pH range namely 2 - 3, as optimum for the studies. Since buffered media are essential for such investigations, a prerequisite has been the selection of appropriate buffers, the criterion being their non-interference in the subsequent microanalytical determinations of lead, phosphate and vanadate. Such a criterion was found to be fulfilled by a combination of potassium acid phthalate - hydrochloric acid within certain specified concentration limits, the limiting concentration being established by separate experiments.

3.2.2 Preparation and Analyses of Saturated Solutions of the Samples

3.2.2.1 Equilibration

Glass containers were found to be unsuitable for housing the systems for purposes of equilibration since Ca^{2+} and SiO_4^{4-} ions dissolved from the glass surface were likely to interfere with the subsequent microanalytical determinations. Polyethylene vessels of about 250 ml capacity provided with air-tight stoppers were found to be suitable for the purpose. The desired solutions were prepared in double - distilled water collected under a CO_2-free atmosphere to avoid the possibility , if any, of formation of of Carbonate-apatite. Atmospheric contamination of the system was avoided by making them air-tight throughout equilibration. Since the activity coefficients of the dissolving species can be maintained effectively constant in a 0.165M sodium chloride solution, the latter was used instead of water for preparing the buffer solutions. Decimolar stock solutions of each of the ingredients of the buffer combinations were prepared for the pH range, 2.0 - 2.7. Care was taken to see that the molarities of these solutions were withinthe stipulated concentration limits required for non-interference in the subsequent microanalytical determinations. The proportions of the ingredients of the buffer combinations were found out by separate experiments for each one of pH values chosen for

equilibration. The pH in all the cases was accurately measured before and after equilibration using a pH meter (Digital pH meter, ELICO, Hyderabad, India). A separate system for each one of the chosen pH values was set up taking 0.2 g of the solute in a polyethylene bottle dried previously.To this were added exactly 100 ml. of the stock solution of appropriate buffer combination. The weight of the solute and the volume of the dissolving medium were maintained scrupulously the same for all the systems in order to eliminate the role, if any, of the slurry density,[159] as a parameter in controlling the solubility of the samples. The systems were equilibrated at $37\pm0.5^{o}C$ at a controlled rate of shaking using a Shaker Bath with a thermostatic arrangement.

3.2.2.2 Filtration

Due to their low solubilities and minute particle size samples of apatites show a tendency to get colloidally dispersed in their solutions resulting in what are known as "slurries". Hence it became necessary to filter off the colloidal component before the solutions were analysed. Further, the filtration was to be carried out at $37^{o}C$, the temperature of equilibration, to avoid any possible alterations in the equilibria consequent upon changes in temperature during filtration.

It was decided to adopt filtration under suction

through a 1G4 sintered glass crucibles for the removal of colloidal component of the solute from the saturated solution of the samples in accordance with the results of earlier investigations.[89,157,244] In order to bring about this filtration at 37 $\pm$ 0.5^{o}C, a thermally insulated wooden cabin, 64 x 54 x 47 cm^{3}, specially prepared for this purpose and maintained at the desired temperature was used. Heating was done by a couple of 200 watt incandescent bulbs positioned appropriately inside the cabin and included in series with a contact thermometer and a relay circuit. The temperature inside the cabin was maintained uniform using an electric fan fabricated specially for the purpose and run at a regulated speed. An assembly fitted with a 1G4 sintered glass crucible suitable for filtration under suction was housed inside this cabin. A desired volume of the filtrate from each one of the equilibrating systems could thus be collected for the subsequent microanalytical determinations.

3.2.2.3 Chemical Analyses of the Saturated Solutions of the Samples.

The OH^{-} ion concentrations of the solutions of the samples required for the calculation of their ionic products could be evaluated from the measured pH values prevalent in the systems after attainment of saturation. A convenient method of determination of concentrations of the remaining ions was provided by the chemical analyses of their saturated solutions and hence was adopted for the purpose. The available

microanalytical methods for the individual quantitative determination of lead, phosphate and vanadate were appropriately modified so that they could be used when all the three were present together.

The micro-determinations of phosphate[69] and vanadate[246] could be achieved spectrophometrically as molybdenum blue and phosphotungsto-vanadic acid respectively. In order to eliminate the interference by PO_4^{3-} and VO_4^{3-} ions in the determination of lead, the latter was separated as lead iodate, dissolved in warm EDTA solution and estimated by back titration of the surplus EDTA against standard $MgCl_2$ solution.

Determination of Phosphate

The determination of phosphate was based on the reaction between orthophosphoric acid and molybdic acid which resulted in the formation of a heteropolyacid. Molybdenum blue formed by the reduction of the heteropoly acid was determined colorimetrically. The details of the experimental procedure were given below:

The required solutions for the determination were prepared as follows:

(i) Ammonium Molybdate Solution.

66.0 g of ammonium molybdate were dissolved in boiling water. The solution was subsequently cooled and made up to 1 litre.

(ii) Ferrous Ammonium Sulphate Solution.

14.0 g of ferrous ammonium sulphate, $FeSO_4(NH_4)_2SO_4.6H_2O$, were dissolved by treating successively with about 500 ml. of water and 4 ml. of sulphuric acid (Sp. gr. 1.84). The volume was then made up to 1 litre.

(iii) 7.5 N Sulphuric Acid

210 ml of sulphuric acid (sp.gr.1.84) when present in 1 litre of its solution gave a diluted acid of normality 7.5 .

(iv) Standard Phosphate Solution:-

1 litre of a standard solution of potassium dihydrogen phosphate containing 0.4387g of it was prepared, the amount taken being such that each ml of this solution contained 100 γ of phosphorus.

For purposes of calibration, each one of several accurately measured volumes of phosphate solution in the range 0.1 to 1.0 ml was taken in a separate 50 ml. standard flask. Each of these aliquots was treated first with 5 ml of ammonium molybdate solution,diluted to about 20 ml and then treated successively with 5 ml each of sulphuric acid and ferrous ammonium sulphate solutions mentioned above and then made up to the mark. The transmittance of the resulting blue solution was measured against a blank using a filter - colorimeter CL20 (ELICO, Hyderabad,India) fitted with a 670 nm filter. It was found

that the transmittance was unaffected by the presence of lead and vanadium enabling the method to be applied for the determination of phospborus in solutions of LPA and LPVA without separating lead and vanadium. The determination of vanadium was based on the reaction between vanadate and sodium tungstate in presence of phosphoric acid to form a yellow solution of phosphotungstovanadic acid, in 0.5 N mineral acid. The following solutions were prepared for this purpose.

i) Standard Vanadium Solution - 1.1460 g of A.R. Ammonium Vanadate were dissolved in double distilled water and the volume of the solution was made up to the mark in a standard 1 litre flask. This solution was further diluted in such a way that 1 ml contained 0.1 mg of vanadium.

ii) Phosphoric Acid Solution

To 500 ml of phosphoric acid (sp.gr. 1.75) 1000 ml of double distilled water were added.

iii) Sodium Tungstate Solution.

0.5M sodium tungstate solution was prepared by dissolving 16.5 g of A.R. Sodium tungstate, $Na_2 WO_4.2 H_2O$ in 100 ml of double distilled water.

iv) Nitric Acid Solution

5 N solution of nitric acid was obtained by diluting ~360 ml of nitric acid (sp. gr. 1.42) to 1 litre.

For purposes of calibration, each one of several accurately measured volumes of vanadate solution in the range of 0.1 to 1.0 ml

was taken in separate beakers. Each of these aliquots was treated first with 5 ml of nitric acid, 5 ml of phosphoric acid and 2.5 ml of sodium tungstate solutions mentioned above. The solutions were brought to boiling on a water bath, cooled, transferred to a 50 ml standard volumetric flask and made up to the mark. The yellow colour produced was measured using a spectrophotometer CL24 (ELICO, Hyderabad, India) at 400 mμ. Since the transmittance was unaffected by the presence of lead this method could be used for the determination of vanadium in LVA and LPVA without separating lead.

Since the presence of Vanadate ions interfered with determination of lead by complexometric back-titration method as described earlier, it was modified in the following way:- From an aliquot of the solution lead was precipitated as lead iodate as mentioned earlier, washed with cold distilled water, dissolved in excess of warm (~ 40°C) 0.01M EDTA solution and titrated against 0.005M $MgCl_2$ solution using 2 ml of a buffer of p^H 10 and Erio-chrome black T as indicator till the colour changed from blue to wine-red.

3.2.2.4. Further purification of solutes by Equilibration with EDTA.

Keeping in view the fact that trace impurities present in the solutes can markedly vitiate solubility data, about 2 g of each sample were subjected to equilibration in polyethylene containers using a mechanical shaker for about 6 hours with

a 2 per cent. solution of E.D.T.A. maintained at p^H 10 using ammonium chloride and ammonium hydroxide as buffer combination in accordance with a procedure adopted by earlier workers.[162] The samples were subsequently washed repeatedly with double-distilled water till the washings were free from the accompanying ions and dried at 110°C.

3.2.2.5 Duration of Equilibration and Determination of Solubility

In order to determine the optimum period required for the attainment of saturation, it was required to investigate kinetics of dissolution of a few representative samples. These investigations were carried out at a p^H of 2.0 setting up a series consisting of 7 systems using LPA as solute. These studies were repeated by taking in turn LVA and a representative solid solution as solutes. At each one of a few convenient time-intervals, the longest being 24 hours, the equilibration of one of the systems was interrupted in each series and the dissolved ingredients estimated as mentioned earlier. It could be confirmed that the saturation was attained in all the series within about 4 hours of equilibration. In the case of regular solubility studies, the duration of equilibration was extended up to lw hours in order to make doubly sure the attainment of saturation. The solubility of each one of these samples was determined at about 4 individual p^H values (2.0 - 2.7). The influence of common ion and the dependence on temperature of the solubility of LPA and LVA were also investigated.

Table 3.1

Microanalytical Determination of Lead, Phosphorus and Vanadium -

Assessment of Attainable Accuracy

S. No.	Wt. of Lead (mg)			Wt. of Phosphorus(mg)			Wt. of Vanadium(mg)		
	Theoretical	Experimental	% Error	Theoretical	Experimental	% Error	Theoretical	Experimental	% Error.
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
1	1.01	1.02	+0.99	0.05	0.05	0.00	0.05	0.05	0.00
2	2.02	2.03	+0.50	0.08	0.08	0.00	0.10	0.10	0.00
3	3.03	3.00	-0.99	1.00	1.00	0.00	0.15	0.15	0.00

Table 3.2

Dissolution Kinetics of Lead phosphate apatite (LPA).

Solute: 0.2 g of $Pb_{10}(PO_4)_6(OH)_2$ (Sample No.1, Table 2.4) washed with a 2 per cent. solution of EDTA maintained at $p^H 10$ using ammonium chloride and ammonium hydroxide.

Dissolving Medium: 100 ml. of a buffer consisting of potassium acid phthalate and hydrochloric acid brought to a molarity of 0.165 with respect to NaCl.

Temperature: $37 \pm 0.5^{\circ}C$

S. No.	Period of Equilibration (hours)	Final p^H	Measured concentrations (g atoms/litre)		g atom ratio
			Pb^{+4} x 10	P^{+4} x 10	Pb/P.
(1)	(2)	(3)	(4a)	(4b)	(5)
1	1.00	1.97	8.075	4.521	1.786
2	2.00	1.94	8.100	4.682	1.730
3	3.00	1.99	8.200	5.069	1.617
4	4.00	1.96	8.999	5.134	1.753
5	6.00	2.18	8.999	5.134	1.753
6	16.50	2.22	8.999	5.134	1.753
7	24.00	1.94	8.999	5.134	1.753

Table 3.3

Dissolution Kinetics of a Representative Solid Solution of LPA and LVA.

Solute: 0.2 g of $Pb_{10}(PO_4)_{2.6}(VO_4)_{3.4}(OH)_2$ (Sample No.6, Table 2.4) washed with a 2 per cent. solution of EDTA maintained at pH 10 using ammonium chloride and ammonium hydroxide.

Dissolving Medium: 100 ml of a buffer consisting of Potassium acid phthalate and hydrochloric acid brought to a molarity of 0.165 with respect to NaCl.

Temperature: $37 \pm 0.5^{\circ}C$

S. No.	Period of Equilibration (hours)	Final pH	Measured concentrations (g atoms/l)			g atom ratio Pb/(P+V)
			Pb_{+4} x 10	P_{+4} x 10	V x 10^{+5}	
(1)	(2)	(3)	(4a)	(4b)	(4c)	(5)
1	0.50	2.04	7.000	3.326	4.711	1.844
2	1.00	2.05	8.000	3.423	8.830	1.817
3	2.00	2.04	9.500	3.713	19.631	1.674
4	3.00	2.07	9.500	3.713	19.631	1.674
5	4.00	2.02	9.500	3.713	19.631	1.674
6	6.00	2.18	9.500	3.713	19.631	1.674
7	24.00	2.02	9.500	3.713	19.631	1.674

Table 3.4

Dissolution Kinetics of Lead Vanadate apatite (LVA)

Solute : 0.2 g of $Pb_{10}(VO_4)_6(OH)_2$ (Sample No.10 Table 2.4) washed with a 2 per cent. solution of EDTA maintained at PH 10 using ammonium chloride and ammonium hydroxide.

Dissolving Medium : 100 ml of a buffer consisting of Potassium acid phthalate and hydrochloric acid brought to a molarity of 0.165 with respect to NaCL.

Temperature: $37 \pm 0.5^{o}C$

S No.	Period of Equilibration (hours)	Final P^H	Measured Contrations (g atoms/l)		g atom ratio Pb/V per mole
			Pb $x10^{+4}$	V $x10^{+4}$	
(1)	(2)	(3)	(4a)	(4b)	(5)
1	1.00	2.25	9.000	5.143	1.750
2	2.00	2.05	9.500	5.497	1.728
3	3.00	2.04	10.000	4.889	1.698
4	6.00	2.05	10.000	5.889	1.698
5	16.50	2.10	10.000	5.889	1.698
6	24.00	2.20	10.000	5.889	1.698

Table 3.5

p^H-Dependence of the solubility Equilibria of Lead phosphate apatite (LPA)

Solute: 0.2 g of $Pb_{10}(PO_4)_6(OH)_2$, (Sample No.1,Table 2.4) washed with a 2 per cent. solution of EDTA maintained at p^H10 using ammonium chloride and ammonium hydroxide.

Dissolving Medium: 100 ml of a buffer consisting of potassium acid phthalate and hydrochloric acid, brought to a molarity of 0.165 with respect to NaCl.

Temperature: 37±0.5°C. p^K_w = 13.54

Dissociation constants of H_3PO_4: $K_1 = 7.51 \times 10^{-3}$, $K_2 = 6.33 \times 10^{-8}$ and $K_3 = 4.73 \times 10^{-13}$

S No.	Final p^H	Measured Conc. (g atoms/l) Pb $\times 10^{\pm 4}$	Measured Conc. (g atoms/l) P $\times 10^{\pm 4}$	g atom ratio Pb/P	Calculated Concentrations(moles or g ions/l) H_3PO_4 $\times 10^{\pm 4}$	$H_2PO_4^-$ $\times 10^{\pm 4}$	HPO_4^{2-} $\times 10^{\pm 9}$	PO_4^{3-} $\times 10^{+20}$
(1)	(2)	(3a)	(3b)	(4)	(5)	(6)	(7)	(8)
1	1.99	8.2000	5.0694	1.618	2.9238	2.1458	1.3271	6.1365
2.	2.55	2.9700	1.7356	1.711	0.4736	1.2620	2.8338	47.5765
3	2.65	2.4800	1.3400	1.851	0.4945	1.3178	2.9591	49.6844
4	2.71	1.9820	1.1382	1.741	0.2346	0.9035	2.9325	71.1592

Table 3.5 (contd.)

Phases expected to be formed and their ionic products.

	$PbHPO_4$		$Pb_2(HPO_4)(OH)_2$		$Pb(H_2PO_4)_2$		$Pb_{10}(PO_4)_6(OH)_2$	
S. No.	$^{*}K_{ip}$ $\times 10^{\pm 13}$	pK_{ip}	$^{**}K_{ip}$ $\times 10^{\pm 40}$	pK_{ip}	$^{***}K_{ip}$ $\times 10^{\pm 12}$	pK_{ip}	$^{****}K_{ip}$	pK_{ip}
(1)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)
1	10.8822	11.9633	70.8820	38.1495	37.7566	10.4230	5.8300×10^{-170}	169.23
2	8.4164	12.0749	261.7510	37.5821	4.7302	11.3251	6.490×10^{-168}	167.20
3	7.3386	12.1344	301.9230	37.5201	4.3068	11.3659	2.197×10^{-168}	167.66
4	5.8122	12.2357	251.9880	37.5986	1.6179	11.7910	2.660×10^{-168}	167.57
							Average	167.91

* = $(Pb^{2+})(HPO_4^{2-})$

** = $(Pb^{2+})^2 (HPO_4^{2-}) (OH^-)^2$

*** = $(Pb^{2+}) (H_2PO_4^-)^2$

**** = $(Pb^{2+})^{10} (PO_4^{3-})^6 (OH^-)^2$

$pK_{ip} = -\log K_{ip}$.

Table 3.6

p^H-Dependence of Solubility Equilibria of Solid Solution of LPA and LVA

Solute: 0.2 g of $Pb_{10}(PO_4)_{5.4}(VO_4)_{0.6}(OH)_2$ (Sample No.2, Table 2.4) washed with a 2 per cent. solution of EDTA maintained at p^H10 using ammonium chloride and ammonium hydroxide.

Dissolving Medium : 100 ml of a buffer consisting of Potassium acid phthalate and hydrochloric acid brought to a molarity of 0.165 with respect to NaCl.

Temperature: 37±0.5°C; p^K_w = 13.54

Dissociation constants of:	K_1	K_2	K_3
H_3PO_4	7.51×10^{-3}	6.33×10^{-8}	4.73×10^{-13}
H_3VO_4	3.98×10^{-4}	1.32×10^{-8}	1.00×10^{-13}

S. No.	Final p^H	Measured Conc. (g atoms/l) Pb $\times10^{+4}$	P $\times10^{+4}$	V $\times10^{+6}$	g atom ratio Pb/(P+V)	Calculated Concentrations (moles or g ions/l) H_3PO_4 $\times10^{+5}$	$H_2PO_4^-$ $\times10^{+4}$	HPO_4^{2-} $\times10^{+9}$	PO_4^{3-} $\times10^{+19}$
(1)	(2)	(3a)	(3b)	(3c)	(4)	(5)	(6)	(7)	(8)
1.	2.09	10.0000	4.8757	122.69	1.639	25.3420	2.3415	1.8233	1.0614
2.	2.51	2.9701	1.6145	3.9262	1.785	4.7064	1.1439	2.3428	3.5876
3.	2.66	2.4800	1.4530	10.9930	1.587	3.2805	1.1249	3.2509	7.0241
4.	2.71	1.7901	1.1624	3.1410	1.500	2.3960	0.9228	2.9949	7.2672

Table 3.6 (contd.)

S. No.	Calculated Concentrations(moles or g ions/l)				Ionic product of the Solute	
	H_3VO_4 x10^{+6}	$H_2VO_4^-$ x10^{+7}	HVO_4^{2-} x10^{+12}	VO_4^{3-} x10^{+22}	K_{ip}	pK_{ip}
(1)	(9)	(10)	(11)	(12)	(13)	(14)
1	116.9600	57.2880	9.2917	1.1432	2.95x10^{-169}	168.53
2	3.4781	4.4811	1.9118	0.6187	5.50x10^{-171}	170.26
3	9.3019	16.9090	10.1790	4.6479	2.29x10^{-169}	168.64
4	2.6086	5.3254	3.6003	1.8463	7.59x10^{-171}	170.12
					Average	169.39

$K_{ip} = (Pb^{2+})^{10} (PO_4^{3-})^{5.4} (VO_4^{3-})^{0.6} (OH^-)^2$

$pK_{ip} = - \log K_{ip}$

Table 3.7

p^H-Dependence of Solubility Equilibria of Solid Solution of LPA and LVA

Solute: 0.2 g of $Pb_{10}(PO_4)_{4.5}(VO_4)_{1.5}(OH)_2$, (Sample No.3 Table 2.4) washed with a 2 per cent. solution of EDTA maintained at p^H10 using ammonium chloride and ammonium hydroxide.

Dissolving Medium: 100 ml of a buffer consisting of Potassium acid phthalate and hydrochloric acid brought to a molarity of 0.165 with respect to NaCl.

Temperature: 37±0.5°C; $p^K w$ = 13.54

Dissociation constants of:

	K_1	K_2	K_3
H_3PO_4	7.51×10^{-3}	6.33×10^{-8}	4.73×10^{-13}
H_3VO_4	3.98×10^{-4}	1.32×10^{-8}	1.00×10^{-13}

S. No.	Final p^H	Measured Conc. (g atoms/l) Pb	P	V	g atom ratio	Calculated Concentrations(moles or g ions/l) H_3PO_4	$H_2PO_4^-$	HPO_4^{2-}	PO_4^{3-}
		$\times 10^{+4}$	$\times 10^{+4}$	$\times 10^{+6}$	Pb/(P+V)	$\times 10^{+5}$	$\times 10^{+4}$	$\times 10^{+9}$	$\times 10^{+19}$
(1)	(2)	(3a)	(3b)	(3c)	(4)	(5)	(6)	(7)	(8)
1	2.12	10.5000	4.4882	166.8600	1.705	22.5600	2.2322	1.8613	1.1604
2	2.35	2.9701	1.6145	9.8155	1.734	6.0212	1.0124	1.4344	1.5194
3	2.64	2.3563	1.4207	7.8524	1.570	3.3197	1.0887	3.0088	6.2171
4	2.73	1.9880	1.1624	2.5913	1.673	2.3074	0.9316	3.1700	8.0644

Table 3.7 (Contd.)

S. No.	Calculated Concentrations(moles or g ions/l)				Ionic product of the Solute	
	H_3VO_4	$H_2VO_4^-$	HVO_4^{2-}	VO_4^{3-}	K_{ip}	pK_{ip}
	$\times 10^{+6}$	$\times 10^{+7}$	$\times 10^{+12}$	$\times 10^{+22}$		
(1)	(9)	(10)	(11)	(12)	(13)	(14)
1	158.4000	83.1600	14.4440	1.9030	3.80×10^{-171}	170.42
2	9.0123	8.0323	2.3706	0.5307	1.78×10^{-176}	175.75
3	6.6893	11.6290	6.6968	2.9234	4.90×10^{-173}	172.31
4	2.1345	4.5685	3.2380	1.7409	2.04×10^{-173}	172.69
					Average	172.79

$K_{ip} = (Pb^{2+})^{10} (PO_4^{3-})^{4.5} (VO_4^{3-})^{1.5} (OH^-)^2$

$pK_{ip} = -\log K_{ip}$.

Table 3.8

p^H-Dependence of Solubility Equilibria of Solid Solution of LPA and LVA

Solute: 0.2 g of $Pb_{10}(PO_4)_{3.69}(VO_4)_{2.31}(OH)_2$, (Sample No.4, Table 2.4) washed with a 2 per cent. solution of EDTA maintained at p^H10 using ammonium chloride and ammonium hydroxide.

Dissolving Medium: 100 ml of a buffer consisting of Potassium acid phthalate and hydrochloric acid brought to a molarity of 0.165 with respect to NaCl.

Temperature: 37±0.5°C; p^K_w = 13.54

Dissociation constants of:

	K_1	K_2	K_3
H_3PO_4	7.51×10^{-3}	6.33×10^{-8}	4.73×10^{-13}
H_3VO_4	3.98×10^{-4}	1.32×10^{-8}	1.00×10^{-13}

S. No.	Final p^H	Measured Conc. (g atoms/l) Pb $\times10^{+4}$	P $\times10^{+4}$	V $\times10^{+5}$	g atom ratio Pb/(P+V)	Calculated Concentrations (moles or g ions/l) H_3PO_4 $\times10^{+5}$	$H_2PO_4^-$ $\times10^{+5}$	HPO_4^{2-} $\times10^{+9}$	PO_4^{3-} $\times10^{+19}$
(1)	(2)	(3a)	(3b)	(3c)	(4)	(5)	(6)	(7)	(8)
1	2.17	9.5000	3.9070	19.1400	1.632	18.5080	20.5620	1.9250	1.3475
2	2.38	2.9700	1.4853	2.1103	1.751	5.3029	9.5503	1.4495	1.6447
3	2.57	2.2325	1.2916	0.7852	1.629	3.4062	9.5096	2.2374	3.9356
4	2.73	1.9880	1.0737	2.0416	1.556	2.1313	8.6056	2.9281	7.4490

Table 3.8 (Contd.)

S. No.	Calculated Concentrations(moles or g ions/l)				Ionic product of the Solute	
	H_3VO_4	$H_2VO_4^-$	HVO_4^{2-}	VO_4^{3-}	K_{ip}	pK_{ip}
	$\times 10^{+5}$	$\times 10^{+6}$	$\times 10^{+12}$	$\times 10^{+22}$		
(1)	(9)	(10)	(11)	(12)	(13)	(14)
1	18.0750	10.6450	20.7590	3.0709	5.30×10^{-173}	172.29
2	1.9264	1.8392	5.8143	1.3943	4.07×10^{-178}	177.39
3	0.6840	1.0123	4.9610	1.8443	2.69×10^{-177}	176.57
4	1.6817	3.5994	25.5110	13.7160	1.94×10^{-174}	173.72
					Average	174.99

$K_{ip} = (Pb^{2+})^{10} (PO_4^{3-})^{3.69} (VO_4^{3-})^{2.31} (OH^-)^2$

$pK_{ip} = - \log K_{ip}.$

Table 3.9

p^H-Dependence of Solubility Equilibria of Solid Solution of LPA and LVA

Solute: 0.2 g of $Pb_{10}(PO_4)_3\ (VO_4)_3(OH)_2$, (Sample No.5 Table 2.4) washed with a 2 per cent. solution of EDTA maintained at p^H10 using ammonium chloride and ammonium hydroxide.

Dissolving
Medium: 100 ml of a buffer consisting of Potassium acid phthalate and hydrochloric acid brought to a molarity of 0.165 with respect to NaCl.

Temperature : 37±0.5°C; p^K_w = 13.54

Dissociation constants of:

	K_1	K_2	K_3
H_3PO_4	7.51×10^{-3}	6.33×10^{-8}	4.73×10^{-13}
H_3VO_4	3.98×10^{-4}	1.32×10^{-8}	1.00×10^{-13}

S. No.	Final p^H	Measured Conc.(g atoms/l)			g atom ratio	Calculated Concentrations (moles or g ions/l)			
		Pb	P	V	Pb/(P+V)	H_3PO_4	$H_2PO_4^-$	HPO_4^{2-}	PO_4^{3-}
		$\times10^{+4}$	$\times10^{+4}$	$\times10^{+5}$		$\times10^{+5}$	$\times10^{+5}$	$\times10^{+9}$	$\times10^{+19}$
(1)	(2)	(3a)	(3b)	(3c)	(4)	(5)	(6)	(7)	(8)
1	2.35	8.8943	3.6329	18.8500	1.612	13.5550	22.7740	3.2245	3.4133
2	2.46	2.9699	1.6145	3.4845	1.512	5.1024	11.0430	2.0141	2.7464
3	2.62	2.2375	1.1786	1.8846	1.636	2.8543	8.9315	2.3553	4.6435
4	2.79	2.0870	1.0737	2.7876	1.543	1.9050	8.8314	3.4502	10.0774

Table 3.9(Contd.)

S. No.	Calculated Concentrations(moles or g ions/l)				Ionic product of the Solute	
	H_3VO_4 x10^{+5}	$H_2VO_4^-$ x10^{+6}	HVO_4^{2-} x10^{+11}	VO_4^{3-} x10^{+22}	K_{ip}	pK_{ip}
(1)	(9)	(10)	(11)	(12)	(13)	(14)
1	17.3085	15.4154	4.5464	10.1710	5.41×10^{-172}	171.27
2	3.1258	3.5863	1.3625	3.9264	4.63×10^{-178}	177.33
3	1.6165	2.6814	1.4729	6.1370	1.05×10^{-177}	176.98
4	2.2377	5.4991	4.4750	27.6230	1.07×10^{-174}	173.97
					Average	174.89

$K_{ip} = (Pb^{2+})^{10} (PO_4^{3-})^3 (VO_4^{3-})^3 (OH^-)^2$

$pK_{ip} = - \log K_{ip}$.

Table 3.10

p^H-Dependence of Solubility Equilibria of Solid Solution of LPA and LVA

Solute: 0.2 g of $Pb_{10}(PO_4)_{2.6}(VO_4)_{3.4}(OH)_2$, (Sample No.6, Table 2.4) washed with a 2 per cent. solution of EDTA maintained at p^H 10 using ammonium chloride and ammonium hydroxide.

Dissolving Medium: 100 ml of a buffer consisting of Potassium acid phthalate and hydrochloric acid brought to a molarity of 0.165 with respect to NaCl.

Temperature : 37±0.5°C; $p^K w$ = 13.54

Dissociation constants of:

	K_1	K_2	K_3
H_3PO_4	7.51×10^{-3}	6.33×10^{-8}	4.73×10^{-13}
H_3VO_4	3.98×10^{-4}	1.32×10^{-8}	1.00×10^{-13}

S. No.	Final p^H	Measured Conc.(g atoms/l) Pb	P	V	g atom ratio Pb/(P+V)	Calculated Concentrations (moles or g ions/l) H_3PO_4	$H_2PO_4^-$	HPO_4^{2-}	PO_4^{3-}
		$\times 10^{+4}$	$\times 10^{+4}$	$\times 10^{+5}$		$\times 10^{+5}$	$\times 10^{+5}$	$\times 10^{+9}$	$\times 10^{+19}$
(1)	(2)	(3a)	(3b)	(3c)	(4)	(5)	(6)	(7)	(8)
1	2.02	9.5000	3.7133	19.6310	1.674	20.7870	16.3470	1.0833	0.5368
2	2.40	2.9702	1.4207	4.4170	1.594	4.9210	9.2857	1.4766	1.7555
3	2.63	2.1138	0.9687	2.1201	1.790	2.3012	7.9854	1.9975	4.0392
4	2.79	1.9880	0.9203	3.5336	1.562	1.6328	7.5692	2.9571	8.6372

Table 3.10(Contd.)

S. No.	Calculated Concentrations(moles or g ions/l)				Ionic product of the Solute	
	H_3VO_4	$H_2VO_4^-$	HVO_4^{2-}	VO_4^{3-}	K_{ip}	pK_{ip}
	$x10^{+5}$	$x10^{+6}$	$x10^{+11}$	$x10^{+22}$		
(1)	(9)	(10)	(11)	(12)	(13)	(14)
1	18.8454	7.8561	1.0845	1.1356	$1.05x10^{-178.}$	177.98
2	4.0154	4.0165	1.3304	3.3427	$4.68x10^{-180.}$	179.33
3	1.8118	3.0825	1.7366	7.4214	$5.89x10^{-179.}$	178.23
4	2.8365	6.9707	5.6726	35.0160	$7.94x10^{-176.}$	175.10
					Average	177.66

$K_{ip} = (Pb^{2+})^{10} (PO_4^{3-})^{2.6} (VO_4^{3-})^{3.4} (OH^-)^2$

$pK_{ip} = -\log K_{ip}$

Table 3.11

p^H-Dependence of Solubility Equilibria of Solid Solution of LPA and LVA

Solute: 0.2 g of $Pb_{10}(PO_4)_{1.9}(VO_4)_{4.1}(OH)_2$ (Sample No. 7, Table 2.4) washed with a 2 per cent. solution of EDTA maintained at p^H10 using ammonium chloride and ammonium hydroxide.

Dissolving Medium: 100 ml of a buffer consisting of Potassium acid phthalate and hydrochloric acid brought to a molarity of 0.165 with respect to NaCl.

Temperature: 37±0.5°C; p^K_w = 13.54

Dissociation Constants of :	K_1	K_2	K_3
H_3PO_4	$7.51x10^{-3}$	$6.33x10^{-8}$	$4.73x10^{-13}$
H_3VO_4	$3.98x10^{-4}$	$1.32x10^{-8}$	$1.00x10^{-13}$

S. No.	Final p^H	Measured Conc. (g atoms/l)			g atom ratio	Calculated Concentrations (moles or g ions/l)			
		Pb	P	V	Pb/(P+V)	H_3PO_4	$H_2PO_4^-$	HPO_4^{2-}	PO_4^{3-}
		$x10^{+4}$	$x10^{+4}$	$x10^{+5}$		$x10^{+5}$	$x10^{+5}$	$x10^{+9}$	$x10^{+19}$
(1)	(2)	(3a)	(3b)	(3c)	(4)	(5)	(6)	(7)	(8)
1	2.13	8.5000	2.6962	24.5390	1.651	13.3910	13,5710	1.1591	0.7402
2	2.37	2.9700	1.2916	4.8587	1.670	4.6819	8.2344	1.2205	1.3525
3	2.57	2.2850	0.9525	2.6502	1.868	2.5121	7.0132	1.6500	2.9024
4	2.60	1.9880	0.8266	7.8524	2.196	2.1078	6.1582	1.5528	2.9272

Table 3.11(Contd.)

S. No.	Calculated Concentrations(moles or g ions/l)				Ionic product of the Solute	
	H_3VO_4 x10^{+5}	$H_2VO_4^-$ x10^{+6}	HVO_4^{2-} x10^{+11}	VO_4^{3-} x10^{+22}	K_{ip}	pK_{ip}
(1)	(9)	(10)	(11)	(12)	(13)	(14)
1	23.2880	12.5120	2.2259	3.0039	$7.59 \times 10^{-179.}$	178.12
2	4.4444	4.1437	1.2793	2.9960	$1.93 \times 10^{-182.}$	181.71
3	2.3085	3.4165	1.6744	6.2244	$3.02 \times 10^{-181.}$	180.52
4	0.6799	1.0531	0.5531	2.2035	$1.26 \times 10^{-183.}$	182.90

$K_{ip} = (Pb^{2+})^{10} (PO_4^{3-})^{1.9} (VO_4^{3-})^{4.1} (OH^-)^2$ Average 180.81

$pK_{ip} = - \log K_{ip}$.

Table 3.12

p^H-Dependence of Solubility Equilibria of Solid Solution of LPA and LVA.

Solute: 0.2 g of $Pb_{10}(PO_4)_{1.2}(VO_4)_{4.8}(OH)_2$ (Sample No.8, Table 2.4) washed with a 2 per cent. solution of EDTA maintained at p^H 10 using ammonium chloride and ammonium hydroxide.

Dissolving Medium: 100 ml of a buffer consisting of Potassium acid phthalate and hydrochloric acid brought to a molarity of 0.165 with respect to NaCl.

Temperature: 37±0.5°C; $p^K w$ = 13.54

Dissociation Constants of:

	K_1	K_2	K_3
H_3PO_4	$7.51x10^{-3}$	$6.33x10^{-8}$	$4.73x10^{-13}$
H_3VO_4	$3.98x10^{-4}$	$1.32x10^{-8}$	$1.00x10^{-13}$

S. No.	Final p^H	Measured Conc. (g atoms/l) ratio			g atom ratio	Calculated Concentrations (moles or g ions/l)			
		Pb	P	V	Pb/(P+V)	H_3PO_4	$H_2PO_4^-$	HPO_4^{2-}	PO_4^{3-}
		$x10^{+4}$	$x10^{+4}$	$x10^{+5}$		$x10^{+5}$	$x10^{+5}$	$x10^{+10}$	$x10^{+20}$
(1)	(2)	(3a)	(3b)	(3c)	(4)	(5)	(6)	(7)	(8)
1	2.14	7.5000	1.0333	35.3360	1.642	5.0616	5.2713	4.5896	2.9996
2	2.36	1.9800	0.5166	6.4782	1.700	1.9004	3.2659	4.7299	5.1214
3	2.67	1.3940	0.3552	3.9262	1.864	0.8764	2.6754	6.8829	13.2390

Table 3.12(Contd.)

S. No.	Calculated Concentrations (moles or g ions/l)				Ionic product of the Solute	
	H_3VO_4 x10^{+5}	$H_2VO_4^-$ x10^{+6}	HVO_4^{2-} x10^{+11}	VO_4^{3-} x10^{+22}	K_{ip}	pK_{ip}
(1)	(9)	(10)	(11)	(12)	(13)	(14)
1	33.4940	18.4180	3.3536	4.6321	$1.32 \times 10^{-180.88}$	179.88
2	5.9373	5.4089	1.6317	3.7339	$3.98 \times 10^{-185.40}$	185.40
3	3.3793	5.4689	2.9308	1.9137	$3.16 \times 10^{-183.50}$	183.50
					Average	182.92

$K_{ip} = (Pb^{2+})^{10} (PO_4^{3-})^{1.2} (VO_4^{3-})^{4.8} (OH^-)^2$

$pK_{ip} = - \log K_{ip}$.

Table 3.13

p^H-Dependence of the Solubility Equilibria of Lead Vanadate apatite (LVA).

Solute: 0.2 g of $Pb_{10}(VO_4)_6(OH)_2$, (Sample No.10 Table 2.4) washed with a 2 per cent. solution of EDTA maintained at p^H10 using ammonium chloride and ammonium hydroxide.

Dissolving Medium: 100 ml of a buffer consisting of Potassium acid phthalate and hydrochloric acid brought to a molarity of 0.165 with respect to NaCl.

Temperature: 37±0.5°C; $p^K w$ = 13.54.

Dissociation Constants of H_3VO_4 K_1 3.98×10^{-4} K_2 1.32×10^{-8} K_3 1.00×10^{-13}

S. No.	Final p^H	Measured Conc. (g atoms/l) Pb $\times 10^{+4}$	V $\times 10^{+4}$	g atom ratio Pb/V	Calculated Concentrations (moles or g ions/l) H_3VO_4 $\times 10^{+5}$	$H_2VO_4^-$ $\times 10^{+5}$	HVO_4^{2-} $\times 10^{+11}$	VO_4^{3-} $\times 10^{+21}$
(1)	(2)	(3a)	(3b)	(4)	(5)	(6)	(7)	(8)
1	2.15	10.0000	5.8893	1.697	56.3740	2.5189	3.7269	0.4183
2	2.53	1.9799	1.2760	1.552	11.2427	1.5172	6.7803	2.2984
3	2.60	0.8000	0.4711	1.698	4.0665	0.6450	3.3876	1.3497
4	2.65	0.8990	0.5104	1.764	4.3338	0.7702	4.5330	2.0237

Table 3.13(Contd.)

Phases expected to be formed and their ionic products								
	$PbHVO_4$		$Pb_2HVO_4(OH)_2$		$Pb(H_2VO_4)_2$		$Pb_{10}(VO_4)_6(OH)_2$	
S. No.	$^{*}K_{ip}$ $\times 10^{+14}$	pK_{ip}	$^{**}K_{ip}$ $\times 10^{+40}$	pK_{ip}	$^{***}K_{ip}$ $\times 10^{+13}$	pK_{ip}	$^{****}K_{ip}$	pK_{ip}
(1)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)
1	3.7269	13.43	3.9124	39.41	6.3449	12.20	8.89×10^{-182}	181.05
2	1.3424	13.87	2.5370	39.59	0.4558	13.34	1.30×10^{-183}	182.07
3	0.2710	14.57	0.2867	40.54	0.0333	14.48	8.58×10^{-189}	188.07
4	0.4075	14.39	0.0608	41.22	0.0533	14.27	3.94×10^{-187}	186.40
							Average	184.60

* = $(Pb^{2+})\ (HVO_4^{2-})$

** = $(Pb^{2+})^2\ (HVO_4^{2-})\ (OH^-)^2$ $\qquad pK_{ip} = -\log K_{ip}$

*** = $(Pb^{2+})\ (H_2VO_4^-)^2$

**** = $(Pb^{2+})^{10}\ (VO_4^{3-})^6\ (OH^-)^2$.

Table 3.14

Ionic products and Free Energies of solution of Lead Phosphate apatite, Lead Vanadate apatite and their solid solutions.

S. No.	Compound	pK_{ip} ($-\log K_{ip}$) (Average)	$\Delta G_{soln.}$ K.Cals/mole
1.	$Pb_{10}(PO_4)_6(OH)_2$ (LPA)	167.91	237.35
2.	$Pb_{10}(PO_4)_{5.4}(VO_4)_{0.6}(OH)_2$	169.39	241.10
3.	$Pb_{10}(PO_4)_{4.5}(VO_4)_{1.5}(OH)_2$	172.79	245.80
4.	$Pb_{10}(PO_4)_{3.69}(VO_4)_{2.31}(OH)_2$	174.99	249.00
5.	$Pb_{10}(PO_4)_3(VO_4)_3(OH)_2$	174.89	248.80
6.	$Pb_{10}(PO_4)_{2.6}(VO_4)_{3.4}(OH)_2$	177.66	252.80
7.	$Pb_{10}(PO_4)_{1.9}(VO_4)_{4.1}(OH)_2$	180.81	257.20
8.	$Pb_{10}(PO_4)_{1.2}(VO_4)_{4.8}(OH)_2$	182.92	260.20
9.	$Pb_{10}(VO_4)_6(OH)_2$ (LVA)	184.6	262.60

Table 3.15

Miscellaneous studies on the Solubility Equilibria of LPA - Proof for constancy of pK_{ip} values and Response of g atom ratios, Pb/P, on Addition of Common ions Pb^{2+} and PO_4^{3-}.

Solute: 0.2 g of $Pb_{10}(PO_4)_6(OH)_2$ (Sample No.1, Table 2.4) washed with a 2 per cent solution of EDTA maintained at pH 10 using ammonium chloride and ammonium hydroxide.

Dissolving Medium: 100 ml of a buffer consisting of Potassium acid phthalate and hydrochloric acid brought to a molarity of 0.165 with respect to NaCl.

Temperature: $37 \pm 0.5^{\circ}C$. $pK_w = 13.54$

Dissociation constants of H_3PO_4 : K_1 7.51×10^{-3} K_2 6.33×10^{-8} K_3 4.73×10^{-13}

S. No.	Common ion added (mg / l) Pb	P	Final pH	Measured Conc. (g atoms/l) Pb $\times 10^{+4}$	P $\times 10^{+4}$	g atom ratio Pb/P	Calculated Conc. (moles or g ions/l) H_3PO_4 $\times 10^{+4}$	$H_2PO_4^-$ $\times 10^{+4}$	HPO_4^{2-} $\times 10^{+9}$	PO_4^{3-} $\times 10^{+20}$	Ionic product of Solute. K_{ip}	pK_{ip}
(1)	(2a)	(2b)	(3)	(4a)	(4b)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
1	40.40	-	1.89	9.9008	4.1573	2.382	2.6261	1.5312	0.7524	2.7641	2.02×10^{-171}	170.69
2	60.60	-	2.03	11.8810	5.7314	2.073	3.1759	2.5555	1.7329	8.7860	2.46×10^{-167}	166.61
3	-	40.00	2.09	5.4454	9.0733	0.600	4.7160	4.3578	3.3930	19.7520	1.71×10^{-168}	167.77
4	-	20.00	2.11	2.4751	1.4692	1.685	7.4666	7.2232	5.8888	35.8990	2.55×10^{-170}	169.59

Average 168.67

$K_{ip} = (Pb^{2+})^{10} (PO_4^{3-})^6 (OH^-)^2$ $pK_{ip} = - \log K_{ip}$.

Table 3.16

Miscellaneous Studies on the Solubility Equilibria of LVA - Proof for constancy of p^{K}_{ip} values and Response of g atom ratios, Pb/V, on Addition of Common ions Pb^{2+} and VO_4^{3-}.

Solute: 0.2 g of $Pb_{10}(VO_4)_6(OH)_2$ (Sample No.10 Table 2.4) washed with a 2 per cent. solution of EDTA maintained at p^{H} 10 using ammonium chloride and ammonium hydroxide.

Dissolving Medium: 100 ml of a buffer consisting of Potassium acid phthalate and hydrochloric acid brought to a molarity of 0.165 with respect to NaCl.

Temperature: 37±0.5°C; p^{K}_{w} = 13.54

Dissociation constants of H_3VO_4 : K_1 3.98×10^{-4} K_2 1.32×10^{-8} K_3 1.00×10^{-13}

S. No.	Common ion added (mg / l)		Final p^{H}	Measured Conc. (g atoms / l)		g atom ratio	Calculated Conc. (moles or g ions / l)				Ionic product of Solute.	
	Pb	V		Pb	V	Pb/V	H_3VO_4	$H_2VO_4^-$	HVO_4^{2-}	VO_4^{3-}	K_{ip}	p^{K}_{ip}
				$\times10^{+4}$	$\times10^{+4}$		$\times10^{+4}$	$\times10^{+5}$	$\times10^{+11}$	$\times10^{+22}$		
(1)	(2a)	(2b)	(3)	(4a)	(4b)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
1	40.40	-	1.93	5.4454	3.7299	1.460	3.6076	1.2223	1.3714	1.1672	3.51×10^{-187}	186.46
2	60.60	-	1.99	10.3960	3.7299	2.787	3.5902	1.3972	1.8004	1.7599	3.48×10^{-184}	183.46
3	-	20.04	2.04	9.9008	7.8524	1.261	7.5239	3.2844	4.7476	5.2057	1.80×10^{-181}	180.75
4	-	40.08	2.05	5.4454	11.8770	0.458	11.3690	5.0779	7.5106	8.4270	1.03×10^{-183}	182.99

$K_{ip} = (Pb^{2+})^{10} (VO_4^{3-})^{6} (OH^-)^{2}$ $p^{K}_{ip} = -\log K_{ip}$. Average 183.42

Table 3.17

Miscellaneous Studies on the solubility Equilibria of LPA - Dependence of Solubility on Temperature.

Solute: 0.2 g of $Pb_{10}(PO_4)_6(OH)_2$, (Sample No.1 Table 2.4) washed with a 2 per cent. solution of EDTA maintained at p^H 10 using ammonium chloride and ammonium hydroxide.

Dissolving Medium: 100 ml of a buffer consisting of Potassium acid phthalate and hydrochloric acid brought to a molarity of 0.165 with respect to NaCl.

Temp.	Dissociation constants of H_3PO_4			p^Kw
	K_1	K_2	K_3	
42°C	$4.47x10^{-3}$	$6.650x10^{-8}$	$4.99x10^{-13}$	13.43
45°C	$5.62x10^{-3}$	$6.645x10^{-8}$	$5.01x10^{-13}$	13.35

S. No.	Temp. °C	Final p^H	Measured Conc. (g atoms/l) Pb $x10^{+4}$	P $x10^{+4}$	g atom ratio Pb/P	Calculated concentrations (moles or g ions/l) H_3PO_4 $x10^{+5}$	$H_2PO_4^-$ $x10^{+4}$	HPO_4^{2-} $x10^{+9}$	PO_4^{3-} $x10^{+19}$	Ionic product of Solute K_{ip}	$p^K{ip}$.
(1)	(2)	(3)	(4a)	(4b)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
1.	42	2.35	3.4653	2.0342	1.704	10.1664	1.0171	1.5142	1.6911	$4.13x10^{-170.}$	169.38
2.	45	2.54	3.9603	2.0988	1.887	7.1151	1.3873	3.1964	5.5548	$6.69x10^{-166.}$	165.18

Table 3.18

Miscellaneous studies on the solubility Equilibria of LVA - Dependence of Solubility on Temperature.

Solute: 0.2 g of $Pb_{10}(VO_4)_6(OH)_2$ (Sample No.10 Table 2.4) washed with a 2 per cent. solution of EDTA maintained at p^H10 using ammonium chloride and ammonium hydroxide.

Dissolving Medium: 100 ml of a buffer consisting of Potassium acid phthalate and hydrochloric acid brought to a molarity of 0.165 with respect to NaCl.

	p^{K_w}
42°C	13.43
45°C	13.35

S. No.	Temp °C	Final p^H	Measured Conc. (g atoms/l) Pb $x10^{+4}$	V $x10^{+4}$	g atom ratio Pb/V	Measured Concentrations (moles or g ions/l) H_3VO_4 $x10^{+4}$	$H_2VO_4^-$ $x10^{+5}$	HVO_4^{2-} $x10^{+11}$	VO_4^{3-} $x10^{+21}$	Ionic product of Solute. K_{ip}	$p^{K_{ip}}$
(1)	(2)	(3)	(4a)	(4b)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
1	42	2.46	1.9803	1.2563	1.576	1.1269	1.2929	4.9122	1.4156	$8.77x10^{-185.}$	184.04
2	45	2.40	1.9803	1.2563	1.576	1.1461	1.1424	3.7893	0.9507	$8.62x10^{-186.}$	185.06

In these calculations the values of K_1, K_2 and K_3 of H_3VO_4 at 25°C were used, since it could be found that data on an analogous system, H_3PO_4, exhibited insignificant temperature dependence.

Table 3.19

Fluctuations in the calculated Ionic Products of Lead Phosphate apatite (LPA). Dependence on the Error Limits in Measurements.

S. No.	Final p^H		Measured Conc.(g atoms/l)		Assumed* Conc(g atoms/l)	
	Measured	Assumed*	Pb $x10^{+4}$	P $x10^{+4}$	Pb $x10^{+4}$	P $x10^{+4}$
(1)	(2)	(3)	(4)	(5)	(6)	(7)
1	1.99	1.89	8.2000	5.0694	8.2800	5.0694
2	2.55	2.45	2.9700	1.7356	2.9990	1.7356
3	2.65	2.55	2.4800	1.3400	2.5046	1.3400
4	2.71	2.61	1.9820	1.1382	2.0016	1.1382

* Each one of the corresponding measured values given in the preceding column was subjected to an alteration equal to maximum negative error observed in the corresponding determination (see Table 3.1) and the resulting value termed as assumed value included in this column.

Table 3.19(Contd.)

S. No.	Calculated concentrations on the basis of assumed Cons.(moles or g ions / l)					Phases expected to be formed and their $p^{K}ip$ values.			
	(OH^-) $x10^{+12}$	H_3PO_4 $x10^{+5}$	$H_2PO_4^-$ $x10^{+5}$	HPO_4^{2-} $x10^{+9}$	PO_4^{3-} $x10^{+19}$	$Pb_{10}(PO_4)_6(OH)_2$ $p^{K}ip^{*}$	$PbHPO_4$ $p^{K}ip^{**}$	$Pb_2HPO_4(OH)_2$ $p^{K}ip^{***}$	$Pb(H_2PO4)_2$ $p^{K}ip^{****}$
(1)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)
1	2.24	32.0410	18.6530	0.9152	0.3357	169.96	12.12	38.51	10.54
2	6.13	5.5650	11.7910	2.1021	2.8019	168.72	12.20	37.90	11.38
3	10.20	3.6581	9.7419	2.1864	3.6686	168.61	12.26	37.85	11.62
4	11.80	2.8084	8.5737	2.2058	4.2427	169.08	12.36	37.91	11.83
					Average	169.09.			

* $- \log(Pb^{2+})^{10} (PO_4^{3-})^6 (OH^-)^2$

** $- \log(Pb^{2+}) (HPO_4^{2-})$

*** $- \log (Pb^{2+})^2 (HPO_4) (OH^-)^2$

**** $- \log (Pb^{2+}) (H_2PO_4^-)^2$

Table 3.20

Fluctuations in the Calculated Ionic Products of Lead Phosphate apatite (LPA) Dependence on the Error Limits in Measurements.

S.No.	Final p^H Measured	Final p^H Assumed*	Measured Conc.(g atoms/l) Pb $x10^{+4}$	Measured Conc.(g atoms/l) P $x10^{+4}$	Assumed* Conc.(g atoms/l) Pb $x10^{+4}$	Assumed* Conc.(g atoms/l) P $x10^{+4}$
(1)	(2)	(3)	(4)	(5)	(6)	(7)
1	1.99	2.09	8.2000	5.0694	8.1500	5.0694
2	2.55	2.65	2.9700	1.7356	2.9358	1.7356
3	2.65	2.75	2.4800	1.3400	2.4554	1.3400
4	2.71	2.81	1.9820	1.1382	1.9624	1.1382

* Each one of the corresponding measured values given in the preceding column was subjected to an alteration equal to maximum positive error observed in the corresponding determination (see Table 3.1) and the resulting value termed as assumed value included in this column.

Table 3.20(Contd.)

Calculated concentrations on the basis of assumed Conc. (moles or g ions / l)						Phases expected to be formed and their $p^{K}ip$ Values.			
S.No.	(OH^-)	H_3PO_4	$H_2PO_4^-$	HPO_4^{2-}	PO_4^{3-}	$Pb_{10}(PO_4)_6(OH)_2$	$PbHPO_4$	$Pb_2HPO_4(OH)_2$	$Pb(H_2PO_4)_2$
	$x10^{+12}$	$x10^{+5}$	$x10^{+4}$	$x10^{+9}$	$x10^{+19}$	$p^{K}ip^{*}$	$p^{K}ip^{**}$	$p^{K}ip^{***}$	$p^{K}ip^{****}$
(1)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)
1	3.55	26.3510	2.4341	1.8949	1.1028	167.53	11.81	37.80	10.32
2	12.90	3.9874	1.3369	3.7771	7.9788	165.70	11.96	37.27	11.28
3	16.20	2.5675	1.0832	3.8515	10.2380	165.62	12.02	37.22	11.54
4	18.60	1.9472	0.9435	3.8525	11.7600	166.11	12.12	37.29	11.76
					Average	166.24			

* - $\log (Pb^{2+})^{10}(PO_4^{3-})^6 (OH^-)^2$

** - $\log (Pb^{2+}) (HPO_4^{2-})$

*** - $\log (Pb^{2+})^2(HPO_4^{2-}) (OH^-)^2$

**** - $\log (Pb^{2+}) (H_2PO_4^-)^2$

Table 3.21

Fluctuations in the calculated Ionic Products of Lead Vanadate apatite (LVA) Dependence on the Error Limits in Measurements.

	Final p^H		Measured Conc.(g atoms/l)		Assumed* Conc. (g atoms/l)	
S.No.	Measured	Assumed*	Pb $\times 10^{+4}$	V $\times 10^{+4}$	Pb $\times 10^{+4}$	V $\times 10^{+4}$.
(1)	(2)	(3)	(4)	(5)	(6)	(7)
1	2.15	2.05	10.0000	5.8893	10.0990	5.8893
2	2.53	2.43	1.9799	1.2760	1.9995	1.2760
3	2.60	2.50	0.8000	0.4711	0.8079	0.4711
4	2.65	2.55	0.8990	0.5104	0.9079	0.5104

* Each one of the corresponding measured values given in the preceding column was subjected to an alteration equal to maximum negative error observed in the corresponding determination (see Table 3.1) and the resulting value termed as assumed value included in this column.

Table 3.21(Contd.)

	Calculated concentrations on the basis of assumed Conc. (moles or g ions / l)					Phases expected to be formed and their pK_{ip} Values.			
S.No.	(OH^-)	H_3VO_4	$H_2VO_4^-$	HVO_4^{2-}	VO_4^{3-}	$Pb_{10}(VO_4)_6(OH)_2$	$PbHVO_4$	$Pb_2HVO_4(OH)_2$	$Pb(H_2VO_4)_2$
	$x10^{+12}$	$x10^{+5}$	$x10^{+6}$	$x10^{+11}$	$x10^{+21}$	pK^*_{ip}	pK^{**}_{ip}	pK^{***}_{ip}	pK^{****}_{ip}
(1)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)
1	3.24	56.3740	25.1880	3.7268	0.4183	181.21	13.42	39.40	12.19
2	7.76	11.5265	12.3356	4.3715	1.1751	184.79	14.06	39.98	13.52
3	9.12	4.1800	5.2710	2.1989	0.6959	189.95	14.75	40.92	14.65
4	10.20	4.4725	6.3140	2.9517	1.0467	188.28	14.57	40.60	14.44
						Average 186.05			

* - $\log (Pb^{2+})^{10}(VO_4^{3-})^6 (OH^-)^2$

** - $\log (Pb^{2+}) (HVO_4^{2-})$

*** - $\log (Pb^{2+})^2 (HVO_4^{2-})(OH^-)^2$

**** - $\log (Pb^{2+}) (H_2VO_4^-)^2$

Table 3.22

Fluctuations in the calculated Ionic Products of Lead Vanadate apatite (LVA) Dependence on the Error Limits in Measurements.

	Final p^H		Measured Conc.(g atom/l)		Assumed* Conc. (g atom/l)	
S.No.	Measured	Assumed*	Pb $x10^{+4}$	V $x10^{+4}$	Pb $x10^{+4}$	V $x10^{+4}$
(1)	(2)	(3)	(4)	(5)	(6)	(7)
1	2.15	2.25	10.0000	5.8893	9.9010	5.8893
2	2.53	2.63	1.9799	1.2760	1.9603	1.2760
3	2.60	2.70	0.8000	0.4711	0.7921	0.4711
4	2.65	2.75	0.8990	0.5104	0.8901	0.5104

* Each one of the corresponding measured values given in the preceding column was subjected to an alteration equal to maximum positive error observed in the corresppnding determination (See Table 3.1) and the resulting value termed as assumed value included in this column.

Table 3.22(Contd.)

	Calculated concentrations on the basis of assumed Conc. (moles or g ions / l)					Phases expected to be formed and their pK_{ip} Values.			
S.No.	(OH^-)	H_3VO_4	$H_2VO_4^-$	HVO_4^{2-}	VO_4^{3-}	$Pb_{10}(VO_4)_6(OH)_2$	$PbHVO_4$	$Pb_2HVO_4(OH)$	$Pb(H_2VO_4)_2$
	$\times 10^{+12}$	$\times 10^{+5}$	$\times 10^{+6}$	$\times 10^{+11}$	$\times 10^{+21}$	pK^*_{ip}	pK^{**}_{ip}	pK^{***}_{ip}	pK^{****}_{ip}
(1)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)
1	5.13	54.9980	38.9610	9.1392	1.6262	177.36	13.04	38.63	13.82
2	12.30	10.9053	18.5534	10.4526	4.4669	180.99	13.69	39.22	13.17
3	14.50	3.9270	7.8370	5.1790	2.5960	186.20	14.39	40.17	14.31
4	16.20	4.1710	9.3290	6.9090	3.8820	184.55	14.21	39.84	14.11
					Average	182.3			

* - $\log (Pb^{2+})^{10}(VO_4^{3-})^6 (OH^-)^2$

** - $\log (Pb^{2+}) (HVO_4^{2-})$ (0

*** - $\log (Pb^{2+})^2 (HVO_4^{2-}) (OH^-)^2$

**** - $\log (Pb^{2+}) (H_2VO_4^-)^2$

Fig. 3.1 Concentration ranges for the Validity of Beer - Lambert's Law for the Determination of Phosphorus.

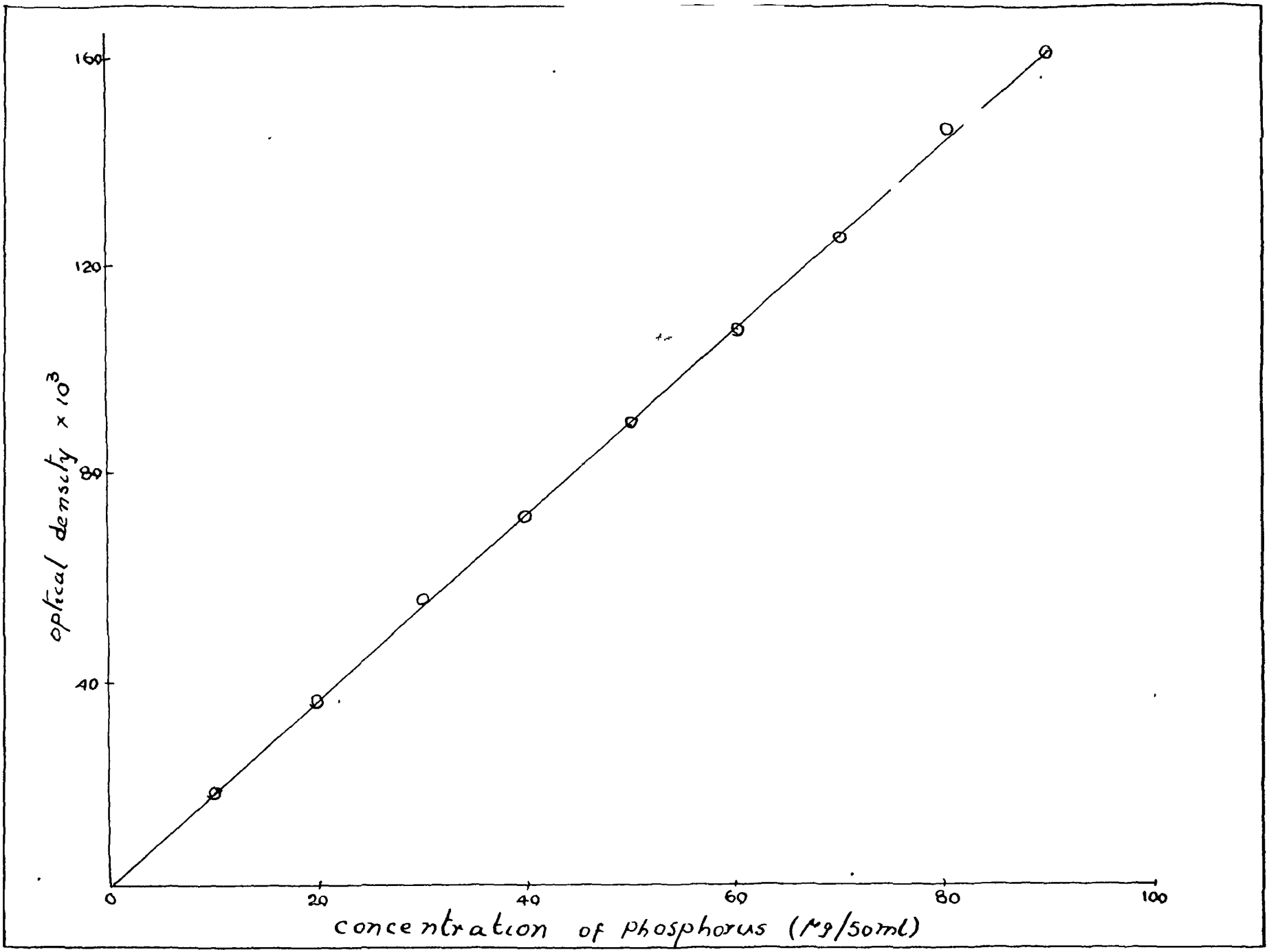

160
120
80
40
optical density $\times 10^3$
0
20
40
60
80
100
concentration of phosphorus (µg/50ml)

FIG 3 1

Fig.3.2 Concentration ranges for the Validity of Beer - Lambert's Law for the Determination of Vanadium.

Fig. 3.3 Studies on Dissolution Kinetics of

(A) Lead Phosphate apatite

A(i) with respect to Phosphorus

A(ii) with respect to Lead

(Table 3.2)

(B) Lead Vanadate apatite

B(i) with respect to Vanadium

B(ii) with respect to Lead

(Table 3.4)

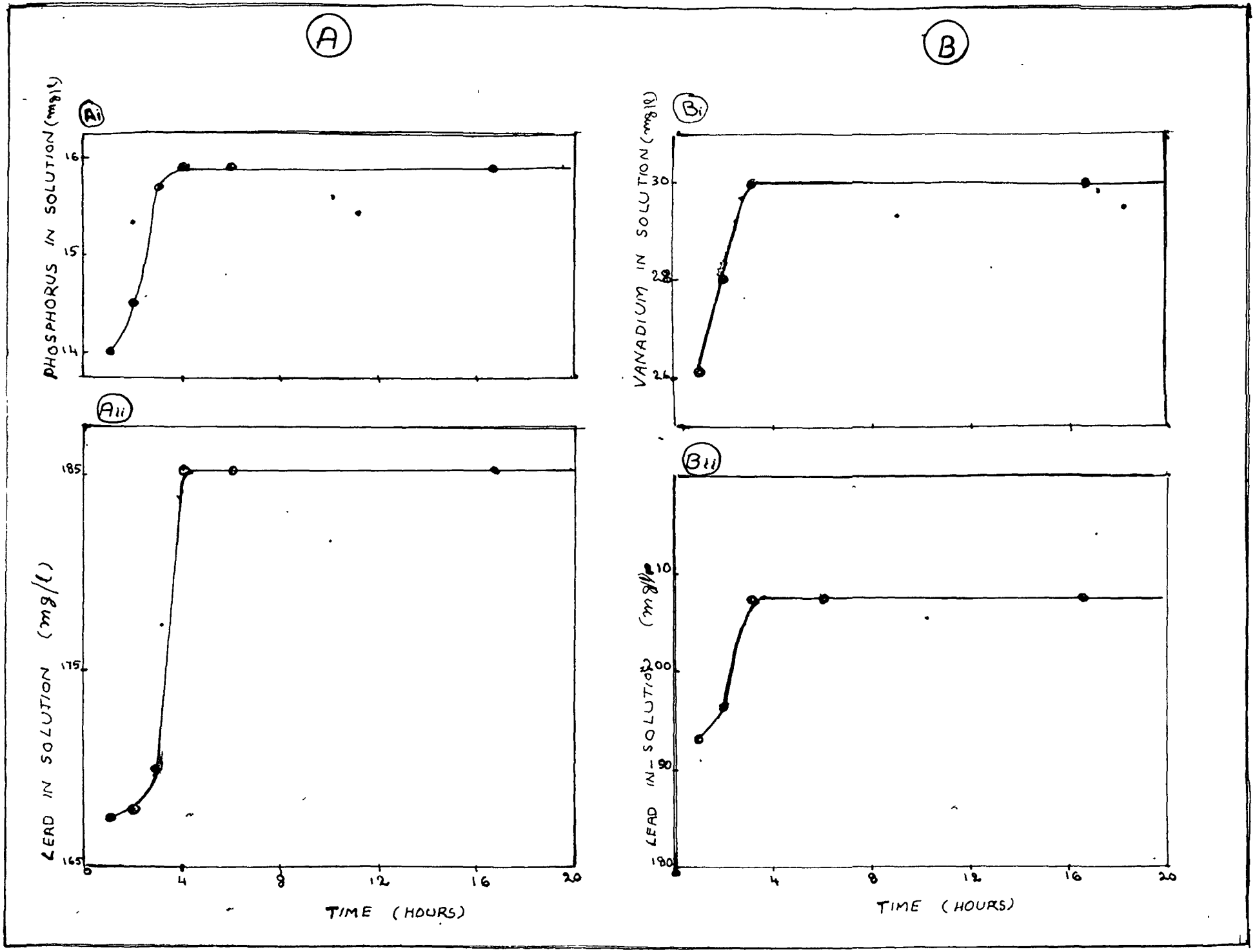

A
B
Ai
Aii
Bi
Bii
PHOSPHORUS IN SOLUTION (mg/l)
VANADIUM IN SOLUTION (mg/l)
LEAD IN SOLUTION (mg/l)
LEAD IN-SOLUTION (mg/l)
16
15
14
30
28
26
185
175
165
10
200
190
180
4
8
12
16
20
TIME (HOURS)
TIME (HOURS)

FIG. 3.3

Fig. 3.4 Studies on Dissolution Kinetics of a representative Solid Solution of Phosphate and Vanadate apatite of Lead.

(i) with respect to Phosphorus

(ii) with respect to Vanadium

(iii) with respect to Lead.

(Table 3.3)

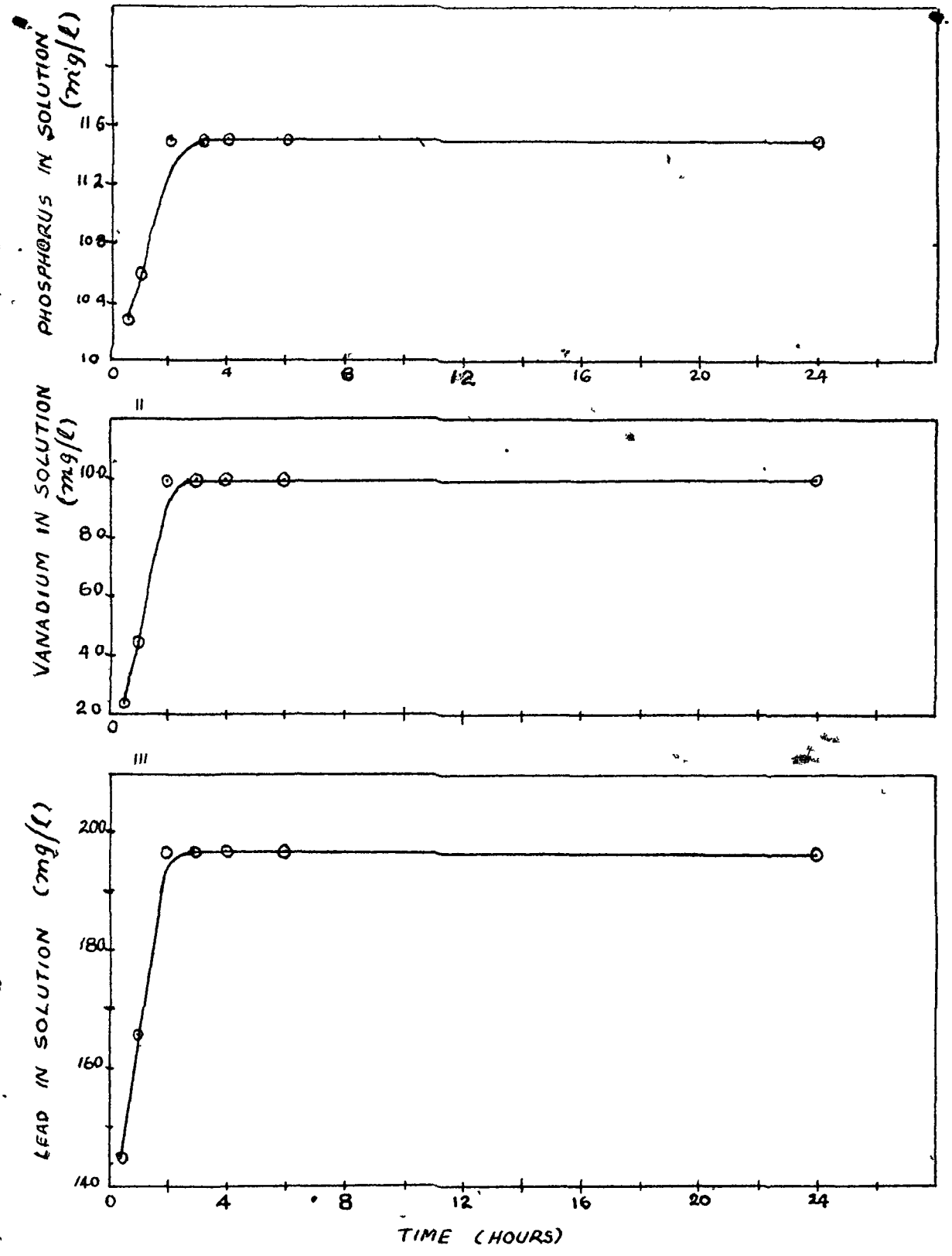
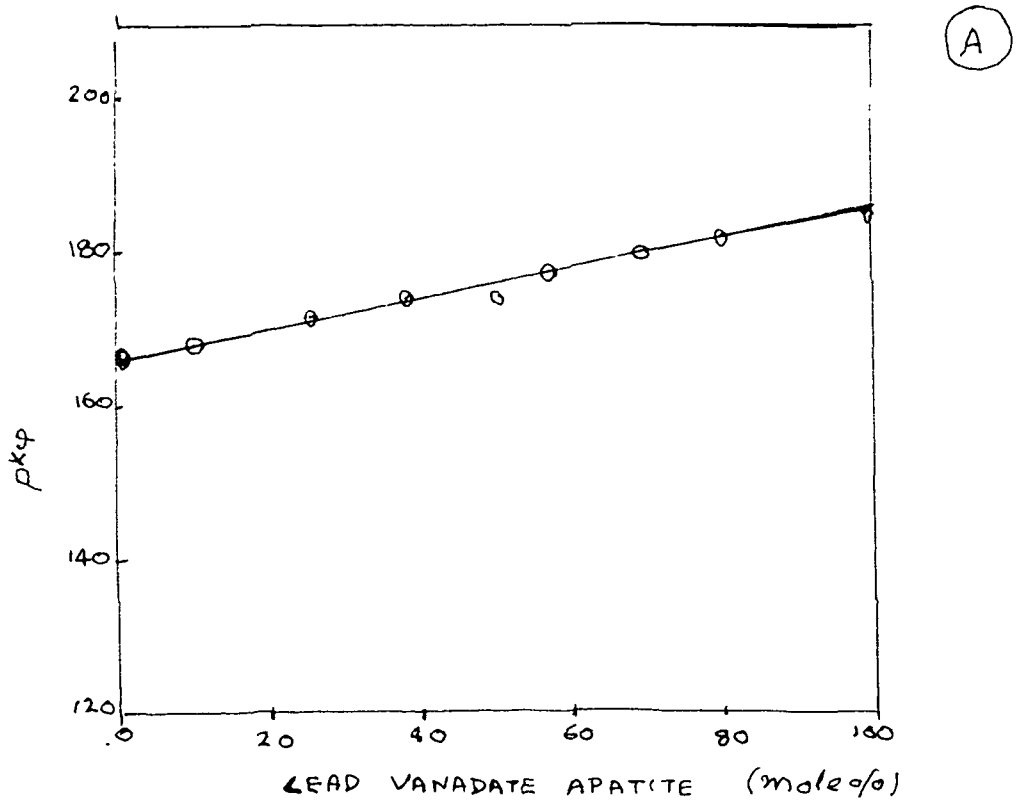

PHOSPHORUS IN SOLUTION (mg/l)
11.6
11.2
10.8
10.4
10
0
4
8
12
16
20
24
II
VANADIUM IN SOLUTION (mg/l)
100
80
60
40
20
0
III
LEAD IN SOLUTION (mg/l)
200
180
160
140
0
4
8
12
16
20
24
TIME (HOURS)

FIG. 3 4

Fig.3.5 (A) Dependence of Ionic Product on mole % of Lead Vanadate apatite

(B) Dependence of $\Delta G_{Soln.}$ on mole % of Lead Vanadate apatite.
(Table 3.14)


A
200
180
160
140
120
pKsp
0
20
40
60
80
100
LEAD VANADATE APATITE (mole%)

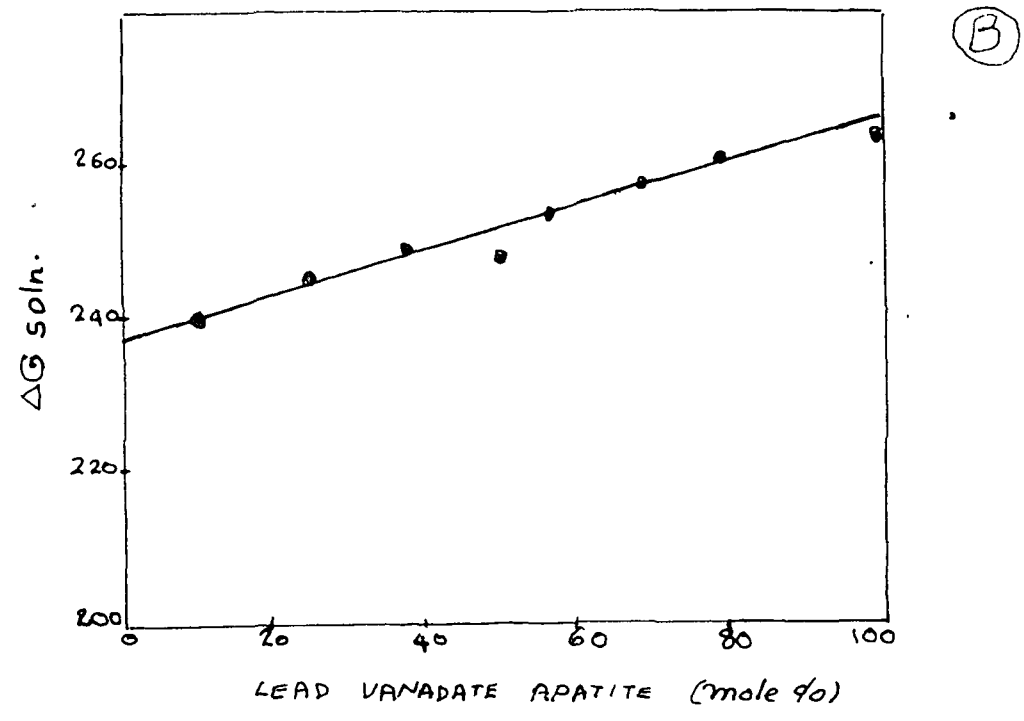

B
260
240
220
200
ΔG soln.
0
20
40
60
80
100
LEAD VANADATE APATITE (mole %)

FIG. 3.5

Clarification of Tables 3.1 to 3.22

Through the analyses of sample solutions containing known amounts of lead, phosphorus and vanadium, the accuracy of the method employed for their individual determinations when present together was scrutinized. The results incorporated in Table 3.1 suggested the maximum weight per cent. error involved in these determinations to be of the order of ± 0.99 for Pb^{2+} ion while the error was nil in the case of P and V.

Based on the results incorporated in columns (4a), (4b) and (4c) of the Tables 3.2 to 3.4 indication of attainment of saturation corresponding to a duration of equilibration equal to 4, 2 and 3 hours for LPA, solid solution and LVA respectively could be obtained by the constancy in the measured concentrations for the subsequent time-intervals. The constancy in g atom ratio reported in column 5 of each Table could show that the dissolution was stoichiometric.

Based on the results incorporated in column 3 of each

of the Tables 3-5 to 3-13, it could be concluded that the concentrations of the dissolved species decreased with increase in pH of the dissolving medium. A marked diminution in the concentration with increase in pH restricted the pH range to be investigated. As in the case of Tables 3.5 to 3.13, proof for the stoichiometric dissolution of the samples could be provided by results incorporated in column (4) of each of the Tables. The equilibrium concentration of OH^- ion present in the saturated solutions, which enters into the calculation of the ionic products of the solutes could be evaluated from the measured final pH of the solutions given in column (2) of the Tables making use of the ionic product of water, K_w, equal to 13.54 at 37°C .

The following aspects were considered to be relevant in understanding the significance of the other columns of the Tables: Orthophosphoric acid[162,247] being a tribasic acid exhibits, when dissociated, the following equilibria:-

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+ \quad \ldots\ldots \quad (3.1)$$

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \quad \ldots\ldots \quad (3.2)$$

$$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+ \quad \ldots\ldots \quad (3.3).$$

It is evident that H^+ ion mentioned in the above equilibria exists as H_3O^+ ion in aqueous media. The total amount of phosphorus present in a solution of LPA, represented as 'P' in column (3) of the Tables can be subdivided into (i) the undissociated acid and (ii) its dissociated ionic species

($H_2PO_4^-$), (HPO_4^{2-}) and (PO_4^{3-}), making use of the pH of the system and the three dissociation constants of the acid. The dissociation constants K_1, K_2 and K_3 and their values at 37°C are given by the following expressions:-

$$K_1 = \frac{(H_2PO_4^-)(H^+)}{(H_3PO_4)} = 7.51 \times 10^{-3} \quad .... \quad (3.4)$$

$$K_2 = \frac{(HPO_4^{2-})(H^+)}{(H_2PO_4^-)} = 6.33 \times 10^{-8} \quad .... \quad (3.5)$$

$$K_3 = \frac{(PO_4^{3-})(H^+)}{(HPO_4^{2-})} = 4.73 \times 10^{-13} \quad ... \quad (3.6)$$

where the quantities in brackets are the activities of the corresponding species. The activity coefficients of all these ions were considered to be unity in a 0.165M solution of NaCl as suggested by La Mer[160] and hence the concentration and activity of each ion were considered synonymous in the following calculations:-

The total dissolved phosphorus in g atoms/l is given by the expression,

$$(P)_{total} = (H_3PO_4) + (H_2PO_4^-) + (HPO_4^{2-}) + (PO_4^{3-}) \quad ... \quad (3.7).$$

The quantities on the right hand side are the concentrations of the respective species, the first being expressed in moles/l and the rest in g ions/l. From equations (3.4) to (3.7) it can be

shown that

$$(H_3PO_4) = \frac{(P) \times (H^+)^3}{q} \quad \ldots \quad (3.8)$$

$$(H_2PO_4^-) = \frac{(P) \times 7.51 \times 10^{-3} \times (H^+)^2}{q} \quad \ldots \quad (3.9)$$

$$(HPO_4^{2-}) = \frac{(P) \times 47.53 \times 10^{-11} \times (H^+)}{q} \quad \ldots \quad (3.10)$$

$$(PO_4^{3-}) = \frac{(P) \times 224.90 \times 10^{-24}}{q} \quad \ldots \quad (3.11)$$

where $q = (H^+)^3 + 7.51 \times 10^{-3}(H^+)^2 + 47.53 \times 10^{-11}(H^+) 224.90 \times 10^{-24}$

Similarly orthovanadic acid being a tribasic acid shows on dissociation the following equilibria:

$$H_3VO_4 \rightleftharpoons H_2VO_4^- + H^+ \quad \ldots \quad (3.12)$$

$$H_2VO_4^- \rightleftharpoons HVO_4^{2-} + H^+ \ldots\ldots\ldots \quad (3.13)$$

$$HVO_4^{2-} \rightleftharpoons VO_4^{3-} + H^+ \quad \ldots\ldots\ldots \quad (3.14)$$

Analogous to the aspects mentioned in the context of dissociation of orthophosphoric acid the following expressions can be arrived at in the case of the above equilibria

$$K_1 = \frac{(H_2VO_4^-)(H^+)}{(H_3VO_4)} = 3.98 \times 10^{-4} \quad \ldots \quad (3.15)$$

$$K_2 = \frac{(HVO_4^{2-})(H^+)}{(H_2VO_4^-)} = 1.32 \times 10^{-8} \quad \ldots \quad (3.16)$$

$$K_3 = \frac{(VO_4^{3-})(H^+)}{(HVO_4^{2-})} = 1.00 \times 10^{-13} \quad \ldots \quad (3.17)$$

$$(V)_{total} = (H_3VO_4) + (H_2VO_4^-) + (HVO_4^{2-}) + (VO_4^{3-}) \quad \ldots (3.18)$$

$$(H_3VO_4) = \frac{(V) \times (H^+)^3}{q} \quad \ldots \quad (3.19)$$

$$(H_2VO_4) = \frac{(V) \times 3.9811 \times 10^{-4} \times (H^+)^2}{q} \quad \ldots \quad (3.20)$$

$$(HVO_4^{2-}) = \frac{(V) \times 5.2483 \times 10^{-12} \times (H^+)}{q} \quad \ldots \quad (3.21)$$

$$(VO_4^{3}) = \frac{(V) \times 5.2483 \times 10^{-25}}{q} \quad \ldots \quad (3.22)$$

where $q = (H^+)^3 + 3.9811 \times 10^{-4}(H^+)^2 + 5.2483 \times 10^{-12}(H^+) + 5.2483 \times 10^{-25}$

where K_1, K_2 and K_3 are dissociation constants of H_3VO_4 at 25°C. While the values of K_1, K_2 and K_3 of H_3VO_4 corresponding to 37°C were not available in literature, it could be found that data on an analogous system, H_3PO_4, exhibited insignificant temperature dependence. The values corresponding to 25°C were therefore used for the present calculations. Thus, knowing the total phosphorus present in a solution of apatite at a given pH, the concentrations of the undissociated orthophosphoric acid and of its three dissociation products can be calculated. Since there were four unknown quantities associated with the four equations (3.8) to (3.11), similar calculations could be made for evaluating the concentrations of orthovanadic acid and its three dissociation products using euqations 3.19 to 3.22. From the measured pH values of the saturated solutions given in column (2) of the Tables, the corresponding OH^- ion concentrations could be calculated making

use of the value of ionic product of water, K_w, at $37^oC(1x10^{-13.54})$. These values were not included in the Tables since they could be obtained from the relationship, $P^H + P^{OH} = P^{K'_w} = 13.54$. Having thus obtained the concentrations of all the species present in the solutions of the apatites the ionic product K_{ip} of each of the possible solutes could be calculated on the basis of the corresponding molecular formula. It is evident that since the temperature was maintained constant, a confirmation that the apatite phase was controlling the solubility could be provided by a constancy of its K_{ip} at all the pH values. While assessing the relative constancies of the K_{ip} and $p^{K_{ip}}$ values of the phases likely to be formed in the solution of apatites, it should be kept in mind that for simple phases like $PbHPO_4$, $Pb\ HVO_4$, $Pb_2HPO_4(OH)_2$ and $Pb_2HVO_4(OH)_2$, the powers to which the measured concentrations of ions such as Pb^{2+}, HPO_4^{2-}, PO_4^{3-}, HVO_4^{2-}, VO_4^{3-} and OH^- ions were to be raised were low in comparison with those required for the apatite phase. Such a disparity in the values of the indices to which the concentrations were to be raised was likely to introduce errors proportionate to the value of the power to which a particular concentration was raised since the corresponding experimental error involved got simultaneously raised to the same power. In the light of these considerations, it could be concluded that the $p^{K_{ip}}$ value of the apatite phase was the most consistent at all the pH values investigated confirming the

occurrence of stoichiometric dissolution of the samples. Further, the g atom ratio, $\frac{Pb}{P}$ or $\frac{Pb}{V}$ given in column (4) of the Tables (3.5) and (3.13) ranged respectively from 1.62 to 1.85 and 1.55 to 1.76 which is very near to theoretical value of 1.67. Results on the solubility equilibria of a total of seven solid solutions of LPA and LVA were subjected to calculations similar to those of the end-members and incorporated in Tables 3.6 to 3.12. As in the case of the end-members, the g atom ratio, $\frac{Pb}{(P+V)}$, of the saturated solutions approached stoichiometry at all the pH values investigated. In addition, the K_{ip}'s and the pK_{ip}'s of the samples of the solid solutions calculated as in the case of the end-members on the basis of their molecular formulae exhibited a constancy at all the measured pH values. The average pK_{ip} value showed a regular increase from LPA (167.9) to LVA (184.6) while the solid solutions had intermediary values.

Making use of the experimentally determined K_{ip} values of LPA, LVA and their solid solutions, the free energy dicrease accompanying the dissolution of each sample was calculated and given in Table 3.14 . A systematic increase in the magnitude of ΔG as one goes from LPA through its solid solutions with LVA to pure LVA confirms the homogeneity of the samples and ensures the formation of the solid solutions.

Results on the dependence of solubility of LPA on the presence of common ions, Pb^{2+} and PO_4^{3-} chosen respectively in the concentration ranges 40-60 mg/l and 20-40 mg/l (expressed in terms of concentration of P) were given in the Table 3.15 .

Similar results on the dependence of solubility of LVA on Pb^{2+} and VO_4^{3-} chosen respectively in the concentration ranges 40-60 mg/l and 20-40 mg/l (expressed in terms of concentration of V) were given in Tables 3.16. For the entire series of concentrations of common ions investigated, the pK_{ip} values of the apatite phase exhibited a constancy proving the response of the solubility of apatite to the common ion effect. As expected, the g atom ratios, $\frac{Pb}{P}$ and $\frac{Pb}{V}$, in these cases were found to be divergent from the stoichiometric value, in accordance with the principle of solubility product. Results on the dependence of solubility of LPA on temperature were included in Table 3.17 while Table 3.18 contains similar results in the case of LVA. In these cases also the pK_{ip} values of apatite phase exhibited a constancy and the g atom ratios, $\frac{Pb}{P}$ and $\frac{Pb}{V}$ approached the stoichiometric value.

An attempt was made to assess the role of experimental errors on the values of ionic products determined. Using a given set of observed Pb^{2+}, P and V concentrations, ionic products of the apatite were calculated after applying corrections to these concentrations on the basis of the error limits involved. The results of such calculations were incorporated in Tables 3.19 to 3.22.

In Tables 3.19 to 3.22 were included results to establish the upper and lower limits of fluctuations in the calculated ionic products of LPA, LVA and other phases likely to control the solubility equilibria. In each set of calculations given

in a row of each Table, the experimentally measured pH values and the concentrations of lead, given respectively in column (6) were subjected to corrections depending upon the observed upper limits of the respective measurements, values of P and V being free from errors were not subjected to such corrections. The pKip values of PbH PO_4, $Pb_2(HPO_4)(OH)_2$, $Pb(H_2PO_4)_2$, $Pb_{10}(PO_4)_6(OH)_2$ and $PbHVO_4$, $Pb_2(HVO_4)(OH)_2$, $Pb(H_2VO_4)_2$ and $Pb_{10}(VO_4)_6(OH)_2$ were calculated using the experimentally measured and corrected values. The difference between two sets of corresponding pKip values gave the range of fluctuations consequent upon the upper limit of experimental errors. Similar calculations were made using the experimental values corrected on the basis of the lower limits of experimental errors. Such a range could help in deciding which among the likely phases constituted the solute to control the solubility equilibria, the criterion for the constancy of the calculated K_{ip} of a given phase being provided by the fact that its values were within the limits of those calculated on the basis of error limits. As an illustration it could be suggested that K_{ip} of the apatite phase of systems involving LPA as solute, taken as a representative set of values, ranged from 5.837×10^{-170} to 2.197×10^{-168} (See Table 3 & 5). While the range of values obtained by taking the error limits into consideration was found to be 1.090×10^{-174} to 2.04×10^{-166} the former range being well within the latter.

The following conclusions could be drawn from the results of the entire series of investigations on the solubility equilibria of LPA, LVA and their solid solutions:-

(i) Attainment of saturation could be achieved within a period of equilibration extending to about 4 hours.

(ii) The concentrations of the dissolution products increased with a decrease in the P^H of the dissolving medium.

(iii) The g atom ratio, $\frac{Pb}{P}$, $\frac{Pb}{V}$ and $\frac{Pb}{(P+V)}$, of the saturated solutions of LPA and LVA and their solid solutions approached the stoichiometric value of 1.67.

(iv) The calculated $P^{K_{ip}}$ values of the apatite phase showed a constancy.

(v) For a given set of experimental conditions the average pK_{ip} value of LVA was found to be greater than that of LPA and the corresponding values of solid solutions ranged between these two extremities. The $P^{K_{ip}}$ values of the solid solutions were found to increase with an increase in VO_4^{3-} content of the solutes which amounts to a decrease in the solubility of the samples with an increase in their VO_4^{3-} content.

(vi) The $P^{K_{ip}}$ values of the samples were found to be unaffected by the addition of common ions.

(vii) No marked dependence of K_{ip} on temperature was observed in the range 37 - 45°C in the case of LPA and LVA.

3.4 Discussion

3.4.1 Fundamental Aspects:

3.4.1.1 Mechanism of Dissolution of Ionic Crystals.

A brief mention of fundamental principles[248,249] governing the solubility of ionic crystals in aqueous media was considered desirable in the present context in order to provide an interpretation of the results on solubility of the samples of apatites investigated. A solution is a homogeneous mixture of two or more substances the composition of which is variable within certain limits beyond which saturation occurs. A crystalline solid is characterised by an orderly alignment of its constituent ions, the forces holding them in their relative positions being a consequence of its lattice energy which is defined as the minimum energy required for the conversion of its constituent ions from solid to gaseous state. When such a solid enters into solution an attraction between the solvent molecules and the constituents of the lattice of the solute caused by the existence of solvation energy occurs. An interplay of lattice and solvation energies controls the dissolution of the solute which is favoured when it is accompanied by a release of energy. It is evident that in polar solvents like water the solvation of the ions constituting the solute is facilitated by the dipolar interaction between

the solvent molecules and these ions. The solubility of a crystalline solid is controlled by size, charge and electronic structure of its constituent ions since both the energies mentioned above are in turn dependent on these parameters. In general, charge remaining the same, large ions pack less tightly than small ones resulting in the formation of a solid of a higher solubility. Similarly, it can be expected that increase in the charge of ions constituting a crystal brings about a greater binding leading to a lowering of the solubility.

In the dissolution studies the role of water as a solvent has been explained on the basis of the polarity of water due to a displacement of electric charges within its molecule. Water molecules which function as dipoles get oriented in an electrostatic field and exert attractive forces on the charged particles. When the ionic crystals come in contact with water, the molecules of the latter align themselves such that their negative and positive ends are oriented respectively towards the oppositely charged ions of the crystal[248]. The interionic attraction within the crystal is weakened consequent upon the dipolar forces exerted by water. The ions are thus pulled into solution. The detached ions move away from the crystal along with the accompanying water molecules. The dissolution of the ionic compounds in polar solvents like water may thus be explained. Additional factors

that greatly influence the dissolution of crystalline solids in polar solvents can be, among others, the proton donating and proton accepting tendencies in acid-base reactions, action of oxidising or reducing agents and formation of complex ions. It is established beyond doubt that water dipoles exist as molecular aggregates due to hydrogen bonding . A prerequisite for a substance to be soluble in water is its ability to weaken the hydrogen bonding such that its particles may be able to penetrate into the intermolecular spaces of the solvent. Such a weakening is brought about by the orientation of the water dipoles in the electrostatic field of an ion.

3.4.1.2 Thermodynamic Aspects of Dissolution:

It is evident that in a saturated solution of an ionic compound an equilibrium is established between the undissociated molecules of the solute and the products of dissociation accompanied by changes in enthalpy as demanded by the laws of thermochemistry. The free energy change, $\Delta G_{soln.}$, accompanying such a process at temperature T can be shown to be given by,

$$\Delta G_{soln.} = - RT \ln K_{sp} \quad \ldots\ldots \quad (3.23)$$

where the other terms involved have their usual significance. On the basis of the fundamental thermodynamic expression used for defining the change in free energy, it can be shown that

$$\Delta G_{soln.} = \Delta H_{soln.} - T \Delta S_{soln.} \quad \ldots\ldots \quad (3.24)$$

where $\Delta H_{soln.}$ and $\Delta S_{soln.}$ are the changes in heat content and entropy of solution respectively.

In order to evaluate K_{sp} of a given solubility equilibrium making use of equation (3.23), $\Delta G_{soln.}$ is desired which in turn is obtained from $\Delta H_{soln.}$ and $\Delta S_{soln.}$ as indicated by equation (3.24). It is evident from equations (3.23) and (3.24) that a theoretical value of K_{sp} of a given solubility equilibrium can be arrived at by making use of values of $\Delta H_{soln.}$ and $\Delta S_{soln.}$ of the process. Visualising dissolution of an ionic compound to be consisting of (i) breaking down of the crystal architecture for which the lattice energy, 'U' , is operative and (ii) the hydration of the constituting ions, so set free, for which the summation of the individual hydration energies is made use of, it can be shown that the overall heat change involved in the process which is the same as the heat of solution, $\Delta H_{soln.}$, is given by

$$\Delta H_{soln.} = \Sigma \Delta H_{hi} + U \quad \ldots\ldots \quad (3.25)$$

where $\Sigma\Delta H_{hi}$ is the sum of heats of hydration of the ions, while ΔH_{hi} is the corresponding value for the i^{th} ion. It is evident that appropriate signs for the quantities involved in the above expression are to be given on the basis of the established conventions. It can be concluded from the above expression that for a highly soluble compound the

absolute value of $\Sigma \Delta H_{hi}$ is greater than that for U while the converse is valid for cases of low solubility. While $\Sigma \Delta H_{hi}$ is the summation of the enthalpy changes involved in the conversion of the products of dissolution to their corresponding hydrated species, U can be shown to be made up of two principal energy terms contributed by Coulombic attraction and repulsion operative among the constituting ions of the crystal lattice and can be shown to be given in K cals/mole at $0^{o}C$ by the expression

$$U = \left(\frac{NAe^2 Z+ Z-}{R_o}\right)\left(1 - \frac{1}{n_B}\right) \quad \ldots\ldots \quad (3.26a)$$

$$= \left(\frac{332\ AZ+ Z-}{R_o}\right)\left(1 - \frac{1}{n_B}\right) \quad \ldots\ldots \quad (3.26b)$$

where N = Avogadro's Number, A = Madelung's constant which depends upon the crystal arrangement, e = electronic charge, Z+ and Z- are the valencies of the cation and anion respectively which constitute the crystal lattice, R_o is the minimum cation to anion distance equal for approximate purposes to $(r_+ + r_-)$ where r+ and r- are respectively the cationic and anionic radii and n_B is the Born exponent which depends upon the electronic configuration of the ions and leads to the evaluation of the repulsive forces operative. Having explained the implications involved in the theoretical evaluation of $\Delta H_{soln.}$ of equation (3.24), a theoretical evaluation of $\Delta S_{soln.}$ involved in this equation which is now desired, can

be obtained from the expression,

$$\Delta S_{Soln.} = \left[\begin{array}{l}\text{(Sum of the entropies of products of}\\ \text{dissolution) - (entropy of solute)}\end{array}\right] \ldots \quad (3.27)$$

It is evident that the quantities on the right hand side of the above expression can be evaluated using the Latimer[250] expression

$$S^{o}_{298} = \left[\frac{3}{2} R \ln.(\text{at. wt. of the species}) - 0.94\right] \quad \ldots \quad (3.28)$$

where S^{o}_{298} refers to the entropy contribution of the desired species at 25°C, the expression being valid only for simple salts such as the alkali halides. Further, in the event of participation of gaseous ions, application of the Sackur - Tetrode equation[249],

$$S^{o}_{g} = 26.0 + \left\{\frac{3}{2} R \ln.(\text{at.wt.})\right\} \quad \ldots \quad (3.29)$$

is also desired where S^{o}_{g} refers to the entropy of the desired gaseous ions. While the above discussion involves a circuitous evaluation of $\Delta G_{soln.}$ desired for arriving at a theoretical basis for dissolution of ionic compounds, a more direct approach is possible as shown below starting with (i) $\Sigma\Delta G_{hydration}$, the summation of the free energy changes of hydration of the constituting ions of the solute and (ii) $\Delta G_{lattice}$, the free energy change of formation of the lattice of the solute,

$$\Delta G_{soln.} = \Sigma\Delta G_{hydration} - \Delta G_{lattice} \quad \ldots \quad (3.30)$$

using a specific example of a solute of general formula, M_mN_n, the quantities on the right hand side of the above expression can be shown to be given by the relationships

(3.31) to (3.35) as given below:-

$$\Delta G_{hydration} = m.\ \Delta G_{h\ M} + n.\ \Delta G_{h\ N} \qquad (3.31)$$

$$= \frac{164\ Z_+^2\ m}{r_+ + 0.85} - \frac{164\ Z_-^2\ n}{r_- + 0.1} \qquad (3.32)$$

The fundamental expression

$$\Delta G_{lattice} = \Delta H_{lattice} - T\ \Delta S_{lattice} \qquad (3.33)$$

assumes the form $\Delta G_{lattice} = - U - T.\ \Delta S_{lattice}$ (3.34)

appropriate signs being given to the terms involved. As explained earlier $\Delta S_{lattice}$ desired in the above expression can be evaluated using the Latimer[252] and Sackur - Tetrode[249] equation provided in equations (3.28) and (3.29). On substitution of the appropriate values for the quantities involved in equation (3.34) expression for $\Delta G_{lattice}$ assumes the following form:

$$\Delta G_{lattice} = \left\{ \frac{332\ AZ_+Z_-}{R_o} \left(1 - \frac{1}{n_B}\right) - 8.03\ (m + n) \right\} \qquad (3.35)$$

substituting the values of $\Delta G_{hydration}$ and $\Delta G_{lattice}$ obtained from the expressions (3.32) and (3.35) $\Delta G_{Soln.}$ in K.Cal/mole at 298°K for such a system is given by the expression.

$$\Delta G_{soln} = -\left\{ \frac{164Z_+^2\ m}{r_+ + 0.85} - \frac{164Z_-^2\ n}{r_- + 0.1} \right\} + \left\{ \frac{332AZ_+\ Z_-}{R_o} \left(1 - \frac{1}{n_B}\right) - 8.03\ (m + n) \right\} \quad K\ cal/mole \qquad (3.36)$$

To emphasize the dependence of $\Delta G_{soln.}$ on the replacement of an anion of the solute by another of a different ionic radius the above expression can be differentiated with respect to r- at

constant r+ which leads to the relationship,

$$\left(\frac{\partial \Delta G_{soln}}{\partial r_+}\right)_{r_-} = \left\{\frac{164\ Z^2_{\pm}\ n}{(r_- + 0.1)^2}\right\} - \left\{\frac{332A\ Z+Z-}{R_o^2}\left(1-\frac{1}{nB}\right)\left(\frac{\partial R_o}{\partial r_+}\right)_{r_-}\right\}$$

.... (3.37)

It is evident that the changes ensuing in $\Delta G_{hydration}$ and $\Delta G_{lattice}$ consequent upon such a replacement are given respectively by the first and second terms on the right-hand side of the above expression.

3.4.1.3 Present results on Solubility

While overall change in the solubility of an ionic compound depends exclusively on the relative variations in ΔG hydration and $\Delta G_{lattice}$ terms as above, for sparingly soluble salts like apatites the latter becomes more dominant. This can be justified by the fact that the alterations in hydration energies[251] for the pair of anions involved (PO_4^{3-} and VO_4^{3-}) in the substitutions investigated are of very small magnitude. The above equation shows that when the lattice energy increases by a larger amount than the hydration energy, a solubility decrease occurs. The inference that the lattice energies increased with the increasing vanadate content in the samples clearly explains the decrease in their solubility as one goes from lead phosphate apatite to lead vanadate apatite as established by the present set of investigations carried out.

While the solubility of a solute in a given solvent under a specified set of experimental conditions is constant, its Kinetics of dissolution is controlled by its particle size and conditions of equilibration such as rate of shaking. It is therefore essential to maintain these parameters constant in comparitive studies of solubility in which a common period of equilibration was adopted for the attainment of saturation. As was to be expected the periods of dissolution required for the attainment of saturation in the present investigations were comparable with those reported earlier[166] under a similar set of experimental conditions. The solubilities of LPA and LVA as well as those of solid solutions studied as a function of pH of the dissolving medium showed a marked increase with a decrease in pH. An interpretation of this observation was provided by the simultaneous equilibria established in systems involving dissolution of apatites. The equilibria which are relevant in the present context for LPA as solute are the following:-

$$Pb_{10}(PO_4)_6(OH)_2 \rightleftharpoons 10Pb^{2+} + 6\ PO_4^{3-} + 2\ OH^- \ldots \qquad (3.38)$$

Among the products of dissolution PO_4^{3-} and OH^- are capable of participating in a few more simultaneous equilibria characteristic of a saturated aqueous solution of an apatite. The presence of PO_4^{3-} in aqueous medium initiates establishment of the following equilibria which are all pH- dependent:-

$$PO_4^{3-} + H_3O^+ \rightleftharpoons HPO_4^{2-} + H_2O \quad .... \quad (3.39)$$

$$HPO_4^{2-} + H_3O^+ \rightleftharpoons H_2PO_4^- + H_2O \quad ... \quad (3.40)$$

$$H_2PO_4^- + H_3O^+ \rightleftharpoons H_3PO_4 + H_2O \quad ... \quad (3.41)$$

The OH^- ion, on the otherhand, takes part in an additional equilibrium characteristic of all aqueous media as shown below:-

$$H_3O^+ + OH^- \rightleftharpoons 2H_2O \quad ..... \quad (3.42)$$

which is also pH dependent. A shift from left to right occurs in all the above equilibria when H_3O^+ ion concentration is increased. While all these equilibria are collectively responsible for influencing equilibrium (3.38), the one in which PO_4^{3-} ion is a direct participant is naturally more dominant for bringing about a shift from left to right resulting in a higher solubility of the solute. Such a shift in equilibrium (3.38) is further accentuated by equilibrium (3.42) which facilitates the removal of OH^- ions which are dissolution products of apatites bringing about an additional enhancement of the solubility of apatite. Such adjustments in these equilibria continue till the solubility product of the solute is attained. The marked pH dependence of the solubilities of LPA and its solid solutions with LVA can thus be accounted for. A saturated solution of LVA is characterised by equilibria analogous to those operative in the system involving LPA.

The foregoing arguments are substantiated by the observed fact that calculated proportion of PO_4^{3-} or VO_4^{3-} ions of the saturated solutions of the samples decreased with an increase in the hydrogen ion concentration of the medium of dissolution (See Table 3.5 to 3.15)

Another important finding of the present investigations was that the solubility of the samples was found to decrease with an increase in the proportion of vanadium. This amounted to LPA exhibiting the highest solubility and LVA the lowest, with the solid solutions exhibiting the intermediary solubilities following the order of diminution with increase in vanadate content under a given set of experimental conditions. Since the covalent radii of P and V are not very much divergent from one another, the factor dominant for controlling the solubility is not evidently the disparity in the lattice energies. The factors which control the solubility of LPA and LVA can be supposed to be related to the release of energy due to hydration of the constituents of the two lattices. The energy associated with hydration of ions evidently depends upon the population of the ions available under the conditions prevalent during dissolution. Experimental conditions being the same, the first dissociation constant of H_3VO_4 is lower than that of H_3PO_4. Based on the consideration that in the case of simultaneous equilibria the ion participating in more than one equilibrium exhibits the same activity in all its equilibria, the population of VO_4^{3-} ions is lower than that of

PO_4^{3-} ions contributing to a lower sum total of hydration energy for the former resulting in a lower K_{sp}.

An additional explanation for the observed K_{sp} of LVA being lower than that of LPA is provided by the fact that the extent of dissocation of H_3VO_4 is lower than of H_3PO_4. The equilibria involving these two acids are evidently the sources for the availability of PO_4^{3-} and VO_4^{3-} ions which in turn participate in the solubility equilibria of LPA,LVA and their solid solutions.

The lower solubilities of the solid solutions over that of LPA can be given an explanation based exclusively on the structural considerations as was shown by Young et al.[118] According to them ions such as F^-, Cl^- and OH^- or a combination of them exist in apatites in columns or linear chains coincident with their six-fold screw axis. It could be shown through infrared spectral studies that the OH^- ions constituting the lattice of a solid solution of LPA and LVA are mutually linked up through a hydrogen bonding. The hindrance caused to the diffusion of the OH^- ion through the columns mentioned above can be a factor in reducing the solubility of solid solutions since the columns offer themselves as the most vulnerable points[252-254] for the diffusion of the ions located in them into the medium of dissolution. In addition, the porosity and the surface activity of the samples of apatites are dependent on the columns in which OH^- ions are located. The crosslinkage of OH^- ions as mentioned above

can contribute to the blockage of these columns resulting in a diminished accessibility of the solvent molecules and release of the OH^- ions explaining thereby the decrease in the solubility of solid solutions.

3.4.1.4 Ionic product and solubility product - Role of Ionic strength.

A saturated solution is characterised by the existence of an equilibrium between the dissolved and undissolved species of the solute. It can be shown on the basis of chemical potential that when the dissolved fraction dissociates completely in a saturated solution, the product of the activities of the constituent ions is a constant at a given temperature known as the activity solubility product, k_{sp}. It is convenient to express solubility in terms of the solubility product since the latter enables the former to be evaluated even in media containing complexing and common ions. Polymorphism, particle size, degree of hydration, occurrence of chemical reactions leading to either hydrolysis or complex formation and surface exchange may be considered as some of the important characteristics of the solute phase which influence its solubility and hence the solubility product. The ionic strength, μ, of a dissolving medium given by half of the summation of the products of molality and square of the charge of all the ionic species present, is another important factor influencing the solubility product. The following expression which can be derived on the

basis of the Debye-Hückel theory gives the solubility of a salt as a function of the ionic strength, , at 25°C

$$\log S = \log S_o + \left\{ \frac{0.509 Z+ Z- \sqrt{\mu}}{(1+0.329\ a\sqrt{\mu})} \right\} \quad .... \quad 3.43$$

where S_o = solubility at zero ionic strength, a = distance of closest approach of the ions and Z+ and Z- are the respective valencies of the positive and negative ions of the salt.

In the present investigations the medium of dissolution adopted was constituted by buffer combinations of desired pH maintained at a molarity of 0.165 with respect to sodium chloride. The ionic strength of the dissolving medium thereby remained virtually constant[160] over the entire compositional range of the buffer combinations. The role of the ionic strength of the medium of dissolution as a parameter of the solubilities of apatites could thus be avoided.

It has been suggested by LaMer[160] that it is complicated to calculate the activity coefficients when ions of high and opposite charge are involved as is the case with solutions of LPA and LVA; the use of the Debye-Hückel equation for the precise calculation of activity coefficients of such ions has been found to be inadequate. It was, therefore, recommended by him that an aqueous solution of 0.165M NaCl, a solvent of

reference in which all activity coefficients may be assigned a value of unity. In the light of such a consideration the concentrations of the ionic species were used instead of their activities for purposes of calculations of K_{ip} - values reported in the present section.

It may be relevant to mention in this context an important concept advanced by Brønsted[255,256] even before the enunciation of the Debye - Hückel theory. Based on an extensive series of investigations he could show that a constant ionic environment contributed by a large excess of an inert neutral salt can ensure a constancy of the activity coefficients of ions present in relatively low concentrations. When such a condition is fulfilled, the ionic product, K_{ip}, of a solute is related to the corresponding activity product by a constant factor enabling thereby the use of the former for purposes of comparison.

3.4.1.5 Stoichiometric Dissolution of Apatites.

Important requirements for a stoichiometric dissolution of an ionic compound leading to the formation of a saturated solution are (i) a constant value for the solubility product at a given temperature even when the rest of the experimental conditions are altered (ii) an agreement of ratios of measured concentrations of the ions of the solute in the absence of

extraneous addition of one or more of these ions and (iii) non-dependence of the evaluated solubility products on the addition of common ions and slurry density. The present investigations on solubility of apatites could convincingly prove that these criteria are fulfilled establishing unambiguously their stoichiometric dissolution. The $p^{K_{ip}}$ values of the samples were calculated from the measured concentrations of the dissolved species of LPA,LVA and their solid solutions at a constant temperature. Each individual solute shows a constant $p^{K_{ip}}$ value within the limits of experimental errors, even under an alteration of the pH of the medium of dissolution. It is clear from the procedure adopted for such calculations that the principal factors which contribute to a deviation of these computed values from those expected are the experimental errors involved in the microanalytical determinations of the dissolved species. Out of these ions, OH^-,with its dominant accompanying effect on the calculated value of the PO_4^{3-} or VO_4^{3-} ion from the measured $(P)_{Total}$ or $(V)_{Total}$ value, as indicated by eqs.(3.8 and 3.18), is of significance. It is evident that an error in its measurement effects not only its own concentration term used directly in the calculation of K_{ip} but also that of PO_4^{3-} or VO_4^{3-} which is computed from the $(P)_{Total}$ or $(V)_{Total}$ and the measured pH value. These errors get accentuated in the $P^{K_{ip}}$ calculations of apatites

the molecular formulae of which involve ten, six and two g ions respectively of Pb^{2+}, PO_4^{3-} or VO_4^{3-} and OH^-. Such computations involve large powers to which the corresponding concentrations are to be raised to get the $p^{K_{ip}}$ values. Based on the fact /that the experimental values of $P^{K_{ip}}$ lie within the error limits consequent upon inaccuracies in the determination of the concentrations of the concerned ions the observed set of values could be considered as constant for a given solute confirming thereby the concept of stoichiometric dissolution.

In order to scrutinize the validity of the concepts advanced earlier[159,161] suggesting the role of additional solid phase such as the secondary salts, $PbHPO_4$ or $PbHVO_4$, a surface complex $Pb_2\ HPO_4(OH)_2$ or $Pb_2\ HVO_4\ (OH)_2$ in controlling the solubility equilibria of apatite systems, the ionic products of these and other solid phases were calculated following the procedures adopted for the apatites.

In general, the errors involved in the measurements of the concentrations of the dissolving species of apatites are likely to magnify the fluctuations in the calculated values of the ionic products since the latter were of a very low order of magnitude involving powers of the ionic concentrations. Since the powers to which the ionic concentrations were to be raised to get the K_{ip} values were much lower in the case of the secondary

salt and the surface complex than for apatite as is evident from the molecular formulae the values of the former were supposed to be lower. The g atom ratio, $\frac{Pb}{(P+V)}$, in the case of additional phases is not stoichiometric as required for apatite phase for which the ratio was found to be close to the stoichiometric value. These considerations could conclusively eliminate the possibility of phases other than apatite controlling the solubility equilibria of the systems. Though the observed constancy in the K_{ip} values of the apatite phase was not very striking, it could still be concluded that their solubility equilibria were characterised by stoichiometric dissolution. This conclusion was justified on the basis of the expected upper and lower limits of fluctuations in the calculated K_{ip} values of all the likely phases. An additional substantiation of the stoichiometric dissolution of apatite could be provided by the remarkable regularity with which the end-members responded to the common ion effect. With the pK_{ip} values calculated remaining unaffected in either case, the g atom ratios $\frac{Pb}{P}$ and $\frac{Pb}{V}$ were found to be divergent from the stoichiometric value as demanded by the principle of solubility product when applied to systems involving common ion.

3.5 SUMMARY

The solubility equilibria of lead phosphate apatite, lead vanadate apatite and a total of seven of of their solid solutions spread over the entire compositional range were investigated with the intention of studying the dependence of their solubility on the extent of isomorphous substitution of PO_4^{3-} by VO_4^{3-} . In order to substantiate the findings the studies were extended to a few chosen buffered dissolving media spread over a narrow p^H range of 2 - 3, higher p^H values being unsuitable due to a marked diminution in solubility in the case of all the solutes. To enable the results of these investigations to be applied to in vivo conditions the studies were restricted to 37°C, although the temperature dependence of solubility was investigated separately.

Equilibrating powdered samples of the solutes with appropriate buffer solutions the colloidal component was separated from the saturated solutions through $1G_4$ sintered glass crucibles and the filtrates were subjected to microanalytical determinations of the concentrations of the dissolved ions. The minimum duration of equilibration required for the attainment of saturation was established through studies on the dissolution Kinetics. The proportion of H_3PO_4 and H_3VO_4 and the corresponding dissociation

products were calculated respectively from the experimentally determined phosphorus and vanadium contents of the solutions using the dissociation constants and the p^H of the medium.

Taking into consideration the possible ionic equilibria which can be established in such systems, the ionic products of primary and secondary phosphates, a complex, $Pb_2(HPO_4)(OH)_2$ and LPA were calculated for systems having the latter as solute. Similar calculations were carried out for the ionic products of the vanadium counterparts in LVA systems. A combination of these two sets of calculations was brought about in the case of systems having the solid solutions of the end-members as solutes. A high concentration of sodium chloride (0.165M) was maintained in the medium of dissolution to maintain the ionic strength constant. This enabled the ionic product of the solute, Kip, to be considered as its solubility product, K_{sp}, assuming the activity coefficients of each one of products of dissolution to be unity in such systems.

Based on the molecular formulae of the solutes, the corresponding ionic products were calculated making use of the sets of concentrations of the products of dissolution. At constant temperature, the ionic product of each solute was found to be constant in all the systems investigated. The assumed constancy was based on the fact

that the observed scatter in $p^{K}ip$ values was within the error limits. Proof for the occurrence of stoichiometric dissolution of the samples could be obtained on the basis of the following:-

(i) a constancy in the $p^{K}ip$ values of the apatite phase in each case

(ii) an agreement of the g atom ratios, $\frac{Pb}{(P+V)}$, of the saturated solutions with the theoretical value and

(iii) a precise response of $\frac{Pb}{P}$ and $\frac{Pb}{V}$ values respectively of LPA and LVA systems to the addition of common ions.

A systematic study of the solubilities of the samples could show that LVA was less soluble than LPA and that the solid solutions exhibited an intermediary behaviour showing a systematic decrease in the solubility product with an increase in the vanadium content. These aspects could be explained on the basis of the concept of hydration and lattice energies of ionic solids supplemented by the disparity in the dissociation constants of ortho-phosphoric and ortho-vanadic acids.

SYNOPSIS

Calcium hydroxylapatite, $Ca_{10}(PO_4)_6(OH)_2$, the principal inorganic constituent of human bones and teeth, belongs to an isomorphous series of substances known as apatites. It has been the subject of extensive investigations because of its biological significance and its remarkable ability to undergo a series of cationic and anionic exchange reactions, the criteria for such an exchange being the identity of charge and the proximity of ionic radii of the pairs of ions involved. Among such diverse exchange reactions a few have attained significance during the recent past consequent upon the toxicity of the elements involved, such an exchange being the mechanism for their incorporation into human skeletal system. Based on the contemporary importance given to the toxicity caused by lead and vanadium to the human system, studies on the replacement of calcium by lead (ionic radii 0.99 and 1.20 Å respectively) and of phosphorus by vanadium (Covalent radii 1.10 and 1.22 Å respectively) have been chosen for the present investigations. It is evident that a complete replacement of Ca^{2+} ions by Pb^{2+} ions leads to lead phosphate apatite, $Pb_{10}(PO_4)_6(OH)_2$, while that of PO_4^{3-} by VO_4^{3-} leads to lead vanadate apatite, $Pb_{10}(VO_4)_6(OH)_2$, both being isomorphs of calcium hydroxyl apatite. A partial replacement in either case leads to formation of solid solutions of the concerned end-members.

It has been established that inhalation of lead in the form of dust or fumes or its absorption through the skin leads to "lead poisoning" (Plumbism) which is, in general, an occupational disease. It is well known that lead salts are extensively used in petrol to improve its quality and in pottery and paints resulting in contamination leading thereby to a possibility of incorporation of this element into the human skeletal system. As in the case of lead the toxic effect of vanadium to human system has been confirmed. In addition, it could be proved that a few species coming under the marine organisms are also vulnerable to such a toxicity. It could be shown that the principal polluting sources of vanadium are its presence in certain varieties of steel as well as the industrial establishments involving the element and its salts as catalysts.

It could be unambiguously established that ions incorporated in the human skeletal system through exchange reactions on calcium hydroxylapatite of bones play a significant role in two principal bone processes, namely, calcification and resorption, the deposition and dissolution respectively of calcium hydroxylapatite at the interface of bone and body fluids. Consequently, any attempt in the direction of elimination or minimization of such a toxicity is associated with a study of the solubility of calcium hydroxylapatite as well as of the products of the exchange

reactions mentioned above under simulated biological conditions

Prompted by such a consideration the present work which deals with the preparation, characterization and solubility equiiibria of lead phosphate apatite, lead vanadate apatite and a series of eight of their solid solutions spread over the entire compositional range, was undertaken. Adopting coprecipitation of the end-members in aqueous media through a judicious modification of the existing methods, the samples were prepared at $37^{o}C$ to simulate biological conditions.

Characterization of these samples was brought about through sophisticated instrumental techniques such as X-ray diffraction, electronmicroscopy,i.r. spectral studies and thermogravimetry in addition to the conventional chemical analyses. Vegard's law demands that the unit cell volume of a series of solid solutions varies linearly with the composition and offers a convenient method of scrutinizing their homogeneity. As is to be expected from the bigger size of vanadate ion, a replacement of phosphate ion by it brings about a dilation of the unit cell. A systematic linear dependence of the unit cell volumes with the proportion of vanadate ion replacing phosphate ion observed in the present

series of solid solutions confirmed their homogeneity. The electronmicrographs of a few representative samples revealed the hexagonal pattern of the crystals confirming the absence of extraneous phases and enabling approximate calculations of the specific surface areas and average dimensions of the individual crystals. The i.r. absorption spectra could confirm the identity of the samples. The predominant absorption peaks recorded in the traces of the samples were found to be due to the orthophosphate and orthovanadate ions. In addition, the absorption peaks due to carbonate and pyrophosphate ions, the two likely impurities, were found to be absent. The absence of carbonate ion eliminates the possibility of atmospheric interaction leading to the formation of carbonate apatite. Thermogravimetric analysis indicated that a temperature of 300^{o}C chosen for driving out volatile impurities from the samples did not inflict a chemical decomposition on them.

Studies on the solubility of the samples were undertaken at 37^{o}C in order to investigate its dependence on the replacement of PO_4^{3-} ion by VO_4^{3-} ion on lead phosphate apatite.Since it was intended to determine the solubility product of each sample from data resulting from the chemical analyses of its saturated solution, a buffered dissolving medium was used to maintain constancy of the activity of OH^- ions

involved in such calculations. In order to investigate the reproducibility of the solubility products so determined, the studies in each case were extended to a few chosen pH values, the range being restricted only from 2.0 to 2.7, since there was a marked fall in the solubility of all the samples at pH value higher than 2.7. In addition, all such buffered dissolving media were maintained at a molarity of 0.165 with respect to sodium chloride to simulate biological conditions. By adopting such a medium of dissolution the complicated process of evaluating accurately the activity coefficients of poly-valent ions could be avoided by assuming all of them to be unity without foregoing accuracy. It is evident that such calculations make the solubility product, K_{sp}, and the ionic product, k_{ip}, synonymous.

Each one of the powdered samples was equilibrated with the chosen buffer combination as the medium of dissolution at a controlled rate of shaking using a constant temperature shaker-bath. The colloidal component of the solute present in its saturated solution due to its low solubility was separated by filtration at 37°C through a 1G4 sintered glass crucible before the solutions were analysed for the products of dissolution. A separate experiment could prove the suitability of such crucibles for colloidal separation.

While phosphorus and vanadium were determined

colorimetrically, complexometry was adopted for the determination of lead, the attainable accuracy in all the cases being scrutinized by analysis of solutions of known compositions.

A scrutiny of attainment of saturation and the minimum period of equilibration required for the purpose were determined through dissolution Kinetics of a couple of representative samples. From among the concentrations of the products of dissolution, the measured total dissolved phosphorus was subdivided into the proportions of orthophosphoric acid and its three dissociation products, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} using the three dissociation constants of the acid and the equilibrium pH of the system, the latter being required also for evaluating OH^- ion concentration needed for the calculation of solubility product.

There exists an ambiguity in the earlier literature regarding the solute phase likely to control the solubility of apatite systems since the dissolution involved is hydrolytic. That the apatites exhibit stoichiometric dissolution could not unambiguously be established by the earlier workers. In order to investigate this significant aspect of dissolution of apatites, the solubility data of the present investigations were subjected to calculations to establish which among the

possible phases exhibited a constancy for the activity product of its ions. It is evident that for the phosphate containing apatites such phases are the primary and secondary phosphates of the metal concerned in addition to the apatite. By analogy with a double salt, $Ca_2(HPO_4)(OH)_2$, a phase reported to control the solubility product of calcium hydroxylapatite by functioning as a surface coating, the ionic product of its lead counterpart, $Pb_2(HPO_4)(OH)_2$, was also calculated for the present system. Examination of the data on solubility of all the phases mentioned above reveals that the ionic product of apatite showed a constancy over the entire pH range investigated and the calculated set of values were found to lie within the error limits. It is evident that the corresponding vanadate phases are relevant for lead vanadate apatite while the phases of both phosphate and vanadate are to be considered for the systems involving the solid solutions. Such calculations were done on the data of solubility of all these samples. That the apatite phase controlled the solubility was further supplemented by the fact that the g atom ratio, $\frac{Pb}{(P+V)}$, of the saturated solutions of all the samples was in the proximity of the theoretical value (1.67) confirming unambiguously stoichiometric dissolution of apatites. An additional substantiation of this fact was that the pK_{ip} values of the samples were found to be unaffected by the addition of common ions.

It could be established further that the solubility product of each sample of the series while remaining constant at all the $\bar{p}^{H}$ values investigated, decreased systematically with an increase in the extent of replacement of PO_4^{3-} by VO_4^{3-}. An interpretation of these results could be provided by the concept of alterations in lattice and hydration energies of ionic crystals consequent upon isomorphous substitution.

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