Calcium hydroxylapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, 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 $1.20 \, \text{Å}$ respectively) and of phosphorus by vanadium (Covalent radii $1.10$ and $1.22 \, \text{Å}$ respectively) have been chosen for the present investigations. It is evident that a complete replacement of $\text{Ca}^{2+}$ ions by $\text{Pb}^{2+}$ ions leads to lead phosphate apatite, $\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$, while that of $\text{PO}_4^{3-}$ by $\text{VO}_4^{3-}$ leads to lead vanadate apatite, $\text{Pb}_{10}(\text{VO}_4)_6(\text{OH})_2$, both being isomorphous 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 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 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, \( k_i \), 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 164 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
olorimetrically, 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, $\text{Ca}_2(\text{HPO}_4)(\text{OH})_2$, a phase reported to control the solubility product of calcium hydroxylapatite by functioning as a surface coating, the ionic product of its lead counterpart, $\text{Pb}_2(\text{HPO}_4)(\text{OH})_2$, 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 $\text{g}$ atom ratio, $\frac{\text{Pb}}{\text{(P+V)}}$, 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 $K_{\text{ip}}$ 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 \( \text{PO}_4^{3-} \) by \( \text{VO}_4^{3-} \). 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.