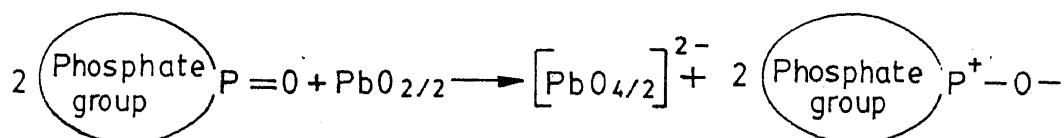


4. Experimental observations reconsidered

We may note here that production of various anions coincidentally produces a large concentration of orthophosphate units. Since the oxygen atoms in orthophosphate ions carry the highest partial charge, Pb^{2+} ions tend to crowd around orthophosphate units. The crowding immobilizes significant numbers of lead ions in the neighbourhood of orthophosphate units. Further orthophosphate ions (and to some extent pyrophosphate ions) enable tight structural packing around themselves, which enhances the barrier for migration of lead ions. Lead ions are also immobilized when they occupy network positions through reactions of the type.



Equation (4), appears as if lead oxide acts as an acid and reacts with phosphate anions which are conjugate bases. Such incorporation of lead into network positions has been noted by us in lead phosphomolybdate glasses (Rao *et al* 1986; Selvaraj and Rao 1988; Damodaran *et al* 1988). It would therefore be reasonable to assume that significant fractions of lead ions are present in four coordinated network positions and are therefore immobilized. Thus the net fraction of free Pb^{2+} ions is low and these are the only ones which can contribute to transport properties, and occupy voids present in the inefficiently packed regions. The large phosphate ions possess topologically restrictive geometries and therefore give rise to inefficiently packed regions. The conductivity behaviour observed in figure 7, is therefore consistent with the motion of a small fraction of lead ions in large voids created in the polymerized anionic matrix, and hence the activation barriers are low. The conductivity itself has a low magnitude because of their small number.

As noted by us in the case of silver pyrophosphate glass (Ananthraj *et al* 1986), large configurational entropy results from the multiplicity of anionic species and gives rise to high values of heat capacity in the glassy region. The presence of Pb^{2+} ions in network and non-network positions may also contribute to the configurational heat capacity.

In our studies we have also noted that although lead metaphosphate glass is soluble in water, lead pyrophosphate glass is completely insoluble. Indeed, we use this property to precipitate lead pyrophosphate. We have therefore examined the electronegativities of the phosphate anions and lead cations vis-a-vis the electronegativity of water itself. Lead ions possess an electronegativity of 2.376, which is slightly higher than but close to the value for $\text{P}_2\text{O}_7^{4-}$ ions. While it is lower than that for PO_3^- ions (2.614), it is significantly higher than that for the PO_4^{3-} ions (1.661). Water has an electronegativity of 2.60. Thus the electronegativities of cations and anions are best matched in pyrophosphate (Brown 1980), which may be the reason why lead pyrophosphate glass, which largely consists of $\text{P}_2\text{O}_7^{4-}$ ions, is least soluble in water. Its absence makes the metaphosphate soluble in water particularly in view of the similarities of the electronegativities of water and meta phosphate ions.

In conclusion we wish to add that a vital chemical parameter like electronegativity, whose quantum chemical origin is well-established can be quite effectively used in