selenium gives glasses with phosphorus over a large range of concentration. These glasses are produced even when the P–Se mixtures are cooled down slowly after thermal treatment. The glassy range spreads over 3–52 at. % P.

The curve of the evolution of the $T_g$ glassy transition temperature of these glasses plotted against the phosphorus content of the sample (Fig. 3) shows that in the 0–52 at. % P range, there are two phosphorus selenides with congruent melting at the Se/P = 2.5 and Se/P = 1 ratios.

The result is confirmed by the P–Se phase diagram. It shows only 3 phosphorus selenides melting congruently: P$_4$S$_{10}$, P$_4$Se$_4$ and P$_4$Se$_3$ (Fig. 4). The compound P$_4$Se$_7$ although described in the literature has not been found, may be due to metastability. The P$_4$Se$_7$ pattern has been observed in the combination formed by reacting P$_4$S$_{10}$ with pyridine.

A. I. 3. Research of phosphorus tellurides

To our knowledge, only a single phosphorus telluride has been described, P$_2$Te$_3$. The preparation consists in heating white phosphorus with powdered tellurium at 320 °C during 1 hour in a sealed tube.

The same procedure has been followed. The product which was obtained corresponds to the author’s description. It presents the same appearance and the same density. However, only tellurium was found by radiocristallographic analysis. The above method gives a mixture of tellurium and red phosphorus, the latter being amorphous to X-ray. It is not necessary to use white phosphorus which is transformed into red phosphorus at 320 °C.

We therefore studied several mixtures of tellurium and red phosphorus systematically by DTA. Different compositions have been chosen, the atomic ratios being P/Te = 2; 1.33; 1; 0.8; 0.4. The DTA curve on heating discloses only two endothermic phenomena due to the elements melting.

The elements mixture were heated up to 800 °C in thick silica tubes (3 mm). Heating was continued during various times up to a week. Then, the samples are slowly cooled (1°/min). X-ray diagrams show not a single line which cannot be assigned to either tellurium or phosphorus.

A. II. Structure of the binary compounds

The different binary compounds of P with S, Se and Te are summarized in the following Table.

The structure of compounds noted with an asterix has been deduced from X-ray on a single crystal. The exact structure of the other compounds has not yet been determined.
The compound $P_4S_2$ is unstable at room temperature and therefore difficult to study.

The compounds $P_4S_4$ and $P_4Se_4$ are insoluble in all solvents. Some arguments are in favour of a cage like structure for these two compounds. In mass spectroscopy, the molecular peaks $P_4S_4$ and $P_4Se_4$ are observed. A fragmentation scheme of $P_4Se_4$ is presented in Fig. 5. The presence of the $P_4Se_3^+$ ion enables one to propose a cage like structure. There is a similar fragmentation for $P_4S_4$.

On the other hand, the IR absorption spectra of $P_4S_4$ and $P_4Se_4$ exhibit a specific band for the exocyclic $P-S$ bond at 690 cm$^{-1}$ and the exocyclic $P-Se$ at 500 cm$^{-1}$. It must be noticed that the IR spectrum of $P_4S_4$ is identical to $P_4S_5$ which confirms again it cage like structure. At last the good agreement between the experimental enthalpy of formation of $P_4S_4$ and the enthalpy of formation calculated from the different bond energies $P-S$ and $P-P$ is another argument in favour of the proposed structural$^{16}$.

$P_4Se_{10}$ is amorphous to X-rays. Many authors gave it the $P_4Se_{10}$ formula in preference to $P_2Se_5$. This former formula $P_4Se_{10}$ is confirmed by our mass and IR spectrometric studies and we propose a structure which is analogous to $P_4S_{10}$$^{12}$. In our mass spectral studies we did not observe the molecular peak corresponding to $P_4Se_{10}$. The largest mass observed corresponds to $P_2Ses$; but the presence of ions with tetrahedral structure as $PSe_3^+$, $P_2Se_2^+$ and $P_5Se^+$ and the likeness of dissociation fragments of $P_4Se_{10}$ and $P_4S_{10}$ show that $P_4Se_{10}$ has also a tetrahedral structure. The lack of molecular peak can be explained by a dissociation of $P_4Se_{10}$ in $P_2Ses$ radicals in the gas phase. The same phenomenon was observed with $P_4S_{10}$.$^{17}$

IR absorption spectra of $P_4Se_{10}$ and $P_4S_{10}$ are presented in Fig. 6. These two spectra have the same general appearance with respect to the absorption bands distribution.

Attempts to obtain $P_4S_4$, $P_4Se_4$ and $P_4Se_{10}$ as single crystals by a vapor transport method are now in progress. The radiocristallographic study on these would confirm the proposed structures without ambiguity.

**A.III. Preparative methods**

A. III. 1. Starting from red phosphorus and sulfur

All phosphorus sulfides can be prepared by this method. The reaction temperature necessary is above 300 °C. A slow cooling process is necessary to obtain the low temperature forms and compounds with incongruent melting.
The action of halogens on the $P_4X_3$ ($X = S$ or $Se$) heterocycles leads to different compounds depending on the halogen.

a) With iodine two compounds are obtained, $P_4S_3I_2$ and $P_4Se_3I_2$. These two iodides possess also a cage like structure. An analogous reaction, with $P_4Se_3$, has been carried out at $0 \degree C$ using the same conditions. After one week, one obtains a dark product which is amorphous to X-ray. Mass spectrometry shows ions resulting from the fragmentation of $P_4Se_{10}$ besides small amounts of $P_4Se_4^+$ and $P_4Se_3^+$ ions. These latter ions do not result from the fragmentation of the $P_4Se_10$ cage. They can only be explained by the existence of the compound $P_4Se_5$. The action of bromine on $P_4Se_4$ selenide is vigorous and is broken. Whatever the temperature, PBr$_3$ and SeBr$_4$ are obtained.

A. III. 4. Reaction of $PCl_3$ with $H_2X$ ($X = S$ or $Se$)

The reaction between $H_2S$ and $PCl_3$ leads to a mixture having a $P_5S_{5,8}$ composition. The action of $H_2Se$ on $PCl_3$ at room temperature has been studied. Phosphorus trichloride has been used pure or diluted in carbon tetrachloride. Hydrogen selenide reacts at once to give a solid. The end of the reaction is marked by evolution of hydrogen chloride.

The residue is amorphous to X-rays: it seems to be a mixture of different phosphorus selenides. From this mixture, it has been possible to extract $P_4Se_2$ by dissolving in carbon disulfide or by sublimation at $10^{-1}$ torr and 215–300 $\degree C$. After purification, IR and mass spectra of the residue show the existence of $P_5Se_{10}$ and $P_4Se_5$.

B. Ternary Compounds

We tried to find ternary compounds based on phosphorus and containing 2 of the 3 elements $S$, $Se$ and $O$ in order to obtain heterocycles. The $P_4O_6S_4$ ternary compound is known and can be obtained according to the scheme:

$$ P_4Se_3 + Se \xrightarrow{300 \degree C} P_4Se_4 $$
$$ P_4Se_3 + 7 Se \xrightarrow{215 \degree C} P_4Se_{10} $$

* Reaction with halogens
The existence of ternary compounds of P, S and Se has been studied systematically by DTA and radiocristallography. We tried to substitute sulfur by selenium atoms in the molecules of phosphorus sulfide and vice versa. The similar properties of the sulfur and selenium compounds let foresee a possible substitution without basic change in the structural properties of the compounds. To this end, we plotted the ternary diagram P–S–Se \(^{35,36}\).

The isometric projection in Fig. 7 gives a general view of the spatial diagram. No mixed phosphorus chalcogenides can be discerned in this diagram.

\[ \begin{align*} 
\text{P}_4\text{O}_6 + 4 \text{S} & \xrightarrow{160 \, ^\circ\text{C}} \text{P}_4\text{O}_6\text{S}_4 \quad \text{(33)} \\
2 \text{P}_8\text{S}_{10} + 3 \text{P}_4\text{O}_{10} & \xrightarrow{450 \, ^\circ\text{C}} 5 \text{P}_4\text{O}_6\text{S}_4 \quad \text{(34)} 
\end{align*} \]

No reaction has been noticed between \( \text{P}_4\text{O}_{10} \) and \( \text{P}_4\text{Se}_{10} \). On the other hand, \( \text{P}_4\text{Se}_{10} \) reacts with \( \text{P}_8\text{S}_{10} \). The reaction is a complex one: \( \text{P}_8\text{S}_7 \) is mainly produced and is easily recognized from its X-ray diagram.

The isometric projection in Fig. 7 gives a general view of the spatial diagram. No mixed phosphorus chalcogenides can be discerned in this diagram.

\[ \begin{align*} 
\text{P}_4\text{O}_6 + 4 \text{S} & \xrightarrow{160 \, ^\circ\text{C}} \text{P}_4\text{O}_6\text{S}_4 \quad \text{(33)} \\
2 \text{P}_8\text{S}_{10} + 3 \text{P}_4\text{O}_{10} & \xrightarrow{450 \, ^\circ\text{C}} 5 \text{P}_4\text{O}_6\text{S}_4 \quad \text{(34)} 
\end{align*} \]