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The Hg-P (Mercury-Phosphorus) System

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The Hg-P system was not studied systematically, and its whole phase diagram is unknown. Hg and αP (white) melt at –38.8290 and 44.14 °C, respectively, and boil at 356.623 and 277 °C, respectively, when the pressure is 0.101325 MPa. P exists in many allotropic modifications [1989Gre]. At least five crystalline and several amorphous or vitreous forms of P are known, but when they melt, they all give the same liquid, consisting of P_4 molecules of tetrahedral structure. This form is also present in the gas phase at temperatures lower than 800 °C. The allotropic forms of P have different colors and other physical properties as well as different chemical reactivities. The most stable allotropes are cubic αP (white) and orthorhombic phosphorus (black).

It is of interest that αP heated at 380 °C in the presence of Hg gives vitreous gray P [1989Gre]. [1911Vou] claimed the formation of a Hg-P compound by heating both components under a layer of paraffin, but no analysis was made to determine the resultant product. Hg_3P_4, Hg_3P_2, and Hg_3P compounds were obtained by indirect chemical reactions [1947Mel], but formation by direct alloying was not observed by [1951Rot]. Therefore, these compounds should be treated as metastable phases.

The melting temperatures of αP and Hg would suggest considerable miscibility of the elements near ambient temperature. According to [1910Ger], molten P dissolves some amount of Hg, and the resulting colorless solution is blackened after solidification due to the rejection of Hg excess. [1951Rot] measured Hg solubility in metastable liquid P at 25 °C by using a chemical analysis of the equilibrated phases. The solubility value found amounts to 0.0176 at.% Hg, which amounts to one-fifteenth of the value predicted from the regular solution model. These authors observed that the solubility of Hg in liquid P increased slightly with temperatures up to 100 °C, but no numerical results were reported therein. Because P is soluble in such metals as Pb and Bi [1947Mel], one may predict that detectable amounts of P should also dissolve in Hg. These facts suggest that the Hg-P diagram should be of a monotectic type, with a critical temperature higher than the boiling point of Hg (at normal pressure).

Crystal structures of the elements and their lattice parameter data are listed in Table 1.

By analogy with an ammonium amalgam [1997Gum], a "phosphonium amalgam" was formed [1889Bes] during the electroreduction of PH_4^+ on a Hg electrode at –25 to –40 °C, The PH_4· radical possesses metallike properties that qualitatively approximate those of the alkali metals. The phosphonium amalgam, like the ammonium amalgam, should be stable in the solid state at temperatures lower than the Hg melting point.

References

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Table 1 Hg-P crystal structures and lattice parameter data according to [Massalski2]

Phase	Composition, at.% P	Pearson symbol	Space group	Strukturbericht designation	Prototype	Lattice parameters, nm			Temperature, °C
						a	*b*	*c*	
Hg	0	*hR*1	$R\bar{3}m$	*A*10	αHg	0.3005	…	α = 70.53°	–48
αP	100	*c***	…	…	αP	0.718	…	…	25
P (black)	100	*oC*8	*Cmca*	*A*17	P (black)	0.33136	1.0478	0.43763	25

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