

Cs-P (Cesium-Phosphorus) System

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Equilibrium Diagram

There are no liquidus or solubility data available for this system [2001Bor]. A large number of Cs-Rb compounds has been prepared and identified. Phosphorus forms many polyatomic groups (rings and cages), and Baudler [1982Bau, 1987Bau] has pointed out the analogies between phosphorus and carbon chemistry.

The preparation and structure of phosphorus compounds with alkali metals were reviewed [1958Waz, 1973Sch, 1977Sch, 1981Sch, 1983Sch1, 1983Sch2]; a later review [1988Sch] is both more detailed and more extensive.

In early study, the reported stoichiometry of some compounds was confused. This was because elemental compositions were not easily distinguished by analytical techniques of the time.

It is appropriate here to distinguish between compounds isolated and characterized as solids and those prepared only in solution or those studied only by theoretical calculations. Unless otherwise noted, red phosphorus was used in preparing Cs-P compounds. Most Cs-P compounds decompose before melting.

Compounds Isolated as Solids

Cs₄P₆ (60.0 at.% P) is prepared by reaction of the elements [1987Sch, 2005Kra]. It was characterized by XRD [1987Sch]. Infrared spectra and ³¹P-NMR spectra (in dimethoxyethane and ethylenediamine solution) were reported [1987Sch].

Cs₃P₇ (70.0 at.% P) in early study was known as Cs₂P₅ (71.4 at.% P). The misidentification was pointed out later [1983Sch1]. Cs₃P₇ (reported as “Cs₂P₅”) was prepared [1912Hac] from the elements. This direct method was used in later study [1985Ten, 1986San, 1987Mey]. The ammoniate Cs₃P₇·3NH₃ was prepared by reaction of the elements in liquid ammonia [1996Kor]; the pure compound may be recovered by removal of ammonia [1996Kor]. It undergoes a first-order crystalline to plastic-crystalline transition αCs₃P₇ → βCs₃P₇ at 295 °C (heating mode) or 191 °C (cooling mode) [1985Ten; 1987Mey] reported 279 °C for the transition temperature. The melting point was given as 944 °C [1985Ten] or 930 °C [1987Mey].

Both forms have been characterized by XRD [1983Hon, 1987Mey]. The ³¹P-NMR spectrum of solvated αCs₃P₇ was measured in ethylenediamine solution [1987Mey].

Cs₃P_{8.33} (73.5 at.% P) is perhaps better understood as a mixed crystal Cs₃(P₇)_{0.67}(P₁₁)_{0.33}. It was prepared by changing conditions of Cs:P ratio during cooling in a reaction of the elements [1987Mey]. It was characterized by XRD [1985Hon, 1987Mey].

Cs₃P₁₁ (78.6 at.% P) is prepared by reaction of the elements [1991Sch] in stoichiometric amounts. The room temperature crystalline form (αCs₃P₁₁) transforms to a plastic-crystalline form (βCs₃P₁₁) in a first-order process at 409 °C [1991Sch]. Both forms were characterized by XRD [1991Sch]. Raman spectra of αCs₃P₁₁ in ethylenediamine solution were reported, as well as the infrared spectrum of the solid [1991Sch].

CsP₇ (87.5 at.% P) was prepared from the elements [1986Kos] and was characterized by XRD [1986Kos, 1988Sch].

CsP₁₁ (91.7 at.% P) is prepared by reaction of the elements (P:Cs = 9:1 or 15:1) [1988Sch] in the same manner as RbP₁₁ [1982Kos]. It was characterized by XRD [1988Sch].

CsP₁₅ (93.8 at.% P). The crystalline compound is prepared from the elements in a solid state reaction, as for KP₁₅ [1967Sch, 1987San]. It was characterized by XRD [1977Sch].

Other Compounds

Cs₃P (25.0 at.% P). There is no report of the preparation of this compound. Its fractional ionic character was calculated by two methods [1990Sha], results of which were 0.96 and 0.76. The presence of solvated Cs₃P was inferred [1987Hon, 1987Sch] from the disproportionation of Cs₄P₆ in ethylenediamine solution (³¹P-NMR measurements).

Cs₂P₄ (66.7 at.% P) was isolated as a solid solvated product Cs₂P₄·2NH₃ which was characterized by XRD [2003Kra, 2005Kra]. These authors prepared the solid by three related routes using P₂H₄, Cs, Cs₄P₆ and NH₃.

Cs₄P₁₄ (77.8 at.% P) in solvated form was detected by ³¹P-NMR as a product of the reaction of Cs₄P₆ with white phosphorus in ethylenediamine [1987Hon]. The solvated molecule has not been isolated from solution.

Crystal Structures and Lattice Parameters

Crystal structures and lattice parameters of Cs phosphides are summarized in Table 1 and 2 respectively. The structural chemistry of these compounds is complex because P can form polyanions of many different configurations [1977Sch, 1983Sch1, 1988Sch].

Compounds Isolated as Solids

Cs₄P₆ is isostructural with Rb₄P₆. There are isolated planar parallel P₆⁴⁻ rings. Each P atom is surrounded trigonally by six Cs⁺ ions [1974Sch, 1977Sch, 1987Sch].

Section II: Phase Diagram Evaluations

Table 1 Cs-P crystal structure data

Phase	Composition, at.% P	Pearson symbol	Space group	Strukturbericht designation	Prototype	Temperature, °C	Reference
Cs	0	<i>cI2</i>	<i>Im</i> $\bar{3}m$	<i>A2</i>	W	25	[King1]
Cs ₄ P ₆	60.0	<i>oF40</i>	<i>Fmmm</i>		Rb ₄ P ₆	25	[1987Sch]
α Cs ₃ P ₇	70.0	<i>tP40</i>	<i>P41</i>		α Cs ₃ P ₇	25	[1988Sch]
β Cs ₃ P ₇	70.0	<i>cF40</i>	<i>Fm</i> $\bar{3}m$		β Rb ₃ P ₇	> 279	[1988Sch]
β Cs ₃ P _{8.3}	73.5	<i>cF40/56</i>	<i>Fm</i> $\bar{3}m$		β Rb ₃ P ₇	(a,b)	[1988Sch]
α Cs ₃ P ₁₁	78.6	<i>oP*</i>				25	[1988Sch]
β Cs ₃ P ₁₁	78.6	<i>cF56</i>	<i>Fm</i> $\bar{3}m$		β Cs ₃ P ₁₁	> 409	[1983Sch1]
CsP ₇	87.5	<i>oP32</i>	<i>Pca21</i>		CsP ₇	25	[1986Kos]
CsP ₁₁	91.7	<i>mP48</i>			RbP ₁₁	25	[1988Sch]
CsP ₁₅	93.8	<i>aP32</i>			KP ₁₅	25	[1988Sch]
P (black)	100	<i>oC8(c)</i>	<i>Cmca</i>			25	[Pearson2]
P (white)	100	<i>c**</i>				25	[Pearson2]
P (red)	100	<i>c*66</i>				25	[Pearson2]

(a) Transition temperature unknown

(b) Mixed crystal

(c) P exists in rhombohedral and cubic forms at high pressures and room temperature

Table 2 Cs-P lattice parameter data

Phase	Composition, at.% P	Lattice parameters, nm			Temperature, °C	Reference
		<i>a</i>	<i>b</i>	<i>c</i>		
Cs	0	0.6141			25	[King1]
Cs ₄ P ₆	60.0	0.9972	1.4999	0.9438	25	[1987Sch]
α Cs ₃ P ₇	70.0	0.9046		1.6714	25	[1987Mey]
β Cs ₃ P ₇	70.0	1.1167			20(a)	[1983Hon]
		1.1193			25(a)	[1987Mey]
		1.1305			300	[1987Mey]
β Cs ₃ P _{8.33}	73.5	1.1495			25(a)	[1985Hon]
β Cs ₃ P ₁₁	78.6	1.195			20(a)	[1983Sch1]
		1.2063			25(a)	[1985Hon]
CsP ₇	87.5	0.9451	0.9150	0.9666	25	[1986Kos]
P (black)	100	0.33136	1.0478	0.43763	25	[Pearson2]
P (white)	100	0.718			25	[Pearson2]
P (red)	100	1.131			25	[Pearson2]

(a) Metastably quenched from high temperature

Alternatively, the structure may be envisioned as a defect-structure derivative of the Al₄B₈ (AlB₂) type: Cs₄P₆□₂. In this case, two P sites remain vacant in an ordered way and leave isolated planar P₆ rings [1988Sch]. This scheme is explained more fully in [1983Nes].

Cs₃P₇: The structure of the room temperature solid (α -form) is tetragonal [1988Sch]; while the high-temperature solid (β -form) is fcc [1983Hon, 1987Mey]. In both forms, there are P₇³⁻ cage groups (formally analogous to nortricycylene in carbon chemistry) [1983Hon, 1987Mey]. The β -form is of the Li₃Bi type, where the P₇³⁻ anions occupy the Bi³⁻ sites.

Cs₃P_{8.33} or Cs₃(P₇)_{0.67}(P₁₁)_{0.33}, is an fcc-mixed crystal [1987Mey, 1988Sch]. [1981Sch, 1983Sch1] show that it derived from Li₃Bi parent structure with statistical distribution and orientation of the cluster anions.

The crystal structure of Cs₃P₁₁ at room temperature (α -form) was not known at first [1988Sch], but later [1991Sch] was identified as the orthorhombic structure of α Na₃P₁₁. The high-temperature (plastic-crystalline) form β Cs₃P₁₁ is cubic [1985Hon, 1991Sch]. Both the forms contain P₁₁³⁻ cages, highly internally connected [1973Wic, 1991Sch]. The corresponding carbon cage compound was given the trivial name “ufosan” [1973Wic, 1988Sch].

Table 3 Experimental thermodynamic properties of Cs phosphides

	$\Delta_f H^0_{298}$, kJ mol ⁻¹	$\Delta_f G^0_{298}$, kJ mol ⁻¹	S^0_{298} , J mol ⁻¹ K ⁻¹	$\Delta_{\text{trs}} H$, kJ mol ⁻¹	$\Delta_{\text{fus}} H$, kJ mol ⁻¹
$\alpha\text{Cs}_3\text{P}_7$	-85(a)	-301(a)	724(a)	19.6(b)	...
$\beta\text{Cs}_3\text{P}_7$	-118(a)	-324(a)	689(a)	...	13.8(b)
CsP_{15}	-108(c)	-238(c)	433(e)
	-109(d)	-238(d)

(a) [1986San]
 (b) [1985Ten] (heating mode)
 (c) [1987San] (2nd law)
 (d) [1987San] (3rd law)
 (e) [1988Sch]

CsP_7 is orthorhombic [1986Kos, 1988Sch]. According to [1977Sch, 1981Sch], the structure contains one-dimensional infinite chains of P_7^- cages. [1986Kos], however, postulated a structure built from P_7^{3-} units. [1977Sch] shows how the two are related.

In CsP_{11} , there are P_7^- and P_{15}^- groups forming infinite tubes in 1:1 ratio [1977Sch]. The Cs^+ ions are situated between the infinite tubes.

CsP_{15} , isostructural with KP_{15} , contains infinite P_{15}^- tubes of pentagonal cross section, resulting from a polymerization of alternating P_7^- and P_8^0 units [1967Sch, 1977Sch]. The Cs^+ ions are situated between the tubes, and each Cs^+ ion has six nearest neighbours.

Other Compounds

Cs_2P_4 is known only as the crystalline ammoniate. The P_4^{2-} anion in this compound is an approximately square, approximately planar group [1988Sch, 2003Kra, 2005Kra]. MINDO/3 calculations suggest that the P_4^{2-} anion by itself has D_{4h} symmetry, i.e., tetrahedral [1981Cut].

Solvated Cs_4P_{14} was found in ethylenediamine solution [1987Hon]. The P_{14}^{4-} anion may [1988Sch] be the same as that found in solvated Na_4P_{14} [1983Sch1]. In this case, the anion consists of two singly joined P_7^{2-} cages.

Thermodynamics

Experimental data are summarized in Table 3. The heat capacity of Cs_3P_7 was measured by differential scanning calorimetry [1985Ten] in the range 120-770 K. From these data were deduced the solid transition temperature and enthalpy of transition. The transition and melting temperatures were measured by differential thermal analysis (DTA) [1987Mey]. The melting temperature and enthalpy of fusion were determined by DTA [1985Ten]. The vapor pressure of this compound was measured by Knudsen effusion/mass spectrometry [1986San] in the range 730-1066 K. From these data were deduced (second law) the thermodynamic properties $\Delta_f H^0_{298}$, $\Delta_f G^0_{298}$ and S^0_{298} of both α - and β -forms.

The vapor pressure of CsP_{15} was measured by Knudsen effusion/mass spectrometry [1987San] in the range 488-577 K. From these data were deduced the formation properties $\Delta_f H^0_{298}$ and $\Delta_f G^0_{298}$.

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