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P-Rb (Phosphorus-Rubidium) System

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Equilibrium Diagram

There are no liquidus or solubility data available for this system [2001Bor]. A large number of P-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 work, 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 P-Rb compounds. Most P-Rb compounds decompose before melting.

Compounds Isolated as Solids

Rb_4P_6 (60.0 at.% P) is prepared by reaction of the elements [1974Sch, 1987Sch, 2005Kra]. It was characterized by XRD [1974Sch, 1987Sch]. Infrared spectra and ^{31}P-NMR spectra (in glyme and ethylenediamine solution) were reported [1987Sch].

Rb_3P_7 (70.0 at.% P) in early work was known as Rb_2P_5 (71.4 at.% P). The misidentification was pointed out later [1983Sch1]. Rb_3P_7 (reported as "Rb_2P_5") was prepared [1912Hac] from the elements. Rb_3P_7 was prepared as the ammoniate and as an ether-solvated ammoniate in liquid ammonia [2005Kra]. It undergoes a first-order crystalline to plastic-crystalline transition $\alpha Rb_3P_7 \rightarrow \beta Rb_3P_7$ at 207 °C [1985Ten]. The melting point was given as 981 °C [1985Ten]. Both forms have been characterized by XRD [1983Hon, 1985Hon, 1988Sch].

Rb_3P_{11} (78.6 at.% P) is prepared by reaction of the elements [1991Sch] in stoichiometric amounts. The room temperature crystalline form (αRb_3P_{11}) transforms to a plastic-crystalline form (βRb_3P_{11}) in a first-order process at 342 °C [1991Sch]. Both forms were characterized by XRD [1983Sch1, 1991Sch]. Raman spectra of αRb_3P_{11} in ethylenediamine solution were reported, as well as its infrared spectrum [1991Sch].

RbP_7 (87.5 at.% P) was prepared from the elements [1977Sch] and was characterized by XRD [1988Sch].

$RbP_{10.3}$ (91.1 at.% P), prepared by direct reaction of the elements, was described by [1988Sch] in preliminary work. The structure, from XRD data, could not be completely elucidated.

RbP_{11} (91.7 at.% P) was prepared by reaction of the elements (P:Rb = 9:1 or 15:1) [1982Kos]. It was characterized by XRD [1982Kos]. The overall composition of this compound is very close to that of $RbP_{10.3}$, but [1988Sch] considers them as two distinct compounds.

RbP_{15} (93.8 at.% P) is a crystalline compound that can be prepared from the elements in a solid state reaction [1977Sch, 1985Ole]. It was characterized by XRD [1985Ole]. Its Raman and photoluminescence spectra were also reported [1985Ole].

Other Compounds

Rb_3P (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 0.74. The presence of solvated Rb_3P was inferred [1987Hon, 1987Sch] from the disproportionation of Rb_4P_6 in ethylenediamine solution (^{31}P-NMR measurements).

Crystal Structures and Lattice Parameters

Crystal structures and lattice parameters of rubidium 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].

In Rb_4P_6, there are isolated planar parallel P_6^{4-} rings. Each P atom is surrounded trigonal-prismatically by six Rb^+ ions [1974Sch, 1977Sch, 1987Sch]. Alternatively, the structure may be envisioned as a defect-structure derivative of the Al_4B_8 (AlB_2) type: $Rb_4P_6\square_2$. In this case, two P sites remain vacant in an ordered way and leave isolated planar P_6 rings [1988Sch]. This scheme is explained more fully in [1983Nes].

Rb_3P_7. The structure of the room temperature solid (α-form) is tetragonal [1988Sch], while the high-temperature solid (β-form) is fcc [1983Hon, 1985Hon]. In both forms, there are P_7^{3-} cage groups (formally analogous to nortricyclene in carbon chemistry) [1983Hon, 1985Hon]. In the low-temperature form, the P_7^{3-} cages are uniformly oriented, whereas in the high-temperature form this is not so. The β-form is of the Li_3Bi type, where the P_7^{3-} anions occupy the Bi^{3-} sites.

Table 1 P-Rb crystal structure data

Phase	Composition, at.% Rb	Pearson symbol	Space group	Strukturbericht designation	Prototype	Temperature, °C	Reference
P (black)	0	*oC*8 (a)	*Cmca*				[Pearson2]
P (white)	0	*c***					[Pearson2]
P (red)	0	*c*66*					[Pearson2]
RbP_{15}	6.3	*aP*32			KP_{15}	25	[1985Ole]
RbP_{11}	8.3	*mP*48	(b)		RbP_{11}	25	[1988Sch]
$RbP_{10.3}$	8.9	*tP*1488			$KP_{10.3}$	25	[1988Sch]
RbP_7	12.5	*oP*32			CsP_7	25	[1988Sch]
αRb_3P_{11}	21.4	*oP*80	*Pnab*		αNa_3P_{11}	25	[1988Sch]
βRb_3P_{11}	21.4	*cF*56	$Fm\bar{3}m$		βCs_3P_{11}	>342	[1983Sch1]
αRb_3P_7	30.0	*tP*40			αCs_3P_7	25	[1988Sch]
βRb_3P_7	30.0	*cF*40	$Fm\bar{3}m$		βRb_3P_7	>207	[1983Sch1]
Rb_4P_6	40.0	*oF*40	*Fmmm*		Rb_4P_6	25	[1974Sch]
Rb	100	*cI*2	$Im\bar{3}m$	*A*2	W	25	[King1]

(a) P exists in rhombohedral and cubic forms at high pressures and room temperature
(b) [1982Kos] reported the space group as *P*2/*m*, *P*2 or *Pm*

Table 2 P-Rb lattice parameter data

		Lattice parameters, nm							
Phase	Composition, at.% Rb	*a*	*b*	*c*	α	β	γ	Temperature, °C	Reference
P (black)	0	0.33136	1.0478	0.43763				25	[Pearson2]
P (white)	0	0.718						25	[Pearson2]
P (red)	0	1.131						25	[Pearson2]
RbP_{15}	6.3	1.220	0.906	0.721	116.6°	101.4°	82.4°	20	[1985Ole]
RbP_{11}	8.3	1.8013	0.9670	0.6511		95.56°		25	[1982Kos]
αRb_3P_{11}	21.4	1.0512	1.4555	1.0754				25	[1991Sch]
βRb_3P_{11}	21.4	1.1592						20(a)	[1983Sch1]
		1.1497						−180(a)	[1991Sch]
βRb_3P_7	30.0	1.0818						20(a)	[1983Hon]
Rb_4P_6	40.0	0.9641	1.4629	0.9010				25	[1974Sch]
Rb	100	0.5703						25	[King1]

(a) Metastably quenched from high temperature

Rb_3P_{11} at room temperature is orthorhombic (α-form), whereas the high-temperature form is cubic [1991Sch]. Both forms contain P_{11}^{3-} cages, highly internally connected [1973Wic, 1991Sch]. The corresponding carbon cage compound was given the trivial name "ufosan" [1973Wic, 1988Sch].

RbP_7 is orthorhombic, isostructural with CsP_7 (Z = 4) [1988Sch]. According to [1977Sch, 1988Sch], the structure contains P_7^- cages in a linear chain.

$RbP_{10.3}$ was described [1988Sch] as having a complicated twofold tubular superstructure, possibly including P_{35}^- units of pentagonal cross-section [1977Sch].

In RbP_{11} there are P_7^- and P_{15}^- groups forming infinite tubes in 1:1 ratio [1983Sch2]. The Rb^+ ions are situated between the infinite tubes [1977Sch].

RbP_{15} contains infinite P_{15}^- tubes of pentagonal cross-section, resulting from a polymerization of alternating P_7^- and P_8^0 units [1967Sch, 1981Sch]. The Rb^+ ions are situated between the tubes, and each Rb^+ ion has six nearest neighbors.

Thermodynamics

Experimental data are summarized in Table 3. Although the compound Rb_3P has not been reported, thermodynamic data were estimated [1980Suu]: $\Delta_f H^0_{298}$ = 189 kJ mol^{-1} and S^0_{298} = 43.9 J mol^{-1} K^{-1}. The heat capacity of Rb_3P_7 was measured by differential scanning calorimetry (DSC) [1985Ten] in the range 120-770 K. From these data the solid transition temperature and enthalpy of transition were deduced. The melting temperature and enthalpy of fusion were determined by differential thermal analysis. The vapor

Table 3 Experimental thermodynamic properties of Rb phosphides

Compound	$\Delta_f H^0_{298}$, kJ mol^{-1}	$\Delta_f G^0_{298}$, kJ mol^{-1}	S^0_{298}, J mol^{-1} K^{-1}	$\Delta_{trs}H$, kJ mol^{-1}	$\Delta_{fus}H$, kJ mol^{-1}
αRb_3P_7	−124(a)		681(a)	5.8(b)	…
βRb_3P_7	−114(a)		612(a)	…	7(b)
RbP_{15}	−113(c)	−238(c)	418(e)	…	…
	−110(d)	−237(d)	…	…	…

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

pressure of this compound was measured by Knudsen effusion/mass spectrometry [1986San] in the range 853-970 K. From these data (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 were deduced.

The vapor pressure of RbP_{15} was measured by Knudsen effusion/mass spectrometry [1987San] in the range 472-555 K. From these data the formation properties $\Delta_f H^0_{298}$ and $\Delta_f G^0_{298}$ were deduced.

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