

Na-P (Sodium-Phosphorus) System

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Equilibrium Diagram

There are no liquidus or solubility data available for this system [2001Bor]. A large number of Na-P compounds has been prepared and identified. Phosphorus forms many polyatomic groups (rings and cages), and Baudler [1982Bau, 1987Bau3] has pointed out the analogies between phosphorus and carbon chemistry.

The preparation and structure of phosphorus compounds with alkali metals has been reviewed [1958Waz, 1977Sch, 1981Sch2, 1983Sch1]; 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 Na-P compounds. Most Na-P compounds decompose before melting.

Compounds Isolated as Solids

Na_3P (25 at.% P) was prepared by reaction of the elements in hydrocarbon solvent [1862Cah, 1881Let] or in liquid ammonia [1894Joa, 1895Hug] or by the reaction of Na with white P in toluene [1966Pet]. It may also be prepared by reaction of the elements in stoichiometric amounts without solvent [1937Bra]. Most recently the reaction of NaN_3 and P with TiN and KI (flux) was used [2005Don]. It was characterized by powder [1937Bra] and single crystal XRD [2005Don]. The melting point of Na_3P was given as 520–550 °C [1959Mor].

NaP (50 at.% P) resulted from the decomposition of “ Na_2P ”, NaPH_2 or $\text{Na}_2\text{P}_2\text{H}_2$ [1955Roy]. A better method is the reaction of the elements in stoichiometric amounts [1979Sch]. It was characterized by single-crystal XRD [1978Hon, 1979Sch].

Na_3P_7 (70 at.% P) in early work [1940Leg, 1955Roy] was prepared from decomposition of products of the reaction of the elements [1955Roy] or of $\text{PH}_3 + \text{K}$ [1940Leg] in liquid ammonia. It is best prepared from stoichiometric amounts of the elements [1985Ten, 1986San, 1995Hon]. It undergoes a first-order crystalline to plastic-crystalline transition at 486 °C (heating mode) [1985Ten], or 522 °C [1986San] or 492 °C [1983Hon]. The melting point was given as 942 °C [1985Ten]. Both forms have been characterized by XRD [1983Hon].

Na_3P_{11} (78.6 at.% P) was reported in early work [1955Roy] as a compound designated “ Na_4P_{15} ” (78.9 at.% P) and was claimed to be among the products of the

reaction between the elements in liquid ammonia. More recently Na_3P_{11} was prepared by direct reaction of the elements without solvent [1973Wic, 1995Hon], from the decomposition of NaP_7 [1973Wic] or by the reaction [1995Hon] $\text{Na}_3\text{P}_7 + \text{P}_4$ (white phosphorus). It was characterized by XRD [1973Wic, 1983Sch1, 1983Sch2]. Vibrational spectra of Na_3P_{11} in ethylenediamine solution were reported [1991Sch]. At 580 °C the crystalline compound transforms to a plastic-crystalline form [1983Sch1] in a first-order process. Both forms have been characterized by XRD [1973Wic, 1983Sch1].

NaP_5 (83.3 at.% P) was prepared by reaction of the elements at 800–950 °C and 3 GPa [2004Che]. It was characterized by single-crystal XRD [2004Che]. The preparation could also be carried out by the reaction of Na with white P in mixed ether solvent [1987Bau1, 1988Bau] or by the reaction $\text{NaPH}_2 + \text{white P}$ [1989Bau]. ^{31}P -NMR, infrared, Raman and ultraviolet spectra of the solvated compound were reported [1988Bau].

NaP_7 (87.5 at.% P) is a product of the reaction of the elements [1972Sch] and was characterized by XRD [1972Sch]. The compound identified by [1955Kre] as “ NaP_x ” was most probably NaP_7 . This compound should not be confused with Na_3P_{21} , which contains isolated P_{21}^{3-} groups (see “Other Compounds” below).

NaP_{15} (93.8 at.% P) is prepared from the elements in a method similar to that for KP_{15} [1967Sch, 1977Sch, 1985Ole, 1987San]. It was characterized by XRD [1985Ole] and x-ray photoemission spectra [1983Goo].

Other Compounds

Na_2P (33.3 at.% P) was claimed as a product of the reaction of Na with white P in liquid ammonia [1951Eve]. These authors allowed that Na_2P is “probably dimeric”. Another investigation of the reaction in liquid ammonia [1953Roy] led to the conclusion that “ Na_4P_2 ” is a mixture of $\text{Na}_2\text{H}_2\text{P}_2$ and NaNH_2 . Theoretical calculations [2004Jin] were made to investigate geometries, electronic structure and vibrational frequencies of the Na_4P_2 molecule, assuming the presence of a P_4 ring.

Na_2P_5 (71.4 at.% P) was reported in early work [1955Roy] as a product of the reaction of the elements in liquid ammonia or without solvent [1912Hac] or from the decomposition of NaPH_2 [1940Leg]. It was later shown [1983Sch1] to have been mistaken for Na_3P_7 (70 at.% P).

Na_4P_{14} (77.8 at.% P) was prepared as a solvated molecule in the reaction of Na_3P_7 and white P in ethylenediamine solution [1983Sch1]. The solvated solid species was characterized by XRD [1988Sch].

NaP_4 (80 at.% P). This molecule has been studied only theoretically. Density functional theory and other methods were used to calculate structural and spectroscopic properties [2002Kuz, 2008Li].

Na₃P₁₉ (86.4 at.% P) was prepared in **dimethoxyethane** or tetrahydrofuran solution by the reaction of Na with white P [1986Bau]. The solvated species was identified through its ³¹P-NMR spectrum [1986Bau].

Na₄P₂₆ (86.7 at.% P) was prepared in tetrahydrofuran solution by the reaction of Na with white P [1984Bau1]. The solvated species was identified through its ³¹P-NMR spectrum [1984Bau1].

Na₃P₂₁ (87.5 at.% P) was prepared in dimethoxyethane or tetrahydrofuran solution by the reaction of Na with white P [1980Bau, 1984Bau2]. The solvated species was identified through its ³¹P-NMR spectrum [1980Bau, 1984Bau2].

Na₂P₁₆ (88.9 at.% P) was prepared in a mixed ether solution (tetrahydrofuran + dimethoxyethane + 18-crown-6) by the reaction of Na with white P [1987Bau2]. The

solvated species was identified through its ³¹P-NMR spectrum [1987Bau2].

Crystal Structures and Lattice Parameters

Crystal structures and lattice parameters of sodium phosphides are summarized in Tables 1 and 2 respectively. These tables include only those compounds isolated and characterized in the pure solid state. The text below includes a description also of compounds prepared only in solution (see “Other Compounds”). These are necessarily descriptions of the phosphorus anions, and are given here to document the ability of P to form cage structures.

Table 1 Na-P crystal structure data

| Phase | Composition, at.% P | Pearson symbol | Space group | Strukturbericht designation | Prototype | Temperature, °C | Reference |
|-----------------------------------|---------------------|------------------|--|-----------------------------|----------------------------------|-----------------|------------|
| βNa | 0 | <i>cI2</i> | <i>Im</i> $\bar{3}m$ | <i>A2</i> | W | 25 | [King1] |
| αNa | 0 | <i>hP2</i> | <i>P6</i> ₃ / <i>mmc</i> | <i>A3</i> | Mg | < -237 | [King2] |
| Na ₃ P | 25.0 | <i>hP8</i> | <i>P6</i> ₃ / <i>mmc</i> | <i>DO</i> ₁₈ | AsNa | 20 | [2005Don] |
| NaP | 50.0 | <i>oP16</i> | <i>P2</i> ₁₂ <i>1</i> ₂ <i>1</i> | ... | NaP | 20 | [1978Hon] |
| αNa ₃ P ₇ | 70.0 | <i>oP80</i> | <i>Pca</i> ₂ <i>1</i> | ... | αNa ₃ P ₇ | 20 | [1983Hon] |
| βNa ₃ P ₇ | 70.0 | <i>cF40</i> | <i>Fm</i> $\bar{3}m$ | ... | βRb ₃ P ₇ | > 492 | [1983Hon] |
| NaP ₅ | 71.4 | <i>oP24</i> | <i>Pnma</i> | ... | ... | 25 | [2004Che] |
| αNa ₃ P ₁₁ | 78.6 | <i>oP56</i> | <i>Pnab</i> | ... | αNa ₃ P ₁₁ | 20 | [1973Wic] |
| β Na ₃ P ₁₁ | 78.6 | <i>t</i> *112(a) | ... | ... | βNa ₃ P ₁₁ | > 580 | [1973Wic] |
| NaP ₇ | 87.5 | <i>tI128</i> | <i>I4</i> ₁ / <i>acd</i> | ... | LiP ₇ | 20 | [1972Sch] |
| NaP ₁₅ | 93.8 | <i>aP32</i> (b) | <i>P</i> $\bar{1}$ | ... | KP ₁₅ | 20 | [1988Sch] |
| P (black) | 100 | <i>oC8</i> (c) | <i>Cmca</i> | ... | ... | ... | [Pearson2] |
| P (white) | 100 | <i>c</i> ** | ... | ... | ... | ... | [Pearson2] |
| P (red) | 100 | <i>c</i> *66 | ... | ... | ... | ... | [Pearson2] |

(a) Information in [1983Sch1] suggests this symbol is *tP**

(b) Also indexed as monoclinic [1985Ole]. See text

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

Table 2 Na-P lattice parameter data

| Phase | Composition, at.% P | Lattice parameters, nm | | | Temperature, °C | Reference |
|----------------------------------|---------------------|------------------------|----------|----------|-----------------|------------|
| | | <i>a</i> | <i>b</i> | <i>c</i> | | |
| βNa | 0 | 0.42096 | ... | ... | 25 | [King2] |
| αNa | 0 | 0.3737 | ... | 0.6154 | < -237 | [King2] |
| Na ₃ P | 25.0 | 0.4990 | ... | 0.8815 | 20 | [1937Bra] |
| | | 0.49512 | ... | 0.87874 | -108 | [2005Don] |
| NaP | 50.0 | 0.6038 | 0.5643 | 1.0142 | 20 | [1978Hon] |
| αNa ₃ P ₇ | 70.0 | 1.3740 | 1.0391 | 1.3446 | 20 | [1983Hon] |
| βNa ₃ P ₇ | 70.0 | 1.0105 | ... | ... | 600 | [1983Hon] |
| NaP ₅ | 71.4 | 1.0993 | 0.6524 | 0.6903 | 25 | [2004Che] |
| αNa ₃ P ₁₁ | 78.6 | 0.9828 | 1.2466 | 1.0410 | 20 | [1973Wic] |
| βNa ₃ P ₁₁ | 78.6 | 1.021 | ... | 0.731 | 600 | [1983Sch1] |
| NaP ₇ | 87.5 | 1.4200 | ... | 1.4666 | 20 | [1972Sch] |
| | | 1.427 | ... | 1.473 | 20 | [1955Kre] |
| 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] |

Section II: Phase Diagram Evaluations

Compounds Isolated in the Pure Solid State

Na₃P has hexagonal structure with isolated P³⁻ anions [1937Bra, 1965Man]. More precise XRD results [2005Don] show that the framework is built of Na⁺ and P³⁻ ions arranged in two kinds of layers perpendicular to the c-axis. One layer may be viewed as consisting of Na and P atoms in chair form cyclohexane-like rings. The other layer consists of planar graphite-like sheets of Na and P atoms. Theoretical calculations [1993Fra] suggest that the Na₃P molecule itself is non-planar. The fractional ionic character of Na₃P, calculated by two different methods, was 0.72 or 0.95 [1990Sha].

NaP is orthorhombic [1979Sch]. The P atoms are arranged in one-dimensional infinite helices of P⁻ anions [1978Hon, 1979Sch].

Na₃P₇ at room temperature (α -form) is orthorhombic, whereas the high-temperature β -form is cubic. In both forms there are P₇³⁻ cage groups (formally analogous to nortricycylene in carbon chemistry) [1983Hon, 1983Sch1, 1983Sch2]. In the α -form they are uniformly oriented, but in the β -form they are not. The β -form is of the Li₃Bi type, where the P₇³⁻ anions occupy the Bi³⁻ sites.

Na₃P₁₁ at room temperature is orthorhombic (α -form), whereas the high-temperature form is tetragonal [1973Wic, 1983Sch1, 1983Sch2]. Both forms contain P₁₁³⁻ cages, highly internally connected. The corresponding carbon compound was given the trivial name “ufosan” [1973Wic, 1988Sch] for trishomocubane.

NaP₅ is orthorhombic [2004Che], with a three-dimensional framework of P₅⁻ anions. The Na ions are placed in channels formed by the anions. The anions themselves are pentagonal, formally analogous to cyclopentadiene in carbon chemistry [1987Bau1, 1988Bau, 2002Zha, 2005Jin]. These rings are stabilized by isomerism.

NaP₇ is isostructural with LiP₇. The P₇⁻ anions are fused groups of the norbornane type, forming infinite helical tubes [1983Sch1, 1988Sch].

NaP₁₅ contains infinite P₁₅⁻ tubes, resulting from a polymerization of alternating P₇⁻ and P₈⁰ units [1985Ole, 1988Sch]. In [1988Sch], NaP₁₅ is described as isostructural with KP₁₅, i.e., triclinic (Table 1). In unpublished thesis work by H. Schmidt and W. Wichelhaus quoted in

[1985Ole], NaP₁₅ is considered to be monoclinic, with $a = 2.2706$ nm, $b = 0.9704$ nm, $c = 0.652$ nm and $\beta = 96.51^\circ$. If NaP₁₅ is assumed to be triclinic, the lattice parameter $a = 1.1353$ nm would be expected [1985Ole] with a unit cell volume of 0.711 nm³; these values are close to those for KP₁₅ and RbP₁₅ [1985Ole].

Other Compounds

Na₂P₄ was studied only theoretically [2004Jin]. Density functional theory and other methods were used in the calculations. It was concluded that the square P₄²⁻ dianion complexes with Na to form a dipyrmidal structure.

Na₄P₁₄, as a solvated molecule, has a dimeric nortricycylene system of condensed P₇⁻ rings [1983Sch1, 1988Sch].

Na₃P₁₉, as a solvated molecule, was described as containing an anion of two P₇⁻ cages attached to two sides of a P₅⁻ ring [1986Bau].

Na₄P₂₆, as a solvated molecule, contains an anion of a central P₁₂⁻ grouping entirely analogous to two condensed norbornane rings, to which are attached two P₇⁻ cages [1984Bau1].

Na₃P₂₁, as a solvated molecule, contains an anion of two P₇⁻ cages attached to a central P₇⁻ norbornane group [1980Bau, 1984Bau2].

Na₂P₁₆, as a solvated molecule, contains two P₇⁻ units coupled by a P₂ dumbbell bridge [1981Sch1, 1987Bau2].

Thermodynamics

Experimental data are summarized in Table 3. The standard enthalpy of formation of Na₃P was estimated [1980Suu] as -202 kJ/mol of formulae. The preferred measured value (Table 3) was determined by solution calorimetry [1959Mor].

The heat capacity of Na₃P₇ per mole of formula was measured in the range 120–770 K [1985Ten] by differential scanning calorimetry (DSC). Transition temperature and enthalpy were determined from these results. The transition temperature in [1986San], attributed to [1985Ten], was

Table 3 Experimental thermodynamic properties of Na phosphides

| Compound | $\Delta_f H^0_{298}$, kJ/mol | S^0_{298} , J/mol·K | $\Delta_f G^0_{298}$, kJ/mol | $\Delta_{trs} H$, kJ/mol | $\Delta_{fus} H$, kJ/mol |
|---|-------------------------------|-----------------------|-------------------------------|---------------------------|---------------------------|
| Na ₃ P | -134(a) | ... | ... | ... | ... |
| α Na ₃ P ₇ | -165(b) | 445(b) | -298(b) | 35.5(c) | ... |
| β Na ₃ P ₇ | -119(b) | 510(b) | -271(b) | ... | 7.8(c) |
| NaP ₁₅ | -153(d) | 364(f) | -261(d) | ... | ... |
| | -139(e) | ... | -256(e) | ... | ... |

(a) [1959Mor]

(b) [1986San]

(c) [1985Ten] (heating mode)

(d) [1987San], 2nd law

(e) [1987San], 3rd law

(f) [1988Sch]

wrongly quoted as 522 °C. Fusion temperature and enthalpy were determined by differential thermal analysis [1985Ten]. The vapor pressure of Na_3P_7 was measured by Knudsen effusion/mass spectrometry [1986San] in the range 752-1066 K. From these data were deduced (second law) the standard thermodynamic properties $\Delta_f H^0_{298}$, $\Delta_f G^0_{298}$ and S^0_{298} for both α - and β -forms. The enthalpy of transition was measured by DSC [1986San].

The vapor pressure of NaP_{15} was measured by Knudsen effusion/mass spectrometry [1987San] in the range 473-529 K. From these data were deduced the standard thermodynamic properties $\Delta_f H^0_{298}$ and $\Delta_f G^0_{298}$.

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