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N-Na (Nitrogen-Sodium) System

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Equilibrium Diagram

The solubility of N in Na was reviewed by [2000Bor] and [2001Bor]. There is no direct N_2-Na reaction unless the gas is under silent electrical discharge at low pressure [1925Gue]. The solubility of N in Na was reported by [1967Caf] and [1968Vel]. The Ostwald coefficient for N_2 dissolved in Na at 500 °C and 3-5 atm was $2.5 \pm 1.5 \times 10^{-7}$ [1967Caf]. This is equivalent to an atom fraction of ~8×10^{-10}. [1968Vel] analyzed liquid Na for nitrogen impurity (this was not a determination of solubility). Their results were represented [1982Rum] as exp[−7.39 − 2780/*T* (K)] atom fraction as 1 bar (pressure assumed by [1982Rum]); at 500 °C this is equivalent to 10^{-11} atom fraction. [2001Bor] represents the same data as exp[−7.12 − 2660/*T* (K)] atom fraction; this gives 3×10^{-11} at 500 °C.

There are two compounds: Na_3N (sodium nitride) and NaN_3 (sodium azide). Na_3N is formed by direct reaction of the elements, but only if N_2 is subject to silent electrical discharge at low pressure [1910Fis, 1929Mol, 1930Wat]. It is also formed from the thermal decomposition of $NaNH_2$ [1954Eph] or by the direct reaction of atomic sodium and molecular nitrogen [2002Fis, 2002Sep]. It decomposes before melting [1930Wat]; its crystal structure has only recently been elucidated [2002Fis, 2002Sep]. Calculations suggest that Na_3N is about 90% ionic [1990Sha].

NaN_3 is formed when Na is contacted with N_2 under discharge [1910Fis, 1929Mol, 1930Wat]. It is usually prepared by the neutralization of HN_3 by NaOH in aqueous solution [1898Cur]. It may also be prepared by the reaction of $NaNH_2$ with N_2O at about 200 °C [1904Den]. NaN_3 decomposes before melting [1926Suh, 1993Bel], and its decomposition temperature lies in the range 275-335 °C [1963Lut, 1990Fuj, 1993Bel]. NaN_3 undergoes a transition not far below room temperature. In a review, [1993Bel] quotes a range of 11-19.5 °C. Individual results are summarized in Table 1. There is no transition above room temperature [1965Mul].

Table 1 $\alpha \rightarrow \beta$ transition temperature of NaN_3 as measured by different methods

°C	Method	Reference
9 (?)	XRD	[1963Pri]
11	Raman	[1973Iqb]
18	DTA	[1957Pet]
	XRD	[1968Pri]
19	ESR	[1963Mil]
20	C_p	[1981Bel]
	C_p	[1976Car]
~20	Raman	[1974Sim]
25	NMR	[1977Jef]

Both forms have been characterized by x-ray and/or neutron diffraction patterns, as well as by Raman, electron spin resonance (ESR), or nuclear magnetic resonance (NMR) spectroscopy in some cases [1925Hen, 1934Wes, 1936Fre, 1939Bas, 1943Bas, 1963Mil, 1966Par, 1968Pri, 1976Cho, 1977Jef, 1977Ste, 1984Agh, 1987Nis].

Crystal Structures and Lattice Parameters

Crystal structures and lattice parameters are summarized in Tables 2 and 3.

Both forms of NaN_3 are layered structures [1968Pri] resembling a sandwich made of alternating layers of Na^+ and N_3^- ions. Each ionic species is surrounded by six of the other species. The N_3 ion is linear and symmetrical [1939Fre]. The low-temperature αNaN_3 is monoclinic and is isostructural with LiN_3 [1968Pri]. The transition to βNaN_3 is of displacive rather than order/disorder nature [1983Agh] and involves shear of the Na atoms and a contraction of the lattice along the monoclinic *a*-axis [1968Pri]. The hexagonal βNaN_3 may also be described using the equivalent rhombohedral unit cell [1939Bas, 1943Bas, 1963Pri, 1977Jef]; the reported lattice parameters for this configuration are: $a = 0.5491$ nm, $\alpha = 38.43°$ [1925Hen] and $a = 0.5488$ nm, $\alpha = 38.43°$ [1939Bas, 1943Bas]. The temperature dependences of the lattice parameters of βNaN_3 were measured by [1966Par] by high-temperature x-ray diffraction (XRD). The reported [1966Par] smoothed linear dependences are: $da/dT = 4.3 \times 10^{-5}$ nm/K and $dc/dT = 7.6 \times 10^{-5}$ nm/K in the range 30-100 °C.

Na_3N was examined by powder XRD at room temperature [2002Fis, 2002Sep], and its structure was found to be simple cubic. The structure was described as anti-ReO_3, with a simple lattice made of corner-shared NNa_6 octahedrons [2002Fis, 2002 Sep].

Thermodynamics

The heat capacity of NaN_3 was measured by adiabatic calorimeter [1966Fri, 1976Car, 1981Bel] and by ice calorimetry [1941Sat]; the total temperature range covered was −269 to +302 °C. The $\alpha \rightarrow \beta$ transition is represented in the C_p-temperature curve by a λ-type anomaly [1976Car, 1981Bel]. The enthalpy change associated with this transition is small, and the reported values, in Joules per mole, are 12.2 [1976Car], 112 [1981Bel], and ~63 [1966Fri]. The lowest value [1976Car] is probably the most accurate. The transition has been described as second order [1976Car], "weakly first order" [1983Agh], or "predominantly second order" [1968Pri, 1984Agh].

From solution calorimetry, the standard thermodynamic formation properties of NaN_3 are $\Delta_f H°_{298} = 21.3$ kJ/mol

Table 2 N-Na crystal structure data

Phase	Composition, at.% Na	Pearson symbol	Space group	Strukturbericht designation	Prototype	Temperature, °C	Reference
αNaN_3	25.0	*mC*8	*C*2/*m*	...	AuSe	<19	[1966Par, 1968Pri]
βNaN_3	25.0	*hR*4	*R*3*m*(a)	$F5_1$	$NaCrS_2$	>19	[1936Fre, 1968Pri]
Na_3N	75.0		$Pm\bar{3}m$	...	...	25	[2002Fis]
αNa	100	*hP*2	$P6_3/mmc$	*A*3	Mg	<–233	[King2]
βNa	100	*cI*2	$Im\bar{3}m$	*A*2	W	25	[King1]

(a) In earlier work, βNaN_3 was assigned a rhombohedral unit cell, space group *R*3*m* (see text).

Table 3 N-Na lattice parameter data

Phase	Composition, at.% Na	Lattice parameters, nm			β	Temperature, °C	Reference
		a	*b*	*c*			
αNaN_3	25.0	0.61654	0.36350	0.52634	107.543°	–261	[1984Agh]
		0.61861	0.36439	0.52888	107.756°	–191	[1984Agh]
		0.61971	0.36432	0.53011	108.166°	–143	[1984Agh]
		0.62233	0.36510	0.53359	108.444°	–113	[1984Agh]
		0.6211	0.3658	0.5323	108.43°	–95	[1968Pri]
		0.62116	0.36419	0.53205	108.806°	–94	[1984Agh]
		0.62520	0.36543	0.53647	109.584°	–46	[1984Agh]
		0.62614	0.36579	0.53842	109.522°	–45	[1984Agh]
		0.62764	0.36558	0.54178	110.108°	–20	[1984Agh]
		0.63043	0.36613	0.54285	110.802°	–1	[1984Agh]
		0.62971	0.36593	0.54369	110.832°	2	[1984Agh]
		0.63016	0.36566	0.54265	111.106°	7	[1984Agh]
		0.63105	0.36578	0.54830	111.212°	9	[1984Agh]
		0.62850	0.36436	0.54379	111.396°	13	[1984Agh]
		0.63264	0.36525	0.54902	112.593°	22	[1984Agh]
		0.6303	0.3657	0.5454	111.33°	RT(a)	[1966Par]
βNaN_3	25.0	0.3646	...	1.5213	...	RT(a)	[1968Pri]
		0.3646	...	1.524	...	20	[1939Bas]
		0.3645	...	1.5231	...	25	[1925Hen]
		0.3646	…	1.5223	...	25	[1977Ste]
		0.362	...	1.513	...	25	[1934Wes]
		0.3647	…	1.522	...	25	[1976Car]
		0.36405	...	1.5195	...	34	[1966Par]
		0.36520	...	1.5210	...	53.5	[1966Par]
		0.36562	...	1.5220	...	74.5	[1966Par]
		0.36682	…	1.5244	...	97.5	[1966Par]
		0.367	...	1.510	...	200	[1934Wes]
		0.47325	...	...	...	25	[2002Fis]
αNa	100	0.3767	...	0.6154	...	<–233	[King2]
βNa	100	0.42906	...	...	...	25	[King1]

(a) RT: room temperature in the original

and S°_{298} = 70.5 J/mol · K [1956Gra1]. The derived lattice energy is 732 kJ/mol [1956Gra2].

The standard enthalpy of formation of Na_3N was estimated [1966Moo] from the Born-Haber cycle to be –151 J/mol. It is metastable at room temperature.

Pressure

The β → α transition can be effected at room temperature by the simple application of pressure [1964Bra], and it was estimated [1968Pri] that the lowering of the transition temperature by 1 °C corresponds to a pressure increase of 35 bar. This estimate is consistent with the pressure dependence of the transition temperature from Raman spectral data [1974Sim], which may be represented by:

$$T_{trs}\ (°C) = 20 + 29P(\text{kbar}) \qquad \text{(Eq 1)}$$

A third form of NaN_3 is said to exist at pressures greater than 30 kbar and temperatures greater than 65 °C [1971Pis], from XRD measurements under these conditions.

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