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Cs-N (Cesium-Nitrogen)

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Equilibrium Diagram

The solubility of N in Cs was reviewed by [2000Bor] and [2001Bor]. The only measurements of solubility in this system are those of [1963Tep] and [1964Tep], who analyzed Cs for N by a modified Kjeldahl method, with stated detection limit 2 mass ppm and sensitivity ±2 ppm. The result of the analysis was a N content of <2 mass ppm. Since this was the result of a simple analysis for impurity and not a solubility measurement, this datum is suggestive only and was given as an upper solubility limit [2000Bor, 2001Bor].

Cs_3N is formed by direct reaction of the elements, but only if N_2 is subject to silent electrical discharge at low pressure [1929Mol]. It is also formed in the decomposition of CsN_3 [1930Clu] or of $CsNH_2$ [1954Eph], or in the reaction of CsH with N_2 at elevated temperatures [1903Moi]. Neither the melting point nor the crystal structure of metastable Cs_3N has been reported. From ab initio calculations, [1990Sha] determined that Cs_3N is approximately 93% ionic.

CsN_3 is most commonly prepared by the neutralization of HN_3 by CsOH [1898Cur, 1966Bry] or Cs_2CO_3 [1956Gra1, 1986Bla] in aqueous solution or by a precipitation reaction such as $Cs_2SO_4 + Ba(N_3)_2$ [1898Cur]. It may also be prepared by the reaction of $CsNH_2$ with N_2O [1954Eph] or CsF with $(CH_3)_3SiN_3$ in SO_2 solvent [2002Gen]. CsN_3 prepared at room temperature undergoes a transition at 151 °C [1965Mul, 1984Sea], and it melts without decomposition at 310-318 °C [1898Cur], 320 °C [1916Tie], 325 °C [1984Sea], or 326 °C [1926Suh, 1965Mul, 1975Win]. It decomposes over a range of temperature 390-460 °C.

Crystal Structures and Lattice Parameters

These are summarized in Tables 1 and 2. There is no information on the crystal structure of Cs_3N.

Crystal structures and lattice parameters of CsN_3 were reviewed by [1959Eva], [1963Gra], and [1993Bel]. The N-N distance is 0.115 ± 0.002 nm [1963Gra]. CsN_3 at room temperature is body-centered tetragonal [1971Hat], space group D_{4h}^{18}-*I*4/*mcm*, $Z = 4$, isostructural with cesium cyanate and KN_3. αCsN_3 has a layered structure, with alternating planes of N_3^- and Cs^+ ions [1972Mul]. The N_3 group is linear and symmetrical [1936Fre]. αCsN_3 is isostructural with KN_3 and RbN_3, each N_3 group being equidistant from eight Cs atoms and vice versa [1972Mul]. The high-temperature form βCsN_3 also has a layered structure but has the cubic CsCl structure [1965Mul].

Thermodynamics

The enthalpy of transition of CsN_3, determined by differential scanning calorimetry, is 3.2 kJ/mol CsN_3 [1965Mul]. The standard enthalpy of formation, from solution calorimetry, is –9.92 kJ/mol [1956Gra1], and the derived lattice energy is 611 kJ/mol [1956Gra2].

Pressure

CsN_3 undergoes a structural transition at room temperature at approximately 6 kbar [1969Pis]. According to [1975Iqb] this high-pressure form involves two crystallographically nonequivalent azide sites.

Table 1 Cs-N crystal structure data

Phase	Composition, at.% N	Pearson symbol	Space group	Strukturbericht designation	Prototype	Temperature, °C	Reference
Cs	0	*cI*2	$Im\bar{3}m$	*A*2	W	25	[King1]
αCsN_3	75.0	*tI*16	*I*4/*mcm*	…	KN_3	<151	[1972Mul]
βCsN_3	75.0	*cP*2	$Pm\bar{3}m$	*B*2	CsCl	>151	[1965Mul]

Table 2 Cs-N lattice parameter data

Phase	Composition, at.% N	Lattice parameters, nm		Temperature, °C	Reference
		a	*c*		
Cs	0	0.6141	…	25	[King1]
αCsN_3	75.0	0.672	0.8045	20	[1957Eva]
		0.65412	0.80908	21	[1972Mul]
		0.647	0.797	25	[1965Mul]
		0.646	0.798	25	[1962Sch]
βCsN_3	75.0	0.4537	…	290	[1965Mul]

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