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K-N (Potassium-Nitrogen)

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Equilibrium Diagram

The solubility of N in K was reviewed by [2000Bor] and [2001Bor]. Although there are no reported experimental data, a lower detection limit of 10×10^{-7} atom fraction was suggested [2000Bor]. There are two compounds, K_3N (potassium nitride) and KN_3 (potassium azide).

K_3N is formed by direct reaction of the elements, but only if N_2 is subject to silent electrical discharge at low pressure [1930Wat]. It is also formed in the decomposition of KN_3 [1930Wat] or of KNH_2 [1954Eph]. It decomposes before melting [1930Wat]; its crystal structure has not been elucidated. K_3N was estimated to be about 93% ionic [1990Sha].

KN_3 is most commonly prepared in aqueous solution, using reagents NaN_3, KOH, K_3PO4, HN_3, and K_2CO_3 [1898Cur, 1939Bro, 1967Sha, 1974Sne, 1986Bla]. It may also be prepared by the reaction $KNH_2 + N_2O$ (or KNO_3) [1954Eph].

KN_3 has been characterized by XRD [1925Hen, 1936Fre, 1957Eva, 1966Par, 1972Mul] and neutron diffraction [1976Cho]. Its melting point has been reported as 343 °C [1926Suh], 345 °C [1975Win], or 350 °C [1916Tie]. Unlike RbN_3 and CsN_3, KN_3 undergoes no high-temperature transition [1965Mul, 1978Car]. It decomposes in the range 320-360 °C [1926Suh, 1993Bel].

Crystal Structures and Lattice Parameters

Crystal structures and lattice parameters are summarized in Tables 1 and 2. There is no information on the crystal structure of K_3N.

KN_3 has a layered structure, with alternating planes of N_3^- and K^+ ions [1972Mul]. The N_3 group is linear and symmetrical [1936Fre]. Each N_3 group is equidistant from eight K atoms and vice versa [1925Hen]. KN_3, RbN_3, and CsN_3 are isostructural with the corresponding cyanates [1959Eva, 1959Wad, 1963Gra]. The arrangement resembles cubic CsCl, the N_3^- ions taking the place of Cl^-. The thermal expansion of KN_3 was measured by [1966Par] in the range 20-340 °C by high-temperature XRD. The smoothed linear temperature dependences of the lattice parameters, as reported by [1966Par], are $da/dT = 2.6 \times 10^{-5}$ nm/K and $dc/dT = 6.7 \times 10^{-5}$ nm/K.

Thermodynamics

The standard thermodynamic formation quantities for KN_3 were determined by solution calorimetry as $\Delta_f H^\circ_{298} = -1.4$ kJ/mol KN_3 [1956Gra1] and $S^\circ_{298} = 86.0$ J/mol · K [1956Gra1]. The derived lattice energy is 657 kJ/mol [1956Gra2].

The enthalpy of formation of K_3N was estimated (from the Born-Haber cycle) to be 84 kJ/mol [1966Moo].

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Table 1 K-N crystal structure data

Phase	Composition, at.% N	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
K	0	*cI*2	$Im\bar{3}m$	*A*2	W	[King1]
KN_3	75.0	*tI*16	*I*4/*mcm*	…	KN_3	[1966Par, 1972Mul]

Table 2 K-N lattice parameter data

Phase	Composition, at.% N	Lattice parameters, nm		Temperature, °C	Reference
		a	*c*		
K	0	0.5321	…	25	[King1]
KN_3	75.0	0.6085	0.6997	−196	[1976Cho]
		0.6106	0.7070	20	[1925Hen]
		0.61131	0.70814	20	[1966Par](a)
		0.61129	0.70943	21	[1972Mul]
		0.61205	0.70748	36.5	[1966Par]
		0.61307	0.71082	75	[1966Par]
		0.61424	0.71302	120	[1966Par]
		0.61491	0.71253	144.5	[1966Par]
		0.61557	0.71708	170	[1966Par]
		0.61606	0.71953	195	[1966Par]
		0.61590	0.72072	200	[1966Par]
		0.61669	0.72016	220	[1966Par]
		0.61742	0.72463	246	[1966Par]
		0.61783	0.72444	280	[1966Par]
		0.61841	0.72470	308	[1966Par]
		0.61960	0.72707	327	[1966Par]
		0.62067	0.72865	340	[1966Par]

(a) The lattice parameter values of [1966Par] reported here are, at each temperature, the mean of the results for Cu and Mo radiation.

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