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N-Rb (Nitrogen-Rubidium)

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Equilibrium Diagram

The solubility of N in Rb was reviewed by [2000Bor] and [2001Bor]. The only report relevant to solubility is the analysis of Rb, under 1 atm of N_2, by a modified Kjehldahl method [1963Tep, 1964Tep]. The lower limit of detection was 2 mass ppm and the sensitivity was ±2 ppm. The result of the analysis was 4.6 mass ppm of N, but since this was a measurement of impurity and not solubility, this value is suggestive only. There are two compounds: Rb_3N (rubidium nitride) and RbN_3 (rubidium azide).

Rb_3N is formed by direct reaction of the elements, but only if N_2 is subject to silent electrical discharge at low pressure [1954Eph]. It is also formed in the decomposition of RbN_3 [1930Clu] or of $RbNH_2$ [1954Eph] or by the reaction of RbH with N_2 gas at elevated temperatures [1903Moi, 1910Fis]. Neither its melting point nor crystal structure has been reported. [1990Sha] determined, from ab initio calculations, that metastable Rb_3N is about 92% ionic.

RbN_3 is most commonly prepared by the neutralization of HN_3 by RbOH [1898Cur] or Rb_2CO_3 [1986Bla] or by the precipitation reaction $Rb_2SO_4 + Ba(N_3)_2$ in aqueous solution. It is also formed by the reaction of $RbNH_2$ with N_2O [1954Eph].

Melting and transition temperatures of RbN_3 were reviewed by [1993Bel]. It melts without decomposition; the melting point has been variously reported to be 300 °C [1916Tie], 317 °C [1965Mul], 321 °C [1926Suh], 330 °C [1898Cur], or 340 °C [1934Pas]. The true melting point is probably near 320 °C. The room temperature form, αRbN_3, transforms to the high-temperature form βRbN_3 at 315 °C [1965Mul]. Both forms have been characterized by x-ray [1929Gun, 1930Pau, 1957Eva, 1965Mul, 1972Mul] or neutron [1976Cho] diffraction. RbN_3 decomposes at about 395 °C [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 Rb_3N. Crystal structures and lattice parameters of RbN_3 were reviewed by [1957Eva], [1959Wad], [1963Gra], and [1993Bel].

αRbN_3 has a layered structure, with alternating planes of N_3 and Rb^+ ions [1972Mul]. The N_3 group is linear and symmetrical [1936Fre], the N-N distance being 0.115 ± 0.002 nm [1963Gra]. αRbN_3 is body-centered tetragonal and is isostructural with KN_3; each N_3 group is equidistant from eight K atoms and vice versa [72Mul]. In the earliest x-ray work on αRbN_3 [1929Gun, 1930Gun], the reflections were indexed on the assumption of 4/*mmm* symmetry, rather than 4/*mcm*, as now preferred (Table 1). The lattice parameters, as originally reported by [1929Gun] were $a = 0.4506$ nm, $c = 0.3714$ nm. The correct interpretation, pointed out by [1930Pau], involves the change D^1_{4h} to D^{18}_{4h} (the value of c is doubled and the elementary cell is rotated 45° around the c axis.). βRbN_3 is also a layered structure (like αRbN_3) but has the cubic CsCl structure [1965Mul].

Table 1 N-Rb crystal structure data

Phase	Composition, at.% Rb	Pearson symbol	Space group	Strukturbericht designation	Prototype	Temperature, °C	Reference
αRbN_3	25.0	*tI*16	*I*4/*mcm*	…	KN_3	25	[1972Mul]
βRbN_3	25.0	*cP*2	$Pm\bar{3}m$	*B*2	CsCl	>315	[1965Mul]
Rb	100	*cI*2	$Im\bar{3}m$	*A*2	W	25	[King1]

Table 2 N-Rb lattice parameter data

Phase	Composition, at.% Rb	Lattice parameters, nm		Temperature, °C	Reference
		a	*c*		
αRbN_3	25.0	0.6161	0.744	−196	[1976Cho]
		0.637	0.743	20	[1930Pau](a)
		0.63098	0.75188	21	[1972Mul]
βRbN_3	25.0	0.435	…	>315	[1965Mul]
Rb	100	0.5703	…	25	[King1]

(a) Recalculated from original measurements of [1929Gun], using corrected unit cell configuration

Thermodynamics

The standard enthalpy of formation of αRbN_3 was reviewed by [1959Eva] and was deduced from solution calorimetry: $\Delta_f H^\circ_{298} = -0.29$ kJ/mol of RbN_3 [1956Gra1, 1986Bla]. The derived lattice energy is 636 kJ/mol^{-1} [1956Gra2]. The enthalpy of transformation of RbN_3 was found to be 4.6 kJ/mol, as measured by differential scanning calorimetry [1965Mul] or 5.24 kJ/mol [1993Bel].

The standard enthalpy of formation of Rb_3N, calculated from the Born-Haber cycle, is 180 kJ/mol [1966Moo].

Pressure

From differential thermal analysis measurements under pressure, it was observed that RbN_3 undergoes a transition at room temperature at about 5 kbar [1969Pis].

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