NITROGEN

References

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N° 2s 2p E.N. 3.0

NH_3, ammonia, g., colrl., pungent, $d = 0.77$, m. p. −78, b. p.−33, $\Delta H = -46$, $(NH_3)_n$ associated by H-bonds, mol.: trig. pyramid (ψ-tetrahedron [:NH_3], sp^3), N—H 1.01, ∠HNH 107, μ = 1.46, ε = 22 (−34°), solv. for M^I, M^{II}, $MHal_n$, S, MNO_3, MNH_2;
$Na + NH_3(liq.) \leftrightarrows Na^+ + e \cdot NH_3$ (blue)
$2\,NH_3(liq.) \leftrightarrows NH_4^+ + NH_2^-$, $[NH_4^+][NH_2^-] = 10^{-33}$ (−50°); H_2O-sol. 34 wt. % = 99 vol. %, pH = 11.8
$NH_3 + H_2O \overset{K=0.2}{\leftrightarrows} \mathbf{NH_3 \cdot H_2O}$ (= H_3N...HOH) $\overset{K=10^{-5}}{\leftrightarrows} NH_4^+ + OH^-$, «ammonium hydroxide», «NH_4OH».
$K = \frac{[NH_4^+][OH^-]}{[NH_3 \cdot H_2O]} = 10^{-5}$
$2\,NH_3 \cdot H_2O$ = $(NH_4)_2O$, m. p.−78 with dec.
$NH_3 \cdot H_2O$ = «NH_4OH», m. p.−77, in struct. chains $(H_2O)_n$, joined mol. NH_3 («NH_4OH» does not exist in the struct.)
$NH_3 \cdot 2\,H_2O$, m. p.−97, in struct. mol. H_2O are disordered [23]
$MX_n \cdot y\,NH_3$, ammoniates

O_2 (t, without cat.); Cl_2 CuO (t)

H_2 (500°, p, Pt; Fe/Al_2O_3)

H_2; NH_3 (t, exp.) > 500°

NaOCl (0.2% gelatin)

N_2H_4, hydrazine (diamide), liq., colrl., fuming, m. p. 2, b. p. 114, $\xrightarrow{t}$ $NH_3 + N_2$, $\Delta H = +52$ (liq.), +95 (g.), μ = 1.83, ε = 52 (25°), N—H 1.02, N—N 1.45, ∠NNH = ∠HNH ~ 110, dihedral ∠90°;
$+ H_2O \leftrightarrows N_2H_5^+ + OH^-$, $K_1 = 10^{-6}$
$N_2H_5^+ + H_2O \leftrightarrows N_2H_6^{2+} + OH^-$, strong Red agent

$[(Me_3Si)_2N{-}N{=}]_2$ CF_3COOH, CH_2Cl_2, −78°

N_4H_4, tetrazene, [17] *trans*-$H_2N{-}N{=}N{-}NH_2$, cr., colrl., subl. vac. −15, $\xrightarrow{t}$ $N_2 + N_2H_4 + NH_4[N_3]$

HNO_2

HN_3, hydrazoic ac., liq., colrl., toxic, pungent, m. p.−80, b. p. 37, $d = 1.13$, exp. 300°, $\Delta H = +293$, 1.24 Å, 1.02 Å, 115°, 1.13 Å; stab. in dil. soln., $K = 10^{-5}$, μ = 0.83, strong Ox (react. with Cu; HN_3 + HCl p. Pt) [20]

NH_4X $MClO_4$·MNO_3·$K_2Cr_2O_7$

N_2, gas., colrl., $d = 1.25$, m. p.−210, b. p.−196, degree of diss. = 0.1% (3000°), $\Delta H_{diss.} = 945$, H_2O-sol. 2 vol. % (0°), v. chem. inert, N—N 1.095 (1σ + 2π bonds), $\nu_{N\equiv N} = 2331\ cm^{-1}$; mol. struct., α-, cub. close pack., $a = 5.66$ ↓ > −238°; β-, hex. close pack., $a = 4.04$, $c = 6.67$ (mol. rotation imitates spheric sym.)

NaOCl NH_3

NH_2Cl, chloramine, oil, colrl., m. p. −60, vac. distillation; $+ H_2O \leftrightarrows NH_3 + HOCl$, Ox, ψ-tetrahedron mol. (sp^3), N—Cl 1.75, ∠ClNH 104, ∠HNH 99

N_2H_5OH, hydrazine hydrate, liq., colrl., m. p.−52, b. p. 119, $K_{bas} = 10^{-6}$, $\Delta H = -243$

Na[N_2H_3], cr., yel., exp.

Na (−H_2)

HX

NH_3 (liq.) [−$(NH_4)_2SO_4$]

Hydrazonium salts
[N_2H_5]Hal, Hal = F, Cl ↑H_2O
[N_2H_6]X_2, X = F, Cl, $TiF_6/2$
[N_2H_6]SO_4 ↓
[N_2H_6]$^{2+}$-*trans*, N—N 1.45, N—H 0.88–1.07 [11]

HX MOH H_2O Na (−H_2; 350°)

Ammonium salts
NH_4Hal $\overset{t}{\leftrightarrows}$ NH_3 + HHal, stab. $NH_4I > NH_4F$
$(NH_4)_2SO_4$, dec. 357
NH_4HSO_4, m. p. 251, b. p. 490
NH_4HCO_3, dec. 40
NH_4X, at X = NO_2, ClO_4, $Cr_2O_7/2$, $\xrightarrow{t}$ $N_2 + H_2O + E_2O_n$
NH_4NO_3 $\xrightarrow{210°}$ $N_2O + H_2O$ (slowly); $\longrightarrow N_2 + H_2O + O_2$ (exp.)
tetrahedron (sp^3) cation, N—H 1.03;
$[R_4N]^+X^-$, tetraalkylammonium salts

Amides
$NaNH_2$, cr., colrl., m. p. 210, b. p. 400, sol. in liq. NH_3;
$Ba(NH_2)_2$, m. p. 280;
$Cr(NH_2)_3$, dec. ~100;
[:NH_2]$^-$-ψ-tetrahedron, N—H 1.03, ∠HNH 104, $+ H_2O \rightarrow NH_3 + M(OH)_n$
$CO(NH_2)_2$, carbamide (urea)
$Ca(CN_2)$, cyanamide, $+ H_2O \xrightarrow{t} NH_3 + CaCO_3$

CaC_2 (1000°, C; cyanamide method of N_2 fixation)

t (−NH_3)

Imides
Li_2NH, $S_n(NH)_{8-n}$, rings

t (−NH_3)

M (−H_2)

Li (20°); Mg–Ba; Al; Ti–Mn; Ln, Mo, W(*t*); MH; TiO_2 + C

Nitrides M_3N_x

Salt-like (*s*-elements)	**Covalent** (*p*-elements)	**Metal-like** (*d*- and *f*-elements)
Li_3N, cr., red, m. p. 814 (p), v. active. **M_2N**, M = Ca—Ba, struct.: anti-$CdCl_2$ [24]	**BN**, cr., wh. m. p. 3000 (p N_2), dec. ~2500, diamond or graphite type struct.	**TiN**, m. p. 3200; **ZrN**, " 2980; **VN** —; **NbN**, " 2300 — NaCl type struct.
Mg_3N_2, dec. 1500; **Ca_3N_2**, m. p. 1195; **Zn_3N_2**, dec. 700 — air stab. Mn_2O_3 type struct.	**AlN**, cr., wh., dec. 2200; **GaN**, yel.; **InN**, blk. — wurtzite type struct. (ZnS)	**CrN**, m. p. 1500; **AnN**, An = Th,U,Pu
Be_3N_2, m. p. 2200 with dec.	**Si_3N_4**, cr., wh., subl. 1900	**Nb_2N, Cr_2N, Fe_4N, Co_3N, Co_2N, Ni_3N, Ni_4N** – N-intercalation phase in M struct., refractory, very hard, friable subst. with metallic thermal and electric conductivity, chem. inert.
Cu_3N, dec. 450, anti-ReO_3 struct. $+ H_2O \rightarrow MOH + NH_3$ semiconductors	**ScN**, NaCl type struct.; dielectrics or semiconductors, thermally stable, stable to Ox and M melts, acid resistant (t)	

$CaHal_2$

Ca_2NHal, Hal = Cl, Br [24]

*) In the Tables, aqueous NH_3 is designated as NH_4OH

NO_2 [H↑]: Pt/C

MNO_2 SO_2; cat., Red

NH_2OH, hydroxylamine, cr., colrl., m. p. 33, b. p. 58/22mm Hg, exp. 100°, $\Delta H = -113$, $+ H_2O \leftrightarrows NH_3OH^+ + OH^-$; $K_{bas.} = 10^{-8}$; conc. sol. $\xrightarrow{(OH^-,\ Pt)}$ $N_2 + NH_3 + N_2O$; strong. Red agent, ψ-tetrahedron mol., N—O 1.48 · **H_2O**

[NH_3OH]$^+X^-$, hydroxylammonium salts, X = Cl (m. p. 151), ClO_4, $SO_4/2$, NO_3, $PO_4/3$, cr., stab., distort. tetrahedron cation, N—H 0.99, N—O 1.41 [9]

ЭF$_5$(HF) M (−N_2–NH_3)

[H_2N_3]$^+$[ЭF$_6^-$], aminodiazonium salts, cr., colrl., stab. at 20°, cation: [$H_2\ddot{N}$—N = N]$^+$ (1.29, 1.10) [22]

M(N_3)$_n$, azides [25]
NaN_3, colrl., dec. 275, **KN_3**, m. p. 350, dec. 355 without exp. M^{II} = Hg, Pb, Ba ($\cdot H_2O$↓); detonators; [SO], [SO_2], [CrO_2]; linear anion: [:$\ddot{N}$ = N = $\ddot{N}$:]$^-$, N—N 1.17

t (−M)

Dinitrogen complexes [7]
[$M(N_2)(NH_3)_5$]Cl_2, M^{II} = Ru, Os, cr., yel., diamagn., stab. to the act. of H_2O and O_2
[$M(N_2)(PR_3)_3$], M^0 = Co, Ni
[$Os(N_2)(PR_3)_3Cl_2$]
[$Ti(N_2)(C_5H_5)_2$]$_2$, $+ RMgH_2Hal \rightarrow NH_3 + ...$;
[$W(N_2)_2(PR_3)_4$], linear [N≡N: → M] gr., N—N 1.12–1.6; ∠MNN 177–179;
[$(NH_3)_5RuN$]$_2X_4$, N—N (br.) 1.25, $\nu_{N\equiv N} = 2050–2150$
K[$Co(N_2)(PR_3)_3$]
$(PR_3)_3Fe(N_2)H_2$
[Na(Thf)][$V(N_2)_2(PR_3)_2$]

$OsCl_3 + PR_3 + Zn/Hg$; $Ti(C_5H_2)_2$
Ni (ac–ac)$_2$ + PPh_3 + eth.
$VCl_3(Thf)_3 + Na + PR_3$

H^+, MCl_3

NH_3, N_2H_4