11.3.4 Thermodynamic relations between N-containing species

The ability of N to exist in its compounds in at least 10 different oxidation states from -3 to $+5$ poses certain thermodynamic and mechanistic problems that invite systematic treatment. Thus, in several compounds N exists in more than one oxidation state, e.g. $[N^{-III}H_4]^+[N^{III}O_2]^-$, $[N^{-III}H_4]^+[N^VO_3]^-$, $[N^{-II}{}_2H_5]^+[N^VO_3]^-$, $[N^{-III}H_4]^+[N^{-\frac{1}{3}}{}_3]^-$, etc. Furthermore, we have seen (p. 423) that, under appropriate conditions, NH_3 can be oxidized by O_2 to yield N_2, NO or NO_2, whereas oxidation by OCl^- yields N_2H_4 (p. 427). Likewise, using appropriate reagents, N_2H_4 can be oxidized either to N_2 or to HN_3 (in which the "average" oxidation number of N is $-\frac{1}{3}$). The thermodynamic relations between these various hydrido and oxo species containing N can be elegantly codified by means of their standard reduction potentials, and these can be displayed pictorially using the concept of the "volt equivalent" of each species (see Panel).

The standard reduction potentials in acidic aqueous solution are given in Table 11.4; these are shown diagrammatically in Fig. 11.8 (p. 437) which also includes the corresponding data for alkaline solutions. The reduction potentials are readily converted to volt equivalents (by multiplying by the appropriate oxidation state) and these are plotted against oxidation state in Fig. 11.9. This latter diagram is particularly valuable in giving a visual representation of the redox chemistry of the element. Thus, it follows from the definition of "volt equivalent" that the reduction potential of any couple is the *slope* of the line joining the two points: the greater the positive slope the stronger the oxidizing potential and the greater the negative slope the stronger the reducing power. Any pair of points can be joined. For example in acid solution N_2H_4 is a

Table 11.4 Standard reduction potentials for nitrogen species[a] in acidic aqueous solution (pH 0, 25°C)

Couple	$E°/V$	Corresponding half-reaction
N_2/HN_3	-3.09	$\frac{3}{2}N_2 + H^+(aq) + e^- \longrightarrow HN_3(aq)$
$N_2/N_2H_5{}^+$	-0.23	$N_2 + 5H^+ + 4e^- \longrightarrow N_2H_5{}^+$
$H_2N_2O_2/NH_3OH^+$	$+0.387$	$H_2N_2O_2 + 6H^+ + 4e^- \longrightarrow 2NH_3OH^+$
$HN_3/NH_4{}^+$	$+0.695$	$HN_3 + 11H^+ + 8e^- \longrightarrow 3NH_4{}^+$
$NO/H_2N_2O_2$	$+0.712$	$2NO + 2H^+ + 2e^- \longrightarrow H_2N_2O_2$
$NO_3{}^-/N_2O_4$	$+0.803$	$2NO_3{}^- + 4H^+ + 2e^- \longrightarrow N_2O_4 + 2H_2O$
$HNO_2/H_2N_2O_2$	$+0.86$	$2HNO_2 + 4H^+ + 4e^- \longrightarrow H_2N_2O_2 + 2H_2O$
$NO_3{}^-/HNO_2$	$+0.94$	$NO_3{}^- + 3H^+ + 2e^- \longrightarrow HNO_2 + H_2O$
$NO_3{}^-/NO$	$+0.957$	$NO_3{}^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O$
HNO_2/NO	$+0.983$	$HNO_2 + H^+ + e^- \longrightarrow NO + H_2O$
N_2O_4/NO	$+1.035$	$N_2O_4 + 4H^+ + 4e^- \longrightarrow 2NO + 2H_2O$
N_2O_4/HNO_2	$+1.065$	$N_2O_4 + 2H^+ + 2e^- \longrightarrow 2HNO_2$
$N_2H_5{}^+/NH_4{}^+$	$+1.275$	$N_2H_5{}^+ + 3H^+ + 2e^- \longrightarrow 2NH_4{}^+$
HNO_2/N_2O	$+1.29$	$2HNO_2 + 4H^+ + 4e^- \longrightarrow N_2O + 3H_2O$
$NH_3OH^+/NH_4{}^+$	$+1.35$	$NH_3OH^+ + 2H^+ + 2e^- \longrightarrow NH_4{}^+ + H_2O$
$NH_3OH^+/N_2H_5{}^+$	$+1.42$	$2NH_3OH^+ + H^+ + 2e^- \longrightarrow N_2H_5^+ + 2H_2O$
$HN_3/NH_4{}^+$	$+1.96$	$HN_3 + 3H^+ + 2e^- \longrightarrow NH_4^+ + N_2$
$H_2N_2O_2/N_2$	$+2.65$	$H_2N_2O_2 + 2H^+ + 2e^- \longrightarrow N_2 + 2H_2O$

[a]All the half-reactions listed in this table have only (Ox), H^+ and e^- on the left-hand side of the half-reaction. Others, such as $N_2/NH_3OH^+ - 1.87$ (i.e. $N_2 + 2H_2O + 4H^+ + 2e^- \longrightarrow 2NH_3OH^+$) can readily be calculated by appropriate combinations (in this case, for example, $N_2/N_2H_5{}^+ - NH_3OH^+/N_2H_5{}^+$). There are also simple electron addition reactions, e.g. NO^+/NO, $E° + 1.46$ V (i.e. $NO^+ + e^- \longrightarrow NO$) and more complex electron additions, e.g. $NO_3{}^-$, $NO/NO_2{}^-$, $E° + 0.49$ V (i.e. $NO_3{}^- + NO + e^- \longrightarrow 2NO_2{}^-$), etc.

Standard Reduction Potentials and Volt Equivalents

Chemical reactions can often formally be expressed as the sum of two or more "half-reactions" in which electrons are transferred from one chemical species to another. Conventionally these are now almost always represented as equilibria in which the forward reaction is a reduction (addition of electrons):

$$(\text{oxidized form}) + ne^- \rightleftharpoons (\text{reduced form})$$

The electrochemical reduction potential (E volts) of such an equilibrium is given by

$$E = E^\circ - \frac{2.3026RT}{nF} \log_{10} \frac{a(\text{red})}{a(\text{ox})} \tag{1}$$

where E° is the "standard reduction potential" at unit activity a, R is the gas constant ($8.3144\,\text{J mol}^{-1}\,\text{K}^{-1}$), T is the absolute temperature, F is the Faraday constant ($96\,485\,\text{C mol}^{-1}$) and 2.3026 is the constant $\ln_e 10$ required to convert from natural to decadic logarithms. At 298.15 K (25°C) the factor $2.3026RT/F$ has the value $0.059\,16$ V and, replacing activities by concentrations, one obtains the approximate expression

$$E \approx E^\circ - \frac{0.059\,16}{n} \log_{10} \frac{[\text{red}]}{[\text{ox}]} \tag{2}$$

By convention, E° for the half-reaction (3) is taken as zero, i.e. $E^\circ(H^+/\frac{1}{2}H_2) = 0.0$ V:

$$H^+(\text{aq}, a = 1) + e^- \rightleftharpoons \tfrac{1}{2}H_2(\text{g, 1 atm}) \tag{3}$$

Remembering that $\Delta G = -nEF$, it follows that the standard free energy change for the half reaction is $\Delta G^\circ = -nE^\circ F$, e.g.:

$$Fe^{3+}(\text{aq}) + e^- \rightleftharpoons Fe^{2+}(\text{aq}); \quad E^\circ(Fe^{3+}/Fe^{2+}) = 0.771 \text{ V} \tag{4}$$

$$\Delta G^\circ = -74.4\,\text{kJ mol}^{-1}$$

Coupling the half-reactions (3) and (4) gives the reaction (5) {i.e. (4) − (3)} which, because ΔG is negative, proceeds spontaneously from left to right as written:

$$Fe^{3+}(\text{aq}) + \tfrac{1}{2}H_2(\text{g}) \rightleftharpoons Fe^{2+}(\text{aq}) + H^+(\text{aq}); \quad E^\circ = 0.771 \text{ V} \tag{5}$$

$$\Delta G^\circ = -74.4\,\text{kJ mol}^{-1}$$

Again, $E^\circ(Zn^{2+}/Zn) = -0.763$ V, hence reaction (6) occurs spontaneously in the reverse direction:

$$Zn^{2+}(\text{aq}) + H_2(\text{g}) \rightleftharpoons Zn(\text{s}) + 2H^+(\text{aq}); \quad E^\circ = -0.763 \text{ V};$$

$$\Delta G^\circ = +147.5\,\text{kJ mol}^{-1} \text{ (note the factor of 2 for } n) \tag{6}$$

In summary, at pH 0 a reaction is spontaneous from left to right if $E^\circ > 0$ and spontaneous in the reverse direction if $E^\circ < 0$. At other H-ion concentrations eqn. (2) indicates that the potential of the H electrode (3) will be

$$E = -0.05916 \log \frac{\{P_{H_2}/\text{atm}\}^{\frac{1}{2}}}{\{[H^+(\text{aq})]/\text{mol l}^{-1}\}} \text{ V}$$

and, in general, the potential of any half-reaction changes with the concentration of the species involved according to the Nernst equation (7):

$$E = E^\circ - \frac{0.05916}{n} \log Q \tag{7}$$

where Q has the same form as the equilibrium constant but is a function of the actual activities of the reactants and products rather than those of the equilibrium state. Note also that the potential is independent of the coefficients of the half-reaction whereas the free energy is directly proportional to these, e.g.:
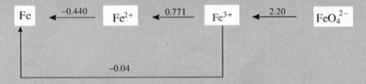
$$\tfrac{1}{2}I_2 + e^- \rightleftharpoons I^-; \quad E^\circ = 0.536 \text{ V}; \quad \Delta G^\circ = -51.5 \text{ kJ mol}^{-1}$$

$$I_2 + 2e^- \rightleftharpoons 2I^-; \quad E^\circ = 0.536 \text{ V}; \quad \Delta G^\circ = -103.0 \text{ kJ mol}^{-1}$$

It is vital to remember that, when half-reactions are added or subtracted, one should not add or subtract the corresponding E° *values but rather* nE°. (We shall return to this point later.)

Lists of standard reduction potentials are given in many books[85] and are extensively quoted throughout this text. Almost all lists now use the IUPAC sign conventions employed above, though some earlier American books (including, unfortunately, the classic early text on the subject[86]) use the opposite sign convention. When standard reduction potentials are listed in sequence from the most negative to the most positive the strongest reducing agents are at the top of the list and a reducing agent should, in principle, be capable of reducing all oxidizing agents lying below it in the table. Conversely, the oxidizing agents are listed in order of *increasing* strength and a given oxidizing agent should be able to oxidize all reducing agents lying above it in the table. Such lists are an extremely compact way of summarizing a great deal of predictive information. For example a list of 100 independent reduction potentials enables the free energy change for $100 \times 99/2 = 4950$ reactions to be calculated and indicates the direction in which a hypothetical reaction would occur under appropriate conditions (which might involve the use of a catalyst).

When an element can exist in several oxidation states it is sometimes convenient to display the various reduction potentials diagramatically, the corresponding half-reactions under standard conditions being implied. Thus, in acidic aqueous solutions

Note that the value of $E^\circ(\text{Fe}^{3+}/\text{Fe}) = -0.04$ V is equivalent to $\{(2 \times -0.44) + 0.77\}/3$. Because the quantity nE° is used in these calculations (rather than E°) it is convenient to define the "volt equivalent" of a species; the volt equivalent of a compound or ion is the reduction potential of the species relative to the element in its standard state multiplied by the oxidation state of the element in the compound (including its sign). The oxidation state is the number of electrons that must be added to an atom of an element to regain electroneutrality when all other atoms in the compound (ion) have been removed as their "normal" ions. For example the oxidation state of Fe is $+6$ in FeO_4^{2-}:

$$\text{FeO}_4{}^{2-} \xrightarrow{-4\text{O}^{2-}} \text{Fe}^{6+} \xrightarrow{+6e^-} \text{Fe}$$

It follows that, in the above example, the volt equivalents of Fe^{2+} and Fe^{3+} are -0.88 and -0.11 respectively and that of $\text{FeO}_4{}^{2-}$ is $+6.49$ {i.e. $(2 \times -0.44) + 0.77 + (3 \times 2.20)$}. This leads to $E^\circ(\text{FeO}_4{}^{2-}/\text{Fe}) = +1.08$ V.

The power of these various concepts in codifying and rationalizing the redox chemistry of the elements is illustrated for the case of nitrogen in the present section. Standard reduction potentials and plots of volt equivalents against oxidation state for other elements are presented in later chapters.

stronger reducing agent than H_2 (slope of tie-line -0.23 V) and NH_2OH is even stronger (slope -1.87 V). By contrast, the couple N_2O/NH_3OH^+ has virtually the same reducing power as H_2 (slope -0.05 V).

It also follows that, when three (or more) oxidation states lie approximately on a straight line in the volt-equivalent diagram, they tend to form an equilibrium mixture rather than a reaction going to completion (provided that the attainment of thermodynamic equilibrium is not hindered kinetically). This is because the slopes joining the several points are almost the same, so that E° for the various couples (and hence ΔG°) are the same; there is consequently approximately zero change in free energy and a balanced

[85] A. J. BARD, R. PARSONS and J. JORDAN *Standard Potentials in Aqueous Solution*, Marcel Dekker, New York, 1985, 834 pp. G. MILAZZO and S. CAROLI, *Tables of Standard Electrode Potentials*, Wiley, New York, 1978, 421 pp.
[86] W. M. LATIMER, *The Oxidation States of the Elements and their Potentials in Aqueous Solutions*, 2nd edn., Prentice-Hall, New York, 1952, 392 pp.
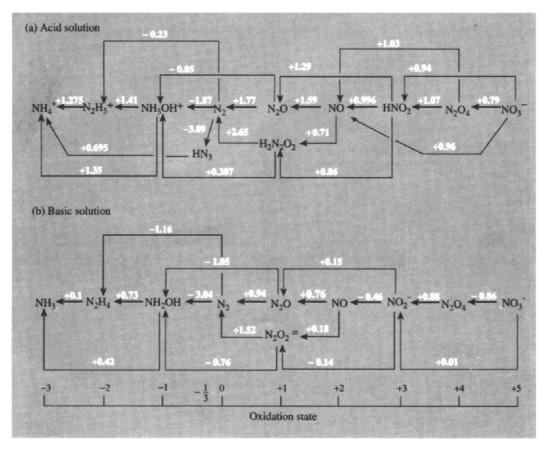
Figure 11.8   Oxidation states of nitrogen showing standard reduction potentials in volts: (a) in acid solution at pH 0, and (b) in basic solution at pH 14.

equilibrium is maintained between the several species. Indeed, the volt-equivalent diagram is essentially a plot of free energy versus oxidation state (as indicated by the right-hand ordinate of Fig. 11.9).

Two further points follow from these general considerations:

(a) a compound will tend to disproportionate into a higher and a lower oxidation state if it lies above the line joining the 2 compounds in these oxidation states, i.e. disproportionation is accompanied by a decrease in free energy and will tend to occur spontaneously if not kinetically hindered. Examples are the disproportionation of hydroxylamine in acidic solutions (slow) and alkaline solutions (fast):

$$4NH_3OH^+ \longrightarrow N_2O + 2NH_4{}^+ + 3H_2O + 2H^+$$

$$3NH_2OH \longrightarrow N_2 + NH_3 + 3H_2O$$

(b) Conversely, a compound can be formed by conproportionation of compounds in which the element has a higher and lower oxidation state if it lies below the line joining these two states. A particularly important example is the synthesis of $HN_3^{-\frac{1}{3}}$ by reacting $N_2^{-II}H_5{}^+$ and $HN^{+III}O_2$ (p. 432). It will be noted that the reduction potential of HN_3 (-3.09 V) is more negative than that of any other reducing agent in acidic aqueous solution so it is thermodynamically impossible to synthesize HN_3 by reduction of N_2 or any of its compounds in such media unless the reducing agent itself contains N (as does hydrazine).
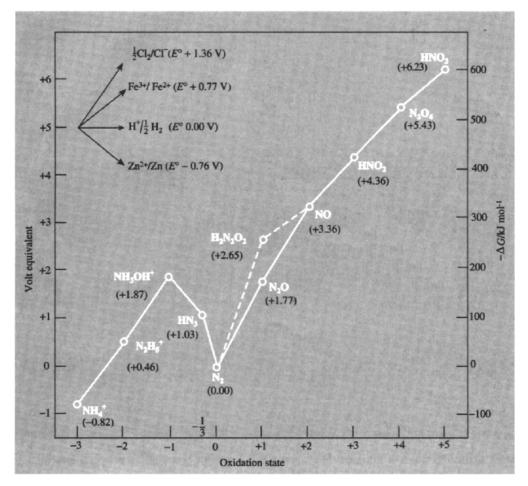
Figure 11.9 Plot of volt equivalent against oxidation state for various compounds or ions containing N in acidic aqueous solution. Note that values of $-\Delta G$ refer to N_2 as standard (zero) but are quoted per mol of N atoms and per mol of N_2; they refer to reactions in the direction $(ox) + ne^- \rightarrow$ (red). Slopes corresponding to some common oxidizing and reducing agents are included for comparison.

In basic solutions a different set of redox equilibria obtain and a different set of reduction potentials must be used. For example:

	$E°/V$
$N_2 + 4H_2O + 2e^- = 2NH_2OH + 2OH^-$	-3.04
$N_2 + 4H_2O + 4e^- = N_2H_4 + 4OH^-$	-1.16
$N_2O + 5H_2O + 4e^- = 2NH_2OH + 4OH^-$	-1.05
$N_2O_2^{2-} + 6H_2O + 4e^- = 2NH_2OH + 6OH^-$	-0.73
$NO_3^- + H_2O + 2e^- = NO_2^- + 2OH^-$	$+0.01$
$N_2H_4 + 4H_2O + 2e^- = 2NH_4^+ + 4OH^-$	$+0.11$
$2NH_2OH + 2e^- = N_2H_4 + 2OH^-$	$+0.73$

A more complete compilation is summarized in Fig. 11.8. It is instructive to use these data to derive a plot of volt equivalent versus oxidation state in basic solution and to compare this with Fig. 11.9 which refers to acidic solutions.

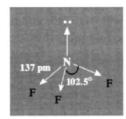### 11.3.5 Nitrogen halides and related compounds [69]

It is a curious paradox that NF_3, the most stable binary halide of N, was not prepared until 1928, more than 115 y after the highly unstable

NCl_3 was prepared in 1811 by P. L. Dulong (who lost three fingers and an eye studying its properties). Pure NBr_3 explodes even at $-100°$ and was not isolated until 1975[87] and NI_3 has not been prepared, though the explosive adduct $NI_3.NH_3$ was first made by B. Courtois in 1813 and several other ammines are known. In all, there are now 5 binary fluorides of nitrogen (NF_3, N_2F_4, *cis*- and *trans*-N_2F_2 and N_3F) and these, together with the cations NF_4^+ and $N_2F_3^+$ and various mixed halides, hydride halides and oxohalides are discussed in this section.

NF_3 was first prepared by Otto Ruff's group in Germany by the electrolysis of molten NH_4F/HF and this process is still used commercially. An alternative is the controlled fluorination of NH_3 over a Cu metal catalyst.

$$4NH_3 + 3F_2 \xrightarrow{Cu} NF_3 + 3NH_4F$$

NF_3 is a colourless, odourless, thermodynamically stable gas (mp $-206.8°$, bp $-129.0°$, $\Delta G_{298}° - 83.3\,kJ\,mol^{-1}$). The molecule is pyramidal with an F–N–F angle of $102.5°$, but the dipole moment (0.234 D) is only one-sixth of that of NH_3 (1.47 D) presumably because the N–F bond moments act in the opposite direction to that of the lone-pair moment:

The gas is remarkably unreactive (like CF_4) being unaffected by water or dilute aqueous acid or alkali; at elevated temperatures it acts as a fluorinating agent and with Cu, As, Sb or Bi in a flow reactor it yields N_2F_4 ($2NF_3 + 2Cu \rightarrow N_2F_4 + 2CuF$). As perhaps expected (p. 198) NF_3 shows little tendency to act as a

ligand, though NF_4^+ is known[88] and also the surprisingly stable isoelectronic species ONF_3 (mp $-160°$, bp $-87.6°$):

$$NF_3 + 2F_2 + SbF_3 \xrightarrow{200°/100\ atm} [NF_4]^+[SbF_6]^-$$

$$2NF_3 + O_2 \xrightarrow[-196°]{electric\ discharge/} 2ONF_3$$

$$3FNO + 2IrF_6 \xrightarrow{20°} ONF_3 + 2[NO]^+[IrF_6]^-$$

ONF_3 was discovered independently by two groups in 1966.[89] Although isoelectronic with BF_4^-, CF_4 and NF_4^+ it has excited interest because of the short N–O distance (115.8 pm), which implies some multiple bonding, and the correspondingly long N–F distances (143.1 pm). Similar partial double bonding to O and highly polar bonds to F have also been postulated for the analogous ion $[OCF_3]^-$ in $Cs[OCF_3]$.[90]

FN_3 is one of the most explosive and thermally unstable covalent azides known. It can be prepared by reacting HN_3 with F_2 and is best handled as a gas at low pressure.[91] The molecular parameters (microwave) are N–F 144.4 pm, N_α–N_β 125.3 pm, N_α–N_ω 113.2 pm, and angles FNN $103.8°$, NNN $170.9°$ (cf HN_3 p. 433) The species NF is known only as a ligand, in the octahedral complex $[ReF_5(NF)]$[92] the complex is made by treating ReF_4N or ReF_3N with XeF_2 and X-ray structural analysis revealed a linear Re–N–F group ($178°$) with N–F 126 pm.

Dinitrogen tetrafluoride, N_2F_4, is the fluorine analogue of hydrazine and exists in both the staggered (*trans*) C_{2h} and *gauche* C_2 conformations

[87] J. LANDER, J. KNACKMUSS and K.-U. THIEDEMANN, *Z. Naturforsch.* **B30**, 464–5 (1975).

[88] K. O. CHRISTE, C. H. SCHACK and R. D. WILSON, *Inorg. Chem.* **16**, 849–54 (1977), and references therein. See also K. O. CHRISTE, R. D. WILSON and I. R. GOLDBERG, *Inorg. Chem.* **18**, 2572–7 (1979). K. O. CHRISTE, R. D. WILSON and C. J. SCHACK, *Inorg. Chem.* **19**, 3046–9 (1980).

[89] See S. A. KINREAD and J. M. SHREEVE, *Inorg. Chem.* **23** 3109–12, 4174–7 (1984) for useful references to preparation and reactions of ONF_3.

[90] K. O. CHRISTE, E. C. CURTIS and C. J. SCHACK, *Spectrochim. Acta* **31A**, 1035–8 (1975).

[91] D. CHRISTEN, H. G. MACK, G. SCHATTE and H. WILLNER, *J. Am. Chem. Soc.* **110**, 707–12 (1988).

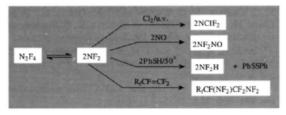[92] J. FAWCETT, R. D. PEACOCK and D. R. RUSSELL, *J. Chem. Soc., Dalton Trans.*, 567–71 (1987).

(p. 428). It was discovered in 1957 and is now made either by partial defluorination of NF_3 (see above) or by quantitative oxidation of NF_2H with alkaline hypochlorite:

$$(NH_2)_2CO(aq) \xrightarrow[\text{(70\% yield)}]{F_2/N_2} NH_2CONF_2$$

$$\xrightarrow[\text{(100\% yield)}]{\text{conc } H_2SO_4} NF_2H \xrightarrow[\text{(100\% yield)}]{NaOCl \ (pH \ 12)} \tfrac{1}{2}N_2F_4$$

N_2F_4 is a colourless reactive gas (mp $-164.5°$, bp $-73°$, $\Delta G_{298}° + 81.2\,kJ\,mol^{-1}$) which acts as a strong fluorinating agent towards many substances, e.g.:

$$SiH_4 + N_2F_4 \xrightarrow{25°} SiF_4 + N_2 + 2H_2$$

$$10Li + N_2F_4 \xrightarrow{-80 \text{ to } +250°} 4LiF + 2Li_3N$$

$$S + N_2F_4 \xrightarrow{110-140°} SF_4 + SF_5NF_2 + \dots$$

It forms adducts with strong fluoride-ion acceptors such as AsF_5 which can be formulated as salts, e.g. $[N_2F_3]^+[AsF_6]^-$. However, its most intriguing property is an ability to dissociate at room temperature and above to give the free radical NF_2. Thus, when N_2F_4 is frozen out from the warm gas at relatively low pressures the solid is dark blue whereas when it is frozen out from the cold gas at moderate pressures it is colourless. At 150°C the equilibrium constant for the dissociation $N_2F_4 \rightleftharpoons 2NF_2$ is $K = 0.03$ atm and the enthalpy of dissociation is $83.2\,kJ\,mol^{-1}$.[93] Such a dissociation, which interprets much of the reaction chemistry of N_2F_4,[94] is reminiscent of the behaviour of N_2O_4 (p. 455) but is not paralleled in the chemistry of N_2H_4:
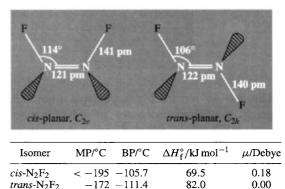

Dinitrogen difluoride, N_2F_2, was first identified in 1952 as a thermal decomposition product of the azide N_3F and it also occurs in small yield during the electrolysis of NH_4F/HF (p. 439), and in the reactions of NF_3 with Hg or with NF_3 in a Cu reactor (p. 439). Fluorination of NaN_3 gives good yields on a small scale but the compound is best prepared by the following reaction sequence:

$$KF + NF_2H \xrightarrow{-80°} KF.NF_2H$$

$$\xrightarrow[\sim 100\% \text{ yield}]{20°} N_2F_2 + KHF_2$$

All these methods give mixtures of the *cis*- and *trans*-isomers; these are thermally interconvertible but can be separated by low-temperature fractionation. The *trans*-form is thermodynamically more unstable than the *cis*-form but it can be stored in glass vessels whereas the *cis*-form reacts completely within 2 weeks to give SiF_4 and N_2O. *Trans*-N_2F_2 can be prepared free of the *cis*-form by the low-temperature reaction of N_2F_4 with $AlCl_3$ or MCl_2 (M = Mn, Fe, Co, Ni, Sn); thermal isomerization of *trans*-N_2F_2 at $70-100°$ yields an equilibrium mixture containing $\sim 90\%$ *cis*-N_2F_2 (ΔH_{isom} $12.5\,kJ\,mol^{-1}$). Pure *cis*-N_2F_2 can be obtained by selective complexation with AsF_5; only the *cis*-form reacts at room temperature to give $[N_2F]^+[AsF_6]^-$ and this, when treated with NaF/HF, yields pure *cis*-N_2F_2. Some characteristic properties are listed below.

cis-planar. C_{2v} *trans*-planar, C_{2h}

Isomer	MP/°C	BP/°C	$\Delta H_f°/kJ\,mol^{-1}$	μ/Debye
cis-N_2F_2	< -195	-105.7	69.5	0.18
trans-N_2F_2	-172	-111.4	82.0	0.00

[93] F. H. JOHNSON and C. B. COLBURN, *J. Am. Chem. Soc.* **83**, 3043–7 (1961).

[94] C. L. BAUMGARDNER and E. L. LAWTON, *Acc. Chem. Res.* **7**, 14–20 (1974).

Several mixed halides and hydrohalides of nitrogen are known but they tend to be unstable, difficult to isolate pure, and of little interest. Examples are[69] $NClF_2$, NCl_2F, $NBrF_2$, NF_2H, NCl_2H and $NClH_2$. The cation $NH_2F_2^+$ has also been prepared as its salts with AsF_6^- and SbF_6^-.[95]

The well known compound NCl_3 is a dense, volatile, highly explosive liquid (mp $-40°$, bp $+71°$, $d(20°)$ 1.65 g cm^{-3}, μ 0.6 D) with physical properties which often closely resemble those of CCl_4 (p. 301). It is much less hazardous as a dilute gas and, indeed, is used industrially on a large scale for the bleaching and sterilizing of flour; for this purpose it is prepared by electrolysing an acidic solution of NH_4Cl at pH 4 and the product gas is swept out of the cell by means of a flow of air for immediate use. NCl_3 is rapidly hydrolysed by moisture and in alkaline solution can be used to prepare ClO_2:

$$NCl_3 + 3H_2O \longrightarrow NH_3 + 3HOCl \text{ (bleach, etc.)}$$

$$NCl_3 + 3H_2O + 6NaClO_2 \longrightarrow 6ClO_2 + 3NaCl$$
$$+ 3NaOH + NH_3$$

$$2NCl_3 + 6NaClO_2 \longrightarrow 6ClO_2 + 6NaCl + N_2$$

The elusive NBr_3 was finally prepared as a deep-red, very temperature-sensitive, volatile solid by the low-temperature bromination of bistrimethylsilylbromamine with BrCl:

$$(Me_3Si)_2NBr + 2BrCl \xrightarrow{\text{pentane}/-87°} NBr_3 + 2MeSiCl$$

It reacts instantly with NH_3 in CH_2Cl_2 solution at $-87°$ to give the dark-violet solid $NBrH_2$; under similar conditions I_2 yields the red-brown solid NBr_2I. The ligands NCl and NBr have been characterized in the purple complexes $[ReF_5(NCl)]$ (mp $\sim80°$, N–Cl 156 pm, angle Re–N–Cl 177°) and $[ReF_5(NBr)]$ (mp $\sim140°$); The preparation parallels that of $[ReF_5(NF)]$ (p. 439), the reagent XeF_2 being replaced by ClF_3 and BrF_3, respectively.[92] The complexes

$[VCl_3(NX)]$ (X = Cl, Br, I) have also been characterized.[96]

Pure NI_3 has not been isolated, but the structure of its well-known extremely shock-sensitive adduct with NH_3 has been elucidated — a feat of considerable technical virtuosity.[97] Unlike the volatile, soluble, molecular solid NCl_3, the involatile, insoluble compound $[NI_3.NH_3]_n$ has a polymeric structure in which tetrahedral NI_4 units are corner-linked into infinite chains of $-N-I-N-I-$ (215 and 230 pm) which in turn are linked into sheets by I–I interactions (336 pm) in the c-direction; in addition, one I of each NI_4 unit is also loosely attached to an NH_3 (253 pm) that projects into the space between the sheets of tetrahedra. The structure resembles that of the linked SiO_4 units in chain metasilicates (p. 349). A further interesting feature is the presence of linear or almost linear N–I–N groupings which suggest the presence of 3-centre, 4-electron bonds (pp. 63, 64) characteristic of polyhalides and xenon halides (pp. 835–8, 897).

Nitrogen forms two series of oxohalides — the nitrosyl halides XNO and the nitryl halides XNO_2. There are also two halogen nitrates $FONO_2$ (bp $-46°$) and $ClONO_2$ (bp 22.3°), but these do not contain N–X bonds and can be considered as highly reactive derivatives of nitric acid, from which they can be prepared by direct halogenation:

$$HNO_3 + F_2 \longrightarrow FONO_2 + HF$$

$$HNO_3 + ClF \longrightarrow ClONO_2 + HF$$

The nitrosyl halides are reactive gases that feature bent molecules; they can be made by direct halogenation of NO with X_2, though fluorination of NO with AgF_2 has also been used and ClNO can be more conveniently made by passing N_2O_4 over moist KCl:

$$2NO + X_2 \longrightarrow 2XNO$$

95 K. O. CHRISTE, *Inorg. Chem.* **14**, 2821–4 (1975).

96 J. STRÄHLE and K. DEHNICKE, *Z. anorg. allg. Chem.* **338**, 287–98 (1965). K. DEHNICKE and W. LIEBETT, *Z. anorg. allg. Chem.* **453**, 9–13 (1979).

97 J. JANDER, Recent chemistry and structure investigation of NI_3, NBr_3, NCl_3 and related compounds, *Adv. Inorg. Chem. Radiochem.* **19**, 1–63 (1976).

$$NO + AgF_2 \longrightarrow FNO + AgF$$

$$N_2O_4 + KCl \longrightarrow ClNO + KNO_3$$

Some physical properties are in Table 11.5. FNO is colourless, ClNO orange-yellow and BrNO red. The compounds, though generally less reactive than the parent halogens, are nevertheless extremely vigorous reagents. Thus FNO fluorinates many metals (nFNO + M → MF_n + nNO) and also reacts with many fluorides to form salt-like adducts such as $NOAsF_6$, $NOVF_6$, and $NOBF_4$. ClNO acts similarly and has been used as an ionizing solvent to prepare complexes such as $NOAlCl_4$, $NOFeCl_4$, $NOSbCl_6$, and $(NO)_2SnCl_6$.[98] Aqueous solutions of XNO are particularly potent solvents for metals (like aqua regia, HNO_3/HCl) since the HNO_2 formed initially, reacts to give HNO_3:

$$XNO + H_2O \longrightarrow HNO_2 + HX$$

$$3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$$

Alkaline solutions contain a similar mixture:

$$4XNO + 3H_2O \longrightarrow HNO_3 + HNO_2 + 2NO + 4HX$$

$$4XNO + 6NaOH \longrightarrow NaNO_3 + NaNO_2 + 2NO$$
$$+ 4NaX + 3H_2O$$

With alcohols, however, the reaction stops at the nitrite stage:

$$XNO + ROH \longrightarrow RONO + HX$$

Nitryl fluoride and chloride, XNO_2, like their nitrosyl analogues, are reactive gases; they feature planar molecules, analogous to the

[98] V. GUTMANN (ed.), in *Halogen Chemistry*, Vol. 2, p. 399, Academic Press, London, 1967; and V. GUTMANN, *Coordination Chemistry in Nonaqueous Solutions*, Springer-Verlag, New York, 1968.

Table 11.5 Some physical properties of XNO[a]

Property	FNO	ClNO	BrNO
MP/°C	−132.5	−59.6	−56
BP/°C	−59.9	−6.4	∼0
ΔH_f°(298 K)/kJ mol^{-1}	−66.5	+51.7	+82.2
ΔG_f°(298 K)/kJ mol^{-1}	−51.1	+66.0	+82.4
Angle X–N–O	110°	113°	117°
Distance N–O/pm	113	114	115
Distance N–X/pm	152	198	214
μ/D	1.81	0.42	—

[a] BrNO dissociates reversibly into NO and Br, the extent of dissociation being ∼7% at room temperature and 1 atm pressure. A similar reversible dissociation occurs with ClNO at higher temperatures.

isoelectronic nitrate anion, NO_3^-. Some physical properties are in Table 11.6. FNO_2 can be prepared by direct reaction of F_2 with NO_2 or $NaNO_2$ or by fluorination of NO_2 using CoF_3 at 300°. $ClNO_2$ can not be made by direct chlorination of NO_2 but is conveniently synthesized in high yield by reacting anhydrous nitric acid with chlorosulfuric acid at 0°C:

$$HNO_3 + ClSO_3H \longrightarrow ClNO_2 + H_2SO_4$$

Reactions of XNO_2 often parallel those of XNO; e.g. FNO_2 readily fluorinates many metals and reacts with the fluorides of non-metals to give nitryl "salts" such as NO_2BF_4, NO_2PF_6, etc. Likewise, $ClNO_2$ reacts with many chlorides in liquid Cl_2 to give complexes such as NO_2SbCl_6. Hydrolysis yields aqueous solutions of nitric and hydrochloric acids, whereas ammonolysis in liquid ammonia yields chloramine and ammonium nitrite:

$$ClNO_2 + H_2O \longrightarrow \{HOCl + HNO_2\}$$
$$\longrightarrow HNO_3 + HCl$$

$$ClNO_2 + 2NH_3 \longrightarrow ClNH_2 + NH_4NO_2$$

Table 11.6 Some physical properties of XNO_2

Property	FNO$_2$	ClNO$_2$	Property	FNO$_2$	ClNO$_2$
MP/°C	−166	−145	Angle X–N–O	118°	115°
BP/°C	−72.5	−15.9	Distance (N–O)/pm	123	120
ΔH_f°(298K)/kJ mol^{-1}	−80	+13	Distance (N–X)/pm	135	184
ΔG_f°(298K)/kJ mol^{-1}	−37.2	+54.4	μ/D	0.47	0.42