109, 579 (1956).
82. A. I. Spasskova and D. I. Rabinovich, Zhur. Obshch. Khim., 30, 2176 (1960).
83. S. Whitby, Ind. Eng. Chem., 47, 807 (1955).
84. E. W. Montroll, J. Amer. Chem. Soc., 63, 1215 (1941).
85. R. F. Tuckett, Trans. Faraday Soc., 41, 351 (1945)
86. S. Ya. Frenkel', "Uspekhi Khimii i Tekhnologii Polimerov" (Progress in the Chemistry and Technology of Polymers), GNTIKhL, Moscow, 1960, pp. 160–183.
87. S. Ya. Frenkel', Vysokomol. Soed., 2, 731 (1960).

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CHEMISTRY OF SOME INORGANIC NITROGEN FLUORIDES

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I. INTRODUCTION

In recent years there has been an increasing number of studies outside the Soviet Union of a new class of compounds characterised by the presence of the NF or NF_2 group. In the USA interest in compounds containing the NF_2 group is due to their use in rocket fuels[1]. The published studies relate mainly to the simplest gaseous nitrogen fluorides, most of which are reagents for the preparation of compounds containing the NF_2 group. These fluorides include tetrafluorohydrazine, the two difluorodiazine isomers, difluoramine, chlorodifluoramine, and fluorine azide.

This review is concerned with the chemistry of these nitrogen fluorides. The chapter on the structure of the nitrogen trifluoride molecule does not embrace all the literature data, but is given solely to provide a more correct understanding of the properties of the nitrogen fluorides.

II. STRUCTURE OF THE NITROGEN TRIFLUORIDE MOLECULE

The geometry of the nitrogen trifluoride molecule has been studied by electron diffraction[2,3] and by microwave spectroscopy[4]; the molecular dimensions have also been obtained from infrared spectroscopy and dipole moment measurements.

The nitrogen trifluoride molecule is an equilateral triangular pyramid in which the apex angle is 102°, N–F distance 1.37 Å, and F... F distance 2.14 Å.

The experimental N–F distance is in good agreement with the interatomic distance calculated from the Schomaker–Stevenson formula[5]:

$$r_{A-B} = r_A + r_B - 0.09(X_A - X_B),$$

where r_A and r_B are the covalent radii of atoms A and B, and X_A and X_B are the corresponding electronegativities. Here $r_F = 0.72$ Å, $r_N = 0.74$ Å, and $X_F - X_N = 0.95$,[6] and hence $r_{A-B} = 1.38$ Å. The above formula takes the ionic nature of the bond into account, and the agreement between the experimental and calculated distances demonstrates that the N–F bond is partially ionic.

The mean energy of the N–F bond, calculated from the heat of formation of NF_3 ($\Delta H = -29.7 \pm 1.8$ kcal mole^{-1} [7]), is 66.3 kcal mole^{-1}. The dissociation energy of the first bond D_{N-F} is determined[8–10] from the thermochemical equation

$$\Delta H_{NF_3} = \Delta H_{NF_2} + \Delta H_F - D_{N-F},$$

where $\Delta H_{NF_2} = 9.8 \pm 2.1$ kcal mole^{-1} (see Section III) and $\Delta H_F = 18.9 \pm 0.5$ kcal mole^{-1};[11] hence $D_{N-F} = 58.4 \pm 4.4$ kcal mole^{-1}. Assuming that the dissociation energies of the other two N–F bonds are the same, these will be 70.5 ± 1.6 kcal mole^{-1}.

Thus, unlike ammonia and many other inorganic substances[12], the energy of dissociation of the first bond in the NF_3 molecule is less than that of succeeding bonds.

Reese and Dibeler[13] recorded the mass spectrum of nitrogen trifluoride, determined the appearance potential of the ions NF_2^+ and NF^+, and calculated the ionisation potentials of the radicals NF_2 and NF. The appearance potential $A \geqslant I + D_{bond}$, where I is the ionisation potential and D_{bond} is the bond energy. The ionisation potentials, calculated from Reese and Dibeler's data using the above values for the N–F bond energies in nitrogen trifluoride and the experimental results of Herron and Dibeler[10], are $I_{NF_2} = 11.9 \pm 0.2$ eV and $I_{NF} = 12.4 \pm 0.3$ eV.

Ramaswamy determined the dielectric constant of NF_3 at -80°, -33°, 25°, and 95°, and calculated the dipole moment to be $\mu = 0.21$ D.[14,15] This low value is surprising (*cf.* the dipole moment of ammonia, which is 1.46 D). Almost all those who have studied the structure of the nitrogen trifluoride molecule have attempted some explanation of this low value, but despite the attempts made[16,17], there is no satisfactory quantitative explanation. The qualitative explanation[2,4,18–20] is that the moment due to the N–F bonds is counteracted by a moment, which must be of opposite sign, produced by the free electrons of N and F because of *sp* hybridisation.

The infrared spectrum of nitrogen trifluoride[21–23] contains four main frequencies: 907 cm^{-1}, $\nu_3(E)$, the doubly degenerate stretching frequency; 1031 cm^{-1}, $\nu_1(A_1)$, the fully symmetrical stretching frequency; 642 cm^{-1}, $\nu_2(A_1)$, the fully symmetrical deformation frequency; and 497 cm^{-1}, $\nu_4(E)$, the doubly degenerate deformation frequency.

The light absorption of nitrogen trifluoride commences at a wavelength < 1800 Å.[24] There are no absorption lines

or bands in the ultraviolet; the whole electronic spectrum appears continuous. An attempt was made[24] to find the absorption coefficient α as a function of the wavelength λ, with the expectation of detecting a discrete spectrum from the nature of the $\alpha-\lambda$ curve but α increases smoothly with decreasing λ. There is intense absorption at 960 Å, which is thought[24] to correspond with the energy of ionisation of NF_3 (934 Å).

III. TETRAFLUOROHYDRAZINE

Tetrafluorohydrazine N_2F_4 was first obtained in 1958 by Colburn and Kennedy[25] from nitrogen trifluoride, and caused great interest among chemists; within two years of its first preparation five different methods for its production had been described.

In Septemper 1960 the Stauffer Chemical Co. (USA) reported its industrial production by conversion of nitrogen trifluoride over carbon[26]. Most of the methods are variations of Colburn's original preparation.

1. Methods for the Preparation of Tetrafluorohydrazine

Colburn and Kennedy[25] obtained tetrafluorohydrazine by thermal conversion of nitrogen trifluoride over stainless steel, copper, arsenic, antimony, or bismuth:

$$NF_3 + M \rightarrow N_2F_4 + MF_n .$$

The reaction was carried out in a flow reactor over copper turnings at 375° with a contact time of 13 min; the degree of conversion of the NF_3 was 42–62%, and the yield of tetrafluorohydrazine was 62–71% based on reacted NF_3. During the reaction a film of copper fluoride is formed, and this hinders the establishment of a steady-state process[27]. The preparative conditions depend on the metal used, *e.g.* a temperature of 250°–300° is used when arsenic is employed[28].

Modifications of Colburn's method are the preparation of tetrafluorohydrazine by thermal conversion of NF_3 over liquid mercury[27] or over carbon[26].

Dresdner *et al.*[27] found that nitrogen trifluoride reacts readily with mercury at optimum temperatures of 320°–330° to form tetrafluorohydrazine, using a flow rate of NF_3 of 40 ml min^{-1}, with the gas bubbling through the liquid mercury for 30–60 sec; the degree of conversion of NF_3 is 72%, and the yield of tetrafluorohydrazine based on reacted NF_3 is 60%†. Water and oxygen-containing substances must be absent.

The method which has attained industrial use is the conversion of NF_3 over carbon[26]. The NF_3 is contacted with a fluidised layer of carbon at 400° ± 10° at a rate of flow of 14.9 ml sec^{-1}, with a time of contact of several seconds. The tetrafluorohydrazine is obtained in 75% yield with 75% conversion of the NF_3. Hexafluoroethane (b.p. -76°), nitrogen trifluoride, and carbon tetrafluoride are also obtained.

Johnson's method for the isolation of tetrafluorohydrazine[29] is based on the differing solubilities of the reaction products in various solvents (chloroform, chlorobenzene, benzene, cyclohexane, or methanol).

† The reported formation in the reaction of small quantities of the active isomer of difluorodiazine is apparently incorrect.

Frazer[30] obtained tetrafluorohydrazine together with difluorodiazine by subjecting nitrogen trifluoride to an electrical discharge in the presence of mercury vapour, using a discharge potential of 2900–3100 V and 1–4 mm Hg pressure. The maximum degree of conversion of nitrogen trifluoride was 16%. The reaction products are tetrafluorohydrazine (50–60% yield based on reacted NF_3), difluorodiazine (12–16% yield), mercury fluoride, and nitrogen.

A process for the preparation of tetrafluorohydrazine based on the reaction

$$2NF_3 + NO = N_2F_4 + 2FNO ,$$

has been proposed[31]. The reaction is carried out at 150°–800°, with contact times between 0.01 sec and 15 min and NF_3 : NO molar ratios of 0.5–2.

The above are the only methods for the production of tetrafluorohydrazine based on the conversion of nitrogen trifluoride.

The presence of nitrogen in the reaction products indicates that the reaction involves the combination of one or more fluorine atoms of the nitrogen trifluoride molecule with the heterogeneous reagent used. In the presence of a heterogeneous reagent the conversion of nitrogen trifluoride comprises three parallel reactions:

$$NF_3 + M \rightarrow N_2F_4 + MF_n,$$
$$NF_3 + M \rightarrow N_2F_2 + MF_n,$$
$$NF_3 + M \rightarrow N_2 + MF_n .$$

The difluorodiazine formed is decomposed by heat or reacts with M, so that under the conditions of the thermal reaction difluorodiazine is effectively absent from the reaction products. When preparing tetrafluorohydrazine by the discharge method, however, the residence time of the gas in the reaction zone is small, conditions are less favourable for the decomposition of difluorodiazine, and its yield is consequently increased.

Tetrafluorohydrazine can be obtained in low yield by the fluorination of ammonia. The homogeneous gas-phase reaction between fluorine and ammonia was studied by Ruff[32]. The main reaction is

$$3F_2 + 2NH_3 = N_2 + 6HF ,$$

but the side-reaction

$$3F_2 + 4NH_3 = NF_3 + 3NH_4F ,$$

was also observed. The yield of nitrogen trifluoride did not exceed 6% based on reacted fluorine. Ruff showed the presence of other nitrogen fluorides, but these were not isolated.

Unlike Ruff, Morrow[33-35] used a copper packing in the reactor, enabling the reaction to be effected under milder conditions (18°). The yield of products depended primarily on the relative amounts of fluorine, ammonia, and nitrogen used, and also on the method of packing the reactor and the quality of the packing. With molar ratios $NH_3 : F_2 : N_2$ = = 1.5–2 : 1.5, the maximum yields were tetrafluorohydrazine 11% and nitrogen trifluoride 24% (based on reacted fluorine).

Cleaver has proposed[36] an electrochemical method for the production of nitrogen fluorides, including tetrafluorohydrazine, which is similar to the usual reactions for preparing nitrogen trifluoride by electrolysis, but with various fluorides (BF_3, PF_5, HF) added to the ammonium hydrogen fluoride electrolyte. The gaseous electrolysis products,

TABLE 1. Physical constants of nitrogen fluorides.

Substance	Mol. wt.	B.p., °C	M.p., °C	Vapour pressure, mm Hg	Heat of vaporisation, kcal mole^{-1}	Trouton's constant	Critical conditions: t, °C	Critical conditions: P, atm	Density, g cm^{-3}	Standard enthalpy of formation, kcal mole^{-1}
Nitrogen trifluoride NF_3	71	−129	−208.5	$\log P = 4.27264 - \frac{613.330}{T}$	2.769	19.94	−40.90	44.72	$d = 2.103 - 3.294 \cdot 10^{-3} T - 4.675 \cdot 10^{-6} T^2$	−29.7±1.8
Tetrafluorohydrazine N_2F_4	104	−73 −74	about −162°	$\log P = -\frac{862.9}{T} + 7.2163$ [41a]	3.170	—	36 37.5	77^{25} 54^{37}	1.5 at −100°	−2±2.5
Difluoramine NF_2H	53	−23	-131^{28} -116^{61}	$\log P = -\frac{1298}{T} + 8.072$	5.940	23.7	130	93	$d = 1.424 - 0.00202t$ $d_{-23} = 1.378$	
Chlorodifluoroamine NF_2Cl	87	−62	between −183 and −196	$\log P = -\frac{950}{T} + 7.478$	4.350	— 21.0		—	—	—
Fluorine azide FN_3	61	approx. −82	approx. −154	—	—	—	—	—	—	—
trans-Difluorodiazine N_2F_2	66	−111.4	−172	$\log P = -\frac{742.3}{T} + 7.470$	3.400		−13	55	—	—
Active difluorodiazine N_2F_2	66	−105.7	below −195	$\log P = -\frac{803.0}{T} + 7.675$	3.670		−1	70	—	+25.3±2.0

* There are also data represented by the equations: $\log P = -\frac{692}{T} + 6.33$ [25] and $\log P = 6.9643 - \frac{811}{T}$. [37]

freed from hydrogen fluoride, contain nitrogen trifluoride (90 mole %), tetrafluorohydrazine (> 4%) and difluorodiazine (> 5%).

Tetrafluorohydrazine has been considered in the USA as an oxidant for rocket fuels[37,38]. It is produced in the USA in two grades by the reaction of nitrogen trifluoride with carbon, a technical grade containing 96% N_2F_4, and 99% N_2F_4. Tetrafluorohydrazine in 1.4 kg amounts is transported in steel cylinders under 7 atm pressure[39].

In 1961 the price of tetrafluorohydrazine in the USA was $200 per kilogramme, but it was considered possible that this could be reduced to the level of prices for fluorine[37].

2. Physical Properties of Tetrafluorohydrazine

Tetrafluorohydrazine is a colourless substance with a characteristic odour resembling that of fluorine‡; its physical properties are given in Table 1. Its heat of formation was determined by Armstrong[40] by the reaction $3N_2F_4 + 4NH_3 = 12HF + 5N_2$. Its infrared frequencies are given in Table 2.[41]

The mass-spectrum of tetrafluorohydrazine[42] consists mainly of the ions NF_2^+ and NF^+. Its nuclear magnetic resonance spectrum has been determined[25].

The structure of the tetrafluorohydrazine molecule has not been fully elucidated. Assuming that the N−F interatomic distances are the same as in nitrogen trifluoride and the N−N distance is the same as in hydrazine, Lide and Mann[43] found that the F−N−F angle is 108°, the N−N−F angle 104°, and the angle of rotation of the NF_2 groups 65°; it was assumed that tetrafluorohydrazine, like hydrazine, has the *cis*-structure.

The dissociation energy of the N−N bond in tetrafluorohydrazine is equal to the heat of the reversible process

TABLE 2. Infrared frequencies of the nitrogen fluorides.

Compound	Lines in the spectrum
Nitrogen trifluoride NF_3	very strong line at 907 cm^{-1} strong line at 1031 cm^{-1} lines of medium intensity at 1809 and 1929 cm^{-1} weak lines at 497, 642, 985, 1135, and 1525 cm^{-1}
Tetrafluorohydrazine N_2F_4	strong lines at 968, 10140, and 700 cm^{-1} lines of medium intensity at 459 and 1937 cm^{-1} weak lines at 469 and 513 cm^{-1}
Nitrogen difluoride NF_2	gas: 1074.3 cm^{-1} matrix: 1069.6, 573.4, and 930.7 cm^{-1}
Difluoramine NF_2H	strong doublet lines at 1430, 1282, and 980 cm^{-1} triplet at 893 cm^{-1}
Chlorodifluoramine $ClNF_2$	strong lines: triplet at 927 cm^{-1} doublet at 855 cm^{-1} triplet at 695 cm^{-1} lines of medium intensity at 747 cm^{-1} weak lines at 1851, 1756, 1696, and 1370 cm^{-1}
trans-Difluorodiazine N_2F_2	strong line at 989 cm^{-1} lines of medium intensity at 1996, 1581, 1434, 1366, 421, and 360 cm^{-1}
Active isomer of difluorodiazine N_2F_2	strong lines at 737, 896, 952, and 1524 cm^{-1} lines of medium intensity at 1774 cm^{-1}

‡ The different colours (pink, blue, green) often observed in liquid tetrafluorohydrazine, which vary with the temperature, are due to the presence of nitric oxide as impurity.

$N_2F_4 \rightleftharpoons 2NF_2$; this was determined experimentally (see below) to be 21.5 ± 1.6 kcal mole^{-1} [10] (*cf.* the dissociation energy of the N–N bond in hydrazine, which is 60 kcal × × mole^{-1} [46]). The values obtained by Herron and Dibeler[44] and Loughran and Mader[45] are high because the reaction $N_2F_4 = 2NF_2$ was not allowed for.

The mean energy of the N–F bond in the NF_2 radical, determined from the heat of formation of the radical (ΔH = 9.8 ± 2.1 kcal mole^{-1}), is 71.0 kcal mole^{-1}; this is the accepted value for the mean energy of the N–F bond in tetrafluorohydrazine.

A most important characteristic of the tetrafluorohydrazine molecule is its reversible dissociation into NF_2 radicals:

$$N_2F_4 \rightleftarrows 2\,NF_2,$$

as found by Colburn and Johnson[8,42]§. This reaction can be considered as definitely established.

The ultraviolet spectrum of tetrafluorohydrazine exhibits absorption bands with a maximum at 2600 Å. The absorption becomes more intense as the temperature is increased and the pressure decreased. This band is considered[8] to be due to absorption by the NF_2 radical.

The infrared spectrum of tetrafluorohydrazine recorded at 1–10 mm Hg and 25°–175° exhibits new lines (at 1074 cm^{-1}) not present in the spectrum of the tetrafluorohydrazine molecule[48]. These lines are fully reversible under changing conditions, and may also be assigned to the NF_2 radical.

The electron paramagnetic resonance spectrum of tetrafluorohydrazine recorded at 20–40 mm Hg and 67°–162° [49] contains a broad band which can be reasonably assigned to the formation of the NF_2 radical, which has one unpaired electron.

The equilibrium $N_2F_4 \rightleftharpoons 2NF_2$ has been studied by several physicochemical methods. Johnson and Colburn[8] used measurements of pressure and of the absorption of monochromatic light (λ = 2600 Å), in each case at 25°–150° and 0.1–0.6 atm. In the first method K_p was found from the pressure increase at various temperatures, and the coefficients A and B of the equation $\log K_p = -A/T + B$ were determined, from which the changes of enthalpy ΔH and entropy ΔS were calculated. In the second method the variation of the intensity of light absorption by the NF_2 radical with the temperature was determined, and the change of enthalpy ΔH calculated.

The dependence of K_p on T is given by the equation

$$\log K_p = -\frac{4.239 \times 10^3}{T} + 8.519,$$

whence ΔH = 19.85 kcal mole^{-1} and ΔS = 39.90 cal mole^{-1} × × deg^{-1}. The light absorption method gives ΔH = = 21.7 kcal mole^{-1}.

From Johnson and Colburn's data[8], the degree of dissociation of tetrafluorohydrazine can be calculated as a function of temperature and pressure (Table 3).

TABLE 3. Degree of dissociation of tetrafluorohydrazine (α)*.

t, °C \ P, atm	1		10^{-1}		10^{-2}		10^{-3}	
	K_p	α	K_p	α	K_p	α	K_p	α
150	$3.67 \cdot 10^{-2}$	0.9	$3.02 \cdot 10^{-2}$	0.26	$2.96 \cdot 10^{-2}$	0.65	$2.95 \cdot 10^{-2}$	0.94
100	$1.94 \cdot 10^{-2}$	0.02	$1.30 \cdot 10^{-2}$	0.05	$1.24 \cdot 10^{-2}$	0.18	$1.23 \cdot 10^{-2}$	0.50
25	$6.3 \cdot 10^{-5}$	0.004	$6.3 \cdot 10^{-5}$	0.01	$6.3 \cdot 10^{-5}$	0.04	$6.3 \cdot 10^{-5}$	0.12
−100	10^{-16}	10^{-8}	10^{-16}	$1.14 \cdot 10^{-8}$	10^{-16}	$4 \cdot 10^{-8}$	10^{-16}	10^{-6}

* The calculation is strictly correct only for the range 100°–150°, for which the conversion factor from K_f to K_p is given. With the other temperature ranges the calculation assumes that the coefficients B_1 and B_2 of the equation $\log K_p = -B_1/T + B_2$ are independent of pressure (concentration).

The equilibrium $N_2F_4 \rightleftharpoons 2NF_2$ has also been studied by electron paramagnetic resonance[49]; ΔH for the reaction was found by measuring the variation of the resonance peak of the radical with the temperature of the gas. The value 19.3 kcal mole^{-1} was found for ΔH (Kennedy and Colburn[50] use the value 19.8 ± 0.8 kcal mole^{-1}).

The mass-spectroscopic method[9] gives ΔH as 21.5 ± ± 1.6 kcal mole^{-1}. Four independent methods thus give values for ΔH for the reaction which agree satisfactorily.

The thermochemical equation

$$\Delta H_{N_2F_4} = 2\Delta H_{NF_2} - D_{N-N},$$

has been used to determine the heat of formation of gaseous NF_2: ΔH = 9.8 ± 2.1 kcal mole^{-1} at 25°.

Harmony and coworkers have studied the infrared spectrum of the NF_2 radical in the gaseous state[48] and in the solid form in a nitrogen matrix at −253° [51] (Table 2). The frequency 1074 cm^{-1} is assigned to symmetrical stretching vibrations. Assuming the N–F distances in NF_2 and NF_3 to be the same, the infrared data were used to calculate the F–N–F angle: this is 104°.

The thermodynamic functions of NF_2 have been calculated[51].

3. Chemical Properties of Tetrafluorohydrazine

Tetrafluorohydrazine can react chemically in two ways:

$$N_2F_4 + M \rightarrow M(NF_2)_n, \quad \text{(I)}$$
$$N_2F_4 + M \rightarrow MF_n + N_2. \quad \text{(II)}$$

Type (I) (radical) reactions arise because of the ready dissociation of tetrafluorohydrazine at the N–N bond, which makes tetrafluorohydrazine a good reagent for the introduction of the NF_2 group. These reactions can arise in two ways. In the first the N–N bond is dissociated by the action on the tetrafluorohydrazine of any free radical produced by the photochemical dissociation of a substance which can react with N_2F_4, and in the second, the NF_2 radicals are produced by the reaction $N_2F_4 \rightleftharpoons 2NF_2$.

According to Frazer[52], a mixture of methyl or ethyl iodide and tetrafluorohydrazine, in which there is no reaction at room temperature in the dark, reacts rapidly on

§ The compound NF_2 was first reported in 1931 by Ruff[47], who obtained a new substance by the reaction between fluorine and ammonia; he determined its boiling point (−125°) and identified it from its molecular weight as NF_2. However, Ruff himself indicated that this conclusion was not necessarily correct, and his results must now be considered as being in error.

irradiation with ultraviolet light of wavelength $\lambda \geq 2600$ Å¶:

$$AlkI + N_2F_4 \xrightarrow{h\nu} AlkNF_2.$$

The reaction products also contain elemental iodine, HCN, and NF_2H. The reaction of CH_3I with N_2F_4 apparently consists of three stages:

$$CH_3I + h\nu = CH_3^{\cdot} + I,$$

$$CH_3^{\cdot} + NF_2 - NF_2 = CH_3NF_2 + NF_2^{\cdot},$$

$$NF_2^{\cdot} + CH_3I = CH_3NF_2 + I.$$

The reaction of AlkI with tetrafluorohydrazine in the presence of nitric oxide gives[53] *N*-fluoro-*N'*-trifluoromethyldiazine-*N'*-oxide $CF_3-N(=O)=N-F$, the first known compound containing the $-N(=O)-N-F$ group. The mechanism of formation of the $=N-F$ group from tetrafluorohydrazine is not clear.

Petry and Freeman[54] have carried out the following photochemical reactions (i)–(v).

$$N_2F_4 + Cl_2 \xrightarrow{h\nu} 2\,NF_2Cl. \qquad (i)$$

The reaction was carried out in a Pyrex vessel at 80° using an excess of chlorine and irradiation with ultraviolet light; it is said to be reversible.

$$N_2F_4 + R-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-R \xrightarrow{h\nu} RCONF_2, \qquad (ii)$$

where R=H, CH_3, or C_6H_5.

A mixture containing 0.06 mole of biacetyl and 0.06 mole of tetrafluorohydrazine irradiated for 16 h with polychromatic light from a mercury lamp gave 0.077 mole of CH_3CONF_2 in 80% yield (calculated on converted tetrafluorohydrazine).

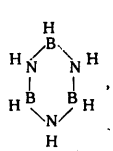
$$N_2F_4 + (CH_3)_2\underset{\underset{CN}{|}}{C}-N=N-\underset{\underset{CN}{|}}{C}=(CH_3)_2 \xrightarrow{h\nu} (CH_3)_2\underset{\underset{CN}{|}}{C}-NF_2, \qquad (iii)$$

$$N_2F_4 + (CH_3)_3C\equiv N-N\equiv CC(CH_3)_3 \xrightarrow{h\nu} (CH_3)_3CNF_2, \qquad (iv)$$

$$N_2F_4 + (C_6H_5)_3C-C(C_6H_5)_3 \xrightarrow{h\nu} (C_6H_5)_3CNF_2. \qquad (v)$$

In reactions (i)–(v) organic radicals or chlorine atoms are apparently first produced photochemically, and then react with the tetrafluorohydrazine.

The second form of the type (I) reaction of tetrafluorohydrazine is found in its reaction with acetaldehyde at 150° [54] and with diborane at 140°–160° and a partial pressure of tetrafluorohydrazine of less than 50 mm Hg.[55] In the latter reaction Pearson and Frazer obtained a mixture of fluoroborazines of general formula $B_3N_3H_nF_{6-n}$, and also BF_3, B_5H_9, H_2, N_2, and $BF_3.NH_3$. Separation of the fluoroborazines gave fractions consisting of mixtures of the isomers $B_3N_3H_5F$, $B_3N_3H_4F_2$, and $B_3N_3H_3F_3$; these are fluoro-derivatives of borazole:



containing the fluorine and hydrogen atoms in different relative positions. Infrared data indicated that the mixture also contained NF_2 derivatives of borazole.

¶ Frazer quotes $\lambda \geq 2750$ Å (Ed. of Translation).

The formation of difluoramine from tetrafluorohydrazine and thiophenol at 50° [56] (see Section IV) is also a reaction of this type.

These two cases of dissociation of the N–N bond are not the only possible type (I) reactions of tetrafluorohydrazine, which would be expected to undergo dissociation at the N–N bond by the direct action of substances having an odd number of outer electrons, such as nitrogen dioxide, nitric oxide, and oxygen.

The ability of tetrafluorohydrazine to undergo type (II) reactions $N_2F_4 + M \rightarrow MF_n + N_2$ is shown by its reaction with aqueous potassium iodide solution[57]. Pankratov and coworkers have shown that two parallel reactions take place:

$$N_2F_4 + 10KI + 8H_2O = 5I_2 + 4KF + 2NH_4OH + 6KOH, \qquad (1)$$

$$N_2F_4 + 4KI = 2I_2 + 4KF + N_2. \qquad (2)$$

Reaction (1) is a type (I) reaction, the tetrafluorohydrazine behaving like an NF_2 radical, which reacts with the potassium iodide solution similarly to difluoramine (see Section IV). Reaction (2) is a type (II) reaction, the tetrafluorohydrazine behaving as a normal fluorinating agent, like nitrogen trifluoride and difluorodiazine.

The relative proportions of reactions (1) and (2) depend on the pH of the medium; tetrafluorohydrazine reacts by reaction (2) to the extent of 65% of the overall process in acid medium and 90% in a neutral medium.

Colburn and Kennedy[56] were probably dealing with a type (II) reaction when reacting tetrafluorohydrazine with thiophenol, arsine, and n-butanethiol (see Section IV), but they did not describe the reaction.

The relative proportions of the two types of tetrafluorohydrazine conversion depend on the actual experimental conditions, but primarily on the other reactant. If this has an odd number of outer electrons (such as the O_2 and NO_2 radicals), the tetrafluorohydrazine undergoes a type (I) radical reaction; if it does not have an odd number of outer electrons, and particularly if it is a reducing agent, it will react with the electronegative fluorine atoms to give a type (II) reaction.

The thermal stability of tetrafluorohydrazine has not been studied. It would appear[29] that under certain conditions tetrafluorohydrazine can explode, producing nitrogen trifluoride and nitrogen.

IV. DIFLUORAMINE AND CHLORODIFLUORAMINE

1. Difluoramine

Three fluorine derivatives of ammonia are possible: the known nitrogen trifluoride NF_3, difluoramine NF_2H, and fluoramine NFH_2.

Ruff[47,58] was the first to refer to fluoramines. In the electrolysis of ammonium hydrogen fluoride to obtain nitrogen trifluoride as the main product, he prepared some new compounds in very small quantities. Separation of the by-products gave fractions of molecular weight corresponding by the formulae NF_2H, NFH_2, and NF_2. Difluoramine was identified by reaction of the gas with molten sodium. For difluoramine, Ruff found b.p. -65° and m.p. -125°.

Ruff identified fluoramine NFH_2 only by its molecular weight; its b.p. was estimated to be -77°. However, later work has not confirmed Ruff's results (method of production, physical constants), nor has the preparation of fluoramine been confirmed.

The data of Ruff and Staub on fluoramines (and especially on nitrogen difluoride), and also the results obtained by Kreft[59] and Ch'ih Chang-li[60] are dubious; Kennedy and Colburn[28] must be considered the first to obtain difluoramine. Nothing has yet been published on fluoramine NFH_2.

Three methods are known for the preparation of difluoramine: (*i*) Kennedy and Colburn's method, by the conversion of nitrogen trifluoride over arsenic in the presence of water vapour[28]; (*ii*) the reaction of tetrafluorohydrazine with mercaptans and arsine[56]; and (*iii*) Lawton and Weber's method, by the fluorination of urea[61]. Attempts to prepare fluoramine by electrolysis of ammonium hydrogen fluoride[28], as in Ruff's method[47], have been unsuccessful.

Kennedy and Colburn[28,56] obtained difluoramine from nitrogen trifluoride over arsenic at 250°–300° in the presence of water vapour; it was obtained as a by-product in low yield, with tetrafluorohydrazine as the main product. The difluoramine is apparently obtained by a secondary reaction of the tetrafluorohydrazine with arsine.

Difluoramine can be obtained by reaction of tetrafluorohydrazine with thiophenol, n-butanethiol, or arsine[56], in each case at 50°. Thiophenol gives the greatest yields:

$$N_2F_4 + 2\,C_6H_5SH = 2\,NF_2H + C_6H_5SSC_6H_5.$$

The reaction is carried out under static conditions in glass apparatus for 4 h with a fivefold excess of thiophenol. The yield of difluoramine was 74%. In metal apparatus there is more formation of nitrogen. This reaction was not identified, but is probably a type (II) conversion:

$$N_2F_4 + M \rightarrow MF_n + N_2.$$

The reaction with n-butanethiol was also carried out under static conditions at 50°–60° for 2 h with a fivefold excess of mercaptan. In this case nitrogen formation was the main reaction, with only a 9% yield of difluoramine. Unlike the reduction with thiophenol, difluoramine is only produced in stainless steel apparatus, and not in glass.

The reaction $N_2F_4 + AsH_3 \rightarrow NF_2H + As$ was carried out under static conditions for 1 h at 50° in a stainless steel cylinder at atmospheric pressure with a 1 : 1 molar ratio of the reactants; difluoramine was produced in 52% yield. The gaseous reaction products contained difluoramine, nitrous oxide (34 mole %), and unreacted arsine (8.5 mole %) and tetrafluorohydrazine (4.3 mole %).

Difluoramine can be obtained analogously in all reactions of tetrafluorohydrazine with organic compounds containing labile hydrogen, the hydrogen being replaced by the NF_2 group[54].

In the method of Lawton and Weber[61] the fluorination of urea produces a yellow liquid containing 16% of active fluorine and 45–55% of total fluorine; difluoramine, CO_2, SiF_4, COF_2, and HNCO have been found in the reaction products. The yield of difluoramine is 15%, based on the fluorine introduced. Apparently all the active fluorine in the urea fluorination products is present as difluoramine. After distillation of the volatile fractions, the residue contains difluoraminourea[62].

The fluorination of ammonia[34] also produced difluoramine, which was not separated, but absorbed in water together with the ammonia. The presence of difluoramine was in fact only deduced from the explosions which occurred during the reaction. Difluoramine is apparently also formed as a by-product in the fluorination of sodamide[63]. It is thus seen that of all the methods for the preparation of difluoramine, only the reduction of tetrafluorohydrazine produces it in good yield.

The physical constants of difluoramine[28,61] are given in Table 1. Attention is directed to the different values reported for the melting point: -131°,[28] and -116°.[61] The infrared frequencies of difluoramine[28] are given in Table 2. There have been no other structural studies on difluoramine.

Difluoramine is an unstable substance which is liable to explode. Solid difluoramine at low temperatures apparently has a greater sensitivity towards explosion. There are indications[34] that liquid and solid difluoramine explodes on contact with air.

An important property of difluoramine is its ability to lose hydrogen and produce tetrafluorohydrazine on contact with various solids[61]; thus with lithium hydride the yield of tetrafluorohydrazine is 70%.

The lability of the hydrogen atom is demonstrated by the reaction of difluoramine with boron trichloride to form the new product chlorodifluoramine[64] (see below).

The reaction of difluoramine with hydriodic acid has been described:

$$NF_2H + 4HI = 2I_2 + NH_4F + HF.$$

The I : F atomic ratio is 2, *i.e.* the reaction can be formally represented as follows:

$$NF_2H + 2HI = I_2 + 2HF + \cdot\ddot{N}H,$$

$$\cdot\ddot{N}H + 2HI = I_2 + NH_3,$$

$$\overline{NF_2H + 4HI = 2I_2 + NH_4F + HF}.$$

Difluoramine reacts with water[34], probably according to the equation

$$NF_2H + 2H_2O = NH_4F + HF + O_2.$$

Difluoramine therefore has (*i*) a strong oxidising action, (*ii*) a labile hydrogen atom, making difluoramine a good reagent for the introduction of NF_2 groups, and (*iii*) it is unstable and liable to explode.

2. Chlorodifluoramine

Chlorodifluoramine NF_2Cl was first obtained by Petry[64] in 1960 by the reaction between difluoramine and boron trichloride. The reactants were condensed into an evacuated flask at -130°, and formed a white solid stable up to -80°. The product decomposed on heating to room temperature to volatile compounds and an involatile solid whose composition was not determined. The volatile products were hydrogen chloride, chlorine, and chlorodifluoramine; the yield of chlorodifluoramine was 50%.

Chlorodifluoramine was also prepared by Petry and Freeman[54] by the photochemical reaction between tetrafluorohydrazine and chlorine; the reaction conditions and yield of chlorodifluoramine were not reported.

Table 1 gives the physical constants of chlorodifluoramine, and Table 2 the frequencies of its infrared

spectrum[64]. Its mass spectrum and nuclear magnetic resonance spectrum have been determined[64].

Chlorodifluoramine is a colourless gas which does not react with atmospheric oxygen. Unlike difluoramine, it is relatively stable: according to Petry, it is not decomposed at room temperature in Pyrex vessels for a long time.

Like difluoramine with its labile hydrogen atom, chlorodifluoramine has a labile chlorine atom. It reacts with mercury at room temperature:

$$2NF_2Cl + 2Hg = N_2F_4 + Hg_2Cl_2.$$

It loses its chlorine when reacted with ammonia at 150°, producing ammonium chloride, and reacts with a solution of sodium in liquid ammonia at -50° to form sodium chloride and fluoride.

Chlorodifluoramine may prove to be of considerable interest as a reagent for the introduction of NF_2 groups.

V. FLUORINE AZIDE AND THE DIFLUORODIAZINE ISOMERS

1. Fluorine Azide

Fluorine azide FN_3 is a very unstable explosive substance which was obtained in 1942 by Haller[65] by the reaction between gaseous hydrogen azide, diluted with nitrogen, and elemental fluorine at 25° in a tubular copper reactor 1 m in length and 0.6 cm in diameter. The optimum temperature is 25°; at 0° the yield of fluorine azide is low, while at 50° the fluorine azide already undergoes decomposition. The yield of fluorine azide was not determined, and the amounts of fluorine, nitrogen, and hydrogen azide used were not measured. The reaction products contain ammonium fluoride but no hydrogen fluoride, and Haller therefore assumes the reaction to proceed according to the equation

$$4HN_3 + 2F_2 = NH_4F + N_2 + 3FN_3.$$

The ammonium fluoride is thought to form by the reaction

$$3HN_3 + HF = NH_4F + 4N_2.$$

The extremely explosive nature of fluorine azide has hindered the study of its properties, and it has only been identified by its molecular weight. Its preparation from hydrogen azide, its explosive nature, and its molecular weight all indicate that the substance obtained by Haller is in fact fluorine azide.

Fluorine azide is a greenish yellow gas resembling chlorine, with an odour like that of ClO_2. It condenses to an oily greenish yellow liquid at -82° and solidifies to greenish yellow crystals at -154°; these temperatures were not accurately determined, and may not be correct. Fluorine azide explodes on evaporation. According to Haller, solid fluorine azide does not usually explode. The liquid explodes when subjected to slight shock or vibration, or to the action of a 100 W lamp at a distance of 30 cm. While the liquid explodes the gas does not detonate at pressures up to 200 mm Hg.

Gaseous fluorine azide is decomposed by heat: at 25° the colour of the gas is completely lost after 1 h, and at 100° the colour disappears within a few minutes. Fluorine azide decomposes to form difluorodiazine:

$$2FN_3 = N_2F_2 + 2N_2.$$

Fluorine azide also decomposes when evaporated. By analogy with the decomposition of HN_3, which according to Audrieth[66] proceeds by way of the biradical $\cdot\dot{N}H$, Haller assumes that the decomposition of FN_3 proceeds by way of the biradical $\cdot\dot{N}F$.

Fluorine azide reacts with elemental fluorine. Reaction is slow at room temperature, but at 80° in excess fluorine all the fluorine azide is converted to nitrogen trifluoride.

With alkali FN_3 reacts to form HF [fluoride? (Ed. of Translation)]; an alkaline solution treated with FN_3 has oxidising properties. Haller considers that nitrous acid is formed during the reaction between FN_3 and KOH, by analogy with its formation in the reaction of HN_3 with alkali.

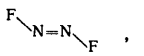
Fluorine azide reacts with water; it reacts explosively at room temperature with gaseous ammonia and with hydrogen. It displaces iodine from aqueous potassium iodide solution.

Dry fluorine azide does not react with glass within 40 h; the moist gas immediately produces a film on the glass.

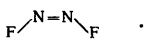
Gaseous fluorine azide dissolves at low temperatures in anhydrous liquid HF, NH_3, HN_3, pentane, acetone, and Freons. Haller estimated the solubility of fluorine azide qualitatively by the solvent's taking on the greenish yellow colour of the FN_3.

2. The Difluorodiazines

Two difluorodiazines are known, the chemically inactive isomer which is *trans*-difluorodiazine:



and the chemically active isomer which is apparently *cis*-difluorodiazine:



The first report on difluorodiazine was by Haller[65], who obtained it by the thermal decomposition of fluorine azide; it was identified only by its molecular weight.

Difluorodiazine is obtained by the electrolysis of ammonium hydrogen fluoride[36,67,68] as a by-product accompanying nitrogen trifluoride.

According to Colburn[67], difluorodiazine is obtained in 5–10% yield (based on the gases condensed in liquid nitrogen) by the electrolysis of fused (120°–130°) ammonium hydrogen fluoride. The current density may be 0.03–0.04 A cm^{-2}.[68] A solution of ammonium fluoride in liquid hydrogen fluoride can also be used as electrolyte. Difluorodiazine is also obtained as a by-product in all preparations of tetrafluorohydrazine[23,25,30,33].

The difluorodiazine isomers have been separated by chromatography[67], which gave 99.7% pure *trans*-isomer. Low-temperature distillation of the isomers gave the active isomer containing not more than 2.1% of *trans*-isomer.

Both isomers are colourless gases with a characteristic odour resembling that of fluorine. The physical constants of difluorodiazine[67] are given in Table 1, and its infrared frequencies[69] in Table 2.

The enthalpy of formation of the active isomer of difluorodiazine, determined by Pankratov *et al.* from its

reaction with acid potassium iodide solution[70], is 25.3 ± ± 2.0 kcal mole^{-1} at 25° and 20.5 ± 2.0 kcal mole^{-1} at -105.7° (for the liquid isomer). Herron and Dibeler[10] refer to a private communication from Armstrong and Marantz, and quote the values 16.4 kcal mole^{-1} and 19.4 kcal mole^{-1} for the enthalpy of formation of the *cis*- and *trans*-isomer respectively, but without giving any experimental data.

The nuclear magnetic resonance spectra of both isomers have been determined[67,71].

The structure of the difluorodiazine isomers was first studied by electron diffraction by Bauer[72], who assumed that the gas is an equimolar mixture of *cis*- and *trans*--difluorodiazine and that both isomers have the same structural parameters. The values obtained by Bauer (r_{N-F} = 1.44 ± 0.04 Å, $r_{N=N}$ = 1.25 ± 0.04 Å, ∠ NNF = = 115° ± 5°) require confirmation. Analysis of the nuclear magnetic resonance spectra of the difluorodiazine isomers has suggested[71] that the valence angles are different in the two isomers.

The question of the structure of the difluorodiazine isomers has not yet been definitely solved. Colburn *et al.*[67] have shown that the isomers have different chemical properties. The chemically inactive isomer was allotted the *trans*-structure, and the chemically active isomer the *cis*-structure, since the inactive isomer has the lower boiling point and higher melting point, as would be expected for the compound with the smaller dipole moment, *i.e.* the *trans*-isomer. It was also reported that there is some evidence for a third very unstable isomer, in all probability of the structure:



The *trans*-structure of the chemically inactive isomer is definitely established, but the question of the structure of the active isomer is still under discussion.

Sanborn[69,73] has suggested that the active isomer has the 1,1-structure:



mainly on the basis of his analysis of the infrared spectrum of the active isomer and because of the similar frequencies of deformation vibrations in this difluorodiazine isomer and in carbonyl fluoride COF_2, which is isoelectronic with 1,1-difluorodiazine. However, mass-spectroscopic studies[10,74] and nuclear magnetic resonance (NMR) data favour the *cis*-structure.

The mass spectra of the active isomer have no peak of mass 52, corresponding to the ion NF_2^+, the expected disintegration product of the 1,1-isomer.

The assignment of the NMR spectra[71] is also in agreement with the *cis*-structure: both nitrogen atoms in the NMR spectrum of the active isomer have the same chemical shift. According to Herron[10], the appearance potentials of the ions NF^+ and N_2F^+ are equal for the active and inactive isomers. He refers to a private communication from Armstrong regarding the enthalpy of formation of the isomers (16.4 kcal mole^{-1} for the active isomer and 19.4 kcal mole^{-1} for the *trans*-isomer); the closeness of these energy values also indicates that the active isomer has the *cis*-structure. The active difluorodiazine isomer is thus apparently the *cis*-isomer.

The bond energies in the molecule of the active difluorodiazine isomer can be calculated from the known enthalpies of formation of the isomer[70] and the NF group. The latter is found from the enthalpy of formation of the NF_2 radical and the average energy of the N–F bond in the NF_2 radical, assuming that the average bond energy is equal to the dissociation energy of the first N–F bond[10]. The energy of the N=N bond is calculated from the thermochemical equation

$$E_{N=N} = 2\Delta H_{NF} - \Delta H_{N_2F_2}.$$

Since ΔH_{NF} = 61.4 ± 4.2 kcal mole^{-1} and $\Delta H_{N_2F_2}$ = 25.3 ± ± 2.0 kcal mole^{-1}, $E_{N=N}$ = 97.5 ± 6.4 kcal mole^{-1}.

Putner[75] has calculated the thermodynamic functions of *trans*-difluorodiazine from the infrared frequencies and Bauer's structural parameters. The functions are given for the range 100°–6000°K.

The difluorodiazines are fluorinating agents, reacting by dissociation of the N–F bond to form fluorides and nitrogen; for example, they react with mercury and potassium iodide to form the corresponding fluorides and nitrogen. Difluorodiazine is a polymerisation initiator for hydrocarbons, such monomers as methyl methacrylate, styrene, and cyclopentadiene polymerising in contact with gaseous difluorodiazine at a pressure of the latter of 300 mm Hg. At room temperature the polymerisation took 12 h or less. Difluorodiazine catalyses the polymerisation of tetrafluoroethylene at 125° and of ethylene and propene at 140°. The polymerisation of ethylene and propene produces polymers containing fluorine[67].

The active isomer reacts considerably more rapidly in all chemical reactions than the *trans*-isomer; thus the former reacts with glass and is completely converted to SiF_4 and nitrogen within two weeks, while with the *trans*--isomer there is no reaction with glass in a month.

The isomers also show different rates of reaction with potassium iodide solution[70] and mercury. This substantial difference in the chemical properties of isomers having close energy characteristics is surprising.

The difluorodiazines do not react with oxygen or water at room temperature.

Both difluorodiazine isomers are relatively stable to heat[67]. On heating, the *trans*-isomer is first converted into the active isomer, but without decomposition into its elements, which does not occur until about 300°. Heating the isomers to 285° produces an equilibrium mixture containing 13% of the *trans*-isomer and 87% of the active isomer.

1. C. J. Hoffman, and R. G. Neville, Chem. Rev., 62, 1 (1962).
2. V. Schomaker and C. S. Lu, J. Amer. Chem. Soc., 72, 1182 (1952).
3. C. S. Lu and V. Schomaker, Acta Cryst., 3, 65 (1950).
4. F. Sheridan and W. Gordy, Phys. Rev., 79, 513 (1950).
5. V. Schomaker and D. P. Stevenson, J. Amer. Chem. Soc., 73, 37 (1941).
6. W. Gordy and W. Thomas, J. Chem. Phys., 24, 439 (1956).
7. G. T. Armstrong, J. Amer. Chem. Soc., 81, 3798 (1959).
8. F. A. Johnson and C. B. Colburn, J. Amer. Chem. Soc., 83, 3043 (1961).
9. J. T. Herron and V. H. Dibeler, J. Chem. Phys., 35, 747 (1961).

10. J. T. Herron and V. H. Dibeler, J. Res. Nat. Bur. Stand., 65A, 405 (1961).
11. W. H. Evans, T. R. Munson, and D. D. Wagman, J. Res. Nat. Bur. Stand., 55, 147 (1955).
12. A. P. Altschuller, J. Chem. Phys., 22, 1947 (1954).
13. R. M. Reese and V. H. Dibeler, J. Chem. Phys., 24, 1175 (1956).
14. K. Ramaswamy, Proc. Indian Acad. Sci., No. 4, 364 (1935).
15. H. Watson, G. Kane, and K. Ramaswamy, Proc. Roy. Soc., 156A, 137 (1936).
16. M. Mashima, J. Chem. Phys., 24, 489 (1956).
17. M. Mashima, J. Chem. Phys., 25, 779 (1956).
18. P. Kisliuk, J. Chem. Phys., 25, 779 (1956).
19. S. N. Ghosh, R. Trambarulo, and W. Gordy, J. Chem. Phys., 21, 303 (1953).
20. P. Kisliuk, J. Chem. Phys., 22, 86 (1954).
21. M. K. Wilson and S. R. Polo, J. Chem. Phys., 20, 1716 (1952).
22. C. R. Bailey, J. B. Hale, and F. W. Thompson, J. Chem. Phys., 5, 274 (1937).
23. E. L. Pace and L. Pierce, J. Chem. Phys., 23, 1948 (1955).
24. S. R. La Paglia and A. B. F. Duncan, J. Chem. Phys., 34, 1003 (1961).
25. C. B. Colburn and A. Kennedy, J. Amer. Chem. Soc., 80, 5004 (1958).
26. Chem. Eng. News, 38, 38, 85 (1960).
27. R. D. Dresdner, F. N. Tlumac, and J. A. Young, J. Inorg. Nuclear Chem., 14, 299 (1960).
28. A. Kennedy and C. B. Colburn, J. Amer. Chem. Soc., 81, 2906 (1959).
29. F. A. Johnson, U. S. P. 3 013 631 (19th Dec., 1961).
30. J. W. Frazer, J. Inorg. Nuclear Chem., 11, 166 (1959).
31. B. P. 895 943 (E. I. Du Pont de Nemours and Co.) (9th May, 1962).
32. O. Ruff and E. Hanke, Z. anorg. Chem., 197, 394 (1931).
33. S. Morrow, D. D. Perry, and M. S. Cohen, J. Amer. Chem. Soc., 81, 6338 (1959).
34. S. Morrow, D. D. Perry, M. S. Cohen, and C. Schoenfelder, J. Amer. Chem. Soc., 82, 5301 (1960).
35. Chem. Eng. News, 38, 16, 82 (1960).
36. C. S. Cleaver, U. S. P. 2 958 634 (Nov., 1960).
37. Astronautics, 6, 80 (1961).
38. A. J. Zaehringer, Missles and Rockets, 5, 36 (1959).
39. Chem. Eng., 68, 92 (1961).
40. G. T. Armstrong, S. Marantz, and C. F. Coyle, U. S. Nat. Bur. Standards, Report No. 6584, October, 1959.
41. C. W. Schoenfelder, J. Chromatog., 7, 281 (1962).
42. C. B. Colburn and F. A. Johnson, J. Chem. Phys., 33, 1869 (1960).
43. D. R. Lide and D. E. Mann, J. Chem. Phys., 31, 1129 (1959).
44. J. T. Herron and V. H. Dibeler, J. Chem. Phys., 33, 1595 (1960).
45. E. D. Loughran and C. H. Mader, J. Chem. Phys., 32, 1578 (1960).
46. M. Szwarc, Proc. Roy. Soc., 198A, 267 (1949).
47. O. Ruff and L. Staub, Z. anorg. Chem., 198, 32 (1931).
48. M. D. Harmony, R. J. Myers, L. J. Schoen, D. R. Lide, and D. E. Mann, J. Chem. Phys., 35, 1129 (1961).
49. L. H. Piette, F. A. Johnson, K. A. Booman, and C. B. Colburn, J. Chem. Phys., 35, 1481 (1961).
50. A. Kennedy and C. B. Colburn, J. Chem. Phys., 35, 1892 (1961).
51. M. D. Harmony and R. J. Myers, J. Chem. Phys., 37, 636 (1962).
52. J. W. Frazer, J. Inorg. Nuclear Chem., 16, 63 (1960).
53. J. W. Frazer, B. E. Holder, and E. F. Worden, J. Inorg. Nuclear Chem., 24, 45 (1962).
54. R. C. Petry and J. P. Freeman, J. Amer. Chem. Soc., 83, 3912 (1961).
55. R. K. Pearson and J. W. Frazer, J. Inorg. Nuclear Chem., 21, 188 (1961).
56. J. P. Freeman, A. Kennedy, and C. B. Colburn, J. Amer. Chem. Soc., 82, 5304 (1960).
57. A. V. Pankratov, L. A. Akhanshchikova, O. N. Shalaeva, and T. V. Kuznetsova, Zhur. Neorg. Khim. (in the press).
58. O. Ruff, Angew. Chem., 47, 739 (1933).
59. O. Kreft, German P. 448 929.
60. Ch'ih Chang-li, Thesis, Breslau, 1937.
61. E. A. Lawton and J. Weber, J. Amer. Chem. Soc., 81, 4755 (1959).
62. E. A. Lawton, E. F. C. Cain, D. F. Shefhan, and M. Warner, J. Inorg. Nuclear Chem., 17, 188 (1961).
63. A. V. Pankratov and E. Ya. Khananova, Zhur. Neorg. Khim., 7, 1743 (1962) [Russ. J. Inorg. Chem., 898 (1962)].
64. R. C. Petry, J. Amer. Chem. Soc., 82, 2400 (1960).
65. J. F. Haller, "Study of the Preparation, Structure, Properties, and Decomposition of Fluorine Azide and Difluorodiazine", Thesis, 1942, Cornell Univ., USA.
66. L. F. Audrieth, Chem. Rev., 15, 191 (1934).
67. C. B. Colburn, F. A. Johnson, A. Kennedy, K. McCallum, L. C. Metzger, and C. O. Parker, J. Amer. Chem. Soc., 81, 6397 (1959).
68. M. Schmeisser and P. Sartori, Angew. Chem., 71, 523 (1959).
69. R. H. Sanborn, J. Chem. Phys., 33, 1855 (1960).
70. A. V. Pankratov, A. N. Zercheninov, O. G. Talakin, O. M. Sokolov, and N. A. Knyazeva, Zhur. Fiz. Khim., 37, 6 (1963) [wrong Ref. (Ed. of Translation)].
71. J. H. Noggle, I. D. Baldeschwieler, and C. B. Colburn, J. Chem. Phys., 37, 182 (1962).
72. S. H. Bauer, J. Amer. Chem. Soc., 69, 3104 (1947).
73. R. H. Sanborn, J. Chem. Phys., 34, 2189 (1961).
74. R. Ettinger, F. A. Johnson, and C. B. Colburn, J. Chem. Phys., 34, 2187 (1961).
75. E. Putner, J. Chem. Eng. Data, 7, 398 (1962).