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Bakh Institute of Biochemistry,
Academy of Sciences of the USSR

PHYSICOCHEMICAL PROPERTIES OF CHLORINE TRIFLUORIDE

Yu. D. Shishkov and A. A. Opalovskii

CONTENTS

Introduction 375

1. Preparation of chlorine trifluoride 358

2. Physical properties of chlorine trifluoride 358

3. Chemical properties of chlorine trifluoride 360

INTRODUCTION

Elemental fluorine can now be made in large quantities and this has facilitated the study of the physical and chemical properties of a number of inorganic fluorides. Among these halogen fluorides are of great theoretical and practical interest. Emeléus and Woolf [1], have shown that the halogen fluorides are ionising solvents which dissociate according to the equation

$$2MF_n \rightleftharpoons MF_{n-1}^{+} + MF_{n+1}^{-}.$$

The physical and chemical properties of the halogen fluorides can be explained by considering them as self-ionising solvents. The great experimental difficulties associated with the handling of these highly reactive compounds did not permit reliable determinations of their physical constants until recently. Table 1 gives some physical properties of known halogen fluorides (figures for elemental fluorine are given for comparison) [2-41].

All the halogen fluorides are powerful fluorinating agents and it is interesting to consider their chemical properties from this point of view. The compounds can be arranged in the following order of reactivity: $ClF_3 > BrF_5 > IF_7 > ClF > BrF_3 > IF_5 > BrF$, although in a number of cases the characteristics of the halogen fluorides as fluorinating agents are known only qualitatively. Chlorine trifluoride is the most reactive of the known halogen fluorides.

The halogen fluorides are of practical importance as fluorinating agents in the preparation of a number of higher fluorides [21-24] and especially of uranium hexafluoride, used in the regeneration of nuclear fuel [25-28]. Complete combustion of the fuel is not achieved in atomic reactors. Consequently several combustion cycles with intermediate regeneration cycles are necessary for its complete utilisation. Fractional distillation is the most suitable method for regenerating nuclear fuel because the technology of this process has been well developed and uranium is regenerated

TABLE 1. Some physical properties of halogen fluorides and fluorine.

Halogen fluoride	m.p., °K	b.p., °K	Heat of formation, kcal mole^{-1}	Conductivity at 25°, ohm^{-1}cm^{-1}	Trouton's constant	Fluorine content, %	Density at 25°, g cm^{-3}
ClF_3	196.84	284,79	37.9+1.0	3.10^{-9}(0°)	20.8	61.62	1.8094
ClF	119	172	13.3±2.1	—	28.0	34.86	—
BrF_5	212.7	313.94	—	$9.1\cdot10^{-8}$	23.2	54.28	2.460
BrF_3	281.93	398.83	75	$8.0\cdot10^{-3}$	25.7	41.60	2.8030
BrF	240	293	18,4±0 5	—	20.5	19.19	—
IF_7	278	277 sublimes	—	—	<26.4	51.15	2.75
IF_5	282.61	373.64	204 7	$5.4\cdot10^{-6}$	27.2	42.79	3.19
F_2	55	86	—	—	—	100.0	—

directly as UF_6 by this method. This compound is advantageous when the regenerated uranium has to be passed to a diffusion plant for concentration[26]. Substantial differences between the volatility of a number of fluorides of fission products and that of uranium hexafluoride enable the latter to be easily purified by fractional distillation[26,27]. The initial attempts to fluorinate uranium metal with elemental fluorine were unsatisfactory, because it was difficult to remove the large quantity of heat evolved in the heterogeneous reaction

$$U(solid) + 3F_2(gas) = UF_6(gas),$$

and in practice the reaction could not be controlled. A practical solution of this problem was found in the use of liquid fluorinating agents, such as the halogen fluorides. These are very suitable because of the range of temperature over which they remain liquid (see Table 1).

The preceding account explains the great interest that has been shown in the halogen fluorides in recent years. Published reviews[29-34] on chlorine trifluoride are largely out of date because of the intensive investigations on these compounds in recent years. None of the reviews deal with the study of systems based on chlorine trifluoride, since investigations on these systems have been carried out and published only recently in connection with the work of the Second International Geneva Conference on the Peaceful Uses of Atomic Energy[35]. This review is devoted to the physical and chemical properties of chlorine trifluoride, the most reactive of the known halogen fluorides.

1. PREPARATION OF CHLORINE TRIFLUORIDE

Chlorine trifluoride, ClF_3, was first prepared in 1930 by Ruff and Krug[15,36], in an apparatus which had been previously used for the synthesis of chlorine monofluoride, ClF.[15,36] Gaseous fluorine and chlorine were led into a heated copper vessel, where they reacted to form chlorine monofluoride and chlorine trifluoride. Three receivers, the first two of quartz and the third of glass, were attached to the reaction vessel. The first receiver, maintained at -70°, served to condense ClF_3; the second, cooled to -150°, was intended to entrain ClF, and the third, surrounded by liquid air, was used to freeze out the excess of fluorine. A copper or glass tube filled with ignited potassium fluoride was attached to the outlet of the third receiver to keep out atmospheric moisture.

The literature on methods of preparation of ClF_3 is practically confined to this work[15]; later papers merely indicate some improvements in the process. For example, ClF_3 has been prepared by the reaction of fluorine and chlorine in a nickel vessel at 280°.[2,13] Pilot-scale production of ClF_3, for use as an incendiary material, was organised in Germany during the Second World War; the method comprised heating a mixture of fluorine and chlorine with a nickel catalyst[37].

Some information on the synthesis of ClF_3 in an experimental pilot plant made of monel metal has also been published[38]: the ClF_3 was prepared by heating a stoichiometric mixture of fluorine and chlorine to 300°. The reaction products were condensed in a helical condenser before passing to a receiver. Condensed chlorine trifluoride can be stored for long periods in steel cylinders[38]. Besides nickel and monel metal, copper can be used in the construction of plant for the production of ClF_3.[15]

2. PHYSICAL PROPERTIES OF CHLORINE TRIFLUORIDE

Under normal conditions chlorine trifluoride is a colourless gas with a molecular weight of 92.457. The melting point is given as -83°[15] and -82.6°[39] in early papers on ClF_3; these values were incorrect and it was later shown that ClF_3 melts at -76.32 ± 0.05°;[2] this conclusion was reached from an examination of the melting point of three samples of ClF_3 containing 0.04, 0.3, and 1.8 mole % of impurities (Fig. 1).

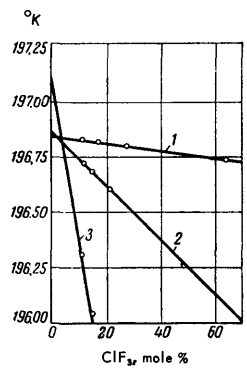


Fig. 1. Determination of the melting point of chlorine trifluoride of different degrees of purity. Impurities: 1) 0.004 mole %; 2) 0.3 mole %; 3) 1.8 mole %.

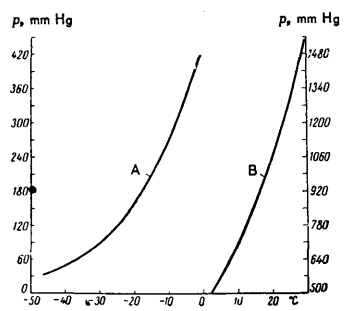


Fig. 2. Vapour pressure of chlorine trifluoride from 0 to 1550 mm Hg.

TABLE 2. Molar heat capacity of chlorine trifluoride,

Temperature, °K	Molar heat capacity, cal mole^{-1}deg^{-1}	Temperature, °K	Molar heat capacity, cal mole^{-1}deg^{-1}	Temperature °K	Molar heat capacity, cal mole^{-1}deg^{-1}
solid		solid		liquid	
14.04	1.03	88.44	11.49	196.84	26.68*
16.60	1.50	95.62	12.03	202.76	26.76
20.10	2.13	103.44	12.47	204.83	26.78
25.88	3.36	111.35	13.03	207.69	26.81
32.59	4.75	126.54	14.16	216.53	26.94
40.67	6.22	141.87	15.28	219.84	26.96
45.88	7.05	156.22	16.28	226.95	27.05
56.27	8.39	171.20	17.36	237.83	27.22
62.67	9.07	180.60	18.04	248.6	27.38
67.82	9.60	184.96	18.46	259.30	27.61
78.96	10.62	196.84	19.18	269.86	27.84
				278.25	28.02

* Values obtained by extrapolation.

The boiling point of ClF_3 was first determined by Ruff and Krug[15] from an empirical relation between the vapour pressure and the temperature:

$$\log P \text{ (mm Hg)} = 7.42 - \frac{1292}{T}.$$

The boiling point found was 11.3°. Values of 12.1°[39] and 12.0° ± 0.1°[16] have also been reported. The vapour pressure–temperature relationship for ClF_3 was later expressed by the equation[2],

$$\log P \text{ (mm Hg)} = 7.3671 - \frac{1096.917}{t + 232.75}.$$

This yields a boiling point of 11.75°, lying between the values given above.

Fig.2 gives data on the vapour pressure of ClF_3. Trouton's constant, according to the equation derived by Ruff and Krug[15], is 20.8 cal deg^{-1}mole^{-1}. Schmitz and Shumacher[40] assume a value of 24.1 cal deg^{-1}mole^{-1} for Trouton's constant, but they do not indicate how this figure was obtained. The critical temperature of ClF_3 as determined by different authors, is close to 154°[15] or 174°;[2] the calculated critical pressure is 57 atm.[2]

The heat capacity of ClF_3 has been measured from 14°K to the boiling point; Table 2 gives heat capacities of solid and liquid ClF_3. It should be noted that the values in this Table have been corrected by the method of Hoge[41] for the heat capacity of the saturated vapour.

The heat of formation of ClF_3 can be found from the heat of formation of ClF and the heat of the reaction

$$ClF + F_2 = ClF_3,$$

for which determinations by independent methods have given the following results: 27.0 ± 1.5, 26.5 ± 0.5, and 25 ± 2 kcal × × mole^{-1}.[42,43] Greenwood[31] accepts 26.5 ± 1 kcal mole^{-1} as the heat of reaction between fluorine and chlorine monofluoride. From this value and the heat of formation of ClF (12.3 ± 1 kcal × × mole^{-1} [44]), the heat of formation of gaseous ClF_3 from the elements,

$$\frac{1}{2}Cl_2 + \frac{3}{2}F_2 = ClF_3,$$

can be found; the actual value is 38.8 ± 2 kcal mole^{-1}. Other data on the heat of formation of ClF_3 have been obtained by combining the data of Schmitz and Shumacher[42] for the reaction

$$ClF \text{ (gas)} + NaCl \text{ (solid)} = NaF \text{ (solid)} + Cl_2 \text{ (gas)}$$

with the data for the same reaction with ClF_3. Two values, depending on the value taken for the heat of formation of ClF, have been obtained for the heat of formation of ClF_3, 32.1 and 36.3 kcal mole^{-1}.[20] The most accurate value is 37.9 ± 1.0 kcal mole^{-1}.[20]

The density of liquid ClF_3 at the boiling point, first measured by Ruff et al.[45], is 1.77 g/cm^3. Banks and Rudge[16] give much more accurate values; they studied the density of liquid ClF_3 under the pressure of its own vapour over the temperature range -5° to +46° and derived the following relationship between the density and the temperature:

$$d_4^t = 1.8853 - 2.942 \times 10^{-3} t - 3.79 \times 10^{-6} t^2.$$

Table 3 gives values for the viscosity of ClF_3, determined by Banks, Davis, and Rudge[46]. The surface tension of ClF_3, determined by the capillary method, is expressed by the equation[46]

$$\gamma = 26.7 - 0.16t \pm 0.2 \text{ dyne cm}^{-1}.$$

Rogers and Garver[47] studied the viscosity and surface tension of the halogen fluorides and put forward the hypothesis that the high surface tension is due to the presence of "fluoride" bonds, similar to hydrogen bonds, the F^- ion playing the part of the proton in the hydrogen bond. The strength of these bonds decreases in the order $BrF_3 > IF_5 > > BrF_5 > ClF_3$.

The conductivity of liquid ClF_3 at 0° is 3×10^{-9} ohm$^{-1} \times \times$ cm^{-1}.[31]

Schmitz and Shumacher[42] first measured the thermal dissociation of ClF_3;[42] the reaction was carried out in a nickel vessel and the pressure measured with a sensitive quartz manometer. Table 4 gives values for the equilibrium constant of the reaction

$$ClF_3 \rightleftharpoons ClF + F_2$$

for different temperatures. The degree of deviation of ClF_3 from the ideal-gas laws can be explained by the association of chlorine trifluoride[40] $2ClF_3 \rightleftharpoons (ClF_3)_2$. The heat of this reaction at room temperature has been calculated as 3.3 ± ± 0.5 kcal mole^{-1}.[40] Table 5 shows values of the equilibrium constant

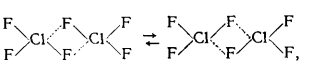
$$K_p = \frac{P^2_{ClF_3}}{P_{(ClF_3)_2}}.$$

Calculated values of K_p for the reverse reaction,

$$(ClF_3)_2 \rightleftharpoons 2ClF_3,$$

are: 0.0372 atm^{-1} at 9.5°, 0.0312 atm^{-1} at 20°, and 0.0283 atm^{-1} at 24.2°. Deductions about the association of ClF_3 have also been drawn from Raman-spectral studies of gaseous and liquid ClF_3.[43,48,49]

A study of the nuclear-magnetic-resonance spectrum[50] has shown that an exchange of fluorine atoms occurs in the ClF_3 molecules. This is evidently due to the presence of dimers,



which are formed through unfilled atomic *d*-orbitals. The exchange of fluorine atoms is possible not only between molecules of ClF_3, but also between ClF_3 molecules, on the one hand, and HF, ClF, or BrF_3 molecules, on the other[51].

TABLE 3. Viscosity of liquid chlorine trifluoride.

Temperature, °C	17.3	17.9	19.4	26.0	32.05	36.3	39.8	48.0
Viscosity, mP	4.48	4.47	4.38	4.07	3.80	3.65	3.52	3.23
Temperature, °C	11.75	15.0	20.0	25.0	30.0	35.0	40.0	50.0
Viscosity, mP	4.78	4.60	4.35	4.12	3.90	3.70	3.51	3.16

TABLE 4. K_p for the reaction $ClF_3 \rightleftharpoons ClF + F_2$.

Temperature, °C	$K_p \times 10^{-4}$ atm
180	0.669
200	0.212
220	0.63
250	2.98
300	24
350	143

TABLE 5. K_p for the reaction $2ClF_3 \rightleftharpoons (ClF_3)_2$.

Temperature, °C	K_p, atm
9.5	26.9
20.0	32.1
24.2	35.4

Studies of the structure of the chlorine trifluoride molecule have been based on determinations of the thermodynamic functions and on optical investigations.

Schafer and Wicke[43] erroneously concluded from Raman-spectral studies that the ClF_3 molecule can be represented by a symmetrical pyramidal model, and Greenwood quotes this in his review[31]. New experimental results show that the symmetrical pyramidal structure for ClF_3 is incorrect. Smith[52,53], on the basis of microwave-spectral studies, considers that the molecule is planar with a C_{2v} axis of symmetry. The moments of inertia obtained[52,53] confirm such a structure and also show that the molecule has a somewhat deformed T-structure with one short (1.598 Å) and two long (1.698 Å) Cl-F bonds. The angle between the different bond types is 87° 29'. The values are 1.621 Å, 1.716 Å, and 86° 59' according to Burbank and Bensey[54]; they put forward the hypothesis that ClF_3 has a layer structure made up of planar triangular molecules, each surrounded by fourteen neighbours. These conclusions are in satisfactory agreement with the presence of a comparatively small dipole moment in ClF_3.

Studies of infra-red absorption spectra, Raman spectra, and nuclear-magnetic-resonance spectra have also confirmed the T-structure for the chlorine trifluoride molecule[50,55]. The deformed T-structure may be considered as being derived from the trigonal bipyramidal molecule[34,56]. The chlorine lies at the centre of the bipyramid and the fluorine atoms are arranged so that two of them are situated at opposite angles of the two pyramide, and the third at one of the angles of the triangle formed by the bases of the pyramids. The two remaining angles of the triangle are occupied by electron pairs of the chlorine atom.

Such a structure satisfactorily explains the tendency of the ClF_3 molecule to form dimers. Muetterties and Phillips[50] believe that the dimer is produced by the formation of bridges from the fluorine atoms between two molecules, the electron pairs from the fluorine atoms occupying 3 d-orbitals of the chlorine atoms. This configuration can be considered to be derived from the octahedral system Sp^3d^2, with two electron pairs occupying two axial positions; the dimer therefore has a planar structure. Because of the increased stability of such a configuration, ClF_3 tends to form dimers.

The same type of structure is also possible for the bromine trifluoride molecule[57]. The halogen fluorides with five atoms of fluorine (BrF_5 and IF_5) form quadrangular bipyramids[58-62], only one angle being occupied by an electron pair. The halogen fluorides with seven fluorine atoms (IF_7) have no lone electron pairs.

3. CHEMICAL PROPERTIES OF CHLORINE TRIFLUORIDE

The distinctive properties of the interhalogen compounds, to which Mendeleev[63] has already drawn attention, are mainly due to the formation of these compounds from atoms of elements belonging to the same Group and sub-group in the Periodic System. The properties of chlorine trifluoride, a compound of two adjacent elements in the same sub-group, clearly reflect this characteristic.

The chemical properties of ClF_3 are to be considered from the point of view of its behaviour as a fluorinating agent. Chlorine trifluoride can react with all the elements with the exception of oxygen, nitrogen, platinum, and the inert gases. According to Ruff and Krug[15], some metals (potassium, molybdenum, tungsten, iron, osmium, iridium) burn in chlorine trifluoride. Sodium, magnesium, aluminium, silver, zinc, and tin react with ClF_3 to form fluorides insoluble in liquid ClF_3, and the metal becomes passive. However, at high temperatures these metals react vigorously with ClF_3.

The metals most resistant to ClF_3 are: mild steel (to 250°), copper (to 400°), and nickel (to 750°)[64]. This is explained by the formation of resistant fluoride films which prevent further attack on the metal.

Chlorine trifluoride acts slowly on dry quartz glass and quartz wool, but in the presence of traces of moisture these are rapidly attacked[16,46,64]. Hydrogen, silicon, phosphorus, arsenic, antimony, sulphur, selenium, and tellurium ignite when acted upon by ClF_3; the composition of the products of most of these reactions has not been established. Many gases (sulphur dioxide, hydrogen sulphide, and ammonia) ignite in ClF_3. ClF_3 reacts with SO_2 to form thionyl tetrafluoride[65,66].

Liquid ClF_3 interacts vigorously with the halogens (Br_2 and I_2) with ignition (and spattering) of the reactants[22] according to the equations

$$2ClF_3 + Br_2 = 2BrF_3 + Cl_2;$$

$$10ClF_3 + 3I_2 = 6IF_5 + 5Cl_2.$$

These reactions have been studied by gradually introducing one reagent into the other with cooling of the mixture and condensation of the products.

Chlorine trifluoride reacts vigorously with water, probably according to the equation[15]

$$3H_2O + 4ClF_3 = 6HF + 3OF_2 + 2Cl_2.$$

Aqueous solutions of alkali decompose ClF_3. Ruff and Krug[15] used this reaction to fix weighed samples in the quantitative analysis of ClF_3. Sulphuric and nitric acids react vigorously with ClF_3.

A study of the isotopic exchange of the fluoride anion between ClF_3 molecules, on the one hand, and molecules of BrF_3 and HF, on the other, has shown that the exchange proceeds according to the reactions

$$HF + ClF_3 \rightleftharpoons ClF_2^+ + HF_2^-;$$

$$BrF_3 + ClF_3 \rightleftharpoons ClF_2^+ + BrF_4^-.$$

The possibility of the formation of an intermediate complex is not excluded. Exchange between gaseous HF and ClF_3 proceeds through the formation of an intermediate complex of composition $ClF_3 . HF$.[67] However, this compound has not been detected in a study of the condensed ClF_3–HF system[68,69]. The $ClF_3 . HF$ is very unstable and is probably present in insignificant quantities in the liquid phase; the presence of a similar complex of bromine trifluoride, $BrF_3 . HF$,[70] has been confirmed. The isotopic exchange of chlorine in ClF_3 has been investigated in studies on the ClF_3–Cl_2 and ClF_3–ClF systems[71].

Gaseous ClF_3 decomposes when it is irradiated with α-particles, the main decomposition products being ClF and fluorine. Calculations show that one molecule of ClF_3 decomposes per 100 eV absorbed by the gas[72].

Organic compounds, as a rule, react with ClF_3 with ignition[42]; for this reason the fluorination of these compounds cannot be controlled. When ClF_3 acts on organic compounds dissolved in fluorinated hydrocarbons[73], carbon tetrachloride[74], or anhydrous hydrogen fluoride, the reaction is relatively mild and can be carried out in the liquid phase; the hydrogen atoms are replaced by fluorine and chlorine. When ClF_3 acts on benzene, toluene or ethylene, addition products of fluorine and chlorine are formed together with some substitution products[50,76,77].

Chlorine trifluoride is widely used to form fluorides by reaction with metals or their compounds. According to Popov and Knudson[21], the oxides of lanthanum and the lanthanides are converted into fluorides by the action of gaseous ClF_3. The degree of fluorination of the oxides and the reaction rates decrease with increasing atomic number; the oxides of the elements from lanthanum to samarium are fluorinated completely to MF_3; Gd_2O_3 is converted to GdF_3 in 80% yield, but the yield of ErF_3 is only 12%. The heavier oxides (Tb to Lu) do not react at all with ClF_3. Yttrium oxide reacts to the extent of only 45% with gaseous ClF_3.

Nikolaev et al.[22,23,24] have synthesised a number of higher fluorides of the transition elements using liquid and gaseous ClF_3. When V_2O_5, WO_3, and MoO_3 react with liquid ClF_3 ignition occurs with atomisation of the reaction products — vanadium pentafluoride, tungsten hexafluoride, and molybdenum hexafluoride. The preparation of these higher fluorides is more conveniently achieved with bromine trifluoride or pentafluoride; with these reagents (for V_2O_5, WO_3, and MoO_3) the reaction is less vigorous. If ClF_3 is used, the gaseous form is more convenient. Gaseous ClF_3 reacts with metallic niobium, tantalum, and molybdenum forming higher fluorides of these metals[23,24]. Quartz apparatus was used in the synthesis of NbF_5, TaF_5, and MoF_6. The reaction starts without external heating; the metal burns in gaseous ClF_3 and the reaction product is distilled into a quartz receiver, cooled with solid carbon dioxide. The reaction can be easily regulated by adjusting the flow of gas. Purification from the excess of fluorine is effected by distillation, by additional fluorination, or by washing the product with liquid hydrogen fluoride at the temperature of dry ice. This synthetic method is applicable in practice to the preparation of a number of higher fluorides.

Hückel[78] prepared HgF_2, AgF_2, CuF_2, TiF_3, PtF_4, and PbF_3 by heating the metals with ClF_3 in an autoclave. When ClF_3 acts on Co_2O_3, cobalt trifluoride is formed[79]. The chlorides of potassium, cobalt, nickel, and silver are converted to the corresponding fluorides by chlorine trifluoride[79,80,81]. The interaction of uranium metal with ClF_3 (both liquid and gaseous) is of great interest; chlorine trifluoride and other known halogen fluorides are used as fluorinating agents in the regeneration of nuclear fuel[25,28,82–86].

The behaviour of ClF_3 as a solvent is best understood from the point of view of the acid-base theory of non-aqueous solvents[13,20,31]. The fluoride ion plays a part similar to that of the proton, addition of a fluoride ion being equivalent to the loss of a proton.

Stein and Vogel[86] considered the fluorination problem from the point of view of the reactivity of uranium metal in different pure halogen fluorides and in mixtures. The experiments were so arranged that it was possible to observe the reaction in both the liquid and the gaseous phases: in all cases uranium was fluorinated with the formation of uranium hexafluoride. The reaction is explosive with gaseous ClF_3. A very large amount of heat (2.2×10^3 kcal kg^{-1})[25] is evolved, which it is practically impossible to remove. Liquid ClF_3 converts uranium metal to UF_6 according to the equation

$$U\ (solid) + 3ClF_3\ (liq.) = UF_6\ (liq.) + 3ClF\ (gas).$$

The use of liquid ClF_3 has several advantages: (1) a high degree of fluorination is achieved at moderate temperatures and pressures; (2) the problem of storing and transporting the fluorinating reagent is simplified; and (3) the problem of heat removal does not arise. However, because ClF_3 is a poor acceptor of fluoride ions in the liquid phase its reactivity to metals is comparatively low (the rate of the reaction between solid uranium and liquid $3ClF_3$ at 30° is $2.5 \times \times 10^{-8}$ moles of uranium per cm^2 of metal surface per second)[72] and is adequate for practical purposes. Anhydrous hydrogen fluoride dissolved in ClF_3 increases the reaction rate[87]. Bernhardt, Barber, and Gustison[72] explain the mechanism of this process in the following way. Pure ClF_3 is slightly ionised:

$$2ClF_3\ (liq.) = ClF_2^+\ (liq.) + ClF_4^-\ (liq.).$$

The instability of the ClF_4^- anion prevents the self-ionisation of ClF_3. The electrical conductivity of ClF_3 at 0°, as already mentioned, is $3 \times 10^{-9} \Omega^{-1} cm^{-1}$. This value is close to that for liquid ammonia, which behaves as an ionising solvent. However, there is a marked difference in the dielectric constants of these compounds (NH_3, 22 at -34°; ClF_3, 4.304 at 25°[34]). The addition of hydrogen fluoride raises the conductivity of the solution because it promotes the formation of the more stable bifluoride anion[72]:

$$ClF_3\ (liq.) + HF\ (liq.) = ClF_3 . HF\ (liq.) = ClF_2^+\ (liq.) + FHF^-\ (liq.).$$

Smith and Pemsler[67] identified the compound $ClF_3 . HF$ in the gas phase; they assumed[72] that the increased activity of ClF_3 when hydrogen fluoride is added is due to the increase in the concentration of the ClF_2^+ ion.

The foregoing explains the importance of a study of the ClF_3–HF system which has been carried out for the solid–liquid equilibrium over a wide range of concentrations (0 to 100% HF) by McGill, Wendolkowski, and Barber[68]. The ClF_3–HF system is of simple type with one eutectic mixture containing 7.5 mole % ClF_3 and having a melting point of -88.8° (Fig.3). The term "molar" is used as equivalent to the term "formula weight", although it is known that hydrogen fluoride must be associated in systems of this type[72]. The authors[68] note the presence of enantiotropy in ClF_3 at -83.1°, significant deviations from the ideal gas laws, and the absence of complex formation in this system.

The liquid–gas equilibrium for the ClF_3–HF system was studied at pressures of 1.5, 2.0, 2.5, 3.0, and 4.0 atm[68,69]. This system forms an azeotropic mixture, containing 67 mole% ClF_3 and 33 mole% HF, whose composition is independent of pressure (Fig. 4). The closeness of this ratio

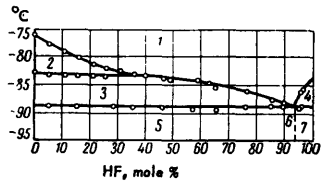


Fig. 3. Solid — liquid equilibrium diagram for the ClF_3—HF system: 1) solution of ClF_3—HF; 2) solid ClF_3 (X-II) + solution; 3) solid ClF_3 (X-I) + solution; 4) solid HF + solution; 5) solid ClF_3 (X-I) + eutectic; 6) eutectic; 7) solid HF + eutectic.

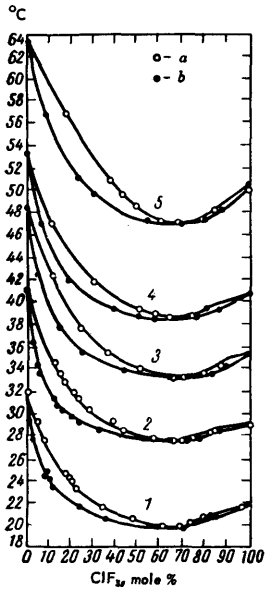


Fig. 4. Liquid — gas equilibrium diagram for the ClF_3 system. Pressure in mm Hg: 1) 1150; 2) 1530; 3) 1900; 4) 2280; 5) 3040. *a*) Vapour; *b*) liquid.

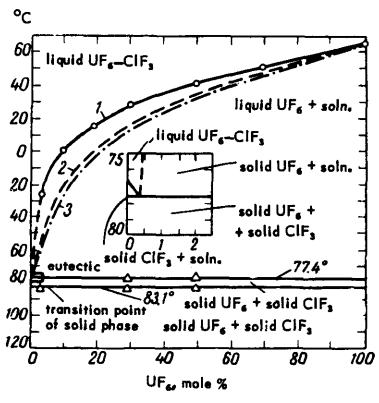


Fig. 5. Solid — liquid equilibrium diagram for the ClF_3 — UF_6 system: 1) experimental curve; 2) theoretical curve; 3) ideal curve.

to the composition of the compound HF . $2ClF_3$ is fortuitous, in spite of the detection of the compound ClF_3 . HF in the gas phase. The melting point for the ClF_3–HF system also gives no indication of the presence of such a compound. At the pressures studied, the boiling point of the azeotrope lies within the range 19.9° to 47.1°.

The solid–liquid and liquid–gas equilibria for the ClF_3–UF_6 system have been studied by Wendolkowski and Barber [88], by Bernhardt, Davis, and McGill [35], and by Ellis and Johnson [89]. The system is simple with a eutectic mixture containing 0.4 mole% of UF_6 and having m.p. -77.4° (Fig. 5). The system shows no compound formation. The liquid–gas equilibrium for the UF_6–ClF_3 system has been studied at the following pressures: 1.5, 2.0, 2.5, and 3.0 atm (Fig. 6). The system does not form compounds of UF_6 and ClF_3 even at higher pressures and there are no azeotropic mixtures. At 67° the components of the system are completely miscible, but at 75° a region of limited miscibility appears within the limit 0.3 to 0.5 mole% UF_6.

Examination of the ClF_3–UF_6 system (liquid–gas) shows that at pressures above 2.5 atm the ClF_3 can be completely separated by fractional distillation from uranium hexafluoride without precipitation of the latter as solid [72,90]; fractional distillation at pressures lower than 2.5 atm is complicated by the formation of solid UF_6.

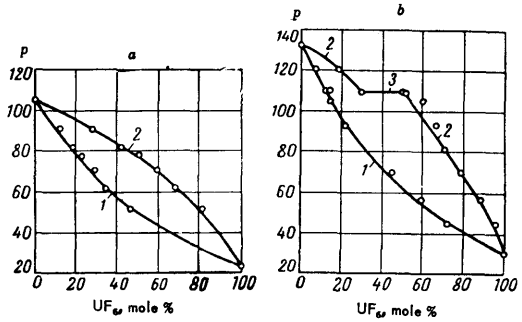


Fig. 6. Liquid — gas equilibrium diagrams for the ClF_3 — UF_6 system: 1) vapour; 2) liquid. *a*) At 67°; *b*) at 75°.

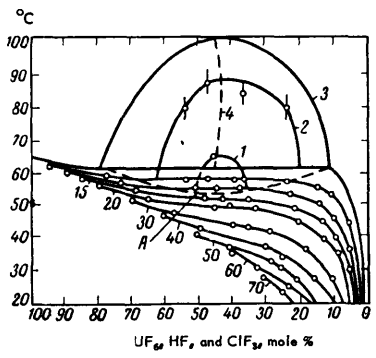


Fig. 7. Solid — liquid — gas equilibrium diagram for the UF_6 — ClF_3 — HF system: 1) 10.0 mole % ClF_3; 2) 5.0 mole % ClF_3; 3) 0.0 mole % ClF_3; A - ternary singular point.

The ternary UF_6–ClF_3–HF system [36,91] (Fig. 7) has been completely studied by way of the systems ClF_3–HF, [68,69] ClF_3–UF_6, [35,88,89] and UF_6–HF. [92,93] The solid–liquid and liquid–gas equilibria were studied over the range -100° to +100°. The UF_6–ClF_3–HF ternary system is of simple type with one eutectic melting at -91°; its composition is 19.5 mole% ClF_3, 80.5 mole% HF, and less than 0.2 mole% UF_6. There is a region of limited miscibility for two liquids saturated with uranium hexafluoride below 53°: at this temperature (composition 13 mole% ClF_3, 38 mole% HF, and 49 mole% UF_6) the two partly miscible liquids become completely miscible. The main features of the liquid–gas equilibrium for the UF_6–ClF_3–HF system [35,72,91,93] were deduced from a study of the three constituent binary systems. The system has no azeotrope, although one is possible for the composition 67 mole% ClF_3 and 33 mole % HF in the UF_6–HF binary system.

The material considered here exhausts the literature data on the systems based on chlorine trifluoride; these are in fact limited entirely to systems that contain uranium hexafluoride and hydrogen fluoride as components. There are no similar studies for systems containing other higher fluorides; the study of these would undoubtedly be of great theoretical and practical interest.

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TERNARY INTERMETALLIC COMPOUNDS

B. K. Vul'f

Institute of Inorganic Chemistry,
Siberian Section of the USSR
Academy of Sciences.

CONTENTS

Introduction 364

1. General features of ternary intermetallic compounds 365
2. Ternary Kurnakov phases 366
3. Ternary intermetallic compounds of normal valency 367
4. Electronic ternary intermetallic compounds 367
5. Ternary Laves phases 369
6. Ternary nickel arsenide phases 369
7. Ternary interstitial phases 370
8. Properties and practical application of ternary metallic compounds 371

INTRODUCTION

A large number of binary intermetallic compounds have now been investigated. The scientific classification of such compounds has been based on Kurnakov's[1] treatment of berthollides and daltonides, and this also enables their precise position among binary metallic phases to be defined. The classification of binary intermetallic compounds according to the types of crystal lattices which they form has been dealt with in several monographs[2-4].

Recent reviews have analysed the general features of the structure, formation, and properties of particular groups of binary intermetallic compounds, and have clarified their role in industrial alloys and the possibilities of their practical utilisation. Data on binary metallic compounds have enabled binary equilibrium diagrams to be studied more completely and more thoroughly.

Three-component systems have received much less attention. Various phases, containing from one to three elements, can be formed in such systems; they are for the most part ternary metallic phases, since the pure components of ternary systems, as well as the binary metallic compounds which are often formed in these systems, are always able to dissolve the components present in excess, to some extent, forming ordinary and "metallide" solid solutions respectively.

The present author[5] has worked out a classification of ternary metallic phases based on a comparison of the nature and extent of the homogeneous regions of the ternary equilibrium diagram. Four of the eight types of ternary metallic phases, including ternary solid solutions based on one of the components of the system, cannot be included among intermetallic compounds.

Ternary phases which are metallide solid solutions of limited solubility are similar in structure and properties to