Meetings

Inorganic Fluorine Chemistry

Inorganic fluorine chemistry was the main theme of a symposium held at Argonne National Laboratory, Argonne, Illinois, 4–6 September 1963. Fluorides of sulfur, nitrogen, oxygen, phosphorus, transition metals, and noble gases and the nonaqueous solution chemistry and thermochemistry of inorganic fluorides were the principal topics of discussion. Approximately 130 scientists from the United States, Canada, Great Britain, France, Denmark, and Germany attended this meeting.

In recent years research on the fluorides of sulfur has been intensified. The tetrafluoride has proven to be a versatile and selective fluorinating agent. The ternary compounds which have been studied include SF_5OF, SF_5Cl, SF_5NF_2, SO_3F_2, SF_5SO_3F, and $S_2O_6F_2$. Some of these are useful intermediates for the preparation of more complex compounds. Reactions of peroxydisulfuryl difluoride, $S_2O_6F_2$, with halogens and with tetrafluorohydrazine revealed the existence of the fluorosulfate free radical, SO_3F, which has now been confirmed by experiments on the thermal dissociation of the peroxy compound (F. B. Dudley and G. H. Cady, University of Washington). Equilibrium constants for the reaction $S_2O_6F_2 \rightleftarrows 2SO_3F$ were determined from 450° to 600°K from both the pressure increase and the light absorbance increase at 474 $m\mu$. [The free radical is yellow, whereas the parent molecule is colorless.] The pressure method yielded $\Delta H = 22.0$ kcal, and the absorbance method $\Delta H = 23.3$ kcal, per mole of $S_2O_6F_2$ dissociated.

Disulfur difluoride, S_2F_2, has been prepared by several methods (F. Seel and D. Gölitz, University of the Saarland, Saarbrücken). The infrared spectrum and fragmentation pattern of the mass spectrum indicate that the compound has the structure $S = SF_2$, similar to $O = SF_2$, the second S being tetravalent. The compound is stable to 200°C but changes to sulfur and sulfur tetrafluoride in the presence of catalysts. Physical and thermodynamic properties, such as the vapor pressure, enthalpy, and entropy of vaporization, have been determined. Since the meeting, a second isomer with the structure F-S-S-F has also been isolated.

Photochemical reactions of SF_5Cl with nitriles, cyanogen, and cyanogen halides are believed to occur by free radical addition to the $-C \equiv N$ function (C. W. Tullock, D. D. Coffman, E. L. Meutterties, E. I. duPont de Nemours). Products such as $SF_5N = CClR$, $SF_5N = CClCCl = NSF_5$, and $SF_5N = CCl_2$ are obtained, which may be used as intermediates to other SF_5 derivatives. The isothiocyanate, $SF_5N = C = S$, for example, and the perfluoro compound, $SF_5N = CF_2$, are readily prepared from $SF_5N = CCl_2$. A variety of more complex derivatives are also known.

Although the dissociation of tetrafluorohydrazine into NF_2 free radicals has been known for several years, a satisfactory electron paramagnetic resonance spectrum of the radical has only recently been obtained in octadecafluoro-2,3-dimethylhexane solvent (R. Ettinger and C. B. Colburn, Rohm & Haas Company). The spectrum consists of nine overlapping lines which are interpreted as consisting of a 1:2:1 triplet, each component being split further into a 1:1:1 triplet. In the F^{19} nuclear magnetic resonance spectrum of tetrafluorohydrazine in the same solvent, the triplet arising from the coupling of the equivalent fluorine nuclei to the nitrogen nuclei has also been observed.

The new compounds, O_2BF_4 and O_2PF_6 oxygenyl salts, have been prepared in reactions of O_2F_2 with BF_3 and PF_5, respectively (I. J. Solomon, J. Keith, R. Uenishi, and J. McDonough, IIT Research Institute). The compounds are believed to contain O_2^+ cations, BF_4^- and PF_6^- anions. The BF_4^- anion remains intact in the reaction of O_2BF_4 with N_2O_4 to form NO_2BF_4. Electron paramagnetic resonance spectra indicate the presence of free electrons in the compounds, but at most, one free electron per three $O_2^+x^-$ units.

Concerning transition metal fluorides, the development of unusual reaction vessels with extreme temperature gradients has permitted the synthesis of a number of new transition-metal hexafluorides. Also, significant results have been obtained by high-pressure reactions, reactions in unusual solvents, and reactions of mild reducing agents. The fluorination of ruthenium by bromine trifluoride in glass apparatus produces a mixture of $RuOF_4$ and RuF_5 from which the pure components can be separated by sublimation in a vacuum (R. D. Peacock, University of Birmingham, England). The action of iodine on RuF_5 in IF_5 produces the yellow compound RuF_4. Similar techniques applied to chromium and technetium yield $CrOF_4$ and CrF_5, $TcOF_4$ and TcF_5. When chromium powder is treated with fluorine at 200°C and a pressure of 200 atm in a nickel autoclave, the product is chiefly red CrF_5, but a small amount of unstable, yellow CrF_6 is also formed (O. Glemser, Institute of Inorganic Chemistry, Göttingen). On increasing the fluorine pressure to 350 atm, the yield of CrF_6 increases. The hexafluoride decomposes to the pentafluoride and fluorine between $-100°$ and $-80°C$.

Complex fluorides of the type MUF_6, M_2UF_7, and M_3UF_8, where M is either potassium, cesium, rubidium, or ammonium, have been prepared by heating UF_5 and the appropriate alkali metal fluoride or ammonium fluoride in a bomb at temperatures up to 350°C (L. B. Asprey and R. A. Penneman, Los Alamos Scientific Laboratory). With lithium fluoride the product is $LiUF_6$; sodium fluoride yields $NaUF_6$ and Na_3UF_8. Stable, bright blue solutions of U(V) in 48 percent HF have also been studied. These produce the crystalline solid $HUF_6 \cdot 2.5H_2O$ on cooling.

In a report reviewing chemical and physical properties of 15 hexafluoride molecules, close correlation was shown to exist between chemical stability, molecular structure, vapor pressure, phase transition temperatures, magnetic and optical properties, and the electronic configuration and atomic mass of the central atom in each compound (B. Weinstock, Ford Motor Company Scientific Laboratory). The hexafluorides of Group VI elements of the Periodic Table and transition series elements all have octahedral symmetry in the gas phase. In the Group VI hexafluorides, the central atom has its maximum valency of six and there are no extra nonbonding electrons. Therefore the compounds are colorless in the gas and liquid states, white in the solid state, and quite stable with respect to dissociation into fluorine and lower nonvolatile fluorides. While the hexafluorides of sulfur, selenium, moylbdenum, tellurium, tungsten, and uranium follow this characteristic pattern, little is known thus far about recently discovered chromium hexafluoride, which may be an exception, or about polonium hexafluoride other than its existence. The hexafluorides of technetium, ruthenium, rhodium, rhenium, osmium, iridium, platinum, neptunium, and plutonium, which contain nonbonding *4d*, *5d*, or *5f* electrons, are colored and are much less stable with respect to dissociation to lower fluorides. Regular trends in vapor pressures may be noted with increasing atomic weight, not only in Column VI of the Periodic Table, but also in the horizontal *4d* and *5d* series. Although the infrared and Raman spectra of all the octahedral hexafluorides show marked similarities, evidence has been obtained for a Jahn-Teller effect in TcF_6, RuF_6, ReF_6, and OsF_6 in abnormalities of the $\nu_2 + \nu_3$ combination bands of these molecules.

Transition metal oxyfluorosulfates, such as $VO(SO_3F)_3$, $NbO(SO_3F)_3$, $TaO(SO_3F)_3$, ReO_3SO_3F, and $ReO_2(SO_3F)_3$, have been prepared in reactions of peroxydisulfuryl difluoride with the metal chlorides, metal oxide chlorides, or pure metals (J. M. Shreeve, University of Idaho). The compounds are highly-colored, hygroscopic liquids, which supercool to glassy solids. The action of SO_3 on SbF_5 is reported to increase the acidity of the system SbF_5–HSO_3F owing to the formation and subsequent ionization of such species as SbF_4SO_3F, $SbF_3(SO_3F)_2$, and $SbF_2(SO_3F)_3$ (R. J. Gillespie, R. J. Rothenbury, K. C. Moss, and R. C. Thompson, McMaster University). The presence of polymeric species containing fluorosulfate linkages in the solutions is also postulated on the basis of F^{19} nuclear magnetic resonance measurements.

Anion-cation interactions have been studied for metal tetrafluoroborates and salts of other complex fluoro acids in solvents such as nitromethane, diethyl ether, and benzene (D. W. A. Sharp, D. H. Brown, M. J. Baillie, Royal College of Science and Technology, Glasgow; K. C. Moss, McMaster University). Tetrafluoroborates of copper, manganese, chromium, iron, cobalt, nickel, and zinc have been prepared in reactions of $AgBF_4$ with the metals or anhydrous metal chlorides. The salts are appreciably soluble in nitromethane, and absorption spectra of the solutions indicate that the salts are present as nitromethanates and free anions. In diethyl ether and benzene, the metal ions are in octahedral fields; cobalt(II) and copper(II) appear to be present as covalent tetrafluoroborate complexes. A comparison of the spectra of $Cu(BF_4)_2$ and $Co(BF_4)_2$ solutions with the spectra of $Cu(SbF_6)_2$ and $Co(SbF_6)_2$ solutions suggests that stronger ligand fields occur in the tetrafluoroborates than in the hexafluoro antimonates.

The blue color in solutions of iodine in iodine pentafluoride is attributed to the uncoordinated paramagnetic species I^+ (N. N. Greenwood, University of Newcastle Upon Tyne, England). The fairly high dielectric constant, weak donor properties, and mild oxidizing property of IF_5 enable it to stabilize I^+. The color of the ion arises from the ligand-field splitting of the outermost *p* orbitals owing to unsymmetrical solvation. Transitions between the $^3\Sigma$ ground state and the $^3\Pi$ excited states produce absorption bands at 15,600, 19,700, and 23,900 cm^{-1}. Solutions of selenium in selenium tetrafluoride show similar behavior, but it is not known at present whether the solutions contain ionic or atomic selenium.

In the rapidly evolving field of noble gas chemistry, xenon compounds continue to play a central role. Methods of preparation, mass spectrometric studies of volatile species, and theoretical treatments of bonding were described (J. G. Malm, M. H. Studier, E. N. Sloth, and G. L. Goodman, Argonne National Laboratory). Both thermal and photochemical reactions of xenon and fluorine yield XeF_2 as the initial product; further fluorination gives rise to XeF_4, and high-pressure fluorination produces XeF_6. Reactions of XeF_6 with H_2O or SiO_2 yield $XeOF_4$. Complete hydrolysis of XeF_6 produces the unstable oxide XeO_3. In exploratory studies of various reactions, new compounds have sometimes been identified in the time-of-flight mass spectrometer as trace components of mixtures before they have been produced in weighable quantities in the laboratory. Thus XeF_2 was detected in initial preparations of XeF_4, and $XeOF_4$ was observed in partially hydrolyzed samples of XeF_6. An additional hydrolysis product, XeO_2F_2, has been observed in the mass spectrometer on several occasions, but macroscopic amounts of this compound have not yet been obtained. The simple fluorides and oxytetrafluoride have now been studied in a number of laboratories. Equilibrium studies of the xenon-fluorine system at one time were believed to indicate the existence of XeF_5, and an infrared absorption band at 520 cm^{-1} was attributed to this molecule. However further measurements show only XeF_2, XeF_4, and XeF_6 in the system (E. E. Weaver, C. P. Knop, and B. Weinstock, Ford Motor Company Scientific Laboratory). The enthalpy change for the dissociation of XeF_6 to XeF_4 and fluorine is calculated to be 18.6 kcal/mole from equilibrium data for the interval from 523° to 623°K.

Dissociation energies and heats of formation of SiF, SiF_2, GeF, and GeF_2 have been obtained from high-temperature mass spectrometric studies (T. C. Ehlert, A. S. Kanaan, A. K. Kuriakose, and J. L. Margrave, Rice University). The volatile species were observed in reactions of silicon and germanium with calcium fluoride. Dissociation energies of the monofluorides and difluorides of beryllium, magnesium, calcium, zirconium, and barium also were obtained in high-temperature reactions in which aluminum was the reducing agent.

In a discussion of heats of formation of ionic fluorides derived by the Born-Haber cycle, the effects of variations in parameters such as the Madelung constant, ionic radius, ionic charge, electron affinity, and ionization potential were described (A. G. Sharpe, Cambridge University, England). In the fluorides of chromium, manganese, iron, cobalt, nickel, copper, and zinc the stability of the trivalent state with respect to the divalent state decreases regularly across the series, as expected from the change in lattice energy and enthalpy. In complex fluorides of the type $M\mathrm{XF}_6$ or $M_2\mathrm{XF}_6$, where M is an alkali metal ion, an increase in the size of M enhances the stability; thus cesium can form such complexes more readily than other alkali metals.

A rotating bomb calorimeter for precisely measuring heats of combustion of metals and other substances in fluorine was described (E. Greenberg, G. K. Johnson, E. Rudzitis, J. L. Settle, S. S. Wise, and W. N. Hubbard, Argonne National Laboratory). Elements and compounds for which thermochemical measurements have been completed include Mg, Zn, Cd, B, Al, Si, Ti, Zr, Hf, Nb, Ta, Mo, U, Ru, BN, SiO_2, and ZrB_2.

Adducts of BF_3, AsF_5, and SbF_5 with halogen fluorides were described (M.

Schmeisser, Institute of Inorganic Chemistry, Aachen). Iodine trifluoride yields the complexes IF_2BF_4, IF_2AsF_6, IF_2SbF_6; chlorine monofluoride yields $ClBF_4$, $ClAsF_6$, $ClSbF_6$. As reported several years ago, the low temperature fluorination of ICl yields progressively IClF, $IClF_2$, and IF_3. Present evidence indicates that the molecular formulas of the compounds are $I \cdot ICl_2$, $IF_2 \cdot ICl_2$, $IF_2 \cdot ICl_2F_2$, and $IF_2 \cdot IF_4$, respectively. The reaction of IF_3 with iodine does not produce three molecules of IF, as previously indicated, but yields the adduct $IF_3 \cdot I_2$.

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Permafrost

About 20 percent of the land area of the earth (50 percent of Canada and the Soviet Union) is located in climatic zones where the mean annual temperature falls below 0°C. As a consequence, the phenomenon of freezing a thin surface crust of soil during the winter months, so familiar in more temperate climates, is reversed; the underlying soils or rocks remain perennially frozen while a thin surface layer ("active zone") temporarily thaws during the summer months. This latter condition is known as permafrost.

The soils in permafrost areas vary from coarse gravels to silts and organic peats and mucks (muskeg). Occasionally plastic clays are encountered. Depending on the soil type and on the drainage and climatic conditions, the proportion and distribution of ice in the ground may vary widely, ranging from partially filling the void spaces between soil particles to lenses and wedges of ice in thicknesses of a few centimeters, to massive zones of ice with dimensions to be measured in meters and even decimeters. Spectacular surface features often manifest themselves either as striking individuals, such as the "pingo" (Fig. 1), or as repetitive patterns over large areas, such as "ice-polygons" (Fig. 2). In recent years, interest in scientific studies of these features has heightened with promising signs of better understanding in such disciplines as geomorphology, glaciology, and historical geology. Moreover, the increasing importance of the arctic (and antarctic) regions, from both military and civilian standpoints, necessitated construction of roads, railways and airfields, dams, water distribution and sewage disposal systems, and structures for all kinds of purposes. Because of limited knowledge and the short time that could be allowed to elapse between the conception of a project and its completion, the design problems involved have been solved by judicious combinations of research, engineering analyses, field experience, and ingenuity. More complex and diverse projects involving the exploitation of mineral resources and the development of electric power on a large scale are now in the offing, requiring more accurate analyses if safe, economic designs are to be achieved.

On 11–15 November 1963 nearly 300 engineers and scientists from 12 countries gathered at Purdue University, Lafayette, Indiana, for the 1st international conference on permafrost. The proceedings of the conference will contain the latest maps defining the occurrence and distribution of permafrost in Eurasia, Alaska, and Canada. New information on permafrost areas reveals that their southern boundaries creep ever further southward—that is, localities heretofore thought to be free of permafrost are now known to have at least sporadic permafrost areas. In fact, permafrost has been discovered near Thompson, Manitoba, and even on Mount Washington, New Hampshire. Air photographs and geophysical methods have been helpful in making these surveys, although additional refinements are necessary where areas of sporadic permafrost are encountered. Vegetal cover may prove promising in this connection and the appearance of lichenaceous cover and the higher incidence of polyploidy are thought to occur where there is permafrost.

Soil genesis in permafrost country, as related to geomorphic conditions, offers a medium of understanding as attractive as that gained by correlating plant communities with soil types, and can even be used where no plants occur. The mechanics of surface-salt accumulation with upward movement of water and the association of soil salinity relations with the "active frost zone" indicate a basis for useful field comparisons and determination of site history. The existence in the normal Arctic soil profile of a permanently frozen organic layer generally 5 to 15 cm thick at a depth of 40 to 130 cm below the surface was reported, and it was suggested that this organic layer represents an accumulation during an abrupt warming of the arctic regions. Carbon-14 dating indicated the age of the warming to be 8000 to 10,000 years. It is worth noting that soil-forming processes are active in the ice-free Lower Wright Valley, Antarctica, under conditions void of humus and almost continuous freezing temperatures.

Fig. 1. Pingo, partially eroded by waves, on an alluvial island in the Mackenzie delta. The pingo is 7.62 m high and consists of a central core of ice doming up 1.5 to 3 m. [J. Ross McKay]

Criticism was made of conventional procedures for calculating thermal changes caused by impounding water or constructing roads and buildings. First, air temperature is only one variable governing the net heat balance at the air-ground interface; in permafrost areas ground and cloud cover may play equally decisive roles. Second, an unfrozen film of water persists around fine grained particles in frozen soils and the percentage of unfrozen water present is dependent on soil type and temperature (and to a secondary degree on the salt content in the pore water). Thus the heat released at the freezing front is not equal to the volumetric latent heat times the total volume of

Fig. 2. Patterned ground near Point Barrow, Alaska. [Philip Johnson, Cold Regions Research and Engineering Laboratories]