HETEROCATIONS

A. A. Woolf

Department of Chemistry, Bristol College of Science and Technology, Bristol, England

I. Introduction

A large part of inorganic chemistry is essentially the chemistry of ions. It follows that any review article about ions of a reasonable length cannot treat every aspect of the topic in depth. In this article some of the heterocations containing two or more different elements, and which have been studied since 1950, are considered. Only the main lines of progress, biased to some extent by the author's particular interests, can be delineated. Solvated cations are dealt with under a number of headings, the main emphasis being directed away from the solvation of simple metal cations toward those solvated cations in which the element is stabilized in an otherwise inaccessible state. While the derivation of cation structures by direct physical methods is accentuated, their deduction from chemical reactivity, although never unequivocal, is also described. Attention is drawn to the effect of the physical method on the event being measured.

A. DEFINITION OF IONS

Every chemist "knows" what is meant by an ion but a comprehensive definition is impossible without discursive qualifications. It is inevitably linked to theoretical concepts and often to the mode of generation of the ion. Thus, in the gas phase, one can define an ion almost mechanistically as a molecule, radical, or atom from which one or more electrons have been completely separated. In practice, the ion must survive for a long enough period to be detected, which in a mass spectrometer is normally of the order of microseconds or orders of magnitude larger than vibration times of the hetero species. An even lower temporal restriction on the definition of an ion is encountered in solution when rapid exchange of charge is occurring. For example, in water the charge on the positive ion species is fluctuating rapidly and any particular hydronium cation can be regarded as having a lifetime of 10^{-12} second (*87*). If there is a reasonable concentration of these cations, as in a solution of a strong acid, the short life does not prohibit recognition of the species, whereas if such a short-lived entity is a reaction intermediate with a low stationary concentration, then indirect methods may be required to identify the species.

A spatial restriction on the definition is just as difficult to impose because in certain structures there is no apparent limitation to the size of the cation. In titanyl sulfate, for example, discrete sulfate ions link together infinite chains of oxygen and titanium atoms (*199*). At the other extreme, difficulties arise in defining cations when they are approached by anions. At some stage the composite begins to differ in physical and chemical behavior from the separate ions. There may not be a point of inflection in the observable properties, and consequently a somewhat arbitrary limit, albeit guided by theory, is set for the definition of such a complex ion. In condensed phases, even more difficult problems of definition arise when there is an incomplete separation of charge. Ideally the electron distribution should be accurately determined by experiment or, alternatively, a model of the structure calculated on wave mechanical principles using appropriate experimental parameters, so that charge distribution is measured quantitatively and the definition of an ion suitably modified. Neither approach is feasible at present. The structure of the compound $ISbCl_8$ as determined by X-ray analysis is a simple example. It consists of octahedral $(SbCl_6)$ groups and angular (ICl_2) units. The former are distorted with a pair of Sb-Cl distances longer than the rest. The chlorine atoms on these bonds are weakly linked to the iodine atoms, and complete a distorted square of chlorine atoms around each iodine. In this arrangement the structure lies between $ICl_2^+SbCl_6^-$ and $ICl_4^-SbCl_4^+$ (*322*).

B. RECOGNITION OF IONS

The main experimental methods applied to the detection of ions are discussed briefly in order to appreciate the particular aspect of ionicity being examined and, as important, any influence exerted by the method on the measurement.

1. Ion Transport

The most obvious property of an ion is the possession of unbalanced charge, which when placed in unidirectional magnetic or electric fields will undergo transport in a direction governed by the sign of charge. Thus in a time-of-flight mass spectrometer the cations move linearly in an electric field, the kinetic energy of the ion being balanced by the field energy, or in a more conventional mass spectrometer on a circular arc in a magnetic field. In both instances the cations of constant mass-to-charge ratio are collected in time or spatial sequence (*205*). Provided the instrument resolution is high enough, the mass of the cation and its identity are readily established, often aided by the presence of satellite peaks due to the less abundant isotopes. For many inorganic applications a low-resolution instrument suffices (*56*). Spurious background from extraneous material can usually be discounted by observing the effects of shielding the ion source, varying the pressure in the system, and altering the conditions of ion generation. However, only matter in the gas state can be examined; although solids and liquids can be vaporized and ionized in suitable sources, the observed ionic distribution will not correspond to that in the solid or liquid state even when the same ions are formed. The method does not provide quantitative information on the distribution of cations in liquids or solids, because of the processes required to separate ions. Nevertheless the simple ions present in liquids or solids can in general be detected qualitatively in mass spectrometers.

In liquids the presence of ions is recognized by electrical conductivity measurements, although a clear distinction is not always possible on these grounds alone. Under normal conditions even hydrocarbons are imperfect insulators, because of the natural ionizing background (*195*). Many ionizing solvents, such as dinitrogen tetroxide, also have very low conductivities of the same order. The full recognition of ionization in these pure liquids relies on their ability to interact with solutes to form acid or base analogs within certain limits of strength. Ionization in solids can be recognized by their dissolution and dissociation in these ionizing solvents and by the magnitude of the conductivity produced. However, the energies involved in dissolution or solvation may be enough to provoke ionization in a solid or liquid which was un-ionized, or only partly ionic, in the crystal state. Ionization in solution or melt is not an unfailing criterion of ionization in the solid.

Conversely, the melt from an ionic solid is not always conducting. Certainly with many heterocations it is unsafe to extrapolate ionicity from one state of matter to another. The nature of the electrical conductivity has also to be considered because modes of charge transport other than by ions are possible. The temperature variation of conductivity provides this information. Ionic conductivity in the liquid state usually possesses a positive and linear temperature coefficient. The conductivity decreases sharply and discontinuously at the melting point. Electronic conduction varies exponentially with temperature without a sharp discontinuity on change of state. Ionic composition and charge have often been deduced from electrolytic transport measurements, but these results can be fully interpreted only if a complete mass balance and knowledge of the ionic equilibria are available. The meaning of transport in molten salts is less clear-cut, because there is no solvent to act as a frame of reference.

A direct influence of the method of measurement on the measurement itself has been pointed out by Wyatt (*339*) with respect to highly conducting liquids, such as sulfuric acid. Application of the field required to measure conductivity causes dissociation in the field direction. This effect is a result of the reduced energy difference between neutral molecules and complex of solvated ion pairs in the field direction. It has been calculated that about one third of the observed conductance in sulfuric acid is due to this assymmetrical dissociation.

Electrical conductance is in general the most widely accepted property for the recognition of ionization and, provided precautions are taken in measurement and interpretation, is a reliable indicator.

2. Interaction with Radiation

In another group of methods for identifying ions, the possession of charge is not recognized as such, but rather the geometrical groupings around a central element. The most generally applicable method is X-ray diffraction by solids. The electron distribution in the solid by cooperative scattering produces well-defined maxima, modified somewhat by physical and chemical imperfections, from the amplitude and direction of which the periodicity of the structure is deduced. The results of such analysis are presented in the form of projections contoured at equal electron intervals on particular planes through the structure. In these projections the heterocation is usually recognized as a finite group of simple shape separated from similar groups by distances greater than the distances within the group.

However, it is not possible to sum the electron density completely enough to assess the charge in a group, mainly because the observed intensities and the atomic structure factors cannot be extrapolated to zero angle of incidence (*35*). In the structure of solid phosphorus pentachloride (Fig. 1) distinct tetrahedral and octahedral groups of chlorine atoms around phosphorus can be seen, but recourse to our knowledge of electron configuration of atoms and theory of bonding is needed to show that the octahedral grouping cannot be a positive entity. (Auxiliary experiments, in which the direction of electrical transport in a solvent is determined, are a useful confirmation of the polarity, but as mentioned previously due regard must be given to the power of the solvent in inducing polarity or changing the direction of polarity in borderline systems.)

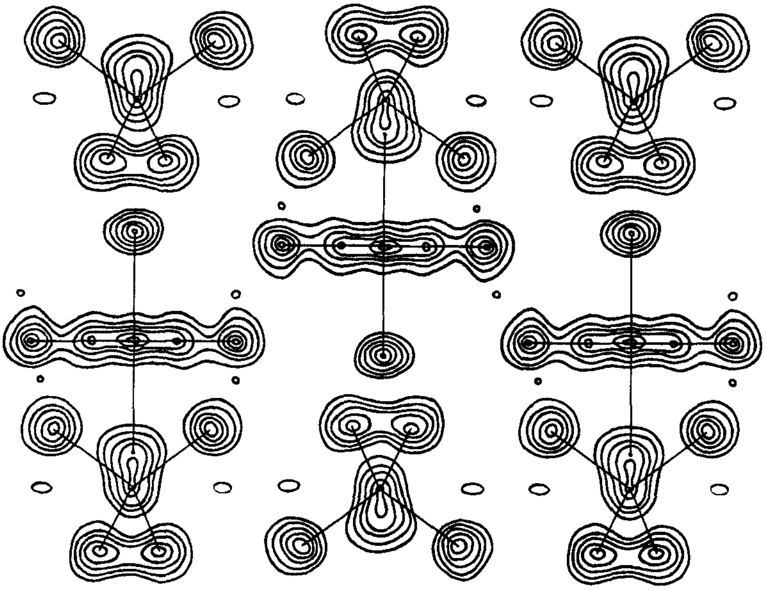


FIG. 1. Fourier synthesis on (100). Tetrahedral PCl_4 and octahedral PCl_6 groups shown by ruled lines.

X-ray diffraction has also been used to examine ions in solution. Again there is coherent scattering in preferred directions, the difference from a solid being the deduction of average distributions only, in the form of radial distribution curves because of the constant movement of atoms in the liquid. If the areas under the peaks of such curves can be resolved, it is possible to calculate the coordination around a particular atom and from a postulated structure to calculate the expected radial distribution (*42*). The location of hydrogen atoms is usually assumed in the X-ray diffraction technique. The most refined measurements can reveal small inflections, or peaks, in the electron-density maps corresponding to the hydrogen positions.

Electron and neutron diffraction methods provide a surer location of hydrogen atoms and for simple geometrical arrangements the best method utilizes proton magnetic resonance (p.m.r.) (*253*). The last technique has been described in detail in an earlier volume (*220*). Briefly, by applying an oscillatory magnetic field at right angles to a permanent field in which nuclei with nonintegral spins are oriented, it is possible to induce nuclear transitions with resonant absorption of energy. The position of the transition is influenced by the surroundings of the particular nucleus, because the nucleus sees, as it were, a magnetic field which differs from the externally applied field. Electron motions near the nuclei screen the latter and produce characteristic chemical shifts. In addition, the presence of neighboring nuclei may modify the field at the central nucleus and produce characteristic fine structure in the absorption of energy. The geometrical arrangement of hetero-ions in solution is deduced by interpreting these spectra. In the solid state the interactions of like and unlike nuclei cause energy absorption over a broader field. The general shape of the absorption curve can be calculated for different geometrical arrangements, and an exact fit obtained by appropriate choice of interatomic distances. Since these factors are not completely independent, it is usual to assume an exact shape for the ion and then calculate precise interatomic distances. The dimensions of the H_3O^+, PH_4^+, and $N_2H_6^+$ ions have been found in this manner (*248*, *254*).

The interpretation of infrared spectra, and the complementary Raman spectra, is the most generally applicable method for determining the configuration of ionic compounds, and as such has been fully described in numerous texts (e.g., *224*). Again, the methods do not reveal ions, insofar as the electron distribution is not measured directly. However, similarity in distribution is readily shown by similarity in force constants and geometry in isoelectronic series, such as the tetrahedral species PH_4^+, CH_4, BH_4^-, or in isoelectronic pairs, such as $PFCl_3^+$, $SiFCl_3$; CH_3CO^+, CH_3CN; NO_2^+, CO_2. For simple ions the shapes can be deduced quite rigorously from group theory and normal coordinate analysis, but in many instances only a partial interpretation of spectra is possible. This may arise because a species is reactive and the spectra are poor and incomplete, or theoretically because of its complexity. This partial assignment has often led to the same spectra being interpreted in different ways, by making analogies with what are regarded as corresponding compounds (*112*, *241*). From the point of view of identifying ionic structures, much needless controversy has arisen when a structure is incompletely ionized and an equilibrium exists between ionic and molecular forms. The nondetection of ionization by examination of infrared spectra, even when clearly indicated by conductivity measurements, is expected when the ionization is small. The extent of ionization when large, however, can be measured quantitatively by infrared or Raman spectroscopy (*70*).

3. Colligative Behavior

Ionization, besides leading to an increase in charge or a change in shape which can be detected by one of the methods described, increases the number of particles in a system and thus affects colligative properties. The depression of freezing point of dilute solutions is one of the most accurately measurable of such properties and for an ideal solution is proportional to the mole fraction of solute. Ionization is inferred by an increased depression over that calculated. In the most extensive study in recent years by this technique, the solvent employed was sulfuric acid (*119*). This has a considerable self-ionization, as well as internal dehydration and subsequent ionization, so not surprisingly the interpretation of ionization in this solvent has been a disputed subject. Originally the deviations from ideality were collected in a single van't Hoff factor, or ratio of the observed depression to that of an equimolecular solution of the ideal nonelectrolyte, which was identified with the number of kinetically separated particles. The factor is actually a combination of this and the interparticulate forces. Gillespie introduced another factor to represent the number of particles, quite separately from these deviations from ideality (*116*). The solvent ionization was repressed in earlier work, but later the ionization was allowed for by means of equilibrium constants obtained from conductivity measurements. When a solute is largely dissociated, the small value of interionic forces in this medium of high dielectric constant is neglected, and the Gillespie factor is sufficiently close to integral values to formulate stoichiometric equations with the equilibrium almost entirely on the ionic side. Certain compounds, which are nonelectrolytes according to spectrophotometric evidence, have been found to give greater depressions than expected for nonelectrolytes in sulfuric acid. This effect has been described as a salt effect since small amounts of electrolytes were also present. Other equilibrium methods, employed to investigate the successive formation of complex cations in solution, are considered later (Section VI).

4. Kinetic Behavior

Kinetic measurements rank equal in importance with equilibrium methods for identifying actual or potential ionic species in reactions, often without the need to isolate them. This holds particularly for electrophilic entities in organic substitution reactions. Thus the following kinetic results are sufficient to identify the nitronium ion as a nitrating entity: the increase in order of reaction in organic solvents to unity with increasing reactivity of aromatic substances, the acceleration of rate by sulfuric acid and retardation by nitrate ions, and the increasing rate of nitration by specific medium effects which favor ionization (*155*). Closely related are some of the reactive entities in Friedel-Crafts types of reaction, such as acylations, for which most evidence suggests an acylium cation as intermediate. Some workers prefer to regard the carbonium ion as a limiting state which is not achieved before attack on the substrate commences, but nevertheless it has proved possible to isolate some of these limiting states in the form of ionic salts (*230*).

The kinetics of metal dissolution have also been used in a semiquantitative fashion to detect the generation of cations in a variety of solvents. The increased rate of metal solution in liquid ammonia by addition of ammonium chloride, of uranium in bromine trifluoride by addition of antimony pentafluoride, or of the same metal in nitrogen tetroxide by addition of amines, is associated with increasing "acidity" of these solvents by generation of cations.

Exchange kinetics of certain nuclei within an entity, or between entities, can be followed by observations of nuclear magnetic resonance (n.m.r.) spectra. The fine structure of a multiplet will often be resolvable only at low temperatures, because the rate of exchange at higher temperatures is sufficient to coalesce the separate peaks. Thus the F^{19} n.m.r. spectrum of sulfur tetrafluoride at −98° consists of a pair of triplets resulting from the interaction of pairs of nonequivalent fluorine atoms. As the temperature increases the spectrum is reduced to a doublet and finally a broad single peak (*219*). In this instance a clear decision between an intermolecular exchange via an ionization, or by association, was not possible, although the ready ionization of sulfur or selenium tetrachloride would be compatible with the former.

Kinetic methods can be applied in a negative way to disprove the existence of ions and with less certainty in the reverse way. Thus if isotopic tracers are incorporated into a solute, then a slow rate or absence of exchange with a solvent implies the absence of ionic intermediaries in the equilibria between solute and solvent. A rapid exchange allows the presence of ions, especially when supported by rate laws appropriate to a feasible exchange mechanism (*312*). The possibility of exchange by nonionic mechanisms, especially in heterogeneous systems, can never be neglected.

C. GENERATION OF CATIONS

1. *Ions in the Gas Phase*

The generation of cations necessarily produces species of opposite charge, which in the solid or liquid associate in stable arrays held by coulombic forces. In the gas phase this stabilization is very limited, and it is usual to make cations by direct ejection and rapid withdrawal of electrons. The free cations are reactive entities and their reactions with molecules can be studied most conveniently by mass spectrometry, although in normal low-pressure operation such reactions are avoided. Appreciable amounts of cations are formed at high temperatures in flames or plasmas or more conveniently at ordinary temperatures in low-pressure discharges. These sources can be sampled by suitable probes and the cations examined inside the mass spectrometer. For example, the ions formed from a glow discharge in water vapor have been measured at various points in the discharge. A series of ions $H(H_2O)_n^+$ ($n = 1$–6) were observed, with the $H_9O_4^+$ ion as a particularly stable species (*170*). Ion production in mass spectrometers is mainly for the purpose of identifying their precursors; stability is not particularly important, provided the ions last long enough to record their presence. The stability, and thermodynamic quantities associated with the ion, can be studied *in situ* as they are produced.

Chemical synthesis has recently been attempted with ion beams of reactive cations directed immediately after generation onto a target (*305*). Nitrogen dioxide at 10^{-3} to 10^{-4} torr was ionized by electron impact in a magnetron ion source. The kinetic energy and the ionizing potential of the nitronium ions were controllable. It was possible to generate milliampere ion currents of 99% nitronium ion content with which to nitrate benzene in good yield. Although the quantities involved were only of the order of microliters, it marks a significant development in controlled ion synthesis. Other types of plasma device such as constricted arcs, high-frequency induced plasmas, and electrically assisted flames generally operate at too high a temperature to generate heterocations directly; larger ions can form only in cooler regions.

2. Ions in Solution

In the liquid state, the principal method of generating ions is by means of ionizing solvents which can directly heterolyze part of the dissolved molecule, or transfer ions from the solvent itself to generate heterocations and the associated complex anions. (The solution or melting of an ionic compound is not regarded as generation of ions in this sense because of preformation elsewhere.) The driving force is obviously the enhanced stability of a regular arrangement of oppositely charged ions aided by the relative ease of charge separation in media of high dielectric constant. The inevitable presence of large dipoles in such solvents limits their applicability because the solvent molecule tends to participate in the ion which is generated. The participation may be limited, as in solvation which helps to spread the ionic charge, or more complete in solvolysis when the ion is replaced by a solvent species. The solvating propensity can be unequal for similar ions of opposite charge if one end of the solvent dipole is sterically hindered, as for example with dimethyl sulfoxide which tends to solvate cations preferentially (*235*). The heterocation can also be sterically hindered with respect to solvent participation, as in the phenyl-substituted ions $(C_6H_5)_3C^+$, $(C_6H_5)_3As^+$, etc. There are enough solvents available to strike a reasonable compromise between solvation and solvolysis and indeed for some ions the choice is very wide. The nitronium ion has been prepared in solvents as diverse as HNO_3, H_2SO_4, CH_3NO_2, CH_3COOH, SO_2, NOCl, HF, and BrF_3.

Heterocations containing halogen or oxygen atoms can usually be generated from the corresponding halide or oxyhalide by abstraction of a halide ion. The abstracting entity may be the solvent or a similar molecule, such as a Lewis acid (an electron pair acceptor), which can form a stable anion. Only wide generalizations concerning the extent of ionization and the nature of the Lewis acid are possible. It is greatest for fluorides, least for iodides; Lewis acids which can be converted to four- and six-coordinated anions are favored compared with odd coordinations. Apart from this, each ionization has to be considered individually and there is no unique order of ionizing ability for Lewis acids. (A closely related problem is that of arranging Lewis acids in order of activity for Friedel-Crafts reactions.)

In solvents of lower dielectric constant the nature of the ions generated is not always easy to assess since the processes of solvation, ionization, and dissociation are intimately linked. One approach is to consider that all ionizing solvents are parent acid-base systems analogous to water or liquid ammonia, and to regard ionization in these solvents as hydrogen ion, halide ion, or oxide ion transfers. Species which become cationic are defined as acids in the particular system. Lewis acids are fitted into this scheme as ansolvo acids which generate the system acid indirectly by combining with the solvent anion and shifting the solvent equilibrium to compensate for this, i.e.,

$$S{-}X \leftrightharpoons S^+ + X^-$$
$$S{-}X + MXn \leftrightharpoons S^+ + MX_{n+1}^-$$

Solvation is not specifically introduced, except when it is obviously incorrect to omit the solvent molecule, as for example the solvation of a proton in acidic solvents. In organic chemistry much more attention has had to be paid to the effect of solvation because of the smaller tendency to ionization in organic systems, and recently Drago and his co-workers have re-emphasized the importance of solvation in inorganic systems. They have proposed a coordination model which focuses attention on the solvating ability of the solvent (*79*). Groenveld proposed much the same ideas more qualitatively (*131, 133*). There is in effect competition between the solvating ability of a solvent and its donor or acceptor strength. When a Lewis acid is dissolved in a solvent the primary step, according to Drago, is the formation of a solvate,

$$p\mathrm{SX} + \mathrm{MX}_n \leftrightharpoons \mathrm{M(SX)}_p\mathrm{X}_n$$

formulated with solvent around the less electronegative atom. The next stage is a stepwise displacement of the more negative group X, as an anion, by more solvent molecules:

$$\mathrm{M(SX)}_p\mathrm{X}_n + \mathrm{SX} \rightarrow \mathrm{M(SX)}_{p+1}\mathrm{X}^{+}{}_{n-1} + \mathrm{X}^{-},\ \text{etc.}$$

The extent of displacement depends on the overall energetics of the system. Although this can be subdivided into simple steps, not all the energy terms can be found experimentally so that only trends can be predicted.

Consider the two approaches when applied to the ionization of ferric chloride in phosphorus oxychloride. On the solvent system concept, the ferric chloride becomes anionic and acts as an acid by increasing the cation content of the solvent:

$$\mathrm{POCl_3} \leftrightharpoons \mathrm{POCl_2^+} + \mathrm{Cl^-}$$

$$\mathrm{POCl_3} + \mathrm{FeCl_3} \leftrightharpoons \mathrm{POCl_2^+} + \mathrm{FeCl_4^-}$$

On the coordination model, assuming octahedral coordination of iron, the following stages are postulated:

$$3\mathrm{Cl_3PO} + \mathrm{FeCl_3} \leftrightharpoons \mathrm{(Cl_3PO)_3FeCl_3}$$

$$\mathrm{(Cl_3PO)_3FeCl_3} + \mathrm{POCl_3} \leftrightharpoons \mathrm{(Cl_3PO)_4FeCl_2^+} + \mathrm{Cl^-}$$

Similarly, for $\mathrm{(Cl_3PO)_5FeCl^{2+}}$ and $\mathrm{(Cl_3PO)_6Fe^{3+}}$ cations

$$\mathrm{Cl^-} + \mathrm{(Cl_3PO)_3FeCl_3} \leftrightharpoons \mathrm{FeCl_4^-} + 3\mathrm{POCl_3}$$

The theories predict different cations; in particular, on the solvent system theory all the ionized iron is expected to be anionic, whereas on the coordination theory part is cationic.

If the solvent phosphorus oxychloride is replaced by triethylphosphate, a solvent with approximately the same dielectric constant and solvating ability, the ionization of ferric chloride to the tetrachloroferrate anion still occurs, although it is no longer possible to express the ionization as a chloride ion transfer from the solvent. An equilibrium of the type

$$\mathrm{FeCl_3} + \mathrm{PO(OC_2H_5)_3} = \mathrm{PO(OC_2H_5)_2^+} + \mathrm{(FeCl_3OC_2H_5)^-}$$

would be required. However, according to the coordination theory, substituting an ethoxy group for chlorine in the above equations leads to essentially similar products and there is no difficulty in understanding the formation of the $\mathrm{FeCl_4^-}$ anion. In fact solvents for ferric chloride can be arranged in order of donating and solvating ability, and related to the ionization induced in ferric chloride. At one extreme, weakly donating and solvating solvents produce mainly $FeCl_2(solvent)_4^+$ and $FeCl_4^-$; at the other extreme, for strongly donating and solvating solvents, only chloride ion and the solvated ferric ion are formed. There are many other examples in which solvation is essential to stabilize cations and in this respect the above theory is satisfactory.

The generation of a tetrachlorostibonium ion by dissolving antimony pentachloride in methyl cyanide can also be formulated according to the coordination theory (*24*, *181*):

$$CH_3CN + SbCl_5 \rightleftarrows CH_3CN \rightarrow SbCl_5$$

$$CH_3CN + CH_3CN \rightarrow SbCl_5 \rightleftarrows (CH_3CN)_2SbCl_4^+ + Cl^-$$

$$Cl^- + SbCl_5 \rightleftarrows SbCl_6^-$$

However, with antimony pentahalides in halide-containing solvents, the antimony is found in the anion only. Thus a solution of antimony pentafluoride in anhydrous hydrogen fluoride behaves similarly to a solution of an alkali hexafluoroantimonate. Similarly, the antimony is anionic in fluorosulfuric acid and in halogen fluorides. The coordination theory has then to be formulated as

$$nXF + SbF_5 \rightleftarrows (n-1)XF\cdot XF\cdot SbF_5$$

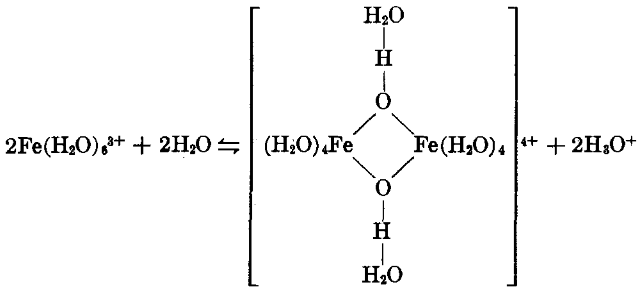
$$XF + (n-1)XF\cdot XFSbF_5 \rightleftarrows (XF)_nX^+ + SbF_6^-$$

where XF is HF, BrF_3, IF_5, AsF_3, which, except for the intermediate adduct, is no different in essence from the solvent system formulation. This would be given more simply, as for example in hydrogen fluoride, by

$$2HF + SbF_5 \rightleftarrows H_2F^+ + SbF_6^-$$

and this is to be preferred since there are strong objections against formulating an un-ionized intermediate, which is anything other than a short-lived transition state in these highly polar media.

The solvation of cations when an ionic solid is dissolved in a solvent will not be considered, but the further reactions with solvents which solvolyze these ions will be described later. Ferric ions in water, for example, are hydrolyzed to a binuclear cation (*212*):



The formation of complex cations, when part of the primary solvation shell is replaced by simple anions, is similar to the above, and is studied by analogous methods. Generally a series of substituted ions coexist and it is impossible to isolate a simple species. The methods of investigation provide no information on the extent of solvent participation. Thus in the hydrolyzed ion above, the octahedral water coordination is assumed to persist from the simple solvated cation.

3. Ions in the Solid Phase

Solid ionic compounds can be generated without solvent participation by merely bringing together volatile nonionic halides and oxyhalides. Admittedly liquids such as halogenated hydrocarbons are sometimes used, but these are inert heat-transfer and collecting media which facilitate the removal of reaction heat and enable solids to be collected conveniently. Thus gaseous sulfur tetrafluoride reacts with boron trifluoride or arsenic pentafluoride to form solid trifluorosulfonium salts (*286*). If one of the halides or oxyhalides is reactive it can act as a halogenating agent and generate a second halide *in situ* to combine with an excess of the first component. Nitrosyl chloride behaves in this way with metals, forming the metal chlorides which then combine with excess nitrosyl chloride to produce nitrosonium salts (*237*). Similar reactions occur with nitryl fluoride and metals (*11*). However, heterogeneous reactions involving solids are less efficient than solution reactions because of limited diffusion rates in solids. Higher temperatures are generally needed and heat transfer is more difficult to control. Alternative solution reactions are therefore preferable, provided solvent participation in the product can be overcome.

The majority of reactions leading to ionic solids involve ion transfers or pairwise electron transfers. It is also possible to form ionic solids by simple electron transfer or mutual oxidation-reduction. A good example is Bartlett and Lohmann's preparation of the oxygenyl ion by electron transfer between oxygen and platinum hexafluoride (*20*):

$$O_2 + PtF_6 = O_2^+(PtF_6)^-$$

Other free radicals, such as NF_2^*, NO_2^*, SO_3F^*, ClO_2^*, can also interact between themselves and with halides although not necessarily to produce ionic compounds (*200*, *279*). Nitronium perchlorate was prepared from nitrogen dioxide, chlorine dioxide, and ozone, presumably by a radical reaction (*124*). Reactions with metals must involve electron transfer in the initial stages, the transferred electron usually being carried off as a volatile species. Thus nitric oxide is liberated in the formation of a nitrosonium complex nitrate from nitrogen tetroxide and zinc or copper, and the fluorination of dinitrogen tetroxide and gold in bromine trifluoride to nitronium tetrafluoroaurate liberates bromine. In the first example the dinitrogen tetroxide is cleaved unsymmetrically to form the heterocation. Other examples of unsymmetrical molecular cleavage are known; in particular the boron hydrides, such as diborane, can be ionized as $BH_2^+BH_4^-$ when the cation is stabilized by solvation.

D. CLASSIFICATION OF HETEROCATIONS

A short survey of the heterocations is now given to show their interrelation, before describing some in more detail. A purely geometrical classification is less informative than one based on the Periodic Table and a formal method of generating ions. The small stable cations are concentrated in earlier periods and toward the center of the periodic classification. There is a tendency for polymeric cations in later periods and for ion pairs with elements of metallic character. In the earlier groups the heterocations also tend to form ion pairs and simple solvated cations. In Fig. 2 these tendencies are represented diagramatically.

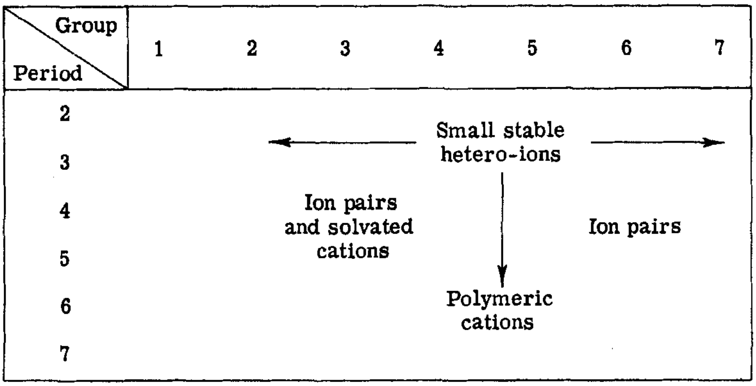


FIG. 2. Cations in relation to the Periodic Table.

The heterocation contains a core element and in order to attain a positive charge the surrounding elements or groups must be of greater electronegativity even if not potentially anionic. Consequently the halogens and oxygen are the main negative functions. This immediately precludes binary oxycations in Group 2; they need to be at least binuclear with respect to the core element. The other main negative species is hydrogen or an analogous group, such as the phenyl group.

Generation of cations can be started formally from carbon tetrachloride. Withdrawal of the chloride ion would leave the trichlorocarbonium cation. In practice this tendency is small in solution, because the inductive effect of three halogens on the heterolysis of the remaining bond will leave the species with a negative charge. Thus the trifluoromethyl group tends to act as a negative substituent or pseudofluoride in many compounds. In the gas phase, however, the generation of CF_3^+ by a homolytic route is feasible and this ion is identified mass spectrometrically as a common product from the breakdown of fluorocarbons. More stable carbonium ions result when alkyl or aryl groups replace halogens. The triphenylcarbonium (trityl) ion is stabilized in numerous salts, but even here the ease of formation of free triphenylmethyl radicals shows how finely balanced are the factors leading to the carbonium ion.

The hydrogen or halogen can also be replaced by oxygen. There is evidence for the formylium cation in some reactions; other acylium or arylium cations are well authenticated. There is no convincing evidence for $COCl^+$ or CO^{++}, although postulated for reactions in solution. These formal relationships are summarized in Fig. 3.

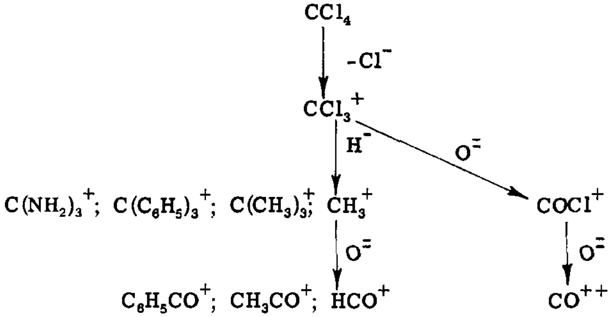


FIG. 3. Formal generation of ions from CCl_4.

The nonclassical carbonium ions, of importance as intermediates in organic chemistry, are not discussed.

Silicon is unable to form this array of small hetero-ions, and the tendency with oxygen is toward polymeric structures as in various forms of silica or in silicones. Simple ions, SiO^+, $Si_2O_2^+$, are encountered only in the gas phase. In the subgroup polymerized oxycations are the rule; the halocations are generally monomeric (e.g., ZrF_2^{2+}, ZrF^{3+}, $ZrCl_3^+$).

In Group 3, boron can form simple heterocations containing hydrogen or halogen, provided the tetrahedral boron coordination is achieved with extra solvent molecules [e.g., BH_2(solvent)$^+$, $B(C_6H_5)_2$(solvent)$^+$, BCl_2(solvent)$^+$]. With oxygen the tendency to three-coordination predominates and results in polymer formation. Boron oxyhalides are cyclic trimers, not salts containing BO^+ cations. With aluminum there is a greater tendency to polymeric cations, especially with oxygen, but thallium again forms dihalo and dialkyl cations.

On the other side of carbon there is a profusion of heterocations in

Group 5, which can be related to phosphorus pentachloride $PCl_4^+PCl_6^-$ by substituting elements or groups of elements for chlorine in the PCl_4^+ cation. This is shown in Fig. 4. Many other more complex phosphonium salts are known.

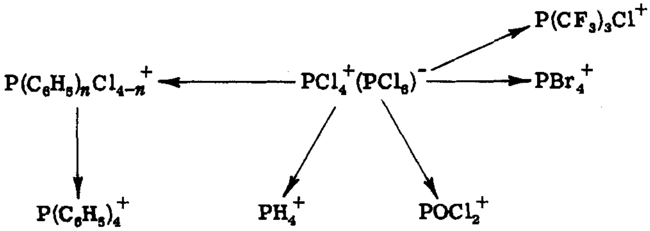


FIG. 4. Formal generation of ions from PCl_5.

The nitrogen heterocations are less extensive in substituents if not in number of salts isolated (e.g., NH_4^+, NO^+, NO_2^+, NF_2^+, N_2F^+). Monomeric tetrahalo cations exist with As, Sb, V, Nb, Ta, as well as polyhalo cations, such as $Nb_6Cl_{12}^{2+}$, in later periods of the group. This polymeric tendency is also shown in oxygen derivatives.

In the next group, while there is only contentious evidence for sulfur and selenium oxycations, there is no doubt concerning the halo derivatives which include $SeCl_3^+$, $TeCl_3^+$, SeF_3^+, SCl_3^+, SCl^+, $S(alkyl)_3^+$. The transition elements in this group again follow the trend from the previous group in forming polynuclear oxyions and some polyhalo cations (e.g., $Mo_6Cl_8^{4+}$).

Group 7 heterocations consist mainly of the interhalogen cations and those derived from oxyfluorides (e.g., ClF_2^+, BrF_2^+, ICl_2^+, I^+(solvent), IF_4^+, ClO_2^+, IO_2^+). Fluorine is too electronegative to be the core element and no fluoronium salts have yet been prepared.

The hydrogen content of heterocations so far mentioned has been electronegative. The positive side of its behavior is even more important, not in the form of the bare proton but associated with water and other protonic solvents or aromatic molecules, as $H(H_2O)_n^+$, $H(HX)_n^+$, and $H(ArH)^+$ ions. The extensive work on this aspect of heterocations merits separate discussion (p. 279).

The principal developments in cation chemistry in the period under consideration can be summarized:

(1) Identification of cations in the gas phase relying mainly on measurement of their mass-to-charge ratio and appearance potential. Little direct information on structure can be obtained for inorganic species.

(2) Production of cations in nonaqueous systems and their isolation as salts. The mechanism of cation production in these systems is the subject of controversy concerning the role of solvation.

(3) Recognition and quantitative measurement of polynuclear complex cations in aqueous solution. The full composition of these species is unknown; they appear as a result of fitting experimental curves with a minimum number of species of different stabilities. More direct experimental methods have provided confirmation for some of these species and shown the reality of the concepts involved.

These developments are not fundamentally different in kind, in that most of the methods and theoretical background already existed. However, the correlation of structural units in the different states of matter can be regarded as novel. Thus large cation units which exist in the solid have now been recognized in the liquid and gaseous states. Presumably the same forces maintain structural integrity.

II. Cations of Nontransition Elements

A. GROUP III

1. *Boron Cations*

The known cations are solvated dihydro or dihalo boronium ions with tetrahedral coordination. Of particular interest are the ions derived from boron hydrides which contain hydroboro anions as well as cations. Parry and his co-workers made a thorough re-examination of the diammoniate of diborane which is admittedly saltlike, but which can be formulated in more than one way by movement of single hydrogen:

$$NH_4^+(H_3B\ NH_2\ BH_3)^-,\ NH_4^+(H_2B\ NH_2)BH_4^-,\ (NH_3\ H_2B\ NH_3)^+BH_4^-$$

The second formula was originally adopted because ammonium borohydride is unstable; the separation of the ions was supposed to stabilize them. It was shown to be a borohydride, and not an ammonium salt, by its reaction with a slurry of solid ammonium chloride in ether. Hydrogen was evolved, a chloride, later indentified as $BH_2(NH_3)_2{}^+Cl^-$, was isolated, and also a borine amine of only half the molecular weight of the original $B_2H_62NH_3$. The reaction can be regarded as a double decomposition reaction (*280*),

$$NH_4Cl + X^+BH_4^- = H_3NBH_3 + H_2 + X^+Cl \qquad (X = BH_2{\cdot}2NH_3)$$

followed by breakdown of the unstable $NH_4^+BH_4^-$. Other reactions which confirmed the borohydride formulation were

$$(1) \qquad [H_2B(NH_3)_2]BH_4 + Na = NaBH_4 + \tfrac{1}{2}H_2 + H_2BNH_2 + NH_3$$

a cation displacement carried out at −78° in liquid ammonia, and the anion displacement,

$$(2) \qquad XBH_4 + HCl = XCl + H_2 + \tfrac{1}{2}B_2H_6 \qquad (X = BH_2{\cdot}2NH_3)$$

Further evidence came from tracer experiments with deuterated compounds which showed that in the sodium reduction (1) the B-H bonds in BH_4^- remained intact whereas the N-H was broken. The presence of the borohydride ion was also established by Raman spectroscopy on a solution of $B_2H_62NH_3$ in liquid ammonia at low temperatures.

The diammoniate of tetraborane, made by adding ammonia to a cold ethereal solution of excess tetraborane, was shown to be $H_2B(NH_3)_2{}^+B_3H_8{}^-$ by analogous methods. Thus in reaction (1) the salt NaB_3H_8 was isolated in 60-70% yield, and from reaction (2) the same XCl salt as from the diammoniate of diborance could be recovered. The B_3H_7 fragment was isolated as the etherate $(C_2H_5)_2O{\cdot}B_3H_7$ (*171*).

The crystal structure of the salt $BH_2(NH_3)_2Cl$ consists of puckered layers of chloride ions interleaved with the cations. Although the hydrogen atoms were not located the B-H distances, equal within experimental error and inclined at 106°, were consistent with a tetrahedral cation. The ammonia groups were surrounded by a distorted square of chlorine atoms with N-Cl distances from 3.39 to 3.45 Å, similar to those in ammonium chloride (*226*). A series of salts with the ammonia in the $BH_2(NH_3)_2{}^+$ cation replaced by amines has been prepared.

Unsymmetrical cleavage of diborane can also be brought about by reaction with dimethyl sulfoxide in the diluent methylene chloride at −78°. The structure of the product was shown to be $BH_2[OS(CH_3)_2]_2{}^+BH_4{}^-$ by $BH_2{}^+$ peaks in the Raman spectrum and the quintet due to $BH_4{}^-$ in the B^{11} n.m.r. spectrum. The compound, however, is not stable above −33° (*201*). A systematic synthesis of a whole range of stable borane cations has now been achieved. Their stability is highlighted by one of the general synthetic methods carried out at temperatures up to 180°. The solvates include tertiary amines, phosphines, arsines, dialkylsulfides, as well as bidendate ligands. The salt anions include halide, polyhalide, fluorophosphate, chloroaurate, and dodecaborane anion $B_{12}H_{12}{}^{=}$. Three synthetic methods were used (*215*):

(1) Base boranes + onium salt of large anions at 100°–180°:

$$D{\cdot}BH_3 + DH^+X = (H_2B)D_2{}^+X^- + H_2$$

If the onium salt was unstable the equivalent D + HX mixture was substituted.

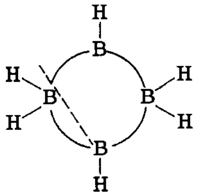
(2) Displacement of the solvate or base in the cation by a stronger base. This could occur simultaneously in the previous method. The displacement series found was diamines > amines > phosphines > arsines > sulfides.

(3) Base borane and diborane.

The cations were thoroughly characterized by the infrared spectra, by the B^{11} n.m.r. spectra, which consisted of 1:2:1 triplets expected from equivalent B-H bands in BH_2, and by the retention of the base in the cation on ion exchange. Substitution reactions in the cation enable the hydrogen to be replaced. Thus SF_5Cl, NCl_3, and aqua regia all monochlorinate, ICI dichlorinates, F_2 with nitrogen difluorinates, and F_2 with the chloride ion can chlorofluorinate. It is even possible to "fluorosulfate" with peroxydifluorosulfate $S_2O_6F_2$. The series of solvated cations of BH_2^+, $BHCl^+$, BCl_2^+, $BClF^+$, BF_2^+, and $B(SO_3F)_2^+$ is now available.

The mechanism of formation of these ions from boranes has been studied and indicates that the initial cleavage of the borane is symmetrical (*236*). Thus tetraborane and sodium tetradeuteroborate in ethylene glycol–dimethyl ether exchange deuterium in the amounts required by the first and not the second equation:

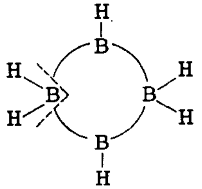
Symmetrical cleavage



$+ NaBD_4 = NaB_3H_7D + B_2H_3D_3$

(12.5% D) (50% D)

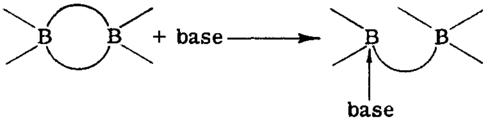
Unsymmetrical cleavage



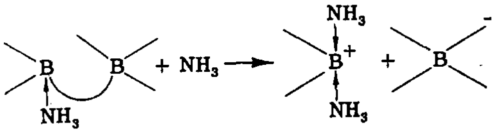
$+ NaBD_4 = NaB_3H_8 + B_2H_2D_4$

(0% D) (50% D)

The reaction of diborane with a base is therefore formulated as a symmetrical bridge opening followed by nucleophilic attack by a second molecule of base:

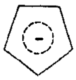


The nature of the nucleophile, and of the base already attached, decides whether the product is symmetrical or not. For ammonia the slow second step is:

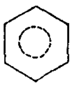


An n.m.r. examination of tetraborane in tetrahydrofuran, on the other hand, suggests an initial nonsymmetrical cleavage. At −68° the B^{11} resonances of tetraborane are observed. They disappear at −50° and at −20° are replaced by a clearly resolved septuplet with the chemical shift and coupling constants of the $B_3H_8^-$ ion (*269*).

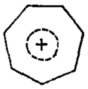
Lipscomb has discussed the possible borane ions from a topological viewpoint and indicated the possibility of purely ionic hydrides, which has now been realized. The $B_6H_{11}^+$ ion has been predicted as one of the triad analogous to the aromatic sequence (*198*). The cations $B_3H_6^+$ and $B_4H_{10}^{2+}$ were also predicted.



$B_4H_7^-$

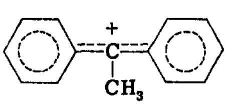


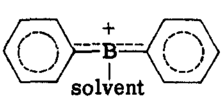
B_5H_9



$B_6H_{11}^+$

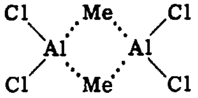
The cations described previously and the chelated cations of boron, with for example acetylacetone, are tetrahedral. Davidson and French (*74*) made a planar cation by dissolving diphenylboron chloride in methyl ethyl ketone and adding aluminum chloride. The production of ions was indicated by a 1000-fold increase in conductivity, equivalent to about 1% ionization. The ultraviolet absorption spectrum had a maximum very close to that of diphenylmethyl bromide in the presence of aluminum chloride. The correspondence of the isoelectronic π systems was taken as evidence for a planar boronium ion.

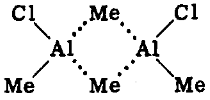




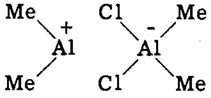
2. Other Cations in the Subgroup

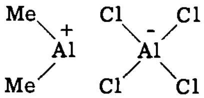
There is some evidence of cations produced by unsymmetrical cleavage of dimeric halides, or substituted halides, with other elements in the subgroup. The dimethyl- and tetramethylaluminum chlorides have been formulated with methyl bridged structures:



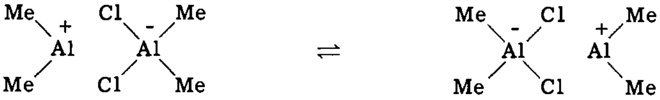


Glick and Zwickel maintain that the Raman spectra are consistent with ionic structures (*122*):



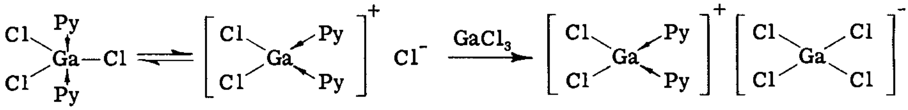


Although the methyl groups are not equivalent in the former ionic structure, they are not distinguished in p.m.r. spectra, presumably because of halogen exchange.



In order to obtain C_{2v} symmetry with bridging methyl groups in the tetramethyl compound the *cis* structure is required. The correct symmetry follows more naturally from the ionic formulation. The dipole moment of 1.9 D is also inconsistent with methyl bridging. This is an interesting illustration of an ion of limited life detected by Raman spectroscopy in the form of an ion pair, but not by n.m.r. because of the time scale of chlorine exchange. The dissolution of aluminum chloride in donor molecules can also induce unsymmetrical ionization. The ion pair $(\mathrm{AlCl_2 \cdot }n\mathrm{CH_3CN})^+$-$\mathrm{AlCl_4^-}$ seems more likely than the ionization $(\mathrm{Al_2Cl_5 \cdot }n\mathrm{CH_3CN})^+\mathrm{AlCl_4^-}$ originally proposed (*276*).

The pyridine adducts of gallium trihalides ionize to a small extent when molten. The amount of ionization with $\mathrm{GaCl_3 \cdot 2C_5H_5N}$ has been estimated at about 7%. The 1:1 adduct is the more stable and ionization of an initial trigonal bidyramidal adduct has been suggested (*130*).



Bidendate ligands on thallic halides can induce similar ionization $\mathrm{TlX_2^+TlX_4^-}$ (*315*).

B. GROUP IV

An extensive account of recent progress in the field of carbonium ions has appeared (*76*), and only a few topics of more general interest are covered here.

1. *Trityl and Related Cations*

Salts of the triphenylmethyl (trityl) and substituted cations are well established. They can be easily prepared by neutralization of the carbinol, or by removal of a chloride ion from trityl chloride by means of a silver salt (*73*). Thus for the tetrafluoroborate:

$$(C_6H_5)_3COH + HBF_4(aq) \xrightarrow{(C_2H_5CO)_2O} (C_6H_5)_3C^+BF_4^- + H_2O$$

$$(C_6H_5)_3CCl + AgBF_4 \xrightarrow{(C_2H_5)_2O} (C_6H_5)_3{}^+CBF_4^- + AgCl$$

The salts of the complex fluoro anions PF_6^-, SbF_6^-, NbF_6^-, and SO_3F^- are particularly stable in the solid state. Delocalization and stabilization of charge in the trityl ion would be optimized if the ion were symmetrical and planar, but the *ortho*-hydrogen atoms on adjacent rings prevent this. A compromise propeller-like structure, with the rings tilted in sequence at 30° to each other, is indicated by both infrared and n.m.r. spectra (*33*). A full interpretation of the former spectra has not been carried out, but qualitatively the main features are accounted for on D_3 rather than D_{3h} symmetry. The absence of covalent bonding between cation and the anions is shown by the characteristic anion absorption bands as in alkali salts. Any distortion of these highly symmetrical ions would lead to splitting of the peaks (*297*).

Less stable tetrahalogenoborates have been prepared by mixing the trityl halide with the boron trihalide in nonionizing solvents, such as methylene chloride or cyclohexane. Thus

$$(C_6H_5)_3CBr + BBr_3 = (C_6H_5)_3C^+BBr_4^-$$

This salt is able to extract a hydride ion from cycloheptatriene to form the tropenium salt $C_7H_7^+BBr_4^-$ (*138*, *139*).

There has been a continuous interest in the ionization of triaryl methyl compounds in solvents. In particular, the distinction between ionization and dissociation, and their variation with substituents in the aromatic portion, or of the group X, has been argued:

$$\begin{array}{ccccccc}
Ar_3CX & \rightleftharpoons & Ar_3C^+X^- & \rightleftharpoons & Ar_3C^+(\text{solvent})X^- & \rightleftharpoons & Ar_3C^+ + X^- \\
\text{(un-ionized and} & & \text{(ionized and} & & \text{(ionized and separated} & & \text{(free ions} \\
\text{undissociated)} & & \text{undissociated)} & & \text{by one or more} & & \text{separated by} \\
 & & & & \text{solvent molecules)} & & \text{many solvent} \\
 & & & & & & \text{molecules)}
\end{array}$$

The method of measurement employed determines which of these stages is detected. Thus conductometry detects the discrete ions in the last stage, and possibly the solvent-separated ions when the ion pairing is weak, whereas spectrophotometry, on a triaryl carbonium absorption peak, is less dependent on the cation-anion separation and both ion pair and free ion are measured.

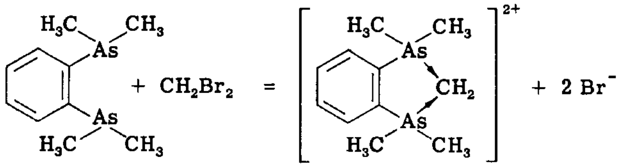
Fairbrother and Wright measured the extent of ionization spectrophotometrically when dilute solutions of arsenic tribromide in various solvents were added to trityl bromide solutions (*95*). The equilibrium constants for ion pair formation varied from about 0.1 to 10 as the solvent was changed from benzene to ethyl bromide. The equilibrium constants, for the stage ion pairs to separated ions, were of the order 10^{-7} to 10^{-4} in these solvents. Even in dilute solutions very few ions were free (e.g., a 0.005 *M* solution in benzene had 0.09% of free ions). With mercuric chloride in benzene there was no evidence for free ions but only for ion pairs. In nitromethane considerable ion pair formation and some dissociation have been claimed (*22*), but this has been disputed by Pocker (*243*), who detected an interaction with the solvent to form hydrogen chloride which contributed to the conductivity and color of solutions. He believes that trityl chloride is ionized in this solvent.

The displacement of chloride in trityl chloride solutions in benzene has been interpreted solely in terms of ion pair formation without dissociation (*154*), but generally the solvent takes a more intimate role in the ionization of trityl compounds, apart from providing a polar medium. This can be appreciated by comparing the minute dissociation of trityl chloride in nitrobenzene (dielectric constant 24.5) with its extensive ionization and dissociation in liquid sulfur dioxide or hydrogen chloride (dielectric constants 15.3 and 9.3, respectively). In the latter solvent, specific interaction by hydrogen bonding to the (Cl——H——Cl)$^-$ anion is likely; in the former, while direct formation of the SO_2Cl^- anion is improbable, the existence of a charge transfer complex between the chloride ion and sulfur dioxide is shown by intensification of the electronic spectrum of the latter (*196*, *197*), i.e.,

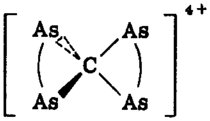
$$(C_6H_5)_3CCl + SO_2 = (C_6H_5)_3C-\underline{Cl}|\ SO_2 \rightleftharpoons (C_6H_5)_3C^+ + Cl^- \text{ (solvated)}$$

This interaction would considerably reduce the energy required for ionization.

Ionic salts of the methyl cation are not known in the solid state, but it has proved possible to make simple carbonium derivatives chelated with diarsines:

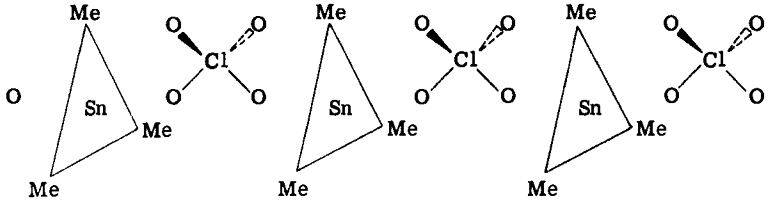


Similarly from carbon tetraiodide the chelated ion results.



Conductivity measurements confirm the cation charges (*64*). There is evidence mainly from n.m.r. spectra for secondary and tertiary alkyl cations produced from the corresponding fluoroalkanes dissolved in antimony pentafluoride (*231*). The planar $C(NH_2)_3^+$ cation has been confirmed by X-ray analysis (*142*).

There are no corresponding stable series of triaryl cations of other Group IVb elements. Thus triphenylsilyl chloride does not ionize in nitrobenzene even in the presence of strong Lewis acids (*316*). Conflicting reasons have been advanced to explain this (*23*). (In Group IVa, delocalization of charge from metal ion to ring systems can form stable cations; these metal-carbon bonded configurations are discussed later.) The full ionicity of many trimethyltin compounds has also been disputed. These volatile solids were formulated as salts $(CH_3)_3Sn^+X^-$ where X^- = halide, NO_3^-, CH_3COO^-, ClO_4^-, BF_4^-, AsF_6^-, or PF_6^-. However, the perchlorate consists of planar trimethyltin groups bridged by bidendate perchlorate groups to form chains (*57*).



The symmetry of the perchlorate group, according to the infrared spectrum, is lowered from the T_d symmetry of the perchlorate ion to C_{2v}. A similar behavior was observed with anhydrous copper perchlorate (*144*). The nitrate contains a unidendate nitrate group, as distinct from the bidendate nitrate group encountered in basic beryllium nitrate, and the tin is tetrahedrally coordinated. The Raman spectra of other halides show halogen bridging between tin groups (*186*). This partial covalent bonding is removed on solvation. Thus the diammoniate of trimethyltin nitrate contains the free nitrate ion and is $(CH_3)_3Sn(NH_3)_2^+NO_3^-$. Tetramethylstannane dissolves in concentrated sulfuric acid with evolution of methane and ionization of the residue to a solvated trimethyltin cation:

$$(CH_3)_4Sn + H_2SO_4 = (CH_3)_3Sn^+ + HSO_4^- + CH_4$$

Trimethyltin sulfate in sulfuric acid produces four particles according to cryoscopic measurements, two of which are shown to be bisulfate ions by conductivity measurements (*119*):

$$[(CH_3)_3Sn]_2SO_4 + 2H_2SO_4 = {}^{+}2[(CH_3)_3Sn{\cdot}H_2SO_4]^+ + 2HSO_4^-$$

2. *Acylium and Arylium Cations*

The main interest in these ions has been in conjunction with their role as reaction intermediates, particularly in the Friedel-Crafts reaction for which Fairbrother's classic experiment on radioactive chlorine exchange during the acetylation of benzene provided prima facie evidence of acetylium ions (*94*). Although stable salts of these ions have been isolated, a detailed examination of the infrared spectra reveals additional lines which indicate some interaction between cation and anion. Susz and coworkers examined the spectrum of acetylium fluoroborate, a compound first isolated by Seel from the component fluorides in liquid sulfur dioxide (*314*). The lines of the fluoroborate anion appeared at frequencies close to those of potassium fluoroborate after precautions were taken to avoid formation of the anion by possible attack on the cell windows by fluoroboric acid. This acid could arise from traces of moisture and partial dissociation of the salt. A strong absorption at 2299 cm^{-1} was ascribed to the cation $CH_3C{\equiv}O^+$. The carbonyl frequencies in acetyl fluoride appeared at 1851 and 1879 cm^{-1}. The assignment was supported by analogy with the bands in $NO^+AlCl_4^-$ and NOCl, which occur at 2236 and 1800 cm^{-1}, respectively (*108*). However, a further absorption occurred at 1619 cm^{-1} and this was interpreted as a contribution from a carbonyl stretching frequency perturbed by an electron drift from oxygen to boron. Similar shifts in carbonyl frequencies occurred when ketones were complexed with Lewis acids (*50*). The lowering of frequencies with various Lewis acids is given in Table I; the uncomplexed ketone frequencies are in parentheses.

TABLE I
LOWERING OF C=O FREQUENCIES BY LEWIS ACIDS

Lewis acid	$C_6H_5COC_6H_5$ (1657)	$C_6H_5COCH_3$ (1675)	CH_3COCH_3 (1710)
$HgCl_2$	—	18	—
$ZnCl_2$	—	47	—
BF_3	112	107	70
$TiCl_4$	144	118	
$SnCl_4$	—	—	75
$AlCl_3$	122	120	—
$FeCl_3$	145	130	—
$AlBr_3$	142	130	85

Thus the main spectral evidence for the acetylium cation rests on the assignment of the 2300 cm^{-1} band, which appears when acetyl halides are mixed with Lewis acids, and similarly a band at 2200 cm^{-1} for arylium ions. However, Cook points out that with some complexes both of these bands are obtained. In $CH_3COCl{\cdot}AlCl_3$ or $CH_3COCl{\cdot}GaCl_3$, for example, there is a strong band at 2300 cm^{-1} and a weak one at 2199 cm^{-1}, as well as a 1616 cm^{-1} band associated with oxygen donation to the halides. He presents evidence for equating the lower frequency with the stretching frequency of CH_3CO^+, and the higher frequency with the carbonyl stretch in a complex $[CH_3CO \cdots GaCl_3]^+Cl^-$ (*67*).

Among the arguments advanced are:

(1) The avoidance of postulating different coordinations, i.e., from oxygen or halogen to the Lewis acid, when the organic chloride is changed and the Lewis acid remains constant in a series, or vice versa. Complex formation always occurs with oxygen on this view.

(2) The mechanism of acetylation requires a more sterically hindered entity than the small CH_3CO^+ cation.

(3) The production of aluminum at both electrodes on the electrolysis of aluminum halides in acyl halide solution.

Much further evidence is needed before the structure of these acylium salts can be satisfactorily resolved. In particular, a study of metal-halogen frequencies should indicate the validity of ionic-coordinated species suggested by Cook, or even further ionization of the Lewis acid in line with Drago's coordination theory (e.g., $[CH_3COGaCl_2]^+Cl^-$). Certainly X-ray structural data are required. The coexistence of more than one species is of course possible, e.g., an equilibrium between ionic species and donor-acceptor complexes.

The evidence for the cations $COCl^+$ and CN^+ relies on the ionizations induced by Lewis acid chlorides in the corresponding chlorides $COCl_2$ and CNCl. Solvates of aluminum chloride can be isolated from solutions in both halides (*111*). The analogies between cyanogen and nitrosyl halides have been discussed (*333*). Thus both chlorides form 1:1 compounds with $AuCl_3$, BCl_3, $AlCl_3$, $SbCl_5$, and $FeCl_3$, and 1:2 compounds with $TiCl_4$. It is therefore tempting to formulate the cyanogen chloride compounds as salts of the cyanogen cation. A comparison of the energetics of salt formation between the cyanogen and nitrosyl positive ions shows that the former is far less favorable, mainly because of the higher ionization potential to produce the cyanogen cation, and the greater dissociation energy of CN-Cl to produce the cyanogen radical. This rules out the cyanogen cation in solid compounds.

The high conductivities of Lewis acid chlorides in solution and transport of aluminum or iron to the anode on electrolysis could be explained by ionization of the solvates without involving a solvent ionization, i.e.,

$$\mathrm{AlCl_3 + Cl{-}CN \rightleftarrows Cl{-}CN \rightarrow AlCl_3}$$
$$\mathrm{Cl{-}CN + Cl{-}CN{\cdot}AlCl_3 \rightleftarrows (Cl{-}CN)_2AlCl_2^+ + Cl^-}$$
$$\mathrm{Cl^- + AlCl_3 \rightleftarrows AlCl_4^-}$$

and similarly for ferric chloride solutions. However, a partial polarization of the cyanogen-halogen bond, which is greater than in the formation of solvates, may be involved in Friedel-Crafts substitutions with cyanogen chloride and bromide. The solvates $CNCl{\cdot}AlCl_3$ and $CNBr{\cdot}AlBr_3$ produce cyanobenzene with benzene, and the yield increases in a more polar medium such as nitromethane (*333*).

C. GROUP V

The nitronium and nitrosonium cations are probably the most intensively studied of all heterocations apart from protonated species. A wide range of other hetero-ions belonging to this group has also been studied but in much less detail.

1. *Halogenated Phosphonium Cations*

The halogenated cations are analogous to the cation in the pentahalides of phosphorus, $PCl_4^+PCl_6^-$, and $PBr_4^+Br^-$. There is some evidence for the existence of all the cations listed in Table II. Reasoning by analogy with the phosphorus halides, one can expect many of their double halides to be ionized. Thus the 1:1 adducts of phosphorus pentachloride with $AuCl_3$, $AlCl_3$, $TlCl_3$, $SnCl_4$, $TiCl_4$, $ZrCl_4$, VCl_4, $NbCl_5$, $TaCl_5$, $SeCl_4$, $TeCl_4$, $MoCl_5$, WCl_5, $CrCl_3$, $FeCl_3$, and $PtCl_4$ and the 2:1 adducts with $SnCl_4$, $ZrCl_4$, $TeCl_4$, and $PtCl_4$ may contain these halides in anions (for references, see *286*).

TABLE II
HALOGENATED CATIONS OF GROUP VB

$PCl_4^+BCl_4^-$	$PCl_4^+PCl_6^-$	$PCl_4^+SO_3Cl^-$	$PCl_4^+F^-$
$PCl_3Br^+BCl_4^-$	$PCl_4^+PCl_5F^-$	$PCl_4^+UCl_6^-$	$PCl_4^+HCl_2^-$
$PCl_4^+BF_3Cl^-$	$PCl_4^+PF_6^-$		$PCl_4^+ICl_2^-$
$PCl_4^+AlCl_4^-$	$PCl_4^+PCl_5Br^-$		$PBr_4^+Br^-$
$PCl_5R^+AlCl_4^-$	$PCl_4^+PNCl_3^-$		$PBr_4^+F^-$
	$PCl_4^+SbCl_6^-$		$PCl(CF_3)_3^+Cl^-$
	$PFCl_3^+SbCl_6^-$		$PCl(CH_3)_3^+Cl^-$
	$PCl_n(C_6H_5)_{4-n}^+SbCl_6^-$		
	$PFC_6H_5\{N(CH_3)_2\}_2^+PF_5C_6H_5^-$		
$AsCl_4^+AlCl_4^-$	$AsCl_4^+AsF_6^-$		$AsCl_4^+$(2 solvent)Cl^-
$AsCl_4^+GaCl_4^-$	$AsCl_4^+SbF_6^-$		
	$SbCl_4^+SbF_6^-$		$SbCl_4^+SO_3F^-$
	$SbCl_4(CH_3CN)_2^+SbCl_6^-$		(SbF_4SO_3F)
	$SbCl_4^+N_3^-$		

Phosphorus pentachloride can exist in an ionic form in solid and solution, and a covalent form in vapor and melt. Many of the compounds listed also have such a chameleonic existence. The acylium ions described previously exhibit this tendency to a lesser extent, and are isolated in one or the other form with relatively small perturbations from an idealized structure. An extreme example of this type of "polarity isomerism" has been encountered in the substituted phosphorus pentafluoride $C_6H_5PF_3N(CH_3)_2$ (*281*). When freshly made by one of the following routes,

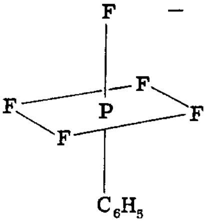
$$\begin{tikzcd}[column sep=small]
C_6H_5PF_3Cl + (CH_3)_2NH \arrow[dr] & \\
C_6H_5PF_4 + (CH_3)_2NH \arrow[r] & C_6H_5PF_3N(CH_3)_2
\end{tikzcd}$$

it is a liquid, boiling at 88° (6.5 torr), soluble in nonpolar solvents. The P^{31} n.m.r. spectrum consists of a doublet of triplets. This spectrum gradually alters and the liquid changes after a few weeks to a crystalline solid of the same empirical composition. The resulting solid forms conducting solutions in the polar solvent, acetonitrile. It is formulated in a dimeric ionic form,

$$[C_6H_5PF[N(CH_3)_2]]^+[PF_5C_6H_5]^-$$

to account for the following features of the n.m.r. spectra:

(1) P^{31}—A 1:1 doublet of the cation to the low field side of the phosphoric acid standard. On the high field side there is another doublet, caused by coupling of phosphorus to an axial fluorine atom, further split into quintets by coupling with four equatorial fluorine atoms. The similarity of coupling constant and chemical shift to that of the hexafluorophosphate anion confirms the anion structure as:



(2) F^{19}—A doublet appears for the cation, a doublet of doublets and a doublet of quintets for the anion.

(3) H^1—A basic doublet appears in the aliphatic region caused by spin coupling of equivalent hydrogens in dimethylamino groups with phosphorus. Each component is further split by coupling to the fluorine in the cation.

The interpretation of these spectra provides an excellent example of the power of the method in structural determination. No other single method would give as much information.

Many workers have provided evidence for halogenated phosphonium, arsonium, and stibonium ions, based on conductivity, transport, and cryoscopic measurements as well as on chemical reactivity. Only a selection from this extensive work can be considered.

The ionization of phosphorus pentachloride itself has been measured in various solvents and the ions PCl_4^+ and PCl_6^- identified by transport measurements (*240*) and infrared spectra. A 1% solution in acetonitrile is completely ionized to unsolvated ions (*325*). If the PCl_4^+ ion is reasonably stable, its survival in chemical reactions in ionizing solvents could be expected. Some indication of stability is provided by the radioactive chlorine exchange between $N(CH_3)_4Cl$ containing Cl^{36} with compounds containing PCl_4^+. The exchange is by a second order reaction of half reaction time from 1 to 19 minutes depending on concentration. The PCl_6^- ion is much less stable and exchanges too quickly to follow by a simple technique (i.e., less than 0.6 second) (*179*). Even in the relatively weak ionizing solvent, hydrogen chloride, neutralization reactions of phosphorus pentachloride, which is readily soluble and slightly ionized, indicate a certain cation stability (*324*):

$$\begin{tikzcd}
& PCl_5 + HCl \rightleftharpoons PCl_4^+HCl_2^- \arrow[dl] \arrow[dr] & \\
PCl_4^+SO_3Cl^- & & PCl_4^+BF_3Cl^-
\end{tikzcd}$$

The chlorosulfate is not stable enough to exist at room temperatures and resembles NO_2SO_3Cl in this respect (*123*).

Phosphorus pentabromide dissociates in acetonitrile similarly to the pentachloride. The equivalent conductivity of these solutions varies in the normal linear way with the square root of concentration. Transport measurements show the solution ionization,

$$2PBr_5 \leftrightarrows PBr_4^+ + PBr_6^-$$

and not the ionization $PBr_4^+Br^-$ of the solid pentabromide (*140*). Mixed halide systems are more complicated and the ionic species have yet to be fully delineated.

The PCl_3–Br_2 system forms compounds at 1:2 and 1:9 proportions. The latter has been equated with a polybromide $PCl_3Br^+[Br(Br_2)_8]^-$ by conductivity and transport measurements (*141*). However, Popov was unable to find simple phases and isolated a solid of composition $PCl_{4.67}Br_{0.33}$ which had a unit cell containing $P_{12}Cl_{56}Br_4$ (*244*). This suggested a packing of $8PCl_4^+$, $4PCl_6^-$, and $4Br^-$ ions. Payne provided cryoscopic evidence for undissociated molecules $PCl_3(Br_2)$ and $PCl_3(2Br_2)$ in equilibrium with small amounts of unspecified ionic species. A simpler product was isolated by employing arsenic trichloride as an ionizing medium with equimolecular proportions of phosphorus trichloride and bromine (*178*). A yellow high melting solid of composition $PCl_{4.5}Br_{0.5}$ was isolated which ionized in acetonitrile, and decomposed to pentahalides in carbon tetrachloride. The structure $PCl_4^+PCl_5Br^-$ was preferred to $PCl_3Br^+PCl_6^-$ because of the retention of the PCl_4^+ ion on fluorination with arsenic trifluoride:

$$3PCl_4^+PCl_5Br^- + 6AsF_3 = 3PCl_4^+PF_6^- + 5AsCl_3 + AsBr_3$$

The suggested mechanism was:

$$PCl_3 + Br_2 \rightarrow PCl_3Br_2 \leftrightarrows PCl_4^+PCl_4Br_2^-$$

$$PCl_4^+PCl_4Br_2^- + AsCl_3 \rightarrow PCl_4^+PCl_5Br^- + AsBr_3$$

The compound $PCl_{4.67}Br_{0.33}$ was believed to be a decomposition product of this salt. The heterocation PCl_3Br^+ has been isolated (*323*) as a tetrachloroborate by the addition of boron trichloride to the ion in liquid hydrogen chloride preformed according to:

$$PCl_3 + Br_2 + HCl = PCl_3Br^+ + HClBr^-$$

The compound $PCl_4^+PF_6^-$, which appears in one of the above equations, was prepared quantitatively by the action of arsenic trifluoride on phosphorus pentachloride dissolved in arsenic trichloride (*173*). It is a white solid which sublimes at 135° and is sparingly soluble in arsenic trichloride. It is quite different in properties from the covalent isomer PCl_2F_3 (boiling point 8°) and the ionic nature is shown by its solubility and conductivity in acetonitrile. This is confirmed by the hydrolysis reaction,

$$PCl_4PF_6 + 7KOH = K_2H_2PO_4 + 5KCl + KPF_6\downarrow + 3H_2O$$

in which the hexafluorophosphate ion in the precipitate could hardly be generated by an aqueous solution and must already exist in the compound. The compound $AsCl_4^+PF_6^-$, which can be prepared similarly, has an isomorphous structure according to the X-ray powder patterns (*174*). The simpler tetrachlorophosphonium fluoride is obtained impure when the hexafluorophosphate is decomposed thermally in suspension (*176*) in arsenic trichloride, or pure by thermal decomposition of the solid under reduced pressure. The reaction can be reversed with phosphorus pentafluoride:

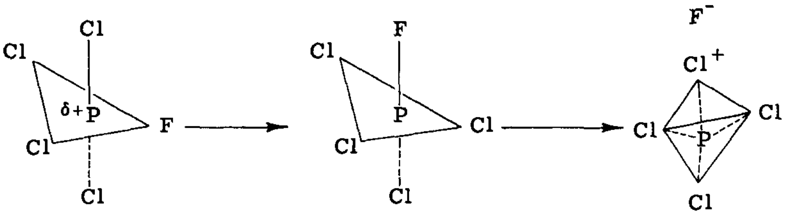
$$PCl_4^+PF_6^- \leftrightarrows PCl_4^+F^- + PF_5$$

However, some PCl_2F_3 is also formed in the reverse reaction since equilibration between the forms is kinetically controlled. This is also illustrated by melting the ionic form to the covalent liquid which slowly reverts to the ionic solid, the rate being apparently dependent on the nucleating surface.

The kinetics of the exchange between covalent and polar forms has been followed quite simply by distilling off the volatile PCl_4F *in vacuo* after holding at constant temperature for various times (*176*). The variation of the first order rate constant with temperature was given by

$$\log K = 4.37 - 10.6/RT$$

where the activation energy is in kcal/mole. At room temperatures the half-life of the covalent form is about 35 hours. The suggested reaction mechanism was by partial ionization of an apical chlorine, followed by exchange of the equatorial fluorine with the other apical chlorine and a simultaneous movement of phosphorus from equatorial plane to tetrahedral position:



The rate-determining step has not been deduced and there is only indirect evidence for the position of fluorine. Thus the apical position of chlorine atoms in PF_3Cl_2 has been shown by electron diffraction, and the reason suggested for its inability to transform to the $PCl_4^+PF_6^-$ isomer was the high activation energy which would be needed for the movement of three fluorine atoms to generate a PCl_4^+ cation. The corresponding trifluoromethyl derivatives behave similarly (see below). Thermochemical measurements on these and related systems would be interesting, especially if the activation energies can be related to energy differences between "polarity" isomers. The ionicity of the compound $PCl_4^+F^-$ follows from the enhanced conductivity of solutions in acetonitrile, from a cryoscopic determination of molecular weight in acetic acid, and from the absence of hexafluorophosphate in the hydrolyzate. The corresponding $PBr_4^+F^-$ is also known (*177*). It is made by keeping a mixture of PBr_2F and bromine below −30° when the molecular PBr_4F changes to the ionic form, a solid decomposing at 87° and forming a conducting solution in acetonitrile. The molecular form decomposed to a mixture of phosphorus pentachloride and pentabromide at room temperatures.

There is one other compound apart from the phosphorus pentahalides for which there is direct X-ray structural evidence for a tetrahalophosphonium salt. This is the compound $IPCl_6$, which crystallizes from iodine monochloride and phosphorus pentachloride in carbon disulfide or tetrachloride. The structure consists of tetrahedral PCl_4^+ and linear ICl_2^- ions. The I-Cl distance of 2.36 Å can be compared with the distance 2.34 Å for

I-Cl in $N(CH_3)_4{}^+ICl_2{}^-$ (*345*). By analogy the other iodine monohalide adducts, $PCl_5 \cdot IBr$, $PBr_5 \cdot ICl$, and $PBr_5 \cdot IBr$, may also contain phosphonium ions.

There is evidence for the $PCl_4{}^+$ ion in solution when the double halide $UCl_5 \cdot PCl_5$ is dissolved in phosphorus oxychloride (*234*). On electrolysis phosphorus tri- and pentachlorides form at the cathode, and chlorine together with a material containing uranium ($2UCl_4 \cdot UCl_6 \cdot 6POCl_3$) at the anode. The low solubility of the compound in toluene (0.014 gm/100 ml) compared with phosphorus pentachloride (6.72 gm/100 ml), and the removal of phosphorus pentachloride in excess of the 1:1 compound from $UCl_5 \cdot 2PCl_5$ and $UCl_5 \cdot 3PCl_5$ by refluxing with toluene, indicate a stability compatible with an ionic salt.

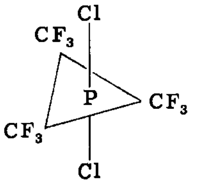
An ionic structure $PNCl_3{}^+PCl_4{}^-$ has been proposed for the compound P_2NCl_7 formed by the reactions $N_4S_4 + PCl_3$ or $(PNCl_2)_3 + PCl_5$ without compelling favorable evidence (*132*).

Later work has shown the compound to be a dimeric salt $\{PCl_3(NPCl_2)Cl\}^+PCl_6{}^-$. The n.m.r. spectrum supports this conclusion (*25*). A similar compound P_3NCl_{12}, prepared from phosphorus pentachloride and ammonium chloride in polar solvents at low temperatures, has the structure $(PCl_3{=}N{=}PCl_3)^+PCl_6{}^-$ (*26*). These compounds are ionic intermediates in the polymerization of phosphonitrilic chlorides (*233*).

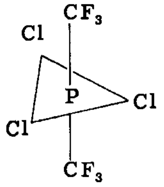
Trifluoromethyl-substituted phosphonium ions have been postulated to explain the conductivity of the substituted pentahalides $PCl_2(CF_3)_3$ and $PBr_2(CF_3)_3$ in acetonitrile or nitromethane (*90*):

$$2PCl_2(CF_3)_3 \rightarrow PCl(CF_3)_3{}^+ + PCl_3(CF_3)_3{}^-$$

The conductivities of these solutions slowly increase to a maximum, again illustrating kinetic control in the transformation. The corresponding disubstituted compound, $PCl_3(CF_3)_2$, is a nonconductor in solution. The possibility of ionicity in these compounds has been related to their configurations. If the chlorine is in an apical position of the trigonal bipyramidal structure it can ionize by heterolysis. The trifluoromethyl group in this position has no tendency to ionize as $CF_3{}^-$.



(a)

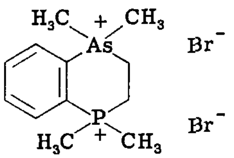


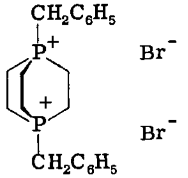
(b)

The C-F stretching frequency observed in the infrared spectrum provides some evidence for apical trifluoromethyl groups in structure (b) (*91*). This type of argument is no longer convincing in view of the recently determined structure of $PF_3(CH_3)_2$ in which the methyl groups are in equatorial positions (*19*).

2. Other Phosphonium Cations

Alkyl- and aryl-substituted phosphonium ions have been known for many years. The synthesis of optically active compounds by differently substituting each tetrahedral position in a cation was the classical method of proving a tetrahedral configuration before X-ray structural analysis had been fully developed. A comprehensive summary of quaternary phosphonium salts should be consulted for details (*222*). Doubly charged cations in which phosphorus or phosphorus and arsenic are linked can be isolated, but salts such as $PCl_3R^+AlCl_4^-$ are more typical examples. They are made according to the reaction:





$$PCl_3 + RCl + AlCl_3 = PCl_3R[AlCl_4]$$

Their ionicity is evidenced by their high melting points, the hydrolyses $PCl_3R^+ + OH^- \rightarrow RPOCl_2 + HCl$, and the anodic transport of aluminum and cathodic formation of $RPCl_2$ by electrolysis in methylene chloride solution (*150*).

A series of phosphonium salts, which span the halogen and organo-substituted salts, have recently been prepared (*262*) by employing antimony pentachloride simultaneously as a chlorinating agent and a Lewis acid:

$$R_3P + 2SbCl_5 = R_3PCl^+SbCl_6^- + SbCl_3$$

The intermediate R_3PCl_2 was not always isolatable. Evidence for ionicity is provided by the high melting points of these compounds, and the equivalent conductivities in nitrobenzene solutions similar to those of quaternary ammonium salts. Spectral evidence for the structure $PCl_3F^+SbCl_6^-$ is provided by the F^{19} n.m.r. spectrum, for which the coupling constant J_{P-F} interpolates in the expected position for tetrahedral hybridization in the series:

PF_3	PCl_3F^+	PF_5	PF_6	
1441	1294	916	710	cycles/sec

The infrared spectrum shows the resemblance of PCl_3F^+ to the isoelectronic molecule $SiCl_3F$.

The simplest of the nonhalogenated ions is the tetrahydrophosphonium ion, for which a more complete assignment of infrared and Raman spectra is possible. This ion is the end member of the isoelectronic triad AlH_4^-, SiH_4, PH_4^+ in which the stretching force constants are inversely related to the cube of the bond lengths (*330*). Tetrahalogenoborates of the same cation can be isolated from liquid hydrogen chloride. Their infrared spectra confirm the presence of a PH_4^+ ion (*324*). A less complete assignment is possible with the trimethylphosphine dihalides, which have C_{3v} symmetry and ionize as $(CH_3)_3PX^+X^-$ (*126*).

3. Arsonium Cations

The tetrachloroarsonium cation is stabilized in many compounds which can be formally represented as double halides with arsenic pentachloride. The latter has never been isolated so that the analogy with PCl_5 cannot be carried over to a salt $AsCl_4^+AsCl_6^-$. The patent instability of arsenic pentachloride, and the hexachloroarsenate ion, among Group Va pentahalides must arise from competing factors (*300*). In contrast, the salt with the hexafluoroarsenate ion is stable. It was first prepared by Kolditz, who passed chlorine through arsenic trifluoride (*172*). A compound of empirical composition $AsCl_2F_3$ separated after some hours from the saturated solution. The compound gave conducting solutions in arsenic trifluoride. The presence of the hexafluoroarsenate cation in the compound was inferred from the hydrolysis reaction,

$$AsCl_4{\cdot}AsF_6 + 7NaOH = Na_2HAsO_4 + 4NaCl + NaAsF_6 + 3H_2O$$

since it could be separated as the well-known "nitron" salt. The slowness of the chlorination of arsenic trifluoride was explained subsequently when it was found that the dry trifluoride would not react with chlorine (*78*). At least 2.5% water was required in the trifluoride to initiate the reaction. The reaction time of 8–10 hours found at this level of water was about twice that encountered by Kolditz. The period decreased to 1/3–1/2 hour at 11% water content. The initiating species was believed to be AsF_2OH, which is susceptible to chlorination since the polarizing effect of the fluorine atoms on the arsenic "inert pair" is decreased:

$$\begin{tikzcd}
AsF_3 + H_2O \arrow[r] & AsF_2OH \arrow[r, "Cl_2"] & AsF_2Cl_2OH \arrow[r, "AsF_3"] & AsF_3Cl_2 + AsF_2OH \arrow[d] \\
 & & & AsCl_4^+AsF_6^-
\end{tikzcd}$$

It is possible to prepare pure $AsCl_4{\cdot}AsF_6$ from the trifluoride and chlorine in arsenic trichloride as a solvent. The corresponding bromine compound $AsBr_4^+AsF_6^-$ could not be isolated. Again there was no reaction between dry arsenic trifluoride and bromine. In the presence of water, reaction occurred with the formation of arsenic acid, arsenic tribromide, and hexafluoroarsenic acid. The explanation advanced was that further hydroxylation of the arsenic trifluoride was required before reaction took place with the weaker oxidant, bromine (*77*). The tetrachloroarsonium cation probably exists in the double halides made by passing chlorine into solutions of phosphorus or antimony pentachlorides dissolved in arsenic trichloride. The double halides $PCl_5 \cdot AsCl_5$ and $SbCl_5 \cdot AsCl_5$ were believed to contain $AsCl_4^+$ cations rather than $AsCl_6^-$ anions. This type of reaction was examined systematically with a series of halides in the expectation that the solution conductivity would increase sharply if a salt formed on chlorination, and would then level out when the solution was saturated. Such behavior was found with $AuCl_3$, $AlCl_3$, $GaCl_3$, $SnCl_4$, $TaCl_5$, and $FeCl_3$. The stability of the salts was judged by following the decrease in conductivity when molecular chlorine in equilibrium with the solution was displaced with nitrogen. The stability order was $AlCl_3 > GaCl_3 > TaCl_5 > FeCl_3 > AuCl_3$. Compounds of the first two were isolated and can be reasonably formulated as $AsCl_4^+AlCl_4^-$ and $AsCl_4^+GaCl_4^-$ (*184*).

The stable hexafluoroantimonate has been prepared by a displacement reaction:

$$SbCl_4^+SbF_6^- + AsF_3 = AsCl_4^+SbF_6^- + SbF_3 \downarrow$$

The presence of the SbF_6^- ion was shown by precipitating the nitron salt of the acid $HSbF_5OH$ from the hydrolyzate in the same way as from an aqueous solution of $KSbF_6$ (*182*). The conductivity in arsenic trifluoride and the cryoscopic molecular weight confirmed the dimeric ionic formula.

The stabilization and ionization of arsenic pentachloride with donor ligands have been suggested. Thus, chlorinating arsenic trichloride in the presence of triphenyl- or trimethylphosphine oxides produces $(AsCl_5)_2$-$OP(C_6H_5)_3$ and $AsCl_5OP(CH_3)_3$ (*277*). The former slowly evolved chlorine. The ionization $AsCl_4[OP(C_6H_5)_3]_2^+Cl^-$ was proposed, in which stabilization arose from the ligand bonding.

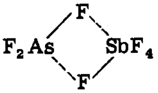
Quaternary organoarsonium salts are well known. The detailed structures of some tetraphenylarsonium salts have been determined by X-ray analysis. In the tetrachloroferrate (*344*), tetrahedral $FeCl_4^-$ groups are packed together with cations in which the phenyl groups are rotated about the C-As axes, thus reducing D_{2d} symmetry encountered in $As(C_6H_5)_4^+I^-$ (*306*). Tetrahydroarsonium ions have also been investigated (*147*).

4. Trivalent Arsenic Cations

Arsenic trichloride functions as an ionizing solvent for chlorides; the proposed self-ionization is

$$2AsCl_3 \leftrightarrows AsCl_2^+ + AsCl_4^-$$

with the ionic product less than 10^{-9}. A conductometric titration of $N(CH_3)_4Cl$ with $SbCl_5$ to form $N(CH_3)_4{}^+SbCl_6{}^-$ provides some evidence for $AsCl_2{}^+$ in solution (*135*). Stabilization of this cation can be achieved by adding pyridine to arsenic trichloride. The moderately conducting solution that results can be titrated conductometrically with halides which behave as "acids" in this system, and this has been explained in terms of the ion pair $(C_5H_5N)AsCl_2{}^+AsCl_4{}^-$. Similar evidence from conductometric and potentiometric titrations in arsenic tribromide has been advanced for the $AsBr_2{}^+$ cation (*159*). The self-ionization of arsenic trifluoride is of a higher order (*338*), and a number of stable salts $M^+AsF_4{}^-$, containing the anion formed on self-ionization, have been isolated (*218*). The existence of simple $AsF_2{}^+$ ions has yet to be proved conclusively in, for example, the compound $AsF_3{\cdot}SbF_5$ made from the conducting solution of SbF_5 in AsF_3.

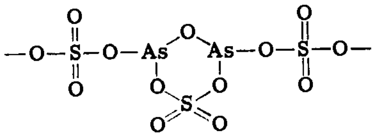


The F^{19} n.m.r. spectrum of this solution has one concentration-dependent peak between that of the component fluorides, indicating fluorine exchange between nonequivalent sets of fluorine atoms (*218*). On a statistical basis it seems that the As-F bond must ionize more frequently than an Sb-F one to obtain exchange equivalence via a bridged structure. This can be regarded as evidence for a short-lived $AsF_2{}^+$ ion in solution. Suitable ligand addition should stabilize this ion and enable stable salts of the cation to be isolated.

An oxycation may exist in dilute solutions of arsenious oxide in sulfuric acid. By analogy with nitrogen trioxide, it should form six particles according to:

$$As_2O_3 + 3H_2SO_4 = 2AsO^+ + H_3O^+ + 3HSO_4{}^-$$

A limiting value of 5.99 was obtained cryoscopically which decreased to 4.79 with increasing concentration, indicating a shift toward unionized $AsOHSO_4$ (*118*). This removal of bisulfate ions, the main current carrier, was shown by a drop in conductivity. The above measurements cannot distinguish the bare AsO^+ ion from its solvated forms such as HO—As$^+$—SO_4H or H_2O^+—$As(SO_4H)_2$. The species which finally separated from solution of empirical composition $(AsO)_2SO_4$ were polymeric, possibly with six-membered rings as structural units:

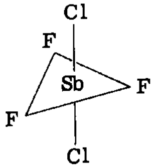


They cannot be regarded as simple arsenyl sulfates.

5. *Stibonium Cations*

The $SbCl_4^+$ ion can be generated from antimony pentachloride by solvation or displacement reactions. Thus the pentachloride forms a conducting solution in acetonitrile. The infrared spectrum has a peak identical with that of pyridinium hexachloroantimonate in the same solvent which serves to identify the $SbCl_6^-$ ion. The cation could not be identified. In the solid adduct $SbCl_5 \cdot 2CH_3CN$ there are bands which can be attributed to *trans*-$(CH_3CN)_2SbCl_4^+$ ions and these are the probable cations in solution (*24*, *181*). It has been pointed out that the Raman spectrum of the pentachloride shows that the antimony is not exactly in the equatorial plane of the trigonal bipyramid, and this indicates an incipient ionization toward $SbCl_4^+$.

Antimony trifluoride reacts with chlorine to form the solid SbF_3Cl_2, which forms a conducting solution in arsenic trifluoride of the same order of conductivity as $AsCl_4^+AsF_6^-$ solutions. The molecular weight determined in the same solvent corresponded to the monomeric composition. The minute conductivity in the melt was associated with a reversion of ionic to a homopolar form (*180*). However, the infrared and Raman peaks of the same substance prepared from $SbCl_5$ and chlorine monofluoride (actually ClF_3 and excess Cl_2) show a close resemblance to the corresponding peaks of SbF_5 and $SbCl_5$. The structure suggested was



An ionic structure $SbCl_4^+SbF_6^-$ was rejected in both solid and liquid states (*75*). Presumably a small amount of ionization or even of asymmetry in the structure, not detectable in the above measurements, would lead to a fuller ionization in the solvent arsenic trifluoride. (Choice of solvents is restricted for this compound because of its reactivity.)

Fluorination of $SbCl_5$ with AsF_3, a milder fluorinating agent than ClF, replaces a single chlorine (*175*):

$$2SbCl_5 + AsF_3 = 3SbCl_4F + AsCl_3$$

The monofluoride sublimes *in vacuo* and melts with decomposition at 83°. The compound formulated as $SbF_5(SbCl_5)_3$ in the SbF_5–$SbCl_5$ system is probably an impure form of $SbCl_4^+F^-$. The ionic nature of the compound was demonstrated by a molecular weight of 138 in arsenic trifluoride and the electrical conductivity in AsF_3 solutions. In contrast, solutions in sulfuryl chloride are nonconducting and the molecular weight is that for undissociated $SbCl_4F$.

Antimony pentachloride reacts with fluorosulfuric acid (*146*) analogously to the displacement reactions of alkali or alkali earth chlorides which form ionic fluorosulfates:

$$SbCl_5 + HSO_3F = SbCl_4SO_3F + HCl$$

The ionization of the product has not been studied but it seems improbable that it should be a simple ionic salt. The corresponding fluorinated derivative SbF_4SO_3F prepared from the pentafluoride and sulfur trioxide is a polymeric liquid in which SO_3F groups act as bridging elements. This was shown by n.m.r., infrared, and Raman spectra (*120*). The fluorosulfate group resembles the perchlorate and nitrate groups in the ability to behave as a bidendate ligand, and for this reason many compounds which appear to be ionic fluorosulfates are more likely homopolar compounds.

A sulfate has been prepared from $SbCl_5$ and SO_3 which, in spite of formulation as $(SbCl_4)_2SO_4$, may be polymeric (*5*).

6. *Trivalent Antimony Cations*

Antimony trichloride is an efficient solvent for many inorganic and organic compounds and in the usual way the self-ionization

$$2SbCl_3 \rightleftarrows SbCl_2^+ + SbCl_4^-$$

is postulated, and supported by conductivity measurements and "neutralization" reactions (*160*). Thus certain Lewis acid chlorides such as $AlCl_3$, $SbCl_5$, or $TeCl_4$ are supposed to generate increased amounts of the $SbCl_2^+$ cation. However, the neutralization reactions can be interpreted by a direct chloride ion transfer from the highly ionized tetrachloroantimonate ion without postulating the $SbCl_2^+$ ion in appreciable amounts:

$$SbCl_4^- + SbCl_5 = SbCl_3 + SbCl_6^-$$

The $SbCl_4^-$ ion is abnormally mobile compared with $SbCl_6^-$ in the solvent (*245*). No solid compounds containing authenticated $SbCl_2^+$ ions are yet known.

The oxycations of antimony are polymeric and simple SbO^+ ions exist only in the gas phase. For example, antimonyl chloride (SbOCl) consists of infinite puckered sheet cations $(Sb_6O_6Cl_4)_n^{2n+}$ held together by chloride ions (*86*). In other oxyhalides, layer and chain cations such as $(Sb_4O_5)_n^{2n+}$ and $[Sb_4O_5(OH)]_n^{n+}$ appear (*85*).

7. *Nitrosonium Ions*

The nitrosonium and nitronium ions have been authenticated in solids and a variety of liquids during the period under review, but only a partial survey of the main lines of investigation can be presented here. Reviews on the chemistry of the nitrosyl group summarized evidence for the nitrosonium ion (*2*, *284*). Spectroscopic and other evidence for the nitronium ion has been summarized more recently (*227*).

There are a number of general methods now available for generating nitrosonium ions either from nitrosyl halides or nitrogen oxides:

(1) Nitrosyl chloride reacts with Lewis acids chlorides to form double halides. The nitrosyl chloride is reactive enough to form many of the metal halides *in situ* from the metals, which then react further with excess of nitrosyl chloride (*237*). Nitrosyl chloride (*47*) or hydrogen chloride (*323*) can be used as ionizing solvent in these reactions. The compounds are listed in Table III [for references see (*283*)].

TABLE III

NITROSYL CHLORIDE ADDUCTS

		MCl_n in MCl_nNOCl		
CuCl	$ZnCl_2$	BCl_3	$AsCl_3$	UO_2Cl_2
$AuCl_3$	$HgCl_2$	$AlCl_3$	$SbCl_3$	$MnCl_2$
		$GaCl_3$	$SbCl_5$	$FeCl_3$
		$InCl_3$	$BiCl_3$	
		$TiCl_3$		
		MCl_n in MCl_n2NOCl		
$SnCl_4$	$TiCl_4$	$FeCl_3$	$PdCl_2$	
$PbCl_4$	$ThCl_4$		$PtCl_4$	

(2) Double fluorides are formed in a similar fashion from the reaction of nitrosyl fluoride with metals (*308*), but a more convenient procedure is to generate the component fluorides in bromine trifluoride and allow them to interact in this solvent. Any material can be used as the starting material if it can be solvolyzed to a soluble fluoride in bromine trifluoride (*331*). Thus nitrosyl chloride or nitric oxide serves as a source of nitrosyl fluoride, and metals, oxides, oxyhalides, or halides as sources of other fluorides. The nitrosyl complex chlorides can also be fluorinated. The double fluorides listed in Table IV have been prepared via bromine trifluoride.

TABLE IV

NITROSYL FLUORIDE ADDUCTS PREPARED VIA BrF_3

		MF_n in MF_nNOF			
AuF_3	BF_3	PF_5	VOF_3	MoF_5	BrF_3
		AsF_5	VF_5	MoF_6	
		SbF_5	NbF_5	WF_6	
			TaF_5	UF_6	
		MF_n in MF_n2NOF			
SiF_4	SnF_4	MnF_4	IrF_4		
GeF_4	TiF_4		PtF_4		

(3) The bromine trifluoride method is limited by displacement reactions when the fluoride is a weak acid in this solvent (see p. 272). Hydrogen fluoride is a more acidic and less oxidizing solvent. Solutions of nitrosyl chloride in this solvent provide another general route to double fluorides. A solvate $NOF \cdot 3HF$ (b.p. 94°) can be distilled from this solution; the solvation energy must be in excess of 13.5 kcal/mole, since this is the positive free energy change for $NOCl + HF \rightarrow NOF + HCl$ (*285*). Various chlorides and metals are converted to double fluorides by reaction with $NOF \cdot 3HF$ in the gas or liquid phase. Reported (*285*) adducts are listed in Table V.

TABLE V
NITROSYL FLUORIDE ADDUCTS PREPARED VIA HF

		MF_n in MF_nNOF			
BeF_2	BF_3	AsF_5	VF_4	SeF_4	IF_5
		SbF_5		TeF_4	$TeOF_4$
		NbF_5		MoF_5	$MoOF_4$
		TaF_5		WF_6	
				UF_5	
		MF_n in MF_n2NOF			
SiF_4	TiF_4	CrF_3			
GeF_4	ZrF_4				
SnF_4	VF_4				

(4) Nitrosyl fluoride can also be stabilized with sulfur dioxide in a 1:1 compound which, although completely dissociated in the gas phase, can act as an effective fluorinating agent below −10°. Again, many metals and halides are converted to double fluorides (*288*). If these reactions are carried out in glass or silica vessels, attack on the containers produces some $2NOF \cdot SiF_4$. This resembles reactions in bromine trifluoride where there is a similar dissociation of a solvate to the reactive nitrosyl fluoride.

Sulfur dioxide can also be employed in a more conventional manner for metathesis leading to nitrosyl salts:

$$NOCl + SbCl_5 \xrightarrow{SO_2} NOCl \cdot SbCl_5 \qquad (282)$$

$$NOCl \cdot SbCl_5 + N(CH_3)_4{}^+PF_6{}^- \xrightarrow{SO_2} NO^+PF_6{}^- + N(CH_3)_4{}^+SbCl_6{}^- \qquad (287)$$

$$\begin{aligned} 2NOCl \cdot SbCl_5 + [N(CH_3)_4{}^+]_2FeNO(CN)_5{}^= \xrightarrow{SO_2} & (NO)_2{}^+Fe(NO)(CN)_5{}^= \\ & + 2N(CH_8)_4{}^+SbCl_6{}^- \qquad (292) \end{aligned}$$

The last is an example of a compound containing both cationic and anionic NO groups.

(5) The nitrosonium ion can also be generated from nitrogen oxides or their hydrates by solution in strong protonic acids such as absolute sulfuric,

nitric, or hydrofluoric acid. Dinitrogen tetroxide, for example, behaves as nitrosonium nitrate. The nitrosyl salts listed in Table VI are derived from strong oxyacids. A simple sulfate has yet to be isolated.

TABLE VI
Nitrosyl Oxyacid Salts[a]

NOP_3O_8	$NOHSO_4$	$NOReO_4$	$NOClO_4$
$(NO)_2P_4O_{11}$	$(NO)_2S_2O_7$		
	$(NO)_2S_3O_{10}$		
$(NO)_2P_6O_{17}$	$NOSO_3F$		
$NOSO_3Cl$			
$NOHSeO_4$			
$(NO)_2SeO_4$			

[a] From (*291*).

(6) The nitrosonium ion can be formed when some metals or their halides are dissolved in liquid nitrogen dioxide. The addition of organic solvents such as ethyl acetate facilitates reaction by increasing ionization. Thus, with zinc, the compound $Zn(NO_3)_2 \cdot 2N_2O_4$ (*3*) and, with ferrous or ferric chloride, $Fe(NO_3)_3 \cdot N_2O_4$ (*1*) are formed. These compounds are electrolytes whose spectra accord with formulas $(NO^+)_2Zn(NO_3)_4$ and $NO^+Fe(NO_3)_4^-$.

The existence of nitrosonium ions in all these substances is possible because of the relatively low ionization potential of the odd electron molecule NO, and the small size of the ion (N-O distance 1.062 Å). The ionization potential can be compared with that of similar diatomic molecules:

$$N_2 \rightarrow N_2^+ \ 15.7; \qquad NO \rightarrow NO^+ \ 9.35;$$
$$O_2 \rightarrow O_2^+ \ 12.2; \qquad CO \rightarrow CO^+ \ 14.1 \text{ ev}$$

These two factors would be consistent with the formation of stable ionic lattices for nitrosonium salts, and indeed Hantzsch provided cryoscopic and spectral evidence for this many years ago (*136*). Other older evidence included the isomorphism of nitrosyl with ammonium salts as shown by X-ray diffraction (*169*), and the identification of a Raman frequency around 2310 cm^{-1} with the NO^+ ion since it was isoelectronic with nitrogen with a frequency of 2330 cm^{-1} (*4*).

Modern evidence relies mainly on behavior in ionizing solvents together with spectral data. Some nitrosyl salts are strong electrolytes in liquid nitrosyl chloride, a solvent of medium dielectric constant (19.7 at $-10°$). Nitric oxide is generated at the cathode on electrolysis, indicating the nitrosyl cation. The latter has a high mobility according to transport measurements. This is also shown by the minimum in the conductivity when ferric chloride solutions are titrated with tetramethylammonium chloride, the nitrosyl ion being replaced by the less mobile ammonium ion (*47*). Radioactive chlorine exchange between NOCl and chlorides in solution is compatible with ionic mechanisms (*194*). In bromine trifluoride the existence of $NOBrF_4$ was postulated as an intermediate to explain the production of other nitrosyl salts (*331*), and it has now been isolated as a solid (m.p. 225°) structurally similar to potassium tetrafluorobromate. The nitrosyl compound is an electrolyte in bromine trifluoride, and can be titrated with stannic or titanic fluoride solutions to a minimum conductance at half a molecule of the latter (*41*) according to the equation:

$$2NOBrF_4 + (BrF_2)_2SnF_6 = (NO)_2SnF_6 + 4BrF_3$$

The structural similarity of $(NO)_2SiF_6$ to K_2TiF_6 was also indicated in this work.

Nitrosyl salts are also strong electrolytes in liquid sulfur dioxide. The equivalent conductivity of nitrosyl hexafluoroantimonate is only a little less than the potassium salt. Again, nitric oxide is liberated cathodically on electrolysis, and conductivity titrations of nitrosyl chloride with antimony pentachloride reach maximum values at the 1:1 composition (*282*). Double decomposition reactions in this solvent illustrate their ionic nature:

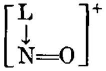
$$NOSbCl_6 + CH_3COBF_4 = NOBF_4 + CH_3COSbCl_6$$

$$NOSbCl_6 + N(CH_3)_4ClO_4 = NOClO_4 + N(CH_3)_4SbCl_6$$

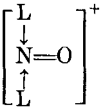
The spectral evidence for nitrosonium salts is convincing. Gerding and Houtgraaf compared the spectra of $NaCl{\cdot}AlCl_3$ with those of $NOCl{\cdot}AlCl_3$ in both the solid and liquid states. The former compound is a salt $Na(AlCl_4)$ containing discrete tetrahedral $AlCl_4$ units as shown by an X-ray structure determination (*108*), and the Raman spectrum is reasonably consistent with a slightly distorted $AlCl_4^-$ tetrahedron. The Raman spectrum for $NOCl{\cdot}AlCl_3$ showed the shifts characteristic of the $AlCl_4^-$ ion, together with an intense line at 2236 cm^{-1} close to that in $NOHSO_4$ or $NOClO_4$ due to the stretching frequency of NO^+. However, this frequency value is significantly lower than that for other nitrosyl salts or nitrogen itself, and suggests that the bonding is incompletely polar. A small contribution from a nonpolar adduct was proposed:

$$Cl_3AlCl{-}N{=}O \rightarrow Cl_3AlCl^-\overset{+}{N}{=}O$$

The nitrosonium ion was also identified by its Raman spectrum in $N_2O_4{\cdot}3SO_3$, i.e., $(NO^+NO_2^+)S_3O_{10}^=$ (*107*), and when the lower oxides of nitrogen N_2O_3 and N_2O_4 were dissolved in sulfuric or nitric acid (*213*). In the latter the NO^+ frequency at 2240 cm^{-1} was again lower than the 2300 value for most nitrosonium salts, and was explained by a more complex ion $NONO_2^+$ held by a single electron bond (*127*). A similar ion $N_2O_2^+$ was obtained by passing nitric oxide into nitrosyl salt solutions in liquid sulfur dioxide or in strong acids. The ion is unstable, the equilibrium constant for $NO + NO^+ \rightleftharpoons N_2O_2^+$ being 6×10^{-3} atm^{-1} at 20° (*290*). An unstable solvated nitrosonium ion $NONOCl^+$ was also encountered in liquid nitrosyl chloride (*47*), and in general ions of the type,



$$\left[\begin{matrix} L \\ \downarrow \\ N{=}O \end{matrix}\right]^+$$



$$\left[\begin{matrix} L \\ \downarrow \\ N{=}O \\ \uparrow \\ L \end{matrix}\right]^+$$

where the ligand L contains an oxygen or nitrogen donor, are not uncommon. These ions account for the increased reaction rates when organic ligand molecules are added to metals dissolving in liquid nitrogen dioxide (*2*).

Finally, two recent extreme examples of nitrosonium salts prepared from chlorine fluorides and nitrosyl fluoride confirm the pattern of ionicity of other nitrosonium salts. These compounds are completely dissociated at room temperatures and can be examined only at low temperatures. Thus $NOF \cdot ClF$ dissolved in chlorine monofluoride at −79° has a low but significant equivalent conductivity. The solid has the usual infrared frequency at 2279 cm^{-1} of the NO^+ ion, and an asymmetrical stretching frequency at 635 cm^{-1} expected for a linear ClF_2^- ion (*51*, *329*).

8. The Nitronium Ion

This ion is the reactive electrophilic entity in aromatic nitration, and there is sufficient evidence for its existence on mechanistic grounds alone. Its existence in salts is considered in the same order as for the corresponding nitrosonium ion. It can be generated by the same general methods:

(1) From nitryl chloride and Lewis acid chlorides. This method is restricted because of the instability of nitryl chloride. The hexachloroantimonate has been precipitated by mixing solutions of nitryl chloride and antimony pentachloride in liquid chlorine (*289*). At room temperature the salt begins to decompose irreversibly. This instability of nitryl salts compared with the corresponding nitrosyl salts is expected because of the much higher ionization potential $NO_2 \rightarrow NO_2^+$ (11.0 ev).

(2) Nitryl fluoride is more stable than the chloride, although the N-F bond is still weaker than in nitrosyl fluoride, and is able to attack elements and convert some to nitronium salts. Others can be obtained by direct combination with fluorides (*11*). Again, a more convenient procedure is to generate the component fluorides with bromine trifluoride and react them *in situ* (*337*). Nitrogen dioxide has been the source of nitryl fluoride but the nitrates would also serve. The method is limited to those "acids" in bromine

trifluoride which are not displaced by the BrF_4^- ion. Nitronium tetrafluorobromate has not been isolated at ordinary temperatures, in accord with the expected lower stability of nitronium salts. The complexes listed in Table VII have been obtained by the above methods.

TABLE VII
NITRONIUM COMPLEX FLUORIDES

NO_2BF_4	$(NO_2)_2SiF_6$	NO_2PF_6	NO_2SeF_5	NO_2IrF_5
	$(NO_2)_2GeF_6$	NO_2AsF_6	NO_2SO_3F	$(NO_2)_2IrF_6$
	$(NO_2)_2SnF_6$	NO_2SbF_6	NO_2IF_6	
		NO_2VF_6		NO_2AuF_4
		NO_2VOF_4		
		NO_2NbF_6		
		NO_2TaF_6		

(3) Nitrogen oxides or nitric acid in protonic solvents have acted as sources of the nitronium ion. Hantzsch, who obtained crystalline compounds from nitric acid–perchloric acid mixtures, believed that acidium ions were formed by proton transfer,

$$HClO_4 + HNO_3 = H_2NO_3^+ + ClO_4^-$$

$$2HClO_4 + HNO_3 = H_3NO_3^{2+} + 2ClO_4^-$$

whereas it has been shown that a mixture of perchlorates is formed:

$$HNO_3 + 2HClO_4 = NO_2^+ClO_4^- + H_3O^+ClO_4^-$$

By working in nitromethane solutions it is possible to isolate single nitronium salts (*123*):

$$NO_2HS_2O_7 \text{ from } HNO_3 + 2SO_3$$

$$(NO_2)_2S_2O_7 \text{ from } N_2O_5 + 2SO_3$$

$$(NO_2)_2S_3O_{10} \text{ from } N_2O_5 + 3SO_3$$

$$NO_2SO_3F \text{ from } N_2O_5 + HSO_3F$$

Similarly, from fluoro acids—generated *in situ* in nitromethane from hydrogen fluoride and a Lewis acid fluoride—and nitrogen pentoxide the salts NO_2BF_4 and $(NO_2)_2SiF_6$ were produced. Alternatively, the complex fluorides are obtained by using hydrogen fluoride as the solvent (*271*):

$$N_2O_5 + 2HF + 3BF_3 = 2NO_2BF_4 + BF_3H_2O$$

Alkyl nitrates can act as a source of NO_2^+:

$$RONO_2 + HF + 2BF_3 = NO_2BF_4 + BF_3ROH$$

(4) Lewis acid fluorides can react directly with nitric acid or nitrogen oxides to form nitronium salts. It should be remembered that nitrogen pentoxide is nitronium nitrate in the solid state.

The experimental evidence for the nitronium ion in the above complexes is firmly based. Refined X-ray structures of $NO_2^+ClO_4^-$ and $NO_2^+NO_3^-$ show almost perfectly linear nitronium ions (*319*), and less precise structures show the same ions in $(NO_2)_2S_3O_{10}$ and $(NO_2)HS_2O_7$ (*110*). Ionization in sulfuric or nitric acid solutions has been demonstrated by cryoscopic measurements (*115*). The following are almost complete:

$$HNO_3 + 2H_2SO_4 = NO_2^+ + H_3\overset{+}{O} + 2HSO_4^-$$

$$N_2O_5 + 3H_2SO_4 = 2NO_2^+ + H_3O^+ + 3H_2SO_4^-$$

$$N_2O_4 + 3H_2SO_4 = NO_2^+ + NO^+ + H_3O^+ + 3HSO_4^-$$

The similarity in cryoscopic behavior between nitronium and ammonium perchlorate in sulfuric acid is due to the liberation of the largely un-ionized perchloric acid from each salt (*113*):

$$\left.\begin{matrix} NH_4^+ClO_4^- \\ NO_2^+ClO_4^- \end{matrix}\right\} + H_2SO_4 = \left.\begin{matrix} NH_4^+ \\ NO_2^+ \end{matrix}\right\} + HClO_4 + HSO_4^-$$

The Raman spectrum seems the most decisive identification for nitronium ions (*158*). In nitric acid the weak lines at 1400 and 1050 cm^{-1} are intensified by adding sulfuric acid or nitrogen pentoxide. Only the 1400 cm^{-1} line is obtained by adding perchloric acid or selenic acid and this highly polarized line is the NO_2^+ line. Such a line is expected for an A-A, A-B, or linear AAA or ABA molecule. In nitric acid the only possible species with this structure would be $N{=}N{=}N^-$ and $O{-}N{-}O^+$ (*68*). The former is excluded by the chemistry and its known spectra, and hence the 1400 cm^{-1} line is the totally symmetrical frequency for NO_2^+. The 1050 cm^{-1} line is the strong Raman line for HSO_4^- and is not observed in sulfuric acid because the amount of ionization is too small. The nitrate ion has three fundamentals but only the 1047 cm^{-1} line is detectable. Using these criteria, the spectra of $NO_2^+ClO_4^-$, $NO_2^+NO_3^-$, and $NO_2^+SO_3F$ are explained:

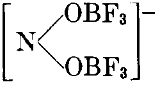
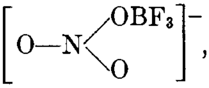
	$\nu_{NO_2^+}$ (cm^{-1})
$(NO_2)ClO_4$	1396.2
$NO_2HS_2O_7$	1396
$(NO_2)S_2O_7$	1401
NO_2SO_3F	1405
NO_2NO_3	1394

The generation of NO_2^+ by passage of boron fluoride or sulfur trioxide into nitric acid, e.g.,

$$HNO_3 + BF_3 = NO_2^+ + BF_3OH^-$$

is shown by the 1400 cm^{-1} Raman line (*107*). Spectral evidence enables the structures of the compounds

$$\begin{matrix} N_2O_3BF_3 & N_2O_4BF_3 & N_2O_5BF_3 \\ N_2O_32BF_3 & N_2O_42BF_3 & \end{matrix}$$

to be decided. Originally these were formulated as nitrosyl and nitronium salts of anions  $\left[\mathrm{N}\begin{matrix}\diagup \mathrm{OBF_3}\\ \diagdown \mathrm{OBF_3}\end{matrix}\right]^-$ and  $\left[\mathrm{O{-}N}\begin{matrix}\diagup \mathrm{OBF_3}\\ \diagdown \mathrm{O}\end{matrix}\right]^-$, but the spectra are not complex enough for salts of these anions and they are now regarded as tetrafluoroborates formed as follows:

$$3N_2O_3 + 8BF_3 = 6NOBF_4 + B_2O_3$$
$$3N_2O_4 + 8BF_3 = 6\left[\frac{NO}{2}\frac{NO_2}{2}\right]BF_4 + B_2O_3$$
$$3N_2O_5 + 8BF_3 = 6NO_2BF_4 + B_2O_3$$

The boric oxide is present in only small amounts and, since it would be near the BF_4^- spectrum, has not been detected (*93*).

Finally, conductivity measurements on the nitronium complex fluorides in tetramethylene sulfone or nitromethane show the ionicity of these compounds (*187*). In these solvents the ion dissociation is incomplete and there is a minimum in the conductivity-dilution curve expected for the equilibrium between ions, ion pairs, and ion triplets. This is confirmed by cryoscopic measurements in the organic solvent.

D. Group VI

The pattern of heterocations in this group follows that in the previous group, except that the maximum valency is not exerted by elements in the nonmetallic subgroup and there is uncertainty concerning the status of oxycations.

Oxygen itself is too electronegative to act as a core element in general. It can appear as a molecular ion in the gas phase, and more remarkably in stable salts. Although the dioxygenyl cation is not strictly a heterocation as originally defined, its importance as the precursor of rare gas chemistry, as well as the method employed in its generation and identification, merits some discussion. It was first encountered in the fluorination of platinum or platinum halides with elemental fluorine at 450° as a red sublimate of composition PtO_2F_6, the oxygen arising fortuitously. It was produced subsequently by tensimetric titration of oxygen with platinum hexafluoride at ambient temperatures. Chemical evidence for its structure relies on displacement reactions in which the relatively unstable O_2^+ is replaced by more stable cations, as shown in Fig. 5. (The structures of the replacing cations are discussed later.)

More direct evidence was provided by X-ray analysis. Cubic and rhombohedral forms exist: the former isomorphous with the well-known $NO^+SbF_6^-$ and $K^+SbF_6^-$, and the latter with $KPtF_6$, $KRuF_6$, and $KOsF_6$. Good agreement with X-ray intensity measurements was obtained with a model based on packing of O_2 and PtF_6 units. The data were not precise enough to distinguish O_2^+ from O_2^- so that recourse was necessary to lattice energy considerations, which easily differentiate $O_2^+Pt^{V}F_6^-$ from $Pt^{VII}F_6^+O_2^-$. The first ionization potential of platinum hexafluoride, obtained from a Born-Haber cycle with the lattice energy calculated by the usual approximation from interionic distances (*166*), would be less than 4.3 ev if the latter formulation were correct. This value is about the same as that for potassium and cannot be correct.

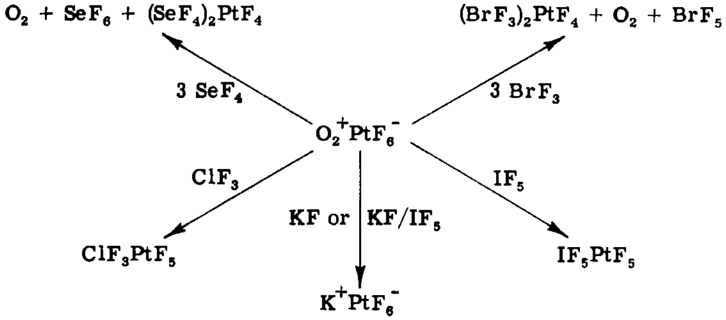


FIG. 5. Displacement reactions on O_2PtF_6 (*20*).

The minimum value of electron affinity for the hexafluoride calculated on the basis of the $O_2^+PtF_6^-$ formulation was -7.0 ev, a value well above that for the halogens and indicative of an extremely powerful oxidant. This is compatible with a direct abstraction of an electron from the oxygen molecule in a redox reaction:

$$\ddot{O}_2 + Pt^{VI}F_6 \rightarrow \dot{O}_2^+Pt^{V}F_6^-$$

The unpaired electron on the cation is shown directly by an e.s.r. spectral measurement on the tetrafluoroborate prepared by the reaction:

$$F_2O_2 + BF_3 = O_2BF_4 + \tfrac{1}{2}F_2$$

(Paramagnetic measurements on bulk samples of $O_2^+PtF_6^-$ are difficult to interpret because there are contributions from both ions, and assumptions about their interaction have to be made before a value can be ascribed to O_2^+.) Other oxygenyl salts have also been prepared from difluorine dioxide and Group V pentafluorides (*342*).

1. *Sulfur Cations*

It has not proved possible to ionize hexavalent sulfur cationically; all examples of sulfonium ions contain S(IV) or S(II). Organosulfonium ions have been well established. Simple examples are the tetrachloroborate $(C_4H_9)\ S^+BCl_4^-$ (*188*) and the tetrafluoroborate $(C_2H_5)\ S^+BF_4^-$ (*211*).

2. Halogeno Sulfur Cations

The halogenated cations are of more recent origin. They were first encountered during investigations into properties of sulfur and selenium fluorides. Boron trifluoride combines equimolecularly with sulfur tetrafluoride to form a colorless crystalline compound which dissociates into its components on heating. The heat of dissociation is close to that of the alkali fluoroborates and is consistent with a formulation $SF_3^+BF_4^-$. This is confirmed by the infrared spectrum in which the boron trifluoride peaks are replaced by those of BF_4^- as in the alkali salts, and a new peak, presumably of SF_3^+, replaces the SF_4 bands (*286*). The compound is isomorphous with NH_4IO_3 (*49*). More stable binary compounds are formed with arsenic and antimony pentafluorides. The latter melts at 253° without decomposition. Its cubic unit cell is compatible with ionic $SF_3^+SbF_6^-$. These compounds undergo displacement reactions with selenium tetrafluoride, which acts as a stronger base than sulfur tetrafluoride toward the Lewis acid fluorides (*21*):

$$SF_3^+MF_n^- + SeF_4 = SeF_3^+MF_n^- + SF_4$$

Selenium tetrafluoride can even displace bromine trifluoride from its adducts to give the isomorphous series $(SeF_4)_2PtF_4$, $(SeF_4)_2GeF_4$, $(SeF_4)_2PdF_4$, a series reasonably formulated as hexafluoro anion salts of SeF_3^+. Another example of a displacement reaction has been given in Fig. 5, in which the similarity of SeF_4 to BrF_3 in the displacement reactions with the oxygenyl cation is illustrated.

Analogous chlorinated cations have also been made. Double halides, thermally much more stable than sulfur tetrachloride, include $SnCl_4{\cdot}2SCl_4$, $SbCl_5{\cdot}SCl_4$, and $FeCl_3{\cdot}SCl_4$ and presumably contain SCl_3^+ cations. Stable hexafluoroarsenates of this cation and of selenium and tellurium analogs have recently been characterized (*183*).

The elements S, Se, and Te can be chlorinated in arsenic trichloride and then arsenic trifluoride is added. This synthesis can be regarded as a displacement reaction by the chalcogen tetrahalides on an intermediate $AsCl_4^+AsF_6^-$ (p. 250):

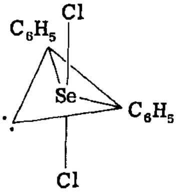
$$AsF_3 + Cl_2 \xrightarrow{AsCl_3} AsF_3Cl_2 \leftrightarrows \tfrac{1}{2}AsCl_4^+AsF_6^-$$

$$AsCl_4^+AsF_6^- + SCl_4 \xrightarrow{AsCl_3} SCl_3^+AsF_6^- + AsCl_3 + Cl_2$$

Iodine trichloride is unable to displace the $AsCl_4^+$ ion, indicating the stability sequence $\left.\begin{matrix}S\\Se\\Te\end{matrix}\right\}Cl_3^+ > AsCl_4^+ > ICl_2^+$. The relative instability of ICl_2^+ is discussed in the next section.

The presence of hexafluoroarsenate anions is inferred from the precipitation of nitron hexafluoroarsenate from the alkaline hydrolyzate. The compounds form conducting solutions in nitromethane with equivalent conductivities similar to those of other binary electrolytes in this solvent. The extent of ionization increases in the expected order from the sulfur to the tellurium compound.

Raman spectroscopy provides confirmatory evidence for the $SeCl_3^+$ and $TeCl_3^+$ cations. In solid $SeCl_4$ and in solid or liquid $TeCl_4$, the four stronger lines are close to those of the respective isoelectronic arsenic trichloride and antimony trichloride. These spectra together with the ionic conductivity of solid and liquid $TeCl_4$ constitute excellent evidence for $Se(Te)Cl_3^+Cl^-$ ionizations (*109*). However, some weak lines in the spectra have not been explained. Perhaps these halides are other examples of a tendency to "polarity" isomerism by a distortion toward a nonpolar form. It should be noted that, if two of the chlorines are replaced by the less electronegative phenyl groups, the substituted compound has the symmetry shown in the solid state and not that of the pyramidal cation:



A similar pattern of lines is observed with the compounds $SCl_4 \cdot AlCl_3$ and $SeCl_4 \cdot AlCl_3$, although the higher frequency values indicate stronger interaction with the anion. The sulfur trioxide adducts of the tetrachlorides are also probably $SeCl_3^+$ and $TeCl_3^+$ chlorosulfates, but the apparent fluorosulfates SF_5SO_3F and $SF_4(SO_3F)_2$ are not simple salts (*279*). They are in all probability covalently linked compounds with fluorosulfate bridging.

Sulfur tetrafluoride has the same trigonal bipyramidal structure shown above with nonbonding electron pair in an equatorial position. The fluorine exchange between nonequivalent fluorine atoms (*219*), observed in the low temperature n.m.r. spectra, may proceed via an ionic intermediate in view of the ionization observed in selenium tetrachloride.

There is also evidence for ionization in the lower sulfur halides. A solvent system, based on the self-ionization of sulfur monochloride,

$$S_2Cl_2 \rightleftharpoons S_2Cl^+ + Cl^-$$

has been postulated and justified by conductometric titrations of "acids" with "bases." The amount of ionization of solvent and solutions is minute.

The value for solutions is 10^{-6} to 10^{-8} ohm^{-1} cm^{-1} and for the solvent 10^{-10} ohm^{-1} cm^{-1} (*309*).

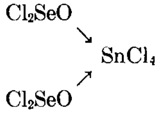
The ionization of sulfur monochloride in compounds with Lewis acids has been examined (*223*).

3. Oxysulfur and Oxyselenium Cations

These have usually been postulated as participants in the self-ionization schemes used to correlate chemical reactions in sulfur and selenium oxides and oxychlorides. Thus, in sulfur dioxide an oxide ion transfer, and in sulfuryl, thionyl, and selenyl chlorines a chloride ion transfer, between molecules is assumed to produce hetero-oxycations:

$$2SO_2 = SO^{++} + SO_3^{=}$$
$$SO_2Cl_2 = SO_2Cl^{+} + Cl^{-}$$
$$SeOCl_2 = SeOCl^{+} + Cl^{-}$$

It is now generally accepted, for at least sulfur dioxide, that metathetical, "neutralization," and displacement reactions need not proceed via the solvent self-ionization. For example, the absence of sulfur or oxygen exchange between thionyl halides and sulfur dioxide precludes the SO^{++} ion. Also the structures of many oxyhalide adducts with Lewis acids, which are supposed to form acids in the oxyhalide systems by halogen abstraction, are in fact bonded via oxygen to the Lewis acid, e.g.,



$$\begin{matrix} Cl_2SeO & \searrow & \\ & & SnCl_4 \\ Cl_2SeO & \nearrow & \end{matrix} \qquad\qquad Cl_2SeO \rightarrow SbCl_5$$

An extensive review of the evidence against SO^{++} has appeared recently and further comment is unnecessary (*323*).

The selenyl ion SeO^{++} has been postulated in the molten state. The conductivity of molten selenium trioxide initially 10^{-7} ohm^{-1} cm^{-1} increases to 5×10^{-3} ohm^{-1} cm^{-1} when the oxide is thermally decomposed at 175°. The conductivity in the supercooled residual Se_2O_5 is ascribed (*161*) to the ionizations:

$$SeO_2 \rightleftharpoons SeO^{++} + O^{=}; \qquad SeO_3 + O^{=} \rightleftharpoons SeO_4^{=}$$

Oxygen ion transfer in molten salts is the basis of Lux and Flood's interpretation of the reactivity of molten oxides (*104*), but the above evidence in a much less conducting medium is hardly definitive. The ionization of selenium dioxide in a particularly favorable medium, sulfuric acid, does not result in oxygen ion transfer to produce SeO^{2+} or $SeOHSO_4^{+}$ cations, but rather it acts as a base (*105*):

$$SeO_2 + H_2SO_4 = SeO_2H^{+} + HSO_4^{-}$$

A planar cyclic ion $S_4N_3^+$ (see Fig. 6) has recently been verified by an X-ray structural determination of thiotrithiazyl nitrate (*68*, *326*). Delocalization of ten electrons in a π system is proposed to account for the stability of the ion and its electronic spectrum (*163*).

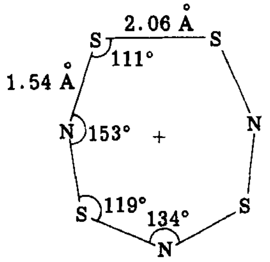


FIG. 6. Dimensions of $S_4N_3^+$ cation.

E. GROUP VII

The heterocations belonging to this group have been encountered during investigations into the reactivity of interhalogen compounds and halogen oxyfluorides. Some cations have been merely postulated in the self-ionization equilibrium of solvents without adequate physical characterization by, for example, spectral methods. However, structures proposed by analogy or extrapolation have generally been confirmed by later studies.

Fluoronium cations have not been prepared. The most feasible preparative route, by interaction of fluorine oxides and strong Lewis acid fluorides, has yielded with dioxygen difluorides the oxygenyl cation rather than an oxyfluoronium one,

$$F_2O_2 + MF_n = O_2^+(MF_{n+1})^- + \frac{1}{2}F_2$$

where M = B(III), P(V), As(V), and Sb(V). These complexes have been recognized by identifying the complex anions, and also by showing their isomorphism with nitrosonium salts of the same anions (*342*).

The compound fluorine fluorosulfate is a covalent one. Similar insertions of sulfur trioxide between halogen atoms occur with halogen fluorides; again, there is no evidence of ionic structures (*255*). Fluorine invariably appears as a negative substituent in other halogen cations.

1. *Difluorohalogen(III) Cations*

The self-ionization in liquid bromine trifluoride is considered in more detail than in previous accounts, because it exemplifies the type of reasoning applied to other interhalogens. The extreme nature of this solvent leads to a simplification of its solution chemistry. Only fluorides, and a few oxyfluorides, of elements in high valency states exist in solution. The effect of traces of moisture on conductivities in this solvent, the usual bane of the experimentalist, is unimportant, since they are eliminated as hydrogen fluoride and oxygen. The high conductivity of bromine trifluoride, which approaches that of sulfuric acid, has been independently confirmed in cells of different materials (Fig. 7) (*16*, *249*). The possible trace impurities Br_2 (or BrF), BrF_5, and HF have been shown to lower the conductivity. The negative temperature coefficient is a sign of ionic instability rather than electronic conduction because of the large drop in conductivity on freezing. The liquid is an associated one, as evidenced by the high Trouton constant and high ratio of energy of evaporation to free energy of viscous flow (*257*).

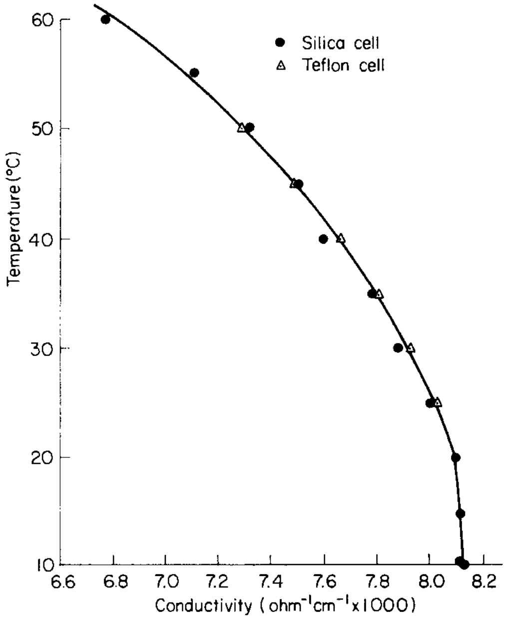
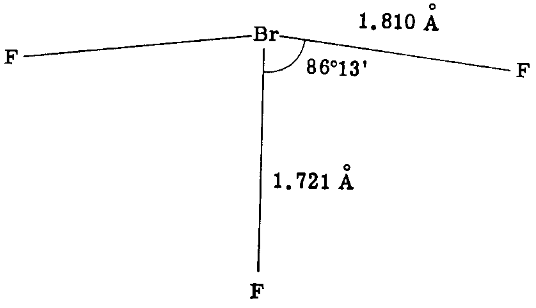


FIG. 7. Variation of conductivity of bromine trifluoride with temperature.



The molecular shape shows that a dipole is present in the direction of the shortest bond (*207*). It is reasonable to assume that in the liquid state the dipoles will orient with fluorine of one molecule close to the bromine of an adjacent molecule, possibly in chain configurations.

This arrangement will facilitate a fluoride ion transfer, which is the most reasonable postulate to explain the solvent conductivity, i.e.,

$$BrF_3 + BrF_3 \leftrightarrows BrF_2^+ + BrF_4^-$$

The ionization is regarded as a mobile one with a continuous but random breaking and remaking of Br-F bonds, so that an instantaneous picture would reveal a few ions in every thousand molecules or, alternatively, observation of a single bond would show it to be ionized for a correspondingly small fraction of the time. The self-ionization equation is only a partial representation of the overall ionization mechanism. The rapid exchange of radioactive fluorine between fluorides and bromine trifluoride agrees with the mobility of the fluoride ion in this solvent. The solvent on electrolysis behaves as an ohmic conductor, but the creation of a sharp color boundary, brown on the cathode side against unchanged yellow, shows that transport occurs. This is explicable as a redox reaction between products at the color junction regenerating solvent and preventing a build-up of products at the electrodes:

At anode: $BrF_2^+ \rightarrow BrF + BrF_3$

At cathode: $BrF_4^+ \rightarrow BrF_5 + BrF_3$

At junction: $BrF + BrF_5 \rightarrow 2BrF_3$

Bromine monofluoride is known to be in equilibrium with bromine and the solvent (*310*):

$$Br_2 + BrF_3 \rightleftharpoons 3BrF$$

Thus the evidence of the high conductivity of the solvent and its behavior on electrolysis by itself requires one to postulate the fluorobromonium cation. The conductivities of fluorides in bromine trifluoride provide confirmatory evidence. In Fig. 8 it can be seen that fluorides divide into two classes (*336*):

(1) The alkali and alkaline earth fluorides, the conductivities of which if extrapolated to zero concentration intercept the conductivity axis below the value of the solvent conductivity.

(2) The fluorides of Groups IV and V, which intercept above the solvent value. Normally the equivalent conductivity is plotted against concentration, but this cannot be done for a highly conducting solvent unless the contribution of solvent ions toward the total conductivity, and how it is affected by solute ions, can be ascertained.

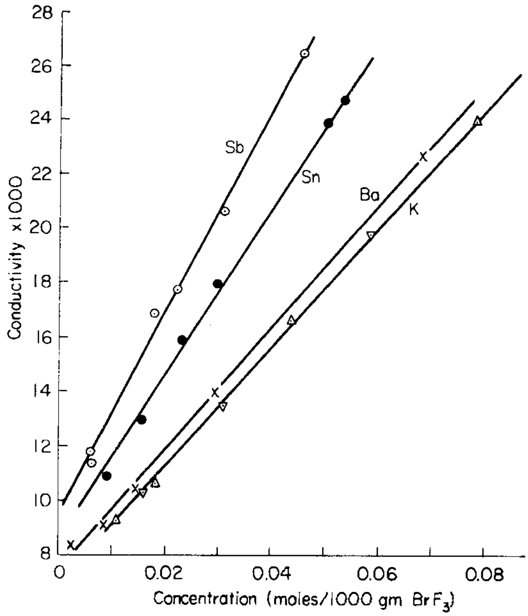


FIG. 8. Conductivity of acids and bases at 25°.

The latter effect is illustrated in Figs. 9a and 9b which show the temperature variation of conductivity for different solute concentrations. For potassium fluoride solutions it can be seen that the temperature variation is linear and positive from the lowest concentrations. (The temperature coefficient extrapolates to zero at just detectable concentration.) This behavior can be compared with the negative and nonlinear variation of the solvent conductivity.

It follows from this effect of the solute on the temperature coefficient, and from the extrapolated value of conductivity below that of the solvent (Fig. 8), that the solvent ionization is being repressed presumably by production of one of the solvent ions by the solute. Since an alkali salt can only ionize to form an alkali cation it follows that the fluoride ion, solvated by the solvent, must be the repressing ion, and indeed ionic salts of composition $MBrF_4$ (*307*) can be isolated from solution.

For antimony pentafluoride, however, although the temperature coefficient becomes positive, the curves remain nonlinear even at the highest concentrations. This fact together with the conductivity intercept above the solvent value (Fig. 8) indicates that the solvent ionization is being stabilized. Antimony pentafluoride is not ionizing as with the alkali fluorides, i.e., $SbF_5 \rightleftharpoons SbF_4^+ + F^-$, but is presumably removing the tetra-

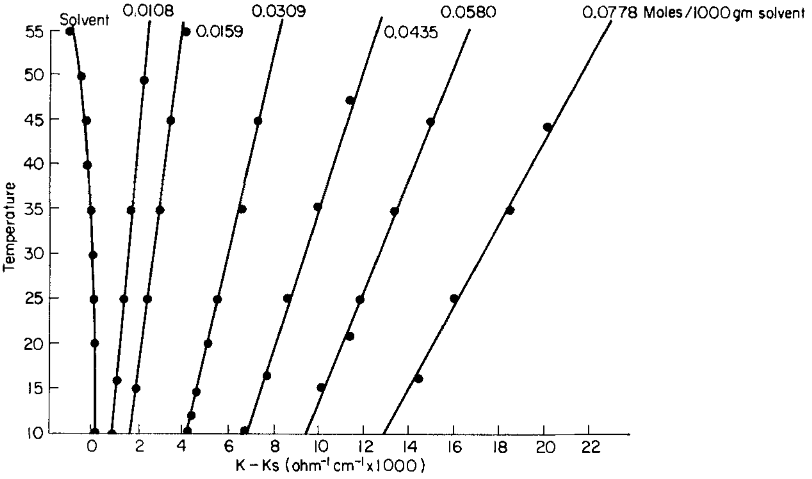


FIG. 9a. Temperature variation of conductivity of $KBrF_4$ solutions.

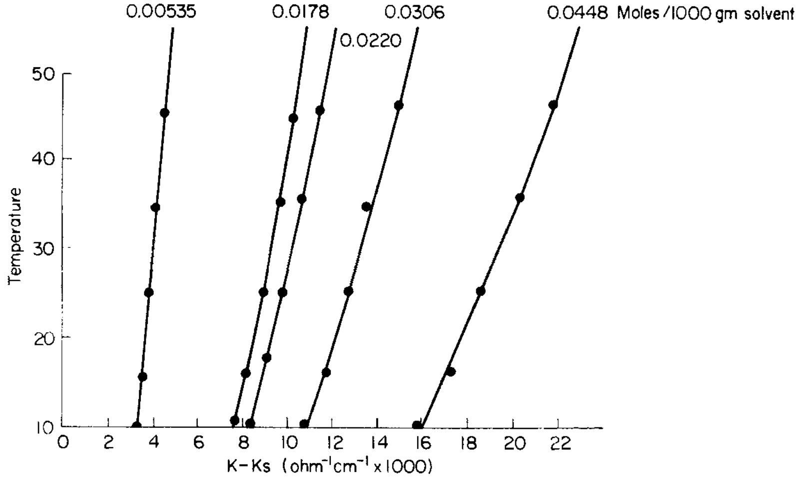


FIG. 9b. Temperature variation of conductivity of BrF_2SbF_6 solutions.

fluorobromate ion from the solvent equilibrium and causing further solvent ionization to replace it:

$$SbF_5 + BrF_4^- = BrF_3 + SbF_6^-$$

Each solute anion must then be balanced by a BrF_2^+ cation. The detailed picture is obviously more complex because it is known that antimony pentafluoride, as well as bromine trifluoride, is associated with short chains of antimony octahedrally coordinated with fluorine (*149*). Thus it is not surprising that compounds other than the least volatile $BrF_3 \cdot SbF_5$ (melting at 130°) exist in the $BrF_3 \cdot SbF_5$ system, namely, another congruently melting compound $BrF_3 \cdot 3SbF_5$ (33.5°) and the volatile incongruently melting compounds $3BrF_3 \cdot SbF_5$ (−16°) and $3BrF_3 \cdot 2SbF_5$ (31°) (*102*). Although the ionicity of these relatively reactive compounds in the solid or molten state has yet to be proven, it seems probable that the 1:1 compound ionizes as $BrF_2^+SbF_6$. It certainly behaves in this way in solution because, when added to a solution of an alkali fluoride or silver fluoride, the conductivity falls until equimolecular amounts are present, i.e., a replacement of BrF_4^- by less mobile SbF_6^-, and then rises at the same rate as a solution with increasing concentration of antimony pentafluoride:

$$Ag^+BrF_4^- + BrF_2^+SbF_6^- = AgSbF_6 + 2BrF_3$$

The unsolvated hexafluoroantimonates can be isolated from the resulting solutions.

The mobilities of ions in this solvent have not been measured directly but, by comparing solutions at 0.01 *M* concentration and assuming that the mobility of the potassium ion is about the same as in water, an assumption based on the validity of Walden's law in both solvents, it follows from the above conductivity measurements that BrF_2^+ and BrF_4^- are the most mobile ions, in that order. This would be expected if fluoride ion transfer proceeded by a chain mechanism. The ionic product $[BrF_2^+][BrF_4^-]$ is approximately 4×10^{-4}.

The description of the antimony pentafluoride ionization on the coordination model advocated by Drago (p. 226) differs from the above insofar as a coordinated intermediate would be the precursor of ionization. If it is accepted that the antimony becomes anionic, then, in the absence of kinetic or thermodynamic data on the intermediate, any difference between the two theories is more in the realm of semantics. The formation of the difluorobromonium ion follows according to the requirement of charge neutrality.

The behavior of other Lewis acid fluorides in this solvent have been studied similarly by conductivity methods or by neutralization and displacement reactions. The generation of extra BrF_2^+ ions, at least in solution, occurs with the addition of the fluorides which form the complex anions listed in Table VIII.

The acid strengths, i.e., the equilibrium constants, for

$$BrF_3MF_n \rightleftharpoons BrF_2^+ + MF_{n+1}^-$$

can be compared by consideration of solvolysis or displacement reactions. For example, hexafluorotitanates when made by neutralization reactions retain solvent because of the reversal of the neutralization $BrF_2^+ + BrF_4^-$

TABLE VIII

COMPLEX ANIONS ASSOCIATED WITH THE BrF_2^+ CATION

AuF_4^-
BF_4^-

PF_6^-
AsF_6^-
SbF_6^-
BiF_6^-

VF_6^-
NbF_6^-
TaF_6^-
RuF_6^-
OsF_6^-
IrF_6^-

$GeF_6^=$
$SnF_6^=$
$TiF_6^=$
$MnF_6^=$
$PtF_6^=$
$PdF_6^=$

VOF_4^-
$CrOF_4^-$
SO_3F^-
$ReOF_4^-$

$\rightarrow 2BrF_3$, whereas hexafluoroantimonates do not (*298*). Hence the titanium acid is much weaker than the antimony acid, in agreement with conductivity measurements. The displacement of the fluorosulfate anion from its nitrosonium salt by other Lewis acids,

$$NO^+SO_3F^- \xrightarrow[\text{in } BrF_3]{MF_n} NO^+MF_{n+1}^-$$

indicates (*331*) the following order of acid strength:

$$\begin{matrix} SbF_5 \\ AsF_5 \end{matrix} > BF_3 > SO_3 > SnF_4\ (> TiF_4)$$

(The relative strength of the last two is indicated from conductivity data. The first pair is not differentiated since both displace SO_3F^- completely.)

A wide range of fluorides has now been examined in bromine trifluoride, and since the majority form the BrF_2^+ ion it is reasonable to assume, even in the absence of quantitative equilibrium data, that the solvent is a basic one. This contrasts with the acid solvent sulfuric acid of the same order of ionization, in which most solutes generate the bisulfate ion.

Liquid chlorine trifluoride is quite different in physical properties from bromine trifluoride, even though the structures are geometrically similar in the gas phase. The solvent conductivity is of the order 10^{-9} ohm^{-1} cm^{-1} and any self-ionization is minute (*15*). The solvating and ionizing ability must also be low because of the small dielectric constant ($\epsilon = 4.3$) and normal entropy of vaporization. The only evidence for association in the liquid state is from n.m.r. measurements, but the traces of hydrogen fluoride required for F^{19} exchange suggest that ionization is more important than association (*217*).

The minuteness of solvent ionization is also shown by the nonformation of tetrafluorochlorates $M^+ClF_4^-$ in solution. These salts are made by fluorination of alkali chlorides with fluorine (*6*). It is therefore remarkable that strong Lewis acids can provoke ionization in solution to produce the difluorochloronium cation:

$$ClF_3 + MF_n = ClF_2^+ + MF_{n+1}^-$$

Thus passage of boron trifluoride increases the solvent conductivity and the 1:1 compound which can be isolated has a melt conductivity of 1.5×10^{-2} ohm^{-1} cm^{-1}. The spectra of the solid show the broad peak characteristic of the BF_4^- anion and the symmetrical and asymmetrical stretching frequencies of the bent ClF_2^+ cation. Solutions of phosphorus, arsenic, and antimony pentafluorides behave similarly but the solution conductivities indicate much smaller ionizations than in bromine trifluoride (*296*). The solids which can be isolated from solution have infrared spectra characteristic of fluoro anions and bent ClF_2^+ cations. Solutions of these compounds in a more effective ionizing solvent, iodine pentafluoride, show their ionic nature. Thus the freezing point depression of $ClF_3{\cdot}AsF_5$ is that for a dissociation into two particles in solution, and a conductometric titration with potassium fluoride is explained by (*52*):

$$ClF_2^+AsF_6^- + KF \xrightarrow{IF_5} ClF_3 + K^+AsF_6^-$$

The heat of dissociation of the $ClF_3{\cdot}BF_3$ compound (23.6 kcal/mole) is also significant, being of the same order as for other fluoroborates, e.g., $SF_3^+BF_4^-$ 25.1, $RbBF_4$ 27.0 (*286*).

The corresponding platinum fluoride adduct $ClF_3{\cdot}PtF_6$, which results from the displacement of the oxygenyl ion in $O_2^+PtF_6^-$ by chlorine trifluoride, is presumably another salt of the ClF_2^+ cation (*20*). The stability of the ClF_2^+ ion is rather low in the order given by displacement reactions, i.e., $K^+ > SF_3^+ > NO^+ > NO_2^+ > BrF_2^+ > ClF_2^+ \geq O_2^+$. Such an order has not been established directly but can be reasonably deduced from partial series in the literature.

The difluoroiodonium cation IF_2^+ should be the most stable of the trivalent halogen ions but, since iodine trifluoride is an unstable solid which disproportionates to iodine and its pentafluoride, there is no direct route to its salts. It may be possible to prepare the IF_2^+ cation by reductive processes from iodine pentafluoride in a suitable solvent in the presence of Lewis acid fluorides, analogously to the formation of the IF_4^- anion (*137*). It should be noted that mixtures of halogens and higher halogen fluorides can behave as a lower halogen fluoride, i.e., $Cl_2 + ClF_3$ is equivalent to ClF, $Br_2 + BrF_3$ to BrF, $I_2 + IF_5$ to IF (*145*).

2. Other Fluoro Cations

Iodine pentafluoride is the most likely of the remaining interhalogen fluorides to exhibit an appreciable self-ionization. The dielectric constant is high and the liquid is associated. The conductivity, 5×10^{-6} ohm^{-1} cm^{-1} at 25°, is probably not the minimum value since it is easily affected by traces of moisture (*258*). There is evidence from neutralization reactions for the self-ionization,

$$IF_5 + IF_5 \rightleftharpoons IF_4^+ + IF_6^-$$

and the adduct $IF_5 \cdot SbF_5$ is a stable solid which ionizes in iodine pentafluoride. The compound $IF_5 \cdot PtF_5$, made by the displacement of the oxygenyl cation in $O_2^+PtF_6^-$ by iodine fluoride, could be $IF_4^+PtF_6^-$. However, the overall evidence for IF_4^+ is somewhat circumstantial. Spectral measurements are badly needed to confirm the postulated ionizations, as well as further investigations in other solvents to confirm equilibrium such as:

$$HF + IF_5 \rightleftharpoons IF_4^+ + HF_2^-$$

$$HSO_3F + IF_5 \rightleftharpoons IF_4^+ + SO_3F^-$$

The basicity of iodine pentafluoride in these solvents has yet to be firmly established (*332*).

Other fluoro heterocations may exist in the adducts which form between iodine heptafluoride and Lewis acid fluorides (*286*):

(1) $IF_7 \cdot BF_3$ has been formulated as $IF_6^+BF_4^-$ but its instability at room temperatures makes this less probable. The alternative formulation as a coordinate compound would require participation of 4*d* orbitals in a bonding scheme and would account for the instability of a covalent form.

(2) $IF_7 \cdot AsF_5$ is a solid with a low vapor pressure at room temperatures, again formulated as the hexafluoroiodine(VII) hexafluoroarsenate.

(3) $IF_7 \cdot 3SbF_5$ is the stablest of the three. It melts at 92°–94° and at 100° the melt has a conductivity of 6.7×10^{-3} ohm^{-1} cm^{-1}. The solid ionization $IF_4^{3+}(SbF_6^-)_3$ is suggested, which in the melt becomes a solution of $IF_6^+SbF_6^-$ in antimony pentafluoride. A less labored explanation would be a partial ionization by fluoride ion transfer to produce $IF_6^+Sb_3F_{16}^-$. The existence of corresponding polymeric fluoro anions of trivalent antimony with fluorine bridging, $(SbF_3)_nF^-$, with $n = 1$–4, is well established (*327*). Other compounds in the IF_7–SbF_5 system are indicated (cf. the BrF_3–SbF_5 system, p. 272).

Fluoro cations derived from bromine pentafluoride, although less probable than those derived from iodine pentafluoride, should also exist in solution.

3. Cations Derived from Other Interhalogen Compounds and Halogens

The heterocation ICl_2^+ is derived from iodine trichloride. The compound $IAlCl_6$ was prepared by heating iodine and aluminum trichlorides in a chlorinated hydrocarbon, the compound $ISbCl_8$ from iodine trichloride in liquid antimony pentachloride. Although the latter conducts in the melt, it is difficult to differentiate from the conductivity of molten iodine trichloride into which it could dissociate. In liquid sulfur dioxide the equivalent conductivity is only a small fraction of the values for hexachloroantimonates. The ultraviolet spectrum in carbon tetrachloride is a superposition of the spectra of ICl_3 and $SbCl_5$.

In the solid the results of X-ray analysis indicate ionization to $ICl_2^+SbCl_6^-$ and $ICl_2^+AlCl_4^-$ but, as commented on in the introduction, there is a considerable interaction between the rectangular ICl_2 unit and pairs of chlorine in the supposed anions. The I-Cl distance between the units is much shorter than the sum of the van der Waals' radii (*322*). It is therefore not surprising that the molecule should revert to its constituents in a nonpolar solvent and only partially ionize in sulfur dioxide, a solvent of low polarity. The cation stability should be enhanced with donor molecules which are themselves stable to chlorination.

The possible occurrence of simple halogen cations X^+ has been discussed, and it appears that almost all the species designated as halogen cations are in fact solvated heterocations (*8*). Even for the conducting melt of iodine monochloride, it is more reasonable to write the self-ionization $3ICl \rightleftharpoons I_2Cl^+ + ICl_2^-$.

Indeed, phase studies of the systems ICl with $AlCl_3$ or $SbCl_5$ show 2:1 adducts and not 1:1, i.e., $I_2Cl^+AlCl_4^-$. When 1:1 adducts are encountered they may contain the ICl_2^- anion, e.g., $PCl_5 \cdot ICl$ is $PCl_4^+ICl_2^-$ (*345*). With organic donor molecules it is possible to isolate the solvated cations in the form of stable salts. A few recent examples are I(py)F, $I(py)_2F_3$, $Br(py)_2NO_3$, and $Br(SR_2)^+B(C_6H_5)_4^-$, where py = pyridine, R = isopropyl (*39, 274, 275*).

Substituted iodonium cations can also be made by metathesis. Thus the diphenyl-substituted iodine(III) chloride and potassium tetrachloroplatinate(II) precipitate $(C_6H_5)_2I^+PtCl_4^-$ from aqueous solutions. The iodonium cation presumably has the same bent shape as in diphenyliodine monochloride (*185*).

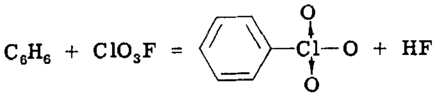
4. *Oxyhalogeno Cations*

The presence of these ions in halogen oxides and as intermediates in reaction mechanisms has often been proposed. Only the solid compounds which may be salts are discussed here. A full series of chlorine oxyfluorides, ClOF, ClO_2F, ClO_3F, ClO_4F with chlorine in an increasingly higher valency state, is known. If the fluorine in these oxyfluorides could be ionized to a simple or complex fluoride ion, the expected order of stability of the resulting cations would be $ClO^+ > ClO_2^+ > ClO_3^+$.

The first of these ions has yet to be studied, presumably because a reliable preparation of chlorosyl fluoride is not available. The first indication of a chloronium ion was the isolation of a red solid $Cl_2O_5 \cdot 3SO_3$, by reaction of sulfur trioxide with potassium chlorate, which is analogous in a formal sense to $N_2O_5 \cdot 3SO_3$ (*190*).

The structure of the latter established by X-ray analysis is that of a nitronium salt $(NO_2^+)_2S_3O_{10}^=$ (*92*). In later work the direct reaction of chloryl fluoride with Lewis acid fluorides (BF_3, SF_4, PF_5, AsF_5, SbF_5, and SO_3) has yielded solid adducts which have been formulated as ClO_2^+ salts by analogy to nitronium salts of the same complex anions (*270*, *272*, *334*). The chloryl ion is isoelectronic with sulfur dioxide and should be a bent ion with a Cl-O distance of about 1.43 Å. This would give an ion of radius about 0.3 Å larger than the nitronium ion, and would result in a larger lattice energy for the chloronium salt of the same anion. The lattice energy difference is believed to be the main energy term which governs the relative stability of the two cations. The relative stabilities can be confirmed by carrying out displacement reactions in bromine trifluoride, which provide the stability sequence $K^+ > NO_2^+ > BrF_2^+ > ClO_2^+$.

Perchloryl fluoride, the most inert of the oxyfluorides, does not complex with the typical Lewis acids $AlCl_3$ or BF_3, but with an active aromatic molecule and aluminum halides the following reaction occurs:



The transient existence of the ClO_3^+ cation in a ternary complex $C_6H_6AlCl_3F^-ClO_3^+$ is part of the suggested mechanism (*228*). It is possible that the formation of salts of the planar perchloryl cation is kinetically limited rather than thermodynamically prohibitive, and that more vigorous reaction conditions may yield stable salts. Fluorine perchlorate resembles the nitrate in being an unstable covalent compound. It would not be expected to act as a source of ClO_3^+ ions.

The evidence for oxyiodonium cations is inconclusive except for spectral evidence of a hexafluoroarsenate salt. The sulfur trioxide adducts of iodine oxides, $I_2O_3 \cdot 3SO_3$, $I_2O_4 \cdot 3SO_3$, $I_2O_5 \cdot 2SO_3$, have been formulated respectively as $(IO^+)_2S_3O_{10}^=$, $(IO^+IO_2^+)S_3O_{10}^=$, and $(IO_2^+)_2S_2O_7^=$, again by analogy to corresponding compounds of nitrogen oxides (*191*). The substitution reactions of aromatics with iodine oxides in sulfuric acid have also been advanced as evidence for iodonium ions in solution and possibly in the solid. However, the infrared spectra show that iodosyl cations are not present in $(IO)_2SO_4$, $(IO)_2SeO_4$, or $IOIO_3$. These compounds, unlike the nitrosyl salts, are insoluble in nitromethane. They are diamagnetic, whereas the iodosyl cation should be paramagnetic in the ground state. The cation should be isoelectronic with tellurium monoxide, but with a slightly higher vibration frequency because of the charge (*72*),

NO_2^+	CO_2	NO^+	CO
2390	2349	2200	2144 cm^{-1}

and hence one would expect the IO^+ stretching frequency at above 800 cm^{-1} compared with 796 cm^{-1} for TeO. The observed absorptions are at much lower frequencies, 553–658 cm^{-1}. It is suggested that the tetrahedral symmetry of the sulfate is retained in iodosyl sulfate by bonding of each oxygen to a neighboring iodine. The yellow color of the compound argues against purely covalent bonding, and the color may be associated with partly charged —I—O—I— chains in a manner reminiscent of the fully ionic titanyl sulfate structure, which has —Ti—O—Ti— chains held together by sulfate ions.

The behavior of iodic acid in sulfuric acid, a solvent capable of stabilizing an iodonium cation, has been examined cryoscopically and conductometrically (*121*). Three modes of ionization were considered:

$$HIO_3 + H_2SO_4 = H_2IO_3^+ + HSO_4^-$$

$$HIO_3 + 2H_2SO_4 = IO_2^+ + H_3O^+ + 2HSO_4^-$$

$$HIO_3 + 2H_2SO_4 = IO_2HSO_4 + H_3O^+ + HSO_4^-$$

The results are consistent with the last ionization, in contradiction to an earlier report (*7*), but involve polymeric forms of iodyl hydrogen sulfate which depolymerize on dilution and are partially ionized.

More recently the existence of an iodonium cation in a complex fluoride has been established. The oxyfluoride IOF_3 made from the pentoxide and pentafluoride was originally considered as $IO_2^+IF_6^-$. Its thermal decomposition to IO_2F at 110° parallels that of alkali hexafluoroiodates and is consistent with its formulation as a hexafluoroiodate (*12*). Iodyl fluoride can be more conveniently made by passing fluorine through a solution of iodine pentoxide in hydrogen fluoride. The purpose of the fluorine is to dehydrate the intermediate iodic acid (*273*):

$$IO_2IO_3 + HF = HIO_3 + IO_2F$$

$$HIO_3 + HF = H_2O + IO_2F$$

$$H_2O + F_2 = 2HF + \tfrac{1}{2}O_2$$

If the iodyl fluoride solution in hydrogen fluoride is treated with arsenic pentafluoride, the compound IO_2AsF_6 can be isolated. The alternative ionization $AsF_4^+IO_2F_2^-$ was suggested as being more probable in view of the existence of stable difluoroiodates (*13*), but it now appears that the ionization originally suggested was the correct one. Examination of the infrared spectra shows the presence of absorptions characteristic of hexafluoroarsenates and the absence of those of difluoroiodates. Another quantitative preparation of the iodyl salt also demonstrates the structure (*242*):

$$K(IO_2F_2) + AsF_5 \xrightarrow{HF} K^+AsF_6^- + IO_2F$$
$$IO_2F + AsF_5 \xrightarrow{HF} IO_2^+AsF_6^-$$

The iodyl fluoride in this instance behaves as a base toward a strong Lewis acid (or ansolvo acid in the hydrogen fluoride system). It can also function as an acid toward fluorides which are basic:

$$K(IO_2F_2) + AgF \xrightarrow{HF} Ag(IO_2F_2) + KF$$

The behavior of the oxyfluoride IOF_3 in fluoride systems is of interest in view of possible amphoteric character (i.e., $IF_4^+IO_2F_2^-$ versus $IO_2^+IF_6^-$).

A substance which can be written in the form of an iodyl salt has been prepared by reaction of iodine pentoxide with peroxydisulfuryl fluoride at 150° when the latter dissociates to SO_3F radicals:

$$I_2O_5 + S_2O_6F_2 = 2IO_2SO_3F + \tfrac{1}{2}O_2$$

This compound is insoluble in fluorosulfuric acid and may be a polymeric substance with SO_3F acting as bidendate bonding groups. It is unlikely to be a simple ionic salt (*9*).

No mention has been made of the xenon fluorides and oxyfluorides which are analogous to the interhalogen compounds, but the resemblances between rare gas and halogen chemistry are such as to allow the possibilities of heterocations of xenon; no doubt this is being actively pursued (*62*, *295*).

III. The Proton in Heterocations

The isolated proton is unlikely to exist to any extent in solution because the ionization potential of elemental hydrogen (13.6 ev) is so much greater than that of other elements which form stable univalent ions in solution. The extreme charge-to-radius ratio for the proton will also encourage polarization of solvent molecules, so that acids in solution once formulated with bare protons are invariably solvated. (Protons can exist under special conditions in solids and liquids, for example during the diffusion of hydrogen in metals or in liquids exposed to intense radiation fields.) An illustrative cross section of the occurrence of complex protons is presented.

A. Aqueous Solutions

Evidence for the hydroxonium ion H_3O^+ and hydronium ion $H_3O^+{\cdot}nH_2O$ in the commonest protonic solvent, water, has been comprehensively reviewed (*38*). X-ray examination of a number of oxyacid hydrates has shown distinct anion units and oxygen atoms. By inference the latter are taken to be hydroxonium ions. Thus in $HClO_4{\cdot}H_2O$, a substance isomorphous with ammonium perchlorate and isostructural with barium sulfate, the almost perfect tetrahedral ClO_4 unit is seen. The H_3O units are coordinated with twelve oxygens from surrounding ClO_4 groups. If molecular $HClO_4$ were present, one of the Cl-O bonds would differ from the others (*189*). In the structure of $HCl{\cdot}H_2O$ the oxygen and chlorine atoms alternate in parallel planes. Each atom is three-coordinate so the units are presumably H_3O^+ and Cl^- (*341*). The hydrogen atoms in these hydrates can be located by examining the shape of p.m.r. absorption curves. Isolated nuclei have narrow resonances, but in solids the resonance is broadened by interaction with fields of neighboring nuclei. These nuclei by exchanging energy levels reduce the time of occupancy of the levels and hence broaden the resonance. The width of the absorption can be related to internuclear distance. By assuming an equilateral triangle of protons of edge 1.72 Å, it is possible to calculate absorption curves in close agreement with experiment. In this way $HNO_3{\cdot}H_2O$, $HClO_4{\cdot}H_2O$, $H_2PtCl_6{\cdot}2H_2O$, and $H_2SeO_4{\cdot}H_2O$ were shown to be hydroxonium salts, whereas $(COOH)_2{\cdot}2H_2O$ contains water molecules (*254*). The p.m.r. spectra are consistent with a pyramidal shaped ion with an approximate O-H distance of 1.0 Å.

The third type of evidence is from infrared and Raman spectra. The spectra of solid $HCl{\cdot}H_2O$ and $HBr{\cdot}H_2O$ are explicable in terms of pyramidal H_3O^+ ions isoelectronic with NH_3, but not in terms of water and hydrogen halide molecules (*96*). The vibrational-rotational bands of H_3O^+ in acid solutions are difficult to detect in the presence of the strong infrared absorption of water itself. Nevertheless the three broad bands at 1205, 1750, and 2900 cm^{-1}, whose intensity increases with acid concentration, can be associated with the hydroxonium ion. This is confirmed by the expected isotope shift which occurs for deuterated acids. There is a true bond between proton and water molecule which lasts long enough for normal vibrations to occur (*97*). More recently it has been shown that $HNO_3{\cdot}H_2O$ contains traces of the covalent form (*267*). In fact this is also detectable from X-ray analysis in the slight asymmetry of the nitrate ion. The equilibrium between covalent and ionic forms in solution can be followed quite precisely by intensity measurements on suitable Raman lines. In aqueous perchloric acid, by using the perchlorate line at 931 cm^{-1}, it has been shown that the ionization is essentially complete from 0.3 to 10 *M* solutions. Above 10 *M* there is insufficient water to solvate the proton as $H_9O_4^+$ and ionization is incomplete (*70*). This ion has been detected directly in a glow discharge in water vapor by mass spectrometry. The suggested mechanism of formation is ionization of a water molecule by electron bombardment followed by reactions with other water molecules (*170*):

$$H_2O^+ + H_2O = H_3O^+ + OH$$
$$H_3O^+ + 2H_2O \rightleftharpoons H_5O_2^+ + H_2O, \text{ etc.}$$

The forward reaction is faster than the reverse. There is a maximum stability at composition $H_9O_4^+$. Further species up to $H_3O^+(H_2O)_9$ have been observed with field emission sources (*27*). The existence of $H_9O_4^+$ in water follows indirectly from studies on the rate of proton transfer by relaxation methods (*88*). The neutralization represented by $H^+ + OH^- = H_2O$ has a rate constant of 1.4×10^{-11} mole^{-1} sec^{-1} at 25°, the maximum rate for an aqueous reaction which is diffusion-controlled. The distance of closest approach of ions which appears in the diffusion rate equation is 8 Å, indicating that the proton is solvated as H_9O_4, an ion of this diameter (*87*).

The presence of the hydroxonium ion in hydrates of mineral acids substituted by electronegative elements or groups such as F or CF_3 can be inferred from their behavior as strong acids in solution. The solid hydrate of trifluoromethylsulfuric acid would be $H_3O^+SO_3(CF_3)^-$. This acid is stronger than perchloric acid when dissolved in acetic acid (*143*). Another example is the solid hydrate of a substituted phosphoric acid, $(H_3O)^+_2$ $(PO_3C_3F_7)^=$ (*91*).

The ionization of halides or oxyhalides by Lewis acid halides is a general method for generating heterocations and many examples have been quoted. An analogous reaction with water would be the formation of boron trifluoride hydrates. The mono- and dihydrate are known; the latter in the solid state is isomorphous with ammonium tetrafluoroborate, and has been formulated as $H_3O^+BF_3OH^-$. The alternative $H_2F^+BF_2(OH)_2^-$, possible because of the similar size of F^- and OH^-, was eliminated by examination of electrolysis products from the melt (*128*). The monohydrate was formulated as $H^+BF_3OH^-$ from electrolysis experiments. The extent of ionization was calculated as 20% for the dihydrate and 10% for the monohydrate (*129*). However, the presence of an unsolvated proton in the latter is incompatible with general views on this species.

The p.m.r. spectra of the hydrates were examined subsequently (*106*). If samples were crystallized slowly, the resonances at 90°K had double maxima whose shape could be calculated on the basis of proton pairs separated by 1.62 Å in the monohydrate, and 1.54 Å in the dihydrate. The monohydrate structure was therefore consistent with a molecular hydrate containing water molecules little different from those in the gas phase. The fluorine resonance was consistent with this picture. In the dihydrate the shorter H-H distance was taken as indicative of different types of water molecule, one-coordinated to boron trifluoride as in the monohydrate, and the other possibly hydrogen-bonded in the lattice. If liquid samples were rapidly quenched the p.m.r. of the solids became single maxima, presumably because the col between the above mentioned double maximum was obscured by new central maxima. For both hydrates a partial ionization to H_3O^+ and BF_3OH^- ions would explain the resonances. The quenched liquids can be regarded as supercooled melts which retain the melt structure. A recent X-ray structural investigation of the dihydrate provides confirmatory evidence (*17*). Although the solid is almost isomorphous with $H_3O^+ClO_4^-$, it is distinctly less symmetrical (monoclinic rather than orthorhombic). It is not possible to locate hydrogen or to distinguish oxygen from fluorine directly. However, the longest of the four bonds around boron must be the B-O bond, and the three shorter bonds B-F. The latter are shorter than in BF_4^- and close to B-F bonds in amine adducts with boron trifluoride. This suggests BF_3H_2O units rather than BF_3OH^- ions. The remaining water is water of crystallization hydrogen-bonded in the structure. The X-ray and p.m.r. spectral evidence, although not decisive, seems to dispose of ionic structures in the solid. Even in the melt the amount of ionization may be less than measured because of the asymmetrical dissociation induced by the measuring field (*339*). This example has been quoted at some length because it demonstrates the uncertainty in transferring structural interpretations from one state of matter to another.

A stabilization of ionization can be achieved by adding a third component, namely, hydrogen fluoride, to the 1:1 system BF_3H_2O when the ternary compound $H_2O{\cdot}HF{\cdot}BF_3$ can partly ionize as $H_3O^+BF_4^-$. Thus the hydroxonium ion can be detected by p.m.r. when water is present in a saturated solution of boron trifluoride in hydrogen fluoride at −75° (*206*). Similarly, addition of alcohol forms the solvated proton $C_2H_5OH_2^+$. The p.m.r. spectrum shows resolved peaks of CH_3, CH_2, and OH_2^+ groups.

B. Solutions in Sulfuric Acid

The ionizations which occur in this solvent have been thoroughly reviewed by Gillespie and Robinson (*119*). The 100% acid has a conductivity at 25° of 1.04×10^{-2} ohm^{-1} cm^{-1}. (This is not the minimum conductivity, which occurs at a slightly weaker composition containing 0.0019 mole of water/kg.) The conductivity is partly due to the proton transfer,

$$H_2SO_4 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$$

and partly to other solvated protons produced in a sequence of reactions,

$$\begin{aligned} H_2SO_4 &= H_2O + SO_3 \\ H_2O + H_2SO_4 &= H_3O^+ + HSO_4^- \\ SO_3 + H_2SO_4 &= H_2S_2O_7 \\ H_2S_2O_7 + H_2SO_4 &= H_3SO_4^+ + HS_2O_7^- \end{aligned}$$

which when summed are equivalent to the above solvent self-ionization and an ionic self-dehydration:

$$2H_2SO_4 \rightleftharpoons H_3O^+ + HS_2O_7^-$$

Sulfuric acid is an acid solvent, consequently the majority of solutes act as bases and the strengths of acids are leveled to a greater extent than in water. Hence few substances can increase the $H_3SO_4^+$ content of the solvent. The strong acids $HClO_4$ and HSO_3F in water are weak acids in sulfuric acid. Only the polysulfuric acids and complex hydrogen-sulfato acids such as $HB(HSO_4)_4$, derived from boric acid in oleum, are strong acids. Both ions produced in the solvent's self-ionization have high mobilities similar to those of H_3O^+ and OH^- in water. This suggests that proton transfer also occurs via hydrogen bonds without actual movement of $H_3SO_4^+$ units. The conductivities of strong acids in sulfuric acid are approximately equal because the $H_3SO_4^+$ ion, or rather the associated proton, is so mobile. Strong acid-base titrations give minimum conductivities at or near equivalence, because of removal of mobile ions as the self-ionization reaction is reversed.

More direct evidence for $H_3SO_4^+$ in sulfuric acid is sparse because the self-ionization, although large by water standards, is still difficult to detect spectroscopically. The detection of a similar ion $H_5SO_5^+$ ($H_3O^+H_2SO_4$) has been claimed in the infrared spectrum of the monohydrate and in more concentrated sulfuric acid solutions (*343*). The same unit may also occur in the crystal structure of the solid monohydrate in which five hydrogen bonds emerge from each sulfate group (*40*). The Raman spectra of concentrated $H[B(HSO_4)_4]$ solutions are quite complex but an assignment has been made for the $H_3SO_4^+$ and $[B(HSO_4)_4]^-$ species (*117*). A pure sample of the solid acid has not been isolated.

The main evidence for $H_3SO_4^+$ therefore relies on the internal self-consistency of a simple self-ionization scheme, and the ability to correlate a large body of cryoscopic and conductivity measurements on this basis.

C. SOLUTIONS IN ANHYDROUS HYDROGEN FLUORIDE

The evidence adduced for a solvated proton in this solvent follows the familiar pattern for other ionizing solvents. The stabilization of protonated aromatic species in anhydrous hydrogen fluoride (A.H.F.) is a unique feature, since it is carried to a higher degree than in other solvents (e.g., H_2SO_4). The solvent itself is associated, as evidenced by a high entropy of vaporization and exceptional boiling point. The dielectric constant (84 at 0°) is higher than that of water at a corresponding temperature (i.e., fraction of boiling temperature). The solvent conductivity is particularly affected by minute traces of water and values have lessened with increasing purification. The lowest values (2.6–5.7×10^{-6} ohm^{-1} cm^{-1} at 0°) are still two orders of magnitude greater than in water (*263*).

The postulated self-ionization, $3HF = H_2F^+ + HF_2^-$, is only a shorthand representation of a more complex situation. It is not believed that large molecular aggregates or ions are present in the liquid, but that ion transfer occurs via short chains and not through three-dimensional networks as in water. Approximate calculations based on an electrostatic model show a gain in stability on passing from HF_2^- to $H_3F_4^-$, and only small differences between $H_2F_3^-$, $H_3F_4^-$, and $H_4F_5^-$. Conductivity measurements show that the proton mobility in A.H.F. is less than that of alkali metal ions and that it is only the fluoride ion which has an exceptional mobility, but even for this ion differences in mobility are mitigated by the low solvent viscosity. The chain cations $H^+(HF)_n$ with n large are improbable; angular H_2F^+ entities isoelectronic with water molecules should occur to some extent.

Protonic acids are unable to function as acids in A.H.F. Even the strong acids $HClO_4$ and HSO_3F are little ionized. The addition of Lewis acid fluorides, however, produces substantial ionization. Antimony pentafluoride in particular forms solutions more highly conducting than solutions of alkali fluorides. The HF–SbF_5 system has been examined in some detail, and two ionic equilibria are postulated to explain the conductivity and spectral data (*156*):

$$2HF + SbF_5 \overset{K_1}{\rightleftharpoons} H_2F^+SbF_6^- \overset{K_2}{\rightleftharpoons} H_2F^+ + SbF_6^-$$

The ion dissociation equilibrium predominates at lower concentrations of the pentafluoride. For example, at 20 mole% SbF_5, $K_1 \simeq 4.4 \times 10^{-4}$ and $K_2 \simeq 1.7 \times 10^{-2}$. The possibility of the SbF_6^- anion being formed from traces of water (i.e., $H_2O + HF = H_3O^+ + F^-$, $SbF_5 + F^- = SbF_6^-$) is no longer important at high concentrations of antimony pentafluoride, so that solvent purification is less critical than for dilute solutions. Addition of A.H.F. raises the very low conductivity of antimony pentafluoride until a maximum is reached at 90 mole% HF. At this point the equivalent conductivity is about 40% of its value at infinite dilution. The Raman spectra show the disappearance of molecular antimony pentafluoride lines at 20–30 mole% HF, and their replacement by the single line of the SbF_6^- anion. There are no HF_2^- lines and hence the solvated proton must accompany the SbF_6^- anion.

The functioning of other fluorides in the production of H_2F^+ or similar solvated protons has been demonstrated more qualitatively by salt formation and attack on metals by solutions of these fluorides (*59*, *61*). The close analogy between fluoride solubilities, as well as acid strengths, in

A.H.F. and bromine trifluoride provides mutual support for the contention that fluoride ion transfer occurs in both solvents. In view of this similarity, the direction of transfer for halogen fluorides dissolved in A.H.F. is of interest. Some workers maintain that iodine pentafluoride is an acid because they isolated salts of the hexafluoroiodate anion (*60*); others were unable to isolate these salts and suggest that the products are bifluorides and that the ionization is $IF_4^+HF_2^-$ rather than $H_2F^+IF_6^-$ (*335*). The extent of ionization is minute, however, and there is no evidence for a 1:1 adduct (*259*). It is also believed that bromine and chlorine trifluorides, which are more conducting, are bases in A.H.F. Xenon hexafluoride is readily soluble in A.H.F. to form highly conducting solutions with equivalent conductivities about a third of those of potassium fluoride solutions (*208*). From the trend with halogen fluorides one would expect the hexafluoride to become acidic in A.H.F. and to generate the solvated proton. Xenon tetrafluoride, the analog of iodine pentafluoride, does not form conducting solutions.

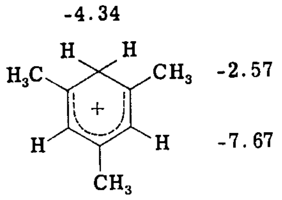
The solubility of aromatic hydrocarbons in A.H.F. has been known for many years and is attributed to the proton-accepting ability of the aromatic nucleus. The resulting arenonium ion can be further stabilized by addition of Lewis acid fluorides, or by increasing the electron availability in the aromatic circuit. The extraction of methylbenzenes with A.H.F. containing controlled amounts of boron trifluoride increases with the basicity of the hydrocarbon from toluene to hexamethylbenzene. The stoichiometry of the interaction can be followed tensimetrically. The vapor pressure of hydrogen fluoride increases with the addition of boron trifluoride, but in the presence of a strongly basic aromatic hydrocarbon the pressure decreases to a minimum at the 1:1 ratio of BF_3:ArH (*204*).

There are similar inflections in the conductivity curves at 1:1 ratios (*168*). The conductivity, however, remains constant after this value is exceeded. The conductivities of the more basic hydrocarbons are similar and approach the potassium fluoride values. The reactions are summarized:

$$ArH + HF \leftrightarrows ArH_2^+ + F^-$$

$$F^- + BF_3 \leftrightarrows BF_4^-$$

With excess of boron fluoride the first equation is displaced to the ionic side, so that conductivities of all the methyl-substituted hydrocarbons approach parity. Further information on the cation produced is provided by spectral methods. The ultraviolet spectra of methylbenzenes in the acid boron fluoride solutions show absorptions characteristic of arenonium ions, which can also be predicted theoretically (*71*). The p.m.r. spectra have been studied at low temperature to slow down proton exchange and separate the peaks. For example, with mesitylene solutions the broadened solvent peak is observed to the low field side followed by that of the ring protons and "aliphatic" methylene group and finally the methyl protons. The chemical shifts relative to trimethylsilane are indicated in the formula:



At higher temperatures the spectra show that the added proton remains attached to the complete ion, but exchanges its position with the other ring protons (*206*). These cations cannot be isolated as tetrafluoroborate salts except at low temperature, but many of the corresponding hexafluoroantimonates are stable at ordinary temperatures, e.g., symmetrical $(CH_3)_3C_6H_3H^+SbF_6^-$ melts at 51° (*229*). The p.m.r. spectra of this salt and related hexafluoro anions measured in liquid sulfur dioxide agree with their formulation as σ-arenonium complexes. Thus, although the solvated proton in hydrogen fluoride has yet to be adequately characterized, there is no doubt about the stabilized protonic species which exist in solution or as salts.

D. Solutions in Liquid Hydrogen Chloride

The existence of H_2Cl^+ in the gas phase has been demonstrated (*98*), but its existence in liquid hydrogen chloride can only be inferred from reactions carried out in this solvent (*323*). It can be stabilized in the presence of Lewis acids and aromatics analogously to the systems just described (*45*).

Brown and Pearsall showed by vapor pressure measurements that dry hydrogen chloride does not combine with aluminum chloride down to as low a temperature as −120° but, in the presence of toluene at −80° for each molecule of aluminum chloride dissolved, one molecule of hydrogen chloride enters the green solution. At higher temperatures, hydrogen chloride is evolved with another region of stability at $AlCl_3$:HCl of 2:1 before all the hydrogen chloride is dissociated from the complex. The reactions are:

$$C_6H_5CH_3 + AlCl_3 + HCl \rightleftharpoons [C_6H_5CH_3H]^+AlCl_4^-$$

$$2[ArH_2]^+AlCl_4^- \rightleftharpoons [ArH_2]^+Al_2Cl_7^- + HCl + ArH, \text{ etc.}$$

The increasing acid strength of the polymeric anions parallels that of polysulfates (*89*).

E. SOLUTIONS IN FLUOROSULFURIC ACID

This solvent has some properties in common with, and some intermediate between, hydrogen fluoride and sulfuric acid. The postulated self-ionization by proton transfer forms another solvated proton:

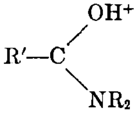
$$HSO_3F + HSO_3F \rightleftharpoons H_2SO_3F^+ + SO_3F^-$$

There is no complication from self-dehydration as in sulfuric acid. The acids which increase the solvated proton content are again the Lewis acid fluorides (*18*), e.g.,

$$HSO_3F + SbF_5 \rightleftharpoons H_2SO_3F^+ + SbF_5SO_3F^-$$

Recent work has shown that the simple antimony acid is only a weak acid in fluorosulfuric acid, but that further substitution with sulfur trioxide forms the acids $H_2SO_3F^+[SbF_{5-n}(SO_3F)_{1+n}]^-$ which increase in strength from $n = 1$ to $n = 3$. The protonated cation species has the abnormally high mobility expected for conduction processes controlled by proton transfers (*317*).

Protonated organic cations are stabilized in solution by these acids or even by the solvent itself. For example, the O-protonation has been shown by p.m.r. measurements on *N*,*N*-dimethylformamide and other amides (*36*, *114*) to produce the cation:



The signal from the bound proton can be observed directly in fluorosulfuric acid solutions at low temperatures when proton exchange is not appreciable as it is in other solvents. Much quantitative work remains to be done with this solvent before an informed comparison can be drawn with hydrogen fluoride and sulfuric acid.

IV. Cations with Metal-Carbon and Metal-Metal Bonding

Although the sandwich-type structure of ferrocene has been well established by spectral and X-ray measurements, the bonding scheme in the compound is far less certain. A strong ligand-field model with ionic bonding to cyclopentadienyl anions is favored (*210*). Whatever the exact nature of the metal-to-carbon bonding, a convenient working rule is to regard the diamagnetism and the stability of ferrocene as arising from a noble gas configuration around the central atom. Appropriate electron contributions come from each type of ligand as this is varied, and in this way a whole series of charged or neutral compounds can be prepared with the same configuration. A selection of heteromononuclear cations is collected in

TABLE IX
ISOELECTRONIC CATIONS WITH METAL-CARBON BONDING[a]

		$Mn(hmbnz)_2^+$	$Fe\cdot Cpd\cdot Bzn^+$	$Co\cdot Cpd\cdot Bzn^{2+}$	
		$Tc(Bzn)_2^+$	$Fe(Mes)_2^{2+}$	$Co\cdot(Cpd)_2^+$	
		$Re(Bzn)_2^+$	$Ru(Mes)_2^{2+}$	$Ir\cdot(Cpd)_2^+$	
			$Ru(Bzn)_2^{2+}$	$Rh(Bzn)_2^{3+}$	
		$MnBzn(CO)_3^+$	$Fe(Cpd)(CO)_3^+$		
	$W(Cpd)_2H_3^+$	$Re(Cpd)_2H_2^+$	$FeH(CO)_5^+$		
$V(Cpd)_2(CO)_2^+$	$Cr(Cpd)(CO)_4^+$	$Re(Etn)_2(CO)_4^+$	$Fe(CO)_6^{2+}$		$Ag(Disn)_2^+$
$VBzn(CO)_4^+$	$CrCht(CO)_3^+$	$Mn(Etn)(CO)_5^+$	$Os(CO)_6^{2+}$		$Cu(PR_3)_4^+$
		$Re(CO)_6^+$			
	$W(hmbnz)(CO)_3Cl^+$	$Mn(CO)_6^+$	$Fe(CNR)_6^{2+}$	$Co(CNR)_5^+$	$Cu(CNR)_4^+$

[a] Bzn = benzene (6); Cpd = cyclopentadiene (5); Cht = cycloheptatriene (7); Disn = diarsine (*o*-phenylenebis-dimethylarsine) (4); Etn = ethylene (2); hmbnz = hexamethylbenzene (6); Mes = mesitylene (6); CO (2); CNR (2); HCl (1). Numbers in parentheses indicate electrons contributed.

Table IX. (If the number of electrons in the outer orbitals of the metal, i.e., the group number, is added to the indicated electron contribution from the ligands less the charge number, it can be seen that all these ions have the same outer configuration of 18 electrons.) The stability of this arrangement is reflected in the variety of preparative methods available. A few illustrative examples are given.

Metal carbonyl cations were isolated in the form of tetrahaloaluminates by reacting metal carbonyl halides directly with aluminum halides in the presence of carbon monoxide (*101*):

$$\mathrm{Mn(CO)_5Cl + AlCl_3 + CO = Mn(CO)_6{}^+AlCl_4{}^-}$$

The compound was decomposed to dimanganese decacarbonyl with water. Its infrared spectra showed the single carbonyl frequency at 2090 $\mathrm{cm^{-1}}$ expected for the hexacarbonyl ion. The corresponding rhenium compound was stable to water so that its ionic nature could be demonstrated by precipitation of an insoluble perchlorate or tetraphenylborate from aqueous solutions (*148*). The carbonyl band of this regular octahedral ion appeared at 2083 $\mathrm{cm^{-1}}$. Doubly charged iron and osmium hexacarbonyl cations were produced by analogous reactions:

$$\mathrm{Os(CO)_4Cl_2 + 2AlCl_3 + 2CO = Os(CO)_6{}^{2+}(AlCl_4{}^-)_2}$$

Ethylene can be used in place of carbon monoxide, or other carbonyl derivatives in place of halides, to make this a general reaction. Thus reactions of the type

$$\mathrm{MCpd(CO)_{\mathit{x}}Br + AlBr_3 + C_2H_4 = [MCpd(CO)_{\mathit{x}}C_2H_4]^+AlBr_4{}^-}$$

lead to ions such as $\mathrm{FeCpd(CO)_3{}^+}$, $\mathrm{Mn(C_2H_4)(CO)_5{}^+}$, $\mathrm{WCpd(CO)_4{}^+}$ (*100*).

An example of direct synthesis for a purely hydrocarbon metal cation is provided by the ruthenium-mesitylene cation. Aluminum chloride was used in a reductive combination with aluminum at 130° and the cation isolated as the insoluble hexafluorophosphate or tetraphenylborate (*99*):

$$\mathrm{RuCl_3 + AlCl_3 + Al + C_6H_3(CH_3)_3 \rightarrow Ru[C_6H_3(CH_3)_3]_2{}^{2+}}$$

The combination of a carbonyl cation with a carbonyl anion in a single salt has been achieved in a recent synthesis (*48*):

$$\mathrm{V^0(CO)_6 + V^{II}(Cpd)_2 + 2CO = V^{III}(Cpd)_2(CO)_2{}^+[V^{-1}(CO)_6]^-}$$

Only the product was diamagnetic. The formal charges on the vanadium in the product were demonstrated by oxidation of the anion with iodine in potassium iodide:

$$\mathrm{V^{III}(Cpd)_2(CO)_2{}^+[V^{-1}(CO)_6]^- + 2I_2 = V(Cpd)_2(CO)_2{}^+ + V^{3+} + 4I^- + 6CO}$$

The triiodide of the cation was precipitated with excess iodine.

Quite obviously the noble gas rule serves as a reliable guide to the preparation of these heterocations, as well as providing a convenient classification of the products.

A number of ionic halides of transition metals in lower valency states have structures containing polymeric units. The metal-metal bond lengths within the units approximate those in the metals. General reviews on this bonding are available for more detailed consideration (*193*, *268*).

The lower molybdenum chloride of empirical composition $MoCl_2$ provides an example. It is extremely stable and can be heated to 800° *in vacuo,* or 300° in air, without change. Concentrated acids displace only a third of the chlorine. The chloro acid of empirical formula $HMo_3Cl_7 \cdot 4H_2O$ can be crystallized from solutions in hydrochloric acid. Part of the chlorine in this acid can be replaced on controlled hydrolysis to form products which include $Mo_3Cl_6 \cdot 4H_2O$ and $Mo_3Cl_4(OH)_2 \cdot 7H_2O$. X-ray structural analyses of these products show the (Mo_6Cl_8) unit consisting of an octahedron of molybdenum atoms oriented at the face centers of an enclosing cube of chlorine atoms. The Mo_6Cl_8 unit is itself enclosed in a surrounding octahedron of six atoms or groups (*44*). The above compounds are now formulated $(H_3O)_2[(Mo_6Cl_8)Cl_6]6H_2O$, $[(Mo_6Cl_8)Cl_4(H_2O)_2]6H_2O$, and $[Mo_6Cl_8(OH)_4(H_2O)_2]12H_2O$, respectively.

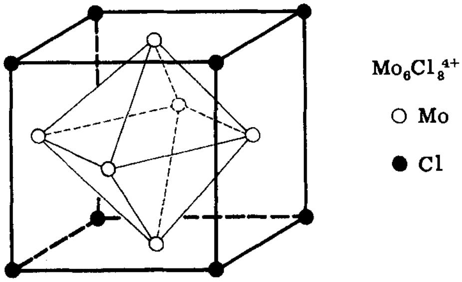


FIG. 10. The $Mo_6Cl_8^{4+}$ ion.

The integrity of the heterocation unit shown in Fig. 10 is evident in all its reactions. A variety of derivatives can be prepared such as $MCl_4(C_5H_5N)_2$, $MCl_4(C_2H_5OH)_2$, $MBr_4(H_2O)_2$, $(H_3O)_2MI_6$, and $K_2MCl_6 \cdot 6H_2O$ where $M = Mo_6Cl_8$. Exchange studies with Cl^{36} showed only six labile chlorine atoms in the last compound (*299*). It has been suggested on the basis of magnetic and spectral data that other lower halides of tungsten and molybdenum probably contain similar trinuclear cations, e.g., $Mo_3Cl_9^{3+}$, $W_3Cl_{12}^{3+}$, $W_3Br_{12}^{3+}$ (*65*).

The lower niobium and tantalum halides $M_6X_{14} \cdot xH_2O$, made by reduction of the pentahalides with metals, have been examined in concentrated solutions by the X-ray scattering technique (*321*). The polynuclear cation in these substances is an octahedron of metal atoms bridged along each edge with halogen atoms, $M_6X_{12}^{2+}$ (Fig. 11). More recently other lower halide phases made by metal reduction in temperature gradients have been identified as salts of similar cations but in different oxidation states (*202*). The equilibrium diagrams of Ta–$TaBr_5$ and Ta–TaI_5 systems have established the phases $TaBr_{2.83}$, $TaBr_{2.5}$, $TaBr_{2.33}$, and $TaI_{2.33}$ as well as the tetrahalides. The nonintegral phases are formulated as

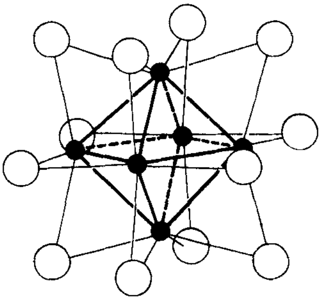


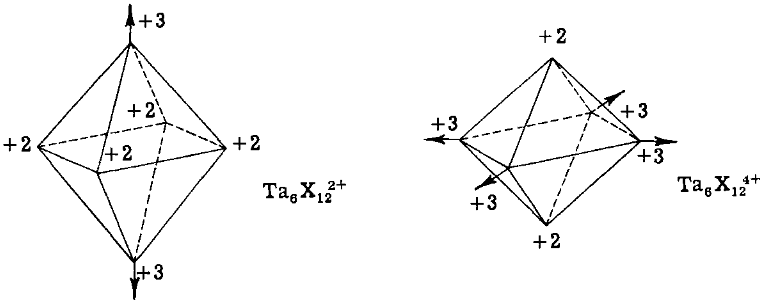
FIG. 11. The $M_6X_{12}^{2+}$ structure (M = Nb,Ta; X = Cl,Br).

$$MX_{2.83} = [M_6X_{12}]X_5$$
$$MX_{2.5} = [M_6X_{12}]X_3$$
$$MX_{2.33} = [M_6X_{12}]X_2$$

The $Ta_6Cl_{12}^{3+}$ ion is unstable in aqueous solution being reduced to $Ta_6Cl_{12}^{2+}$, whereas the phases $TaBr_{2.33}$ and $TaI_{2.33}$ provide stable aqueous solutions of $Ta_6X_{12}^{4+}$ (*203*).

The nature of the bonding in these ions is of special interest. Sheldon has given a valence-bond interpretation of the $MCl_6^{=}$ structure in which the tetragonal pyramidal configuration around each Mo employs $d_{x^2-y^2}sp^3$ hybrid orbitals and the square planar Mo-Mo bonding utilizes d_{xz}, d_{yz} orbitals. The two remaining electrons from molybdenum are supposed to pair their spins and strengthen the metal-metal bonding.

A more general molecular orbital approach is favored by Cotton and Haas (*69*), who discuss the difficulties in treating these systems in terms of two center bonds. Thus in $M_6Cl_{12}^{2+}$ the formal metal oxidation number is 2, or in Pauling's terminology the metal-metal links have a bond order of 2/3 (*239*). The similarity in the square planar environment around metal atoms in the ions $M_6X_8^{4+}$, $M_6X_{12}^{2+}$, and $M_3X_{12}^{3-}$ encourages a common treatment of bonding rather than a special treatment for each species. Energy level diagrams were derived using appropriate L.C.A.O.-M.O. wave functions for each of the three systems. Robin and Kuebler (*256*) relied on direct spectral evidence to obtain an order of energy levels different from that of Cotton and Haas. The spectral effects of metal-ligand bonding were distinguished from those of metal-metal bonding by comparing spectra of $Nb_6Cl_{12}^{2+}$ with $Nb_6Br_{12}^{2+}$, and of $Nb_6Cl_{12}^{2+}$ with $Ta_6Br_{12}^{2+}$. (A change of ligand has a large effect on metal-ligand bonding and little effect on metal-metal bonding.) A complicating factor in the interpretation was the splitting of some of the bands observed in spectra of niobium complexes into two components in the corresponding tantalum spectra. This was attributed to a tetrahedral elongation in the tantalum octahedra giving rise to a formal charge distribution, shown in Fig. 12a.



(a) (b)

FIG. 12. Charge distribution in distorted octahedral ions. See text for explanation.

The expected alteration in charge distribution on a two-electron oxidation is shown in Fig. 12b, and this was again supported by the spectra obtained in solution. Distortions are supposed to occur in order to separate high charge entities as well as to produce integral valencies. This is feasible because it can be shown that coulombic repulsions between like ions are less if part of the charge from the equatorial plane of an equi-charged octahedron is transferred to the apical positions. The amount of charge transferred, and especially the absence of detectable transference in niobium compounds, is not explained, but certainly the avoidance of nonintegral or unusual valencies by charge separation is in line with previous work on colored complexes ($[Fe_2(CN)_6]^-$ contains Fe^{2+} and Fe^{3+}; $SbBr_6^{2-}$ contains Sb^{3+} and Sb^{5+}).

The nontransition metal complex $Bi_6(OH)_{12}^{6+}$ has a structure similar to the M_6X_{12} units described above (see p. 291).

V. Ions in the Gas Phase

Mass spectrometry is the method most frequently employed for detecting such ions (*205*). The main interest has not been in the ions themselves but rather in their neutral precursors, which in effect have been recognized by ionizing them. Nevertheless these studies have revealed a surprising complexity for many gaseous ions and have demonstrated the stability of structural units encountered in other phases. Certainly modern determinations of vapor pressure at high temperature cannot afford to ignore some of the vapor phase species if they are to be meaningful. Conversely, these studies imply that a number of structural entities in the gas phase may also exist in the solid or liquid state. For example, the species formed by surface ionization from rhenium, which had been treated with nitric acid, included considerable amounts of the primary ReO_4^+ in addition to ions derived from rhenium heptoxide and its fragmentation (*313*). The neutral tetroxide, which has been claimed to result from the oxidation of the metal, has not been taken seriously and is usually ascribed to traces of water forming anhydrous perrhenic acid (*318*). From the mass spectral evidence it could well be a genuine species at ordinary temperatures. A selection of heterocations encountered during mass spectrometric observations is collected by Reed (*252*).

The primary aim of many studies has been to obtain thermochemical data such as dissociation energies and heats of evaporation. A common high temperature technique employs a Knudsen cell containing the specimen to be vaporized, with a small orifice area in comparison with its total internal surface in order to obtain equilibrium inside the cell. This is heated resistively, or by electron bombardment, at low pressures and the emerging molecular beam is ionized by a cross beam of electrons controlled at a voltage a little above the required ionization potentials. (A compromise voltage which gives a sufficient yield without undue fragmentation is needed.) The ion beam is then analyzed in a mass spectrometer of moderate resolution (1 in 600). It is important to distinguish ionization of the Knudsen cell beam from that of extraneous sources such as deposits or residual gases. This is possible if a plate with a defined aperture is inserted in the beam path under operating conditions, which can either stop the beam completely or allow through a cross section of the beam (*55, 56*). The beam intensity profile varies according to the place of origin of a particular ion. Photo-ionization of metal vapors by the cell acting as a light source must also be allowed for. The ion current, derived from neutral species and collected by a photomultiplier detector, is related to the concentration of neutral species in the ionizing region by

$$I_+ = \eta Q I_e l n$$

where η is the collection efficiency, Q is the ionization cross section, I_e is the electron beam current, l is the active path length of electrons, and n is the concentration of neutral species. Substituting for n according to the ideal gas law shows that the pressure $p = kI_+T$, where k is a combined constant usually determined with a standard element such as silver in the Knudsen cell. The variation of p with T for any particular species provides data for calculating the thermochemical quantities. Recent reviews on other ion sources (*251*), and on time-resolved spectrometry (*251*), serve to illustrate the potential of the method.

Much of the earlier work was concerned with the vapor of elements (*301*). In particular, the existence of polymeric ions derived from neutral species helped to resolve the controversy concerning the heat of sublimation of carbon. At the sublimation point of carbon the relative amounts of the species were (*80*):

C^+	C_2^+	C_3^+	C_4^+	C_5^+	C_6^+	C_7^+
1	2.8	4.5	0.35	0.5	<0.0005	

The heats of sublimation of the separate species were derived from

$$\frac{d \ln (I_+T)}{d(1/T)} = \frac{-\Delta H_s}{R}$$

and the overall value for carbon vapor was derived (*55*). Similar studies have been carried out on silicon, germanium, and their carbides (*81, 82, 83, 153*).

More recently the measurement of polymeric sulfur cations S_n^+ (n = 2–8) over a range of temperatures has reiterated their persistence outside the liquid phase (*209*). Their stability decreases with temperature so that only monomeric sulfur exists above 2500°. The species observed by electron impact on metal sulfide vapors, which give undersaturated sulfur vapor in the gas phase, are summarized:

Sulfide	Temperature (°K)	n for S_n^+ ions
FeS	1323	1,2
ZnS	1244	1,2,3,4
CdS	1014	1,2,3,4
HgS	581	1–8

By comparing the ions produced from pure sulfur with those from mercuric sulfide, it was shown that S_2^+ ions were in large part derived from S_8^+ ions. The mean degrees of polymerization obtained from these results are in close agreement with vapor pressure measurements. The mole fraction of all the species can be plotted as a function of temperature. Such a diagram demonstrates the unique stability of S_8^+, which can be rationalized as the least strained of the puckered ring structures, being closest to the natural dihedral angle for the unit S—S—S (*238*):

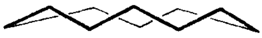
S_6

69°34'

S_8

102°6'

S_{10}



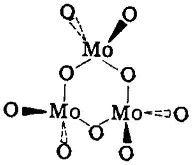
118°59'

Mean angle in $(CH_3)_3S_3$, $(CF_3)_3S_3$, and BaS_3 is 104°.

Investigations of oxide vapors have also shown polymeric and presumably cyclic ions. Molybdenum trioxide at 850° gave the following relative yields of ions (*32*):

$Mo_3O_9^+$	$Mo_4O_{12}^+$	$Mo_5O_{15}^+$	MoO_3^+	$Mo_2O_6^+$
1	0.33	0.05	~0.01	~0.01

The low monomer and dimer yields resulted from fragmentation of higher polymers. Polymers higher than a pentamer, if present, were in less than 10^{-5} yield. The structure suggested for the trimer was a cyclic one with the d^5s hybridization of the molybdenum orbitals reinforced by π-bonding. The ring would be puckered if the molybdenum angles approached the tetrahedral values.



Similar results were obtained with tungsten trioxide vapor. The monomer and dimer ions arose by fragmentation. At 1492°K the ion yields were:

$(WO_3)_3^+$	$(WO_3)_4^+$	$(WO_3)_5^+$	$(WO_3)^+$	$(WO_3)_2^+$
1	0.32	0.002	<0.05	

A rich spectral pattern was observed for each of the ions because of the number of tungsten isotopes. The trimer, for example, had twelve values ranging from 690 to 702 a.m.u. (*28*).

The refractory oxide of beryllium, when ionized in the vapor phase at 2000°–2400°K, produced mainly $(BeO)_4^+$ and some trimer and pentamer (*54*). Only traces of monomer and dimer were detected. The polymeric ions derive from primary ionization of molecules since a low potential electron beam was employed. Apart from the dimer, these ions are believed to be cyclic by analogy to ions in solution or in solids. The trimeric ion would be a six-membered ring similar to the cation in $Be_3(OH)_3(H_2O)_6^+Hg_2I_7^-$ and consisting of beryllium tetrahedra linked at two of their apices. A tungsten container which held the sample became oxidized, presumably by the oxygen dissociating from the beryllium oxides, and a series of mixed oxides was detected. The most abundant of these ions were $WO_2(BeO)_2^+$ and $WO_3(BeO)_2^+$, which can also be represented as hexagonal rings. The adventitious production of these mixed ions during primarily thermochemical investigations suggests that a more systematic approach could provide valuable information on a whole series of mixed complex ions.

Vanadium pentoxide was not investigated in detail because its ready decomposition prevented thermochemical measurements (*29*). The results obtained are of interest, however, for comparison with solid state structures. The monomer ion was not detected but only the dimer and dissociated products from this and the trimer: $V_4O_8^+$, $V_3O_6^+$, $V_4O_9^+$, and $V_6O_{14}^+$, $V_6O_{12}^+$. Fragmentation ions from higher polymers $V_2O_3^+$, $V_3O_6^+$, $V_4O_9^+$ were also observed. The $V_4O_{10}^+$ peak diminished with time as the oxide dissociated. The oxide compositions encountered in the solid state range from $VO_{0.8}$ to $VO_{2.5}$ including a series $V_nO_{2n-1}(n = 3\text{–}8)$ and V_6O_{13} (*328*). These are infinite structures. The oxide V_6O_{13} consists of distorted oxygen octahedra around vanadium atoms, linked by some corners and edges into a rather complex double chain cum layer structure. The smaller units encountered in the gas phase are relatively oxygen-rich compared with the solid units, presumably because of unshared oxygen atoms at the surface of the finite units. Cyclic structures seem improbable for these ions. The actual structures would be of considerable interest in view of the range of vanadium coordinations which must exist in the series.

The ions of lower oxides, which may be unstable at lower temperatures, can be produced *in situ* by reduction of oxides with metals. Again the reduction may be unintentional if metal containers are used at high temperatures under reduced pressures. Tantalum pentoxide was reduced by tantalum to yield mainly TaO^+ and TaO_2^+ (*157*). The Ta-O bond strength is particularly high, almost as great as for the multiple-bonded carbon monoxide or nitrogen. Titanium dioxide reduced by titanium gave simple TiO^+ and TiO_2^+ ions (*31*). The polymeric nature of TiO units in titanyl salts, both solid and in solution, is not carried over to the vapor phase. Also in the reduction of alumina with tungsten the primary hetero-ions AlO^+, Al_2O^+, and $Al_2O_2^+$ are less complex than in some of the aluminum oxyhalides and basic salts (*83*). Reduction with aluminum gave Al_2O^+ almost exclusively. A silicon-silica mixture yielded SiO^+ and $Si_2O_2^+$ with SiO_2^+ at higher temperatures (*246*).

The ionization of oxyhalides has been examined in a cursory manner compared with oxides. One example is provided by the mass spectra of chromyl halides (*103*). Ions from the halide CrO_2ClF can be detected in an equimolecular mixture of chromyl chloride and fluoride, but even for a simple halide it has not been possible to ascertain the processes leading to the great variety of ions produced. Dimeric ions and fragment ions were present (CrO_2F_2, CrO_2F, CrO_2, $CrOF_2$, CrOF, CrO, CrF_2, CrF, Cr, $Cr_2O_4Cl_3$, $Cr_2O_4Cl_2$, Cr_2O_4Cl, $Cr_2O_3Cl_3$, Cr_2O_3Cl, and CrOCl ions).

Halides, especially the alkali halides, have been examined in much greater detail. The alkali halide vapors contain appreciable amounts of dimers and trimers (Table X) and even traces of tetrameric molecules, which yield the ions M_2X^+, $M_3X_2^+$, and $M_4X_3^+$ by electron impact (*30*). The amount of MX^+ ion is low and decreases with increasing cation size. The degree of dimerization also follows a regular pattern, being greatest for lithium salts and for chlorides. The forces binding these structures are the same as in solid alkali halides, since it is possible to treat the gas molecules as ion pairs which polarize one another. The potential energy of the molecules is compounded of electrostatic and small van der Waals' attractions less an exponential repulsion energy. There is good agreement between experimental and calculated values. The dissociation energies can also be calculated on an ionic model (*31*). The polymers from which the ions derive can be recognized as fragments of the solid state structures.

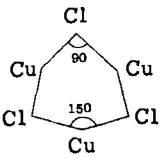
TABLE X

IONIZATION OF THE ALKALI FLUORIDES

MF	Temperature (K°)	Relative ion intensities M_2F^+/M^+	 M_3F_2/M^+
LiF	954	3.3	0.31
NaF	1017	0.8	0.015
KF	1031	0.93	0.013
RbF	888	0.59	0.0055
CsF	764	0.29	0.0022

The vapors of alkali hydroxides resemble those of alkali fluorides and the main ions are MOH^+ and M_2OH^+ (*278*).

Polymeric structures have also been found in other halide vapors. The predominant ion from cuprous chloride is $Cu_3Cl_3^+$, which is undoubtedly cyclic since electron diffraction of the molecular vapor has given the molecular shape shown (*260*). This ring is part of the solid state structure (zinc blende type).



The aluminum halide ions in the vapor are less directly related to solid state structures (*247*). The layer lattice of solid aluminum chloride is converted to dimeric species in the vapor. Mass spectra show $Al_2Cl_5^+$ as the predominant ion followed by $AlCl_2^+$. However, traces of trimeric species are also present and these are obviously not detectable by the electron diffraction technique used to examine the structure of the vapor species. (The relative ion intensities were $Al_2Cl_5^+$, 187; $AlCl_2^+$, 100; $Al_3Cl_9^+$, $Al_3Cl_8^+$, $Al_3Cl_7^+$, total 0.86.) The bromide is dimeric in the solid, in nonpolar solvents, and in the vapor. The mass spectra show the expected main ions $AlBr_2^+$ and $Al_2Br_5^+$ and no trimeric species. Aluminum fluoride vapor is almost exclusively monomeric with predominance of AlF_2^+ ions and only traces of $Al_2F_5^+$. A time-resolved study of the vaporization process might be more informative with respect to evaporation of units from the solid structures.

Ions derived from glow discharges in water vapor have been mentioned. An example of a monohydrated metal ion, $K{\cdot}H_2O^+$, has been observed when traces of water vapor contaminated alkali halides (*53*). This ion contrasts with the $K(H_2O)_4^+$ ion in aqueous solutions where the potassium ions are inserted substitutionally in the water lattice (*42*).

Finally, to complete this brief survey of the types of ion investigated by mass spectrometry, mention should be made of ion-molecular reactions. If the pressure in a mass spectrometer is allowed to rise, the chance of ions interacting with molecules as they move from source to detector is correspondingly increased. The process has been considered theoretically and experimentally for rare gas-hydrogen molecule interactions (*311*). The ions ArH^+ and KrH^+ have been measured when the pressure in the ion source was higher than normal. The corresponding neutral molecules would not of course be stable.

VI. Heterocations in Aqueous Solution

Heterocations in aqueous solution have been studied intensively in recent years and a more detailed picture of the species qualitatively designated as solvated cations is beginning to emerge. The extent of this work is reflected in, for example, compilations of stability constants (*37*, *340*) and texts devoted wholely or in part to the determination of stability constants (*216*, *261*).

A. ION PAIRING

The concept of ion pairing in solution arose from deviations between experimentally determined activity coefficients of the more polarizing ions in dilute solutions, and the values calculated on the simple Debye-Hückel theory. Two methods have been proposed to remove the discrepancy. In one approach it was no longer assumed that the energy required to place an ion in the vicinity of another ion was negligibly small compared with thermal energies, and hence a more accurate solution of the Poisson-Boltzmann expression was found (e.g., *134*). The alternative approach was to assume that some of the ions became paired with ions of opposite charge and thereby lessened the energy needed to place ions in their ion atmospheres. The association constant for ion pairing, K, relative to the separate ions was evaluated by Bjerrum as

$$1/K = 4\pi \int_a^q \exp\,[Z_1Z_2e^2/DKTr]r^2dr$$

where r is the distance between ion centers of charge Z_1e, Z_2e, in a medium of dielectric constant D at temperature T, and K is Boltzmann's constant. The lower limit of the integral is the distance of closest approach of oppositely charged ions. Oppositely charged ions have been considered to pair and become nonelectrolytes when they approach closer than a distance $q = Z_1Z_2e^2/2DKT$. The sharp distinction between ions and ion pairs at distance q is of course a mathematical device without necessarily having a particular physical significance.

Other arbitrary choices of q and hence association constants are possible. For example, precise cryoscopic measurements with aqueous copper sulfate solutions showed negative deviations from the values expected for 1:1 electrolytes and hence suggested incomplete dissociation (*46*). The calculated minimum q value (13.9 Å) was much larger than Cu-S distances in solid $CuSO_4{\cdot}5H_2O$ which vary from 3.6 to 5.5 Å. The latter would approximate the distance of closest approach for the ion pair (a), and the former distance (q) would allow insertion of five to six water molecules. It was found that almost constant values for an association constant were obtained from the data for values of q from 5 to 6.9 Å; the "constant" then increased with increase of the chosen q. These results could therefore be taken to indicate an intimate ion pair, although the theory allows longer-range attractions.

Other methods for detecting ion interaction may yield quite different results, depending on the range of interaction susceptible to the measurement; in particular, spectrophotometric investigations of ion pairing, when a new visible or ultraviolet absorption band is generated on addition of anions to a particular cation in solution. It is assumed on good evidence that the new bands arise when an electron is transferred from anion to cation, or at least to the aquated cation. Hence only ion pairs in fairly close proximity would be detectable by optical methods and the association constant could be less than that found as above. These indirect methods of measuring ion association depend on the model assumed and the derived theoretical equation used in computation (*63*).

It is therefore of considerable interest that ion pairing of a hydration cation has now been observed directly in solution by the X-ray scattering technique. With solutions of erbium chloride at various concentrations the radial distribution curves peak first at 2.3 Å, corresponding to the sum of Er^{3+} and H_2O radii, and the area under the peak corresponds to octahedral coordination (*43*).

There is a further peak at 4.6 Å that corresponds to an Er^{3+}-Cl^- distance which would place the chloride ions in the position shown (Fig. 13) with an overall D_{3h} symmetry, the same symmetry required to explain the visible spectra of the solution.

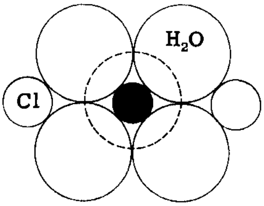


FIG. 13. $Er^{3+}(Cl^-)_2$ pairing.

The direct measurement of coordinated water in alkali cations has also been made by X-ray scattering from solutions (*42*). Another method which distinguishes the first coordination shell of water molecules around cations from the rest employs n.m.r. techniques (*66*). If cobalt perchlorate is added to solutions of diamagnetic salts in water enriched with O^{17}, it is possible to separate the O^{17} resonances arising from water molecules in the first coordination shell from those of unbound water molecules. The paramagnetic cobalt ion interacts much more strongly with O^{17} in the latter and shifts the resonance to lower field values. The sixfold coordination of $(Al \cdot 6H_2O)^{3+}$ was found from the area under the resolved absorption curve. The absorption curves for beryllium solutions, besides showing the $(Be \cdot 4H_2O)^{2+}$ ion, were slightly asymmetrical because of exchange of the free and coordinated water molecules. The lifetime of the coordinated water, determined from the temperature dependence of resonance, was about 3×10^{-4} second. This value can be compared with a lifetime of about 3×10^{-12} second for the proton in its hydrate complex $(H \cdot 3H_2O)^+$.

B. HYDROLYTIC EQUILIBRIA

Many hydrated cations can interact further with water molecules and the nature of the hydrolytic equilibria has been the subject of numerous investigations, especially by Scandinavian chemists (*303*). In addition to mononuclear products, polynuclear ones containing two or more metal ions linked by ligand bridges can also form. It is not possible to formulate the resulting heterocations unambiguously because of the excess of solvent molecules and salts added to provide a constant ionic medium. Their concentrations remain approximately constant during the formation of the complex cations and hence equilibrium equations convey no information about these species. The hydrolytic cations are formulated with OH^- as ligands, omitting solvent and electrolyte participation (*302*). Hydrolytic reactions are a special instance of a quite general formation of complexes in solution.

The thermodynamic equilibrium constant for complex formation would normally be expressed in terms of activities but, since these are readily accessible only for dilute solutions where activity coefficients can be calculated from the Debye-Hückel formula, it is usual to add large amounts of supporting electrolyte consisting of noncomplexing, or at most weakly complexing, ions. In such swamping media the ionic strength and activity coefficients remain constant as the complexes are formed. A stability constant can then be given in terms of concentrations which will be valid for the particular medium used. Complex formation involves the successive substitution of the originally solvated cation by ligands (anions or neutral molecules); the successive steps usually overlap and it is difficult to separate the participating equilibria.

These would be disturbed if chemical methods were employed to follow them, so that only physical methods are practicable in these labile systems. It can be shown for mononuclear complexes that the average number of ligands (L) for each metal ion (M) is related to the stability constants β_n for $ML_{n-1} + L = ML_n$ by:

$$\bar{n} = \sum_{n=1}^{n=n} n\beta_n[L]^{n-1}/1 + \sum_{n=1}^{n=n} \beta_n[L]^n$$

For polynuclear complexes M_mL_n a new set of stability constants β_{nm} are defined, which are similarly related to the average ligand number. The latter is determined, and the problem is to find the values for m and n and the stability constants which fit the equation. Experimentally the free metal ion concentration is found potentiometrically or polarographically, the free ligand concentration by pH measurement if the ligand is the anion of a weak acid, or the complex by solvent extraction into a nonmiscible solvent. The pH method is the commonest; among others are solubility, cation exchange, and spectrophotometric and other spectral measurements (for details of which the cited references should be consulted).

The hydrolysis of the uranyl ion provides a good example, being one of the most thoroughly studied equilibria. A summarizing paper compares the complexes and their stability constants as determined in a number of ionic media (*84*). Solutions are made up with a constant concentration of uranyl ion and supporting electrolyte, e.g., 3 *M* $NaClO_4$, but with varying amounts of acid or alkali. The solution pH is then measured and the average number of OH groups bound to the uranyl groups ($\bar{n}$), which is equivalent to the number of protons released on hydrolysis, is deduced from the measured hydrogen ion concentration and the number of protons introduced into the solution:

$$n\mathrm{H_2O} + m\mathrm{UO_2^{2+}} \leftrightarrows [(\mathrm{UO_2})_m(\mathrm{OH})_n]^{(2m-n)+} + n\mathrm{H^+}$$

A series of curves of $\bar{n}$ against pH at constant uranyl concentrations is plotted and values for m, n, and the stability constants chosen to fit the curves over the widest range. In earlier studies these values were obtained by graphical methods, but nowadays more accurate values are obtained by suitable computer programming shortened by using approximate graphical values (*266*, *304*). Often there is no unique solution and with increasing accuracy of data the number of species tends to increase. The main species are not usually in dispute but the choice of minor species is more contentious. Since the interpretation can be no more accurate than the experimental data will allow, it is important that alternative methods be used to avoid undetectable systematic errors of a single method. In the work on uranyl ion hydrolysis it is interesting to follow the changing interpretation as the data become more precise or are reinterpreted by more accurate procedures. Originally the mononuclear ion $UO_2(OH)^+$ was assumed, then the parallel $\bar{n}$-pH curves were interpreted as indicating an unlimited series $[(UO_2)_{n+1}(OH)_{2n}]^{2+}$. More refined results in a variety of media showed deviations from parallelism in some of the media and the following assignments were made:

Ionic medium	n,m for $(UO_2)_m(OH)_n$
$SO_4^{=}$	2,2; 4,3; 6,4; 8,5
NO_3^-	2,2; 4,3; 6,4; 5,3
Cl^-	2,2; 4,3; 6,4; 5,3; 7,4
ClO_4^-	2,2; 4,3; 6,4; 5,3

In addition, the mononuclear 1,2 complex was needed in the most concentrated uranyl solutions (about 0.1 *M* in U compared with 3 *M* perchlorate substrate), and the 1,1 complex at low uranium concentrations (down to 0.00025 *M*) to obtain a better fit with the data. Other authors fit their results with a smaller number of species. Thus in nitrate media only the 1,1, 2,2, and 5,3 species were used to explain the pH measurements. The increasing stability of the dimeric species with increasing temperature was noted (*14*). The difference in species produced in different media suggests additional complexing by the medium anions.

It is possible to compare the complexing tendency relative to the perchlorate medium, and this shows that sulfates are stronger complexing media with nitrates approximately the same as perchlorates (*84*). Chloride ion complexing in sodium chloride media is also indicated by optical absorption measurements (*265*) for the 4,3 ion but not for the 2,2 and 5,3 ions, which have the same extinction coefficients in perchlorate as in chloride media. $(UO_2)_3(OH)_4^{2+}$ is present in substantial amount in chloride but not in perchlorate media.

A more direct method for measuring polynuclear species is obviously desirable since the e.m.f. results do not give unique schemes. Ultracentrifugation provides such a method. This is a weight-sensitive technique in which sedimentation is followed by optical interferometry, and weight-average degrees of polymerization are obtained. The degree of polymerization is plotted against $\bar{n}$ and the curve is fitted with species of the appropriate stability constants. Thus in sodium chloride media the e.m.f results can be fitted to 2,2 and 5,3 species and with less certainty to 4,3 and 6,4 species. The agreement is just as good for 4,3 and 6,4 species alone, or together, or even with an unlimited series $2n$, $n + 1$. The ultracentrifugation data rule out the last possibility, and best agreement is obtained with only the three species 2,2, 4,3, and 5,3 (*264*).

C. STRUCTURES IN SOLUTION

The existence of polynuclear cations in solution, as indicated by the above work, led to the hypothesis that these cations were the precursors of the solids which precipitated when sufficient hydroxyl ion was added. The structures in solution were therefore regarded as related to solid structures. In uranyl salt solutions, for example, the series of polynuclear ions $UO_2[(OH)_2UO_2]_n^{2+}$ was related to units in the sheetlike crystal structure of α-$UO_2(OH)_2$ and related salts (*34*, *303*). This attractive hypothesis is no longer tenable and the relation between solution and solid structure in this particular instance has yet to be elucidated.

The relationship is more clearly indicated for aluminum ions. Alkali can be added to aluminum chloride solution to near the ratio OH^-/Al^{3+} of 2.5 without forming a permanent precipitate. From these solutions it is possible to obtain well-crystallized salts. The structure of the selenate salt has been determined by X-ray analysis (*162*). The solid contains alkali ions, which seem essential to the structure, as well as a large amount of water, some of it zeolitic. The significant structural feature is the large discrete group of twelve AlO_6 octahedra surrounding a central AlO_4 tetrahedron, i.e., $Al_{13}O_{40}H_{48}^{7+}$. The salt can be written as:

$$Na^+[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}(SeO_4^=)_4 \cdot 13H_2O$$

The hydrogen atoms are located by inference in a hydrogen-bonding scheme based on Pauling's rules for packing of polyhedra. The $PW_{12}O_{40}^{3-}$ anion has an analogous structure (*167*). The early e.m.f. results for hydrolysis in solution were fitted to an infinite series, $Al[(OH)_5Al_2]_n^{(3+n)+}$, or preferably to a single species, $Al_6(OH)_{15}^{3+}$. Only recently has more direct evidence been adduced for the higher polymeric species $Al_{13}(OH)_{32}^{7+}$ as a result of ultracentrifugation studies which show mean degrees of polymerization up to about 12. The best fit to the degree of polymerization versus $\bar{n}$ curve is obtained by assuming only the $Al_2(OH)_4^{4+}$ and $Al_{13}(OH)_{32}^{7+}$ species, and the stability constants derived for them from acidity measurements (*10*). Other species could be introduced at low $\bar{n}$ values, but the activity coefficients alter most in this region and any improvement in curve fitting is not meaningful. The apparent discrepancy between the cation formulas in solid and solution arises from the nondetectability of complexed water molecules in solution. Evidence from X-ray scattering in solution also substantiates this hetero species (*250*).

The hydrolysis of bismuth solutions in perchlorate media has been followed by measuring the free bismuth ion concentration or the acidity, and also by ultracentrifugation (*151*, *232*). The curves can best be fitted with the two species $Bi(OH)^{2+}$ and $Bi_6(OH)_{12}^{6+}$. The structure of the latter has been examined in concentrated solution (5.8 *M* $BiO(ClO_4)$ in 0.95 *M* $HClO_4$) by X-ray scattering (*192*). Maxima are observed at 3.71 and 5.25 Å due to Bi–Bi interactions. Excellent agreement with the intensity measurements are obtained with an octahedral distribution of bismuth atoms bridged by oxygens along the octahedral edges, in the same structure type encountered for $Nb_6Cl_{12}^{2+}$ (p. 291).

The hydrolyses of zirconium and hafnium halides apparently produce hydrated oxyhalides $MOX_2 \cdot 8H_2O$. The actual structures, confirmed by X-ray scattering in solution and by X-ray structural determination in the solid, are tetrameric with no metal-halogen bonds (*58*, *221*). Ultracentrifuge studies also show this degree of polymerization (*164*). Zirconium atoms are bridged by pairs of OH and each zirconium is coordinated by a distorted antiprismatic arrangement of eight oxygen atoms (Fig. 14).

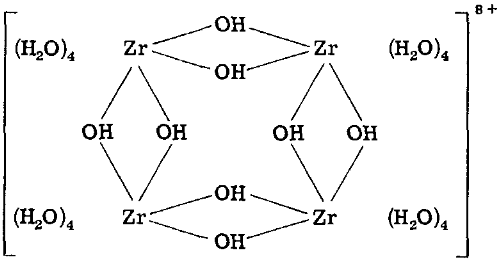


FIG. 14. The cation in zirconium oxyhalides.

The presence of a cyclic polymeric cation in hydrolyzed beryllium solutions has also been suggested. The acidity curves are fitted with $Be(OH)_2$ and the cations Be_2OH^{3+} and $Be_3(OH)_3{}^{3+}$. The last is the predominant species and the proposed structure (Fig. 15) utilizes the tetrahedral coordination of beryllium, known for example in the $(Be{\cdot}4H_2O)^{2+}$ cation (*165*).

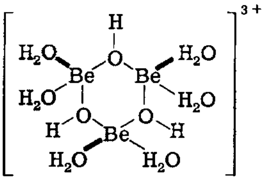


FIG. 15. The main cation in beryllium solutions.

The beryllium oxide trimer in the gas phase and the volatility of beryllium oxide in the presence of traces of water are explicable on the basis of similar cyclic structures.

It can be concluded that many of the species which emerge from a purely mathematical treatment of hydrolytic data have a truly physical significance.

VII. Concluding Remarks

Although the above account has been confined mainly to heterocations formed by the nontransition elements, there has been a corresponding large amount of work with transition metals, exemplified by review articles on a single species VO^{2+} (*293*), and oxycations in general (*294*). The emphasis of this work with transition elements has been the explanation of spectral and magnetic properties in terms of modern theories of bonding, the results of which are too extensive to consider here. With the nontransition elements one of the main aims has been to extend the range of heterocations, and consequently less attention has been paid to the detailed structure and configuration of the hetero-ions. One of the most interesting problems raised has been the relation between polar and homopolar forms of the simple and substituted Group V halides (*152*). The ionic form seems to be the thermodynamically stable form at room temperatures. With some solids, conversion to the covalent form occurs in the melt and reversion on cooling is slow; with others, the ionic form is the only stable form at room temperatures.

Equilibrium and kinetic data are badly needed on these compounds before a rational interpretation is possible. Interconversion of forms is unlikely to admit of a universal interpretation, as can be seen by comparing aluminum trichloride with iodine trichloride. The former ionic solid melts to a nonconducting liquid, whereas the latter solid consists of I_2Cl_6 molecules which produce a conducting melt. It should also be noted that a low volatility is not a universal criterion of ionicity. Nitrogen pentoxide, for example, is nitronium nitrate in the solid with a sublimation pressure of 200 torr at 15°. The low heat of sublimation for this compound can be explained by the ionic lattice energy being nearly compensated with the formation energy of covalent N-O bonds (*214*).

The exact nature of the cation bonding in various double halides such as $NOSbCl_6$, $NOAlCl_4$ (*108*), and $CH_3COGaCl_4$ (*67*) is far from clear. There are additional lines in the infrared spectra which are incompatible with the simple ionic formulations. An X-ray structural investigation, preferably at low temperatures, should help resolve the cation-anion interaction in these substances. Even with $NO_2^+ClO_4^-$ the spectra are not consistent with a purely ionic structure held by electrostatic forces (*225*).

The bonding in many nitrates, sulfates, fluorosulfates, and iodates, in which these groups act as bidendate ligands rather than anions, is a more extreme deviation from conventional ionic bonding. Again, a precise description of the charge distribution in such polymeric structures has yet to be achieved.

Apart from these finer structural details, the broad relationship between structures in the different states of matter is also of great interest. There are various lines of evidence which have related the physical properties of liquid to solid structures in the region of the melting point (*320*). Supercooling phenomena in liquids or premelting effects in solids are examples. It is therefore attractive to consider certain common units which survive a phase change. The precipitation of basic salts in aqueous solution has been regarded as a build-up of the crystal structure by a stepwise succession of hydrolytic equilibria. Evidence for this has been controverted in part, but there are still examples of smaller cations of bismuth and aluminum which are common to both solids and aqueous solutions. Even in the gas phase there are polymeric ions which resemble those of cations in solution.

The isoelectronic principle has been widely applied in the recognition of cation spectra, but less attention has been paid to it as a guide to synthetic possibilities. The proliferation of "diamond-type" semiconductors in recent years (*125*) is an example of the systematic application of this principle. It would seem that a similar approach could provide substitutional series of polymeric cations with interesting electrical properties when incorporated in suitable salts.

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