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Inorganic Polymer Chemistry

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Inorganic Polymer Chemistry

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INTRODUCTION AND SURVEY

Inorganic chemistry is to a great extent the chemistry of high polymers. This is not apparent from reading much of the inorganic literature of the last quarter-century, since the research problems described therein have often been carefully selected to avoid complications due to high-polymer formation. Nevertheless, the physical properties of many of the reaction products described in the early inorganic-chemistry literature prior to 1900 clearly show these materials to be macromolecular. In the recent inorganic literature there is a growing trend toward considering the chemistry of the larger molecular structures instead of merely ringing the changes of substituents on a single atom. Thus, we see that inorganic polymers are at once very old and very new.

One might ascribe the present-day interest in inorganic polymers to the millions of dollars that the governments of the United States and the Soviet Union have poured into this subject as part of the search for high-temperature-resistant materials of construction. Much of the resulting work, however, has dealt with small molecules, the so-called model compounds, and with small ring structures which, though polymers (trimers, tetramers) in the strict sense of the word, can in no way be considered polymers in the popular sense, i.e., high polymers or, more precisely, macromolecules. In my opinion, the increasing interest in inorganic molecules from the moderately sized up to the very large (oligomers to high polymers) is due to the fact that the level of sophistication in chemistry is presently reaching the point where it has become profitable to attack scientific problems in this field. In other words, the availability of new or previously poorly exploited physical techniques and also the growing use of high-speed computers (necessary in solving the mathematics of equilibrium-controlled chemistry involving complicated molecular structures) are causing the subject of inorganic high polymers to become a profitable area for scientific study rather than a topic to be avoided, like sex in a Victorian novel.

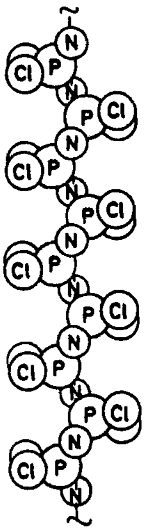
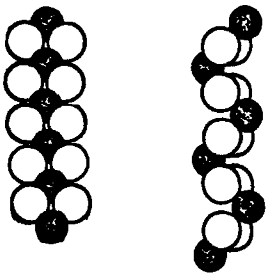


FIG. 1. Chain configuration in stretched $PNCl_2$.



Planar $PdCl_2$

Zigzag $Th(OH)_2^{++}$

FIG. 2.

The structural chemistry of inorganic compounds is generally equilibrium-controlled, so the relative proportions and kinds of reaction products are more readily interpreted in terms of equilibrium constants than of the reaction mechanisms used to explain the kinetically controlled processes of organic chemistry. Thus, in order to understand inorganic polymers it is necessary to delve deeply into thermodynamics and its underlying sciences, particularly statistical mechanics and the application of mathematical stochastics to molecular structures. Since the technique of obtaining desired reaction products in kinetically controlled chemistry is well developed, having been a primary concern of chemistry during the last hundred years, organic polymer chemists have been able to tailor-make the kinds of high polymers they desired, i.e. uncharged straight-chain macromolecules, since these are the most amenable to laboratory manipulation and theoretical explanation and, therefore, to commercial exploitation. The opposite has been true of inorganic polymers, in that the investigator has generally obtained the equilibrium or near-equilibrium products corresponding to the over-all stoichiometry regardless of the synthetic route chosen. For example, intractable amorphous-network molecular structures often result from laboratory operations aimed toward inorganic high polymers, and inorganic polyelectrolytes were pre-

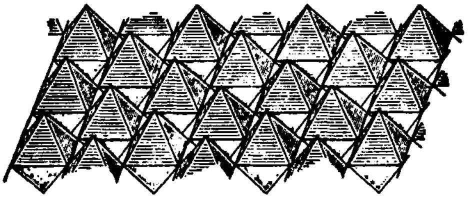


FIG. 3. A plane of AlF_6 octahedra in NH_4AlF_4 (an Al is in the center of each octahedron and fluorine is at the corners).

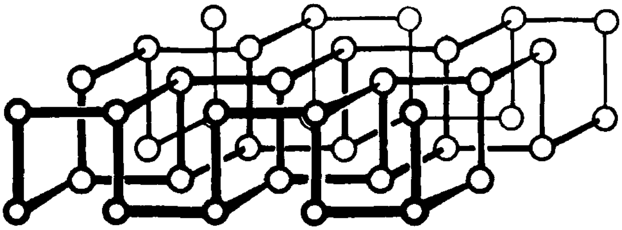


FIG. 4. Arrangement of atoms in crystalline black phosphorus.

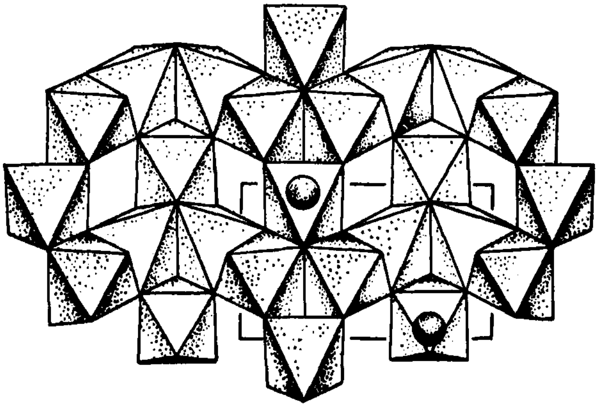
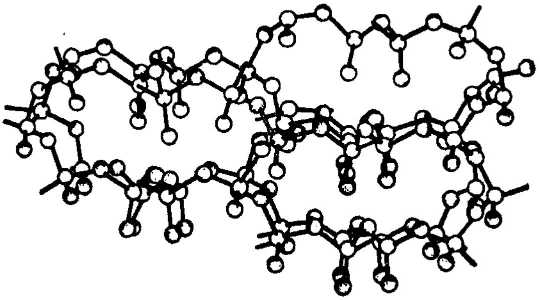
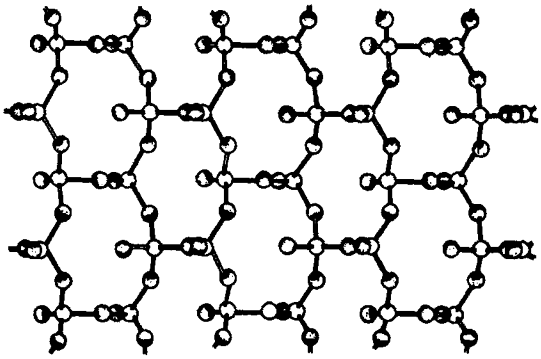


FIG. 5. Part of an undulating sheet of interconnected VO_6 octahedra in potassium trivanadate. The two balls represent interlayer potassium ions.



The *O*-form



The *O'*-form

○ Oxygen

◐ Phosphorus

FIG. 6. Structure of two crystalline forms of phosphorus pentoxide. The white balls represent phosphorus and the shaded ones oxygen.

pared and studied about a century before there was any pertinent theory or, indeed, the term "polyelectrolyte." As a further example, it should be noted that the elegant work of Huggins and the Braggs in the first quarter of this century in using x-ray diffraction to elucidate the polymeric structure of many of the silicate minerals has had little impact on preparative inorganic chemistry or the development and application of other methods of polymer physics to inorganic polymers. This is because these crystalline salts of the polysilicate anions with multiply charged cations could not be dissolved in any solvent without complete destruction of the molec-

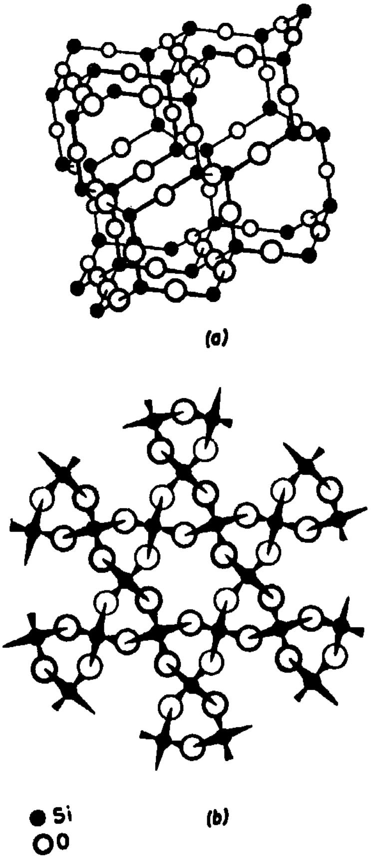


FIG. 7. The structure of silica: (a) β-tridymite and (b) β-quartz. The open circles represent oxygen atoms and the black circles silicon or aluminum atoms.

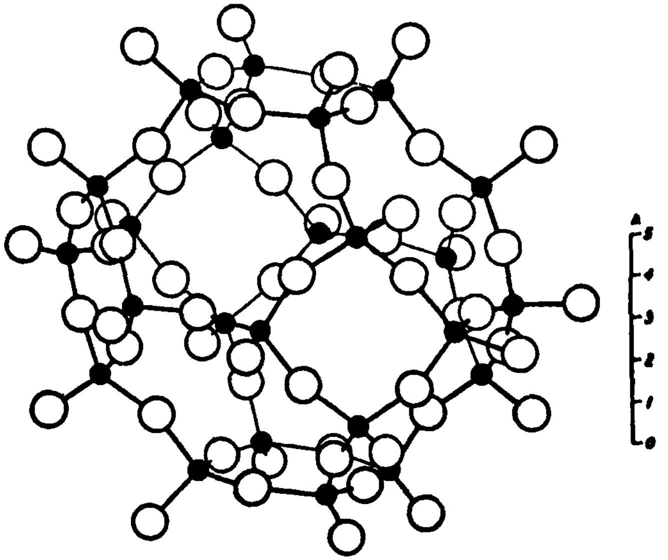


FIG. 8. A cubooctahedral cavity composed of interconnected AlO_4 and SiO_4 tetrahedra in certain zeolites and feldspathic minerals. The open circles represent oxygen atoms and the black circles silicon or aluminum atoms.

ular structure of the polyanions. It should be noted that the calcium and aluminum salts of organic polyelectrolytes are exceedingly intractable likewise, so there is essentially no literature on them.

A classification of inorganic macromolecules and oligomers as representative major structural types is presented in Table 1 with examples of some well-established high polymers. In the table, as well as throughout this discussion, a substance is called "inorganic" if at least half of the atoms making up the molecular backbone are other than carbon. There are several features of inorganic high polymers that differentiate them from the organic macromolecules, and these features can be classed under the two main categories of utilization of low-lying orbitals in bonding and equilibrium control of molecular structure. Some discussion of each of these categories is given in the following paragraphs.

UTILIZATION OF LOW-LYING ORBITALS IN BONDING

Three-Center and Four-Center Bonds

For first-row elements of the periodic table, such as carbon, *d* orbitals are unavailable, so no more than four σ bonds, correspond-

TABLE 1

Some Common Types of Atomic Geometries in Inorganic Polymers

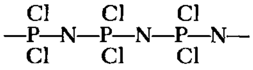
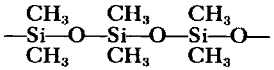
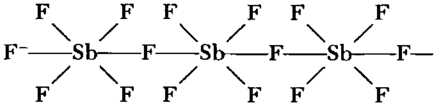
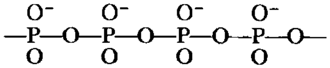
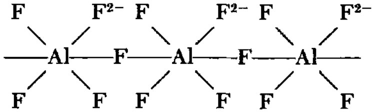
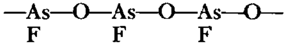
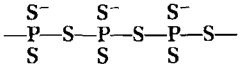
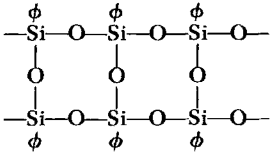
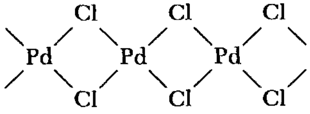
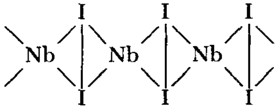
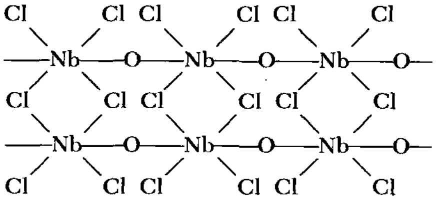
Structure Class	Subclass		Examples
Unbranched chains, generally with alternating atoms	Neutral	 $-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{P}}}-\mathrm{N}-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{P}}}-\mathrm{N}-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{P}}}-\mathrm{N}-$ (See Fig. 1.)	Polyphosphonitrilic chlorides
		 $-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}-$	Polydimethylsiloxanes
		$-\mathrm{S}-\mathrm{S}-\mathrm{S}-\mathrm{S}-\mathrm{S}-\mathrm{S}-$	Polysulfides (sulfanes)
	Anionic-terminated neutral chains		Fluoride-terminated antimony pentafluoride
	Polyanionic	 $-\overset{\mathrm{O^-}}{\underset{\mathrm{O}}{\mathrm{P}}}-\mathrm{O}-\overset{\mathrm{O^-}}{\underset{\mathrm{O}}{\mathrm{P}}}-\mathrm{O}-\overset{\mathrm{O^-}}{\underset{\mathrm{O}}{\mathrm{P}}}-\mathrm{O}-\overset{\mathrm{O^-}}{\underset{\mathrm{O}}{\mathrm{P}}}-\mathrm{O}-$	Polyphosphate anion
			Anion of the complex between thallous fluoride and aluminum fluoride
Predominately branched chains	Neutral	 $-\underset{\mathrm{F}}{\mathrm{As}}-\mathrm{O}-\underset{\mathrm{F}}{\mathrm{As}}-\mathrm{O}-\underset{\mathrm{F}}{\mathrm{As}}-\mathrm{O}-$	Polyarsenous oxyfluorides

TABLE 1 (*Continued*)

Structure Class	Subclass		Examples
	Anionic	 $-\overset{S^-}{\underset{S}{P}}-S-\overset{S^-}{\underset{S}{P}}-S-\overset{S^-}{\underset{S}{P}}-S-$	Polyphosphothioates
Chains of fused rings with alternating atoms	Neutral		Polymonophenylsiloxanes
		 (See Fig. 2.)	Palladous chloride
			Niobium tetraiodide
			Niobium oxytrichloride

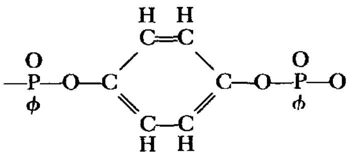
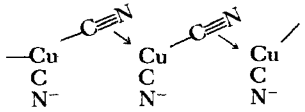
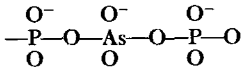
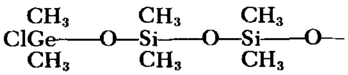
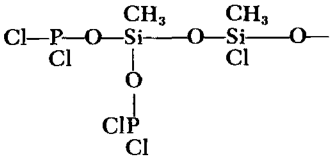
Chains based on several different atoms in an identically repeating sequence	Neutral		Condensation product of phenylphosphonic dichloride with hydroquinone
	Anionic		A complex between KCN and CuCN
Irregular chains based on several different atoms	Randomly scattered in a straight-chain anion	 $-\overset{O^-}{\underset{O}{P}}-O-\overset{O^-}{\underset{O}{As}}-O-\overset{O^-}{\underset{O}{P}}-O$	Polyarsenatophosphate anion
	Preferentially arranged in a straight chain	 $Cl\overset{CH_3}{\underset{CH_3}{Ge}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-$ (Ge at the ends)	Chloro-terminated mixed polydimethylgermoxosiloxanes
	Preferentially arranged branched chains	 (P at the ends)	Chloro-terminated oxygen-bridged mixed polymers based on triply connected phosphorus and the methylsilicon moiety
Sheet polymers with identical layers	Planar layer, ionized	See Fig. 3.	Anion of ammonium tetrafluoroaluminate, NH_4AlF_4

TABLE 1 (*Concluded*)

Structure Class	Subclass		Examples
	Corrugated layers, not ionized	See Fig. 4.	Black phosphorus
	Corrugated layers, ionized		Sheet silicates, such as mica
	Wavy layers, ionized	See Fig. 5.	Potassium trivanadate
	Randomized, not ionized	Irregular, primarily sheet-type, structure exhibiting variously sized rings (See Fig. 6 for two crystalline forms.)	Glassy P_2O_5
Sheet polymers with different kinds of layer	Triple-decker layer, not ionized	Layers consisting of three decks each of: hexagonally arranged S hexagonally arranged Mo hexagonally arranged S each Mo being bonded to six S	MoS_2
Three-dimensional networks	Neutral, small cavity	See Fig. 7.	Forms of SiO_2
	Ionized, large cavity	See Fig. 8 for a picture of a single cavity in the network polymer.	Zeolites, molecular sieves
	Neutral or ionized, variously sized cavities and irregularities		Glasses involving silicates, phosphates, borates, etc.

ing to the sp^3 hybrid, are expected for any atom. From carbon through fluorine the first-row elements have sufficient electrons to donate at least one to each total bond (consisting of the σ plus π_x and π_y orbitals). For boron and the covalent compounds of beryllium, however, there is a deficiency of electrons, so bonding of a type not found in classical organic chemistry (the chemistry of C, H, N, and O in various combinations) is observed. Since atoms tend to use all of their energetically available outer orbitals in bonding, even when these exceed the number of electrons available for bonding, one finds such unusual structures as the long-chain polymeric molecules of dimethylberyllium (see Fig. 9). The electronic interaction causing a methyl group to link a pair of beryllium atoms together is a so-called three-center bond, in which there is overlapping of three orbitals instead of the usual pair of orbitals making up the conventional σ bond. A diagramatic representation of this overlap is given in Fig. 10.

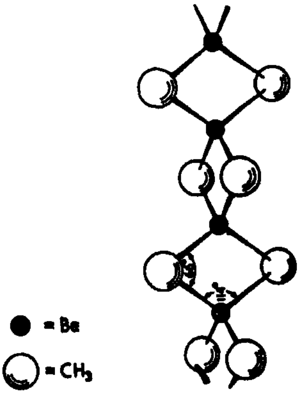


FIG. 9. Chain structure of dimethyberyllium.

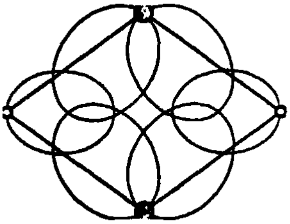


FIG. 10. Orbital overlap between Be (black balls) and C (white balls) of the methyl group.

High-molecular-weight boron hydrides are held together in part with similar three-center bonds in B—H—B linkages. There are also a number of aluminum compounds in which three-center bonds are important. This type of bonding is found in some of the chemistry of the transition metals. An important example is found in the compound $[(CH_3)_4Pt]_4$, which exhibits methyl bridges between three platinum atoms. In this case four-center bonds, involving one orbital each from the methyl group and the three platinum atoms, are invoked to explain the structure in which the platinum atoms are too far apart for an effective Pt—Pt bonding.

π Complexes

In the chemistry of inorganic high polymers π complexes (including the "sandwich compounds") have been investigated. For example, when ammoniacal solutions of cuprous salts are treated with acetylene or monosubstituted acetylenes, yellowish-colored precipitates, which are insoluble in all nonreactive solvents, are formed. Blowing acetylene through such a copper solution gives a quantitative yield of $Cu_2C_2 \cdot H_2O$, the postulated structure of which is shown in Fig. 11; the acetylenic π orbitals donate electrons to the empty orbitals of the copper. Ferrocene-type sandwiches have been incorporated into high polymers as dangling groups and also in the chain. To my knowledge, however, the structures of these compounds have not been thoroughly characterized.

Available *d* Orbitals and Unusual Bridging Atoms

For the second-row elements of the main group (particularly Si, P, and S) *d* orbitals have a sufficiently low energy to be available

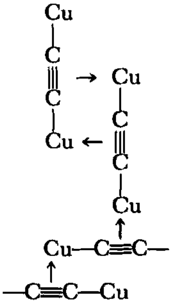


FIG. 11.

for bonding. Although the use of *d* orbitals in σ bonding is found in the chemistry of these elements, it is not important, and *d* orbitals are primarily used for π bonding in the common sp^3, p^3, and p^2 types of gross hybridization. This π-bond feedback stabilizes the molecules, partially by avoiding large charge separations due to differences in electronegativity. Generally speaking, molecules incorporating silicon, phosphorus, and sulfur in their backbones are the most stable of the inorganic polymers to rearranging.

The main-group elements of the fourth row (particularly Sn, Sb, Te, and I) show a much greater propensity than their second-row analogues for utilizing *d* orbitals in their σ-bond structure; that is, octahedral rather than tetrahedral coordination is common in the high-polymer chemistry of these elements. The π-bond feedback, however, is also important. As would be expected, the third-row elements (particularly Ge, As, and Se) are intermediate in their behavior, most of their polymer chemistry studied to date being similar to that of their second-row analogues.

For the transition metals (subgroup elements) as well as the main-group elements toward the bottom of the periodic table and the rare-earths there is often a dynamic equilibrium between molecular species of different coordination numbers (such as an equilibrium between tetrahedral and octahedral coordinations) in solution. For example, oxygens bridging between a pair of neighboring metal atoms in tetrahedral coordination may donate either one or even both of its unshared pairs of electrons to a low-lying vacant orbital of one or two other atoms of the metal, thereby increasing the coordination number of these electron-pair-accepting atoms. As a result of this we find many familiar elements exhibiting coordination numbers that are unfamiliar to the average chemist. Thus, halogens, particularly fluorine, may act as bridging atoms in molecular structures. Therefore, in inorganic polymer chemistry difunctional and also monofunctional halogens are commonplace. Also, oxygen may range from monofunctional to tetrafunctional. Four tetrafunctional oxygen atoms (exhibiting approximately sp^3 hybridization) are seen symmetrically arranged around the center of the valence-bond diagram presented on the right-hand side of Fig. 13 on p. 48.

The bridging halogens and oxygens bonded to three or four neighboring atoms are found in stable structures. For example, when it is very pure, antimony pentafluoride, $(SbF_5)_n$, is a highly viscous liquid made up of macromolecular —Sb—F—Sb—F—Sb—F— chains terminated by trace impurities, particularly fluoride ions due to the HF resulting from partial hydrolysis. Except for its ready hydrolysis, this is a very stable compound under ambient conditions. The heteropoly salts and acids based on molybdenum, tungsten, vanadium, or chromium are also generally stable in the usual nonreducing atmosphere, even though they contain oxygen atoms exhibiting a functionality greater than 2.

EQUILIBRIUM CONTROL OF MOLECULAR STRUCTURES

Preparative Chemistry

As in organic chemistry, many reactions of inorganic-polymer synthesis are carried out in single-phase liquids. These reactions commonly involve substitutent-exchange processes, and it is often found during the preparation of the polymers that the various molecules scramble or exchange parts with each other. Of the two well-known classes of organic-polymerization reactions, addition and condensation, probably the most important to inorganic polymer chemistry is condensation. Thus, it is common to condense two M—O—H functions to form an M—O—M linkage with elimination of water or an M—O—R with an M—Cl to give M—O—M and the alkyl chloride. Such condensation reactions may be caused to proceed by driving off a volatile (water, alkyl chloride, etc.), or the equilibrium may be such that there is no need for volatilization. Another main preparative procedure might be called ring-opening polymerization. This process may involve polymerization of a low-molecular-weight material coupled with depolymerization of a network polymer, the polymerization-depolymerization occurring through exchange of parts between the molecules. On the other hand, simple rings may be opened to give long chains, as in the organic-polymer example of preparing nylon-6 from caprolactam. Addition polymerization in the inorganic field is generally restricted to the donation of π electrons or electron pairs to the low-energy orbitals of a metal, as exemplified by the π-complex polymer of Fig. 11 and the formation of halogen bridges discussed previously. It should be noted that addition polymerization in inorganic chemistry (exclusive of carbon) seldom if ever involves opening a multiple bond as in, say, vinyl polymerization.

Scrambling of Substituents

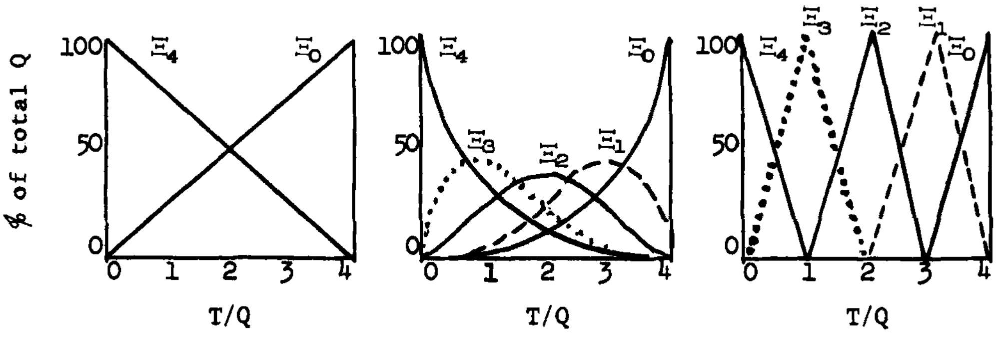
To a first approximation, the scrambling of substituents on a given central atom is controlled by the nearest-neighbor atom of the substituent, so that with respect to this property an —NH_2 group is similar to an —NR_2 or even to an —$N[Si(CH_3)_3]_2$ group. In other words, scrambling reactions of the type shown in general form in Eq. (1), where a T substituent is exchanged for a Z substituent on a central Q moiety having ν exchangeable sites, are applicable not only when the Z and T substituents are monofunctional but when one or both of them is polyfunctional as well:

$$(\nu - i)QT_\nu + (i)QT_\nu \rightleftarrows \nu QT_{\nu-i}Z_i, \qquad \text{for } i = 0, 1, 2, \ldots, \nu \quad (1)$$

Studies of scrambling equilibria involving monofunctional substituents thus give considerable information concerning the equilibria pertaining to polymers. In our laboratories we have often studied, exchange of, say, monofunctional methoxyl groups for another substituent and have then applied the resulting information to polymers in which the same central atoms are linked together by oxygen bridges (considered to be approximately thermodynamically equivalent to the methoxyl groups). In this case the deviations from random sorting of the T and Z substituents—deviations which are due primarily to the enthalpy of the appropriate reaction(s) of the form of Eq. (1)—can thereby be deduced for the equivalent polymers from relatively simple experimental data.

In the case in which T stands for a monofunctional substituent and Z for a bridging atom (or, indeed, a bond to another Q atom) the assemblage of atoms $QT_{\nu-i}Z_i$ shown on the right-hand side of Eq. (1) represents only part of a molecule, a part which we have called a building unit of functionality i. In the special case of $i = 0$ the resulting QT_ν structure is called the *neso* compound and represents the smallest molecule in that particular family of chemical structures. Similarly for, say, $i = 3$ the unit is trifunctional. Such a trifunctional unit is exemplified by the tertiary carbon group, in which Q = C, $\nu = 4$, T = H, and Z = a C—C bond, and by the arsenous trioxide group, in which Q = As, $\nu = 3$, and Z = a bridging oxygen. The character of the molecular mixture obtained from a polymerization reaction is greatly affected by the $(i-1)$ equilibrium constants, K_{fi}, corresponding to the reaction of Eq. (1), the integer values of i ranging from 1 to $\nu-1$. This is demonstrated by Fig. 12, from which it can be seen that, if the values of the various K_{fi} are either very large or very small, there will never be detectable amounts of more than two units of different functionality present at one time at equilibrium.

When these constants are very large, the only observable molecules must be unbranched chains plus more or less of the possible simple ring molecules in the composition range corresponding to an over-all T/Q mole ratio between $\nu-1$ and $\nu-2$, since all measurable building units must then be either mono- or difunctional. In this case, when there are no rings, the average chain size becomes very large as the T/Q mole ratio approaches $\nu-2$. On the other hand, when the values of K_{fi} are very small, one has only a mixture of the neso compound, QT_ν, and the most branched building unit (the zeugotatic structure), QZ_ν. An example of the latter situation is found when Z stands for a bond between two Q atoms —that is, when there is *catenation*. In this case, K_{fi} is usually small, so that the predominate species are the neso compound and the zeugotatic building unit either in infinite polymers or ring structures, including bird-cage compound. This explains the often-remarked absence of catenation in inorganic chemistry, except for nonequilibrium polymerized mixtures and those structures for which $\nu = 2$ (exemplified by catenation of elemental sulfur and selenium, which are both bifunctional).



(a) small $\underline{K}_{fi}$ (b) random $\underline{K}_{fi}$ (c) large $\underline{K}_{fi}$

FIG. 12. Properties of ith-functionality building units, $QT_{4-i}Z_i$, symbolized in the graphs as Ξ_i as a function of the over-all concentration (T/Q mole ratio) in the system QT_ν versus QZ_ν, where $\nu = 4$.

Just as one can treat experimental data in the scrambling of Z and T substituents on a Q moiety in terms of deviations from random sorting of the substituents, so the various building units, $QT_{\nu-i}Z_i$, may be scrambled into pairs, these pairs into triplets. In this latter type of scrambling there is no longer stoichiometric additivity, since a given atom may be part of several overlapping scrambled assemblages of atoms. Again, experimental data may be treated in terms of deviation from randomness. In the detailed mathematical treatment of this idea (*1*) we have introduced the concept of reorganizational heat order (RHO), symbolized by ρ, which for ring-free chains is a measure of the smallest size of assemblages of building units from which any larger assemblage is randomly composed. This RHO concept is based on the rationale that the thermodynamic properties of a given bond are increasingly less affected by atoms on either side of the bond as these atoms are situated at increasingly greater distances from the bond. Except for a few systems (thus far, the aliphatic hydrocarbons, as evaluated from thermodynamic data, the polyphosphates from paper chromatography, and the polysulfates from NMR), it appears that the experimental data on the molecular constitution of many families of compounds can be approximated by $\rho = 1$; that is, it is assumed that the statistical sorting of the building units into larger assemblages or molecules is random.

Straight Chains and Simple Rings

In any system for which $\nu = 2$ or, as previously described [see Fig. 12(c)], for which the equilibrium constants of the form of K_{fi} are very large, one can discuss molecules exclusively based on mono and difunctional groups without complications due to groups of higher functionality. If we donote a monofunctional group by E (for end) and a difunctional group by M (for middle), equilibria involving all molecules except the neso are summarized in Eqs. (2) and (3):

$$2\ EM_nE \rightleftharpoons EM_{n-i}E + EM_{n+i}E \tag{2}$$

$$EM_rE \rightleftharpoons EE + M_r \quad \text{or} \quad EM_nE \rightleftharpoons EM_{n-r}E + M_r \tag{3}$$

Equation (2) deals with the chain-chain equilibria, those reactions whereby the size distribution of the (unbranched) chains is established. For $\rho = 1$, i.e. random sorting of building units, the equilibrium constant corresponding to Eq. (2) can be shown to be equal to unity when either building unit or molecular concentrations are employed. Furthermore, chain-chain equilibria are not dependent on dilution, since there are the same number of molecules on both sides of the chemical equation for exchange of parts between the molecules. Equilibria between cyclic molecules of size r (denoted by M_r) and the chains are handled by Eq. (3). From its form it is obvious that the equilibrium of Eq. (3) must be shifted to the right by increasing dilution.

By the same statistical reasoning whereby it is demonstrated that the equilibrium constant of Eq. (2) is unity the equilibrium constant of Eq. (3) may be shown to have the following form for $\rho = 1$:

$$K_r^{\circ} = \frac{[\text{middles in the } r\text{-sized ring}]}{(1+D)\{V_2 + (R/2)(V_0 - V_2)\}} \left[\frac{[\text{ends}] + 2[\text{chain middles}]}{2[\text{chain middles}]}\right]^r \tag{4}$$

where D is the dilution expressed in volumes of diluent per volume of neat sample, V_0 and V_2 are the molar volumes in liters per mole of the neso and bifunctional units, respectively, R is the overall T/Q mole ratio, and all bracketed concentrations, [ ], are measured in terms of mole fractions of the total building units. In this expression it is assumed that the molar volume of the various building units is linearly proportional to their functionality and, further, that the molecular volume of a molecule is additively composed of the volumes of the constituent building units. By dividing K_r° by r we obtain the usual equilibrium constant for molecules, $K_{\text{mol}} = [M_r][EE]/[EM_rE]$.

By combining several equations of the form of Eqs. (2) and (3) it is possible to set up equilibrium constants between the variously sized cyclic molecules. From such a mathematical operation one can obtain the following chemical equation, which embodies the idea of large rings twisting off to give smaller rings or, conversely, smaller rings coalescing to give large ones:

$$M_r \rightleftarrows M_{r-s} + M_s \tag{5}$$

Equations (2), (3), and (5) emphasize the following: (1) if there are inappreciable rings, the distribution of chains is expected to be unaffected by finite dilution, and (2) if rings are present in moderately concentrated solutions, increasing dilution will drive the equilibria to more and more rings. For the limiting case of achieving equilibrium at infinite dilution there will be no chains but only the smallest-sized ring and the neso compound, if functionality-change as described by Eq. (1) is allowed. If the functionality of the building units is fixed, as for the alkyl-terminated dialkysiloxanes, then all of the monofunctional units will be in the EE or di chain and all difunctional units in the smallest ring. Incidentally, the size of the smallest ring is determined by the bond angles and steric hindrance. Further, upon approaching infinite dilution an infinite time will be needed for equilibration.

Branching and the Gel Point

When there are detectable amounts of building units exhibiting a functionality greater than 2, infinite, or wall-to-wall, polymers may exist over a more or less extensive region of composition (as measured by the T/Q mole ratio). This occurs where there are not enough monofunctional units available to cap off all of the branches in at least one chain molecule. In a ring-free system for $\rho = 1$ the composition, called the gel point, at which a wall-to-wall molecule first appears is given by Eq. (6), in which z_i stands for the fraction of total building units present as the building unit having a functionality of i:

$$\Sigma_{i=0}^{\nu} i(i-2)z_i = 0 \tag{6}$$

When this equation is solved for $\nu = 6$, we see that

$$z_1 = 3z_3 + 8z_4 + 15z_5 + 24z_6 \tag{7}$$

This means that, in order to avoid infinite network molecules, there must be at least 24 monofunctional units for each hexafunctional unit, 15 monofunctional units for each pentafunctional one, etc. The fact that much of the polymer chemistry of noncrystalline compositions based on the transition metals deals with intractable amorphous materials follows from Eq. (7). A good example of this may be found in rust, amorphous hydrated ferric oxide, the molecular constitution of which has not been open to experimental investigation, since there is no nondestructive solvent and the material decomposes (by giving off water) upon heating.

The presence of rings in the composition range where there are sufficient monofunctional units to assure that all molecules are finite will necessarily cause the gel point of the system to shift to lower values of the composition ratio T/Q, since incorporation of rings into a molecular structure will cut down the number of monofunctional units needed to cap it off. From Equations 18 and 21 of Reference 1 it can be shown that the gel point in the presence of rings is given by the following expression, in which c is the number of ring closures per building unit:

$$\Sigma_{i=0}^{\nu} i(i-2)z_i = 2c(\Sigma_{i=0}^{\nu} i^2 z_i / \Sigma_{i=0}^{\nu} i z_i) \qquad (8)$$

According to this equation, the higher the functionality of the building units, the more effective they are in shifting the gel point to lower values of T/Q. This is consistent with the highly cyclized oligomers characteristic of transition-metal chemistry; see Fig. 13.

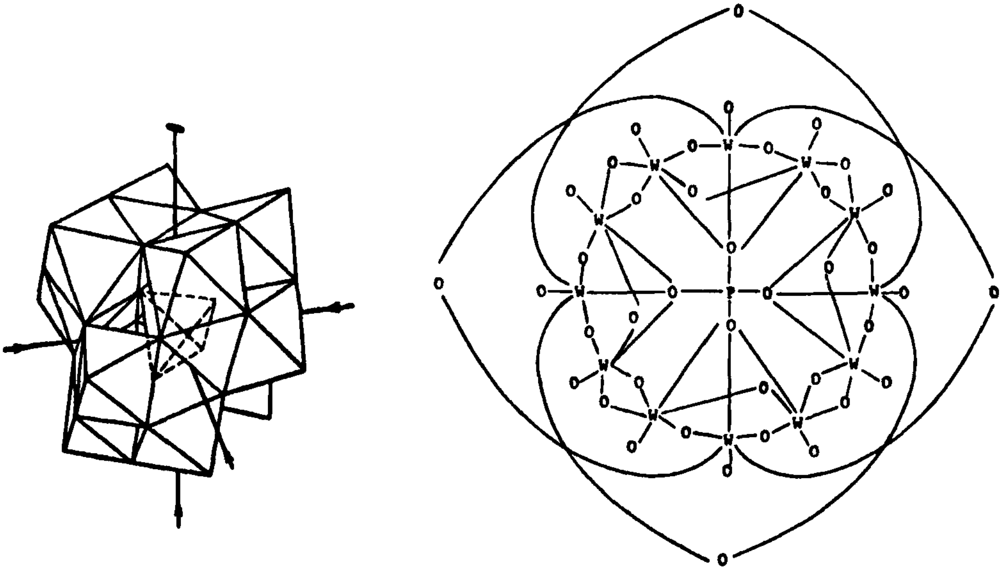


FIG. 13. A phosphotungstic anion of a 12-polyacid, $PW_{12}O_{40}^{3-}$. In the spatial diagram on the left, the PO_4 tetrahedron (dashed) is shown surrounded by WO_6 octahedra. The equivalent chemical-bond diagram is given on the right.

In the region of wall-to-wall molecules beyond the gel point there must necessarily be rings, owing to crowding. Thus, no matter where the starting point is chosen in a highly branched infinite molecule, it can be shown that the average number of chains per cross-sectional area will increase rapidly with distance from this point, so that ring closure imposed by physical crowding must occur. In this region of composition the rings induced by crowding are expected to be rather large and will have a high probability of being fused with neighboring rings in the molecule. Fused rings are also found in the smaller bird-cage and basket-type molecular structures, which are so prevalent in inorganic chemistry. A typical, relatively simple, structure exhibiting a large number of fused rings is shown in Fig. 13. The reason that investigators favor the depiction of the chemical structure of many transition-metal compounds as joined octahedra, each consisting of the central metal atom and its bridging substituents, is seen in the great complexity of the usual molecular-bond diagrams when applied to this chemistry, as exemplified by Fig. 13.

Inorganic Polymers Not at Equilibrium

Thus far the discussion has been centered around polymer systems in which the kind and relative amounts of the various molecules are equilibrium-controlled. Although it seems certain that the majority of inorganic polymers lie in this class, there are also many examples of nonequilibrium inorganic polymers. Kinetically controlled products are expected from transitory preparative techniques such as (1) passing a gas through an arc of glow discharge (in which case polymeric solids often result), (2) passing a gas over a heated solid (such as one of the elements) and then rapidly quenching the products, or (3) carrying out a reaction in a shock tube. Inorganic polymers exhibiting catenation have generally been made by this technique. However, it is usually found that such polymers with only one kind of backbone atom, even when present in solid form as cross-linked molecules, commonly undergo rearrangement: rapidly, when heated, and slowly in storage.

For example, Si—Si chains having alkoxyl groups bonded to each silicon undergo an insertion-type rearrangement, whereby the oxygen moves over to act as a bridge between the silicon atoms and the alkyl group is left affixed to the silicon. Likewise, a methyl group bonded directly to an Si—Si chain can, under some circumstances, form a methylene bridge between the silicon atoms, the remaining hydrogen taking the position in the molecule originally held by the methyl group. Likewise, structures based on a P—P backbone, on which the substituents are not organic groups, undergo rapid dismutation to give the neso compound plus polymers approaching red phosphorus in their structure. All of these reactions are in accord with the previously discussed statement that the values of K_{fi} [the equilibrium constants corresponding to the reaction of Eq. (1)] are small for molecules in which the backbone consists of a sequence of the same atom. The C—C backbone of organic molecules corresponds to a similar nonequilibrium situation for which K_{fi} is small. Although chain molecules having a C—C backbone are extremely stable at ambient temperatures, charring is a common fate of the organic polymers at high temperatures when equilibrium control takes over.

Although they may be quite labile, highly cross-linked inorganic polymers are often not at equilibrium, because the rate of equilibration is greatly diminished through diffusion control. Examples are readily found in the numerous accounts of nonstoichiometric amorphous solids in the inorganic literature prior to 1900, in which small amounts of such elements as oxygen, nitrogen, and hydrogen are combined with a preponderance of such elements as silicon, phosphorus, and arsenic. For example, phosphorus polyhydrides rapidly dismutate to form the neso compound PH_3 and a network polymer of indefinite composition, which was formulated by some of the early workers as P_2H. Depending on such parameters as the time and temperature of heating, state of subdivision, and whether or not the sample was held in a well-pumped vacuum, this "P_2H" polymer may exhibit an over-all P/H mole ratio ranging from 1.5 to very large numbers. When this ratio becomes larger than about 5 to 10, the polymer is called red phosphorus rather than phosphorus hydride.

Kinetics of Equilibration

The main feature that differentiates organic chemistry from the rest of chemistry is the unusually slow rate at which organic compounds come to equilibrium when present in fluid form. Inorganic chemistry is generally characterized by moderate to very fast rates of equilibration. Thus, the half-lives for exchange of parts (*5,12, 13,18,19,20*) in a neat liquid consisting of polymer molecules based on backbones in which silicon or quadruply connected phosphorus atoms alternate with other atoms generally range from about a week at room temperature to a month or two at about 200°, depending on the particular substituents and bridging atoms involved and the presence of catalysts. However, the same kind of structures based on tin or triply connected arsenic have half-lives (*6,7,14,16*) under the same conditions, in the range of 10^{-3} to 1 sec at room temperature.

Because the values of K_{fi} are small for structures based on C—C chains, and because carbon compounds exhibit the rather unique property of becoming unsaturated (i.e., C going to a lower coordination with concomitant transfer of electrons from σ into π orbitals), the chemist mainly familiar with the behavior of organic compounds tends to equate chemical lability with "degradative processes." Thus, he expects reactions similar to charring and elimination of volatiles when the temperature is sufficiently high. In equilibrium-controlled polymers, however, this situation may not exist at all. For example, a molten silicate or phosphate glass, in which exchange of parts within and between molecules is proceeding at a mad pace, is stable practically indefinitely when exposed to the normal oxidizing atmosphere and held in a container with a frozen lining of the glass. On the other hand, many inorganic polymers because of their lability are highly reactive with atmospheric moisture. Thus, the "inorganic rubber," which has been known for many years, $PNCl_2$ (see Fig. 1), is effectively an acid chloride, so that it reacts with moisture in the air to give off HCl vapor and thereby cross-link through oxygen atoms.

Although special reaction-mechanism paths lead to gross exceptions, it is possible to postulate some broad generalizations concerning the rates of exchange processes involved in the equilibration and related chemical properties of inorganic polymers. These generalizations are as follows.

1. Bonds between carbon and another element, for which the energetically available orbitals are filled, are generally the most stable bonds to that element. Bonds between that element and other elements exhibiting filled available orbitals are found to decrease in stability as the other element appears at a greater distance from carbon in the periodic table. (For silicon this rule

gives the following order of increasing reactivity: Si—C < Si—Si, Si—P, Si—N < Si—O, Si—Ge < Si—S < Si—Ge, Si—Te, etc.)

2. Atoms having energetically available orbitals which are vacant (that is, the transition elements and main-group elements of groups II and III in their lower coordinated states) are often highly reactive, so that half-lives for exchange of parts between molecules in the neat liquid will be of the order of magnitude of 10^{-4} sec. A glaring exception to this generalization appears to be found in the square-planar complexes of platinum.

3. When the ΔH of the reaction is very large, the rate will generally be much faster than would otherwise be expected.

Consideration of gel-point phenomena is often complicated by kinetic effects. Thus, for polymers whose molecules exchange parts rapidly one can observe flow beyond the gel point (*6*); that is, this flow occurs through making and breaking of bonds. Related to this phenomenon is stress relaxation occuring by the same mechanism. A false or kinetic gel point is sometimes observed in the chemistry of inorganic polymers. Thus, when a bird-cage molecule such as P_4O_{10} reacts in a "ring-opening" polymerization process, network polymers are sometimes initially formed in compositions which correspond at equilibrium to mixtures of relatively low-molecular-weight molecules.

CHEMICAL ANALYSIS OF POLYMER MIXTURES

As pointed out previously, the molecules of many inorganic polymers readily exchange parts with each other and, concomitantly, these molecules are often quite reactive (as with atmospheric moisture). Because of this fact rapid analytical methods must be used, and great care is often necessary to avoid contamination. In fact, with respect to the lability and general sensitivity of the molecules involved, the chemistry of inorganic polymers is much more similar to that of biological polymers than to that of the usual organic polymers. Indeed, it is the predominance of oxygen, sulfur, and nitrogen linkages in the biological polymers (which, by the way, are apparently generally formed *in vivo* by equilibrium processes)—that is, their "inorganic" constituents—which give them their lability.

An extremely fruitful method for the study (*4–20*) of families of inorganic compounds (from the neso molecule up through the macromolecular region) is nuclear magnetic resonance. Other spectral methods, such as Raman spectroscopy, are also useful, but the data are not as readily interpreted. The various solution chromatographic methods (paper, thick-layer, column, etc.), which have proved so fruitful in biochemistry, offer great promise for the study of inorganic polymers and should be exploited further.

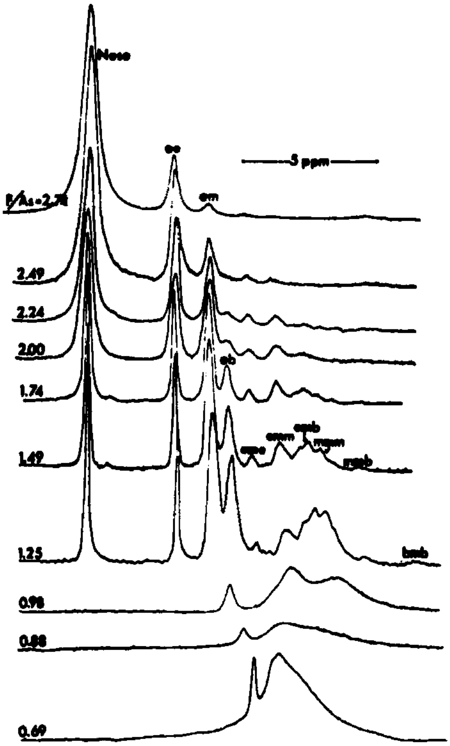


FIG. 14. F^{19} NMR spectra of equilibrated mixtures of AsF_3 with As_2O_3 at various F/As ratios. See J. R. Van Wazer, K. Moedritzer, and D. W. Matula, *J. Am. Chem. Soc.*, **86**, 807 (1964), for the interpretation of these spectra in terms of As—O—As bridged molecules.

Thus far there has been a tendency in the study of inorganic polymers to substitute hypothesis and speculation for sound measurements, but the situation is changing, and precise physical methods of determining molecular structure and evaluating physical properties are now being more generally applied, as we hope will be evident from the reports of this symposium.

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