

# INORGANIC POLYMERS

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## Introductory Paper

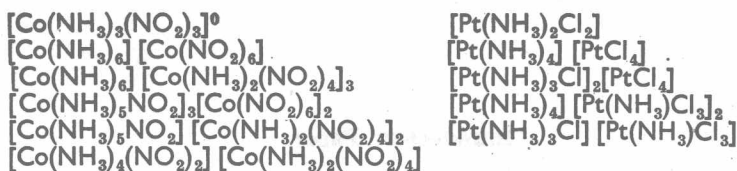
By J. S. Anderson

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In selecting the subject of Inorganic Polymers as the topic for discussion at the International Symposium, the Chemical Society has sought out one of the growing points of chemistry. Our meeting brings together workers on different aspects of a field that impinges on many aspects of inorganic chemistry, and so provides an opportunity to assess the present state of knowledge and the more important questions that need to be answered. This has frequently happened in the past and we look forward to an equally useful clash of ideas at this meeting. The purpose of this introductory paper is presumably to set the matter in perspective against the rest of inorganic chemistry, to state—or question—the objectives of inorganic polymer work and to point to some, at least, of the problems which will, we hope, be dealt with in our lectures, contributed papers, and discussions. In attempting to do this I have tried not to trespass on ground which will be covered more authoritatively by those who follow.

Our current interest in inorganic polymers is based, in large measure, on the concepts and possibilities of experimental study worked out in connection with the organic chemistry of high molecular substances. In the past 20–25 years, these have undergone a subtle development that has modified our thought more profoundly than is often appreciated. For the purpose of the Symposium we may note that the term “polymer” is being interpreted in at least three distinct ways that parallel the historical development of the concept.

We may recollect that the term was originally coined to denote the fact that (without any implications as to structure) two compounds were analytically identical; but the molecular formula of one compound was some multiple of that of another, simpler molecule. Recognition of the monomer–polymer relationship was thus necessarily concerned, in practice, with what we would now term a low degree of polymerization. We would now restrict the monomer–polymer relationship to substances that are closely related in structure; this is a more recent refinement of thought. It may be recalled that the term was introduced into an inorganic context when Werner pointed out the existence of monomer–polymer relationships in the broader sense amongst the co-ordination compounds. *E.g.:*



In the stricter sense, the chemistry of such diverse groups of substances as metallic alkoxides, the cyclic phosphonitric halides, and the new polymeric borazines exemplifies the existence of series of inorganic polymers differing in their degree of complexity. We shall be concerned with several such groups of compounds in this symposium.

The second use of the term "polymer" was a logical extension of the first: to denote the relation between substances of high molecular weight based strictly on the replication of a simple monomer unit, such as the vinyl group. Polymers of this kind are typically derived from monomers with double bonds; their formation involves a bond rearrangement which is possible in carbon chemistry because of the properties of the  $\pi$ -bonded systems typified by  $\text{C}=\text{C}$ ,  $\text{C}=\text{O}$ , or  $\text{C}=\text{N}$  double bonds. Professor Burg and Professor Laubengayer, in their main lectures, seem likely to discuss bond types and the pseudo-unsaturated or pseudo-aromatic properties of bonds between pairs of atoms other than carbon atoms, so it may suffice to point out that inorganic chemistry can show rather few strict parallels with carbon chemistry in this respect. It is, of course, the possible analogy between the  $[sp^2] p^\circ \pi$  boron- $[sp^2] p^2 \pi$  nitrogen and the  $[sp^2] p^1 \pi$  carbon- $[sp^2] p^1 \pi$  carbon atom pairs that is the basis of interest in boron-nitrogen polymers. We look forward to hearing more about these and, in Professor Laubengayer's lecture, to an account of the formally analogous aluminium-nitrogen system. There may still be questions that should be asked about the structure of these substances. The extent of overlap between the filled  $p_\pi$  orbital of nitrogen and the vacant  $p_\pi$  orbital of boron is the crux of the matter. There must be sufficient  $\pi$ -bonding to stabilize an unfamiliar electronic configuration of the nitrogen. In the infinite polymer of hexagonal boron nitride there is no doubt about the matter. Electron diffraction measurements on borazole vapour confirmed Stock's hypothesis that the molecule was planar, and it appears that there is room on the experimental side for (e.g.) some detailed crystal-structure determinations on suitable substituted borazoles and similar compounds and, on the theoretical side, for more refined molecular orbital treatments of the borazole ring. Indeed, the whole question of extended  $\pi$ -bond systems involving the B-N, P-N, Al-N, S-N groups (and others) still needs to be cleared up. Craig and Dewar have made a start, but the state of the molecular orbital theory is at present quite

unsatisfactory. Those working on the experimental aspects of these polymer systems would like to refer their structures and reactions to a sound background of theory, which would enable some predictions to be made about reactivity and pseudo-aromatic character.

There are a few other aspects of the straightforward monomer-polymer relation that may be mentioned at this point. One of these is that the lability shown by a number of inorganic systems is apparently greater than that of  $\sigma$ -bonded chains and skeletons of carbon compounds. Thus every student of chemistry is familiar with the reversible polymerization of sulphur, involving the cleavage of the  $\sigma$ -bonds between sulphur atoms for the interconversion of cyclic  $S_8$  molecules into quasi-infinite chains. Is this a matter of bond energies or of reaction mechanisms? In recent years our knowledge of polythiane chemistry has been greatly extended, and we have examples of numerous sulphur-chain compounds, with quite long thiane chains, terminated by a range of end groups—halogen atoms, sulphydryl groups, sulphonic groups, etc. From a very recent review of the field by M. Schmidt, in *Angewandte Chemie*, it would appear, indeed, that the covalent bond between sulphur and a number of other elements of comparable electronegativity is very susceptible to reaction with  $S_8$  molecules, thereby extending the sulphur chain. Particular interest thus attaches to the mechanism of such reactions. Professor Gee's lecture should touch on these questions, and the study of the reaction processes, as well as the equilibria, in sulphur may well be relevant to other cases.

In general, the idea of straightforward polymerization is less applicable in inorganic chemistry than is that of recurrent condensation processes. It will be recalled that although the essence of the matter was already there, in polysaccharide and polypeptide chemistry and elsewhere, the understanding of high-molecular organic compounds received a great impetus from the study of reactions between polyfunctional molecules. It is now obvious that, unless particular stereochemical conditions are fulfilled, like, or alternating, structural units thereby get strung together in extended arrays as a result of the repeated elimination of water (or other reaction product). Where there is unsatisfied functionality, further elimination steps can link together adjacent polymer skeletons, or segments of the same skeleton, quite fortuitously. A great many of the high molecular weight substances of inorganic chemistry are based on polycondensation reactions, and especially on the elimination of water between structural units. This is also true in the low-molecular weight range of discrete "polymers" and a good deal of this symposium deals with substances that are analytically quite distinct-polycondensation products, but not polymers

in the original sense. Thus we have several papers on the discrete isopolyanions of molybdenum and tungsten, as well as on such substances as the polysulphuric acids. The latter represent the reversible first stages of that process of linear polycondensation which Professor Thilo has so successfully interpreted in his elegant work on the polyphosphates, and which leads, through the gradations in properties along the series of elements Si-P-S, to the chemistry of the silicic acids, based very largely on infinitely polymeric linear and cross linked structures.

With the concepts of polyfunctional units, condensation reactions, and cross-linking, the study of high molecular weight compounds took a step that was so far-reaching and so subtle that we rarely comment upon it; it has passed unnoticed into our assumptions and outlook. This is the extension of quite detailed structural chemistry into the domain of the inherently amorphous, structurally irregular, and analytically uncharacterizable materials. A highly cross-linked polymer is necessarily a completely random structure; the possibilities for coiling, entanglement, and cross connection between segments and skeleton chains or sheets are infinite, so that there can be no long-range order. However, by regarding the whole as built up through condensation reactions between similar (or at least only a few kinds of) polyfunctional units, we recognize a higher degree of local order. The sequence of linkage of the atoms within each structure unit is known, and the bond properties of those atoms determine, within the limits of molecular flexibility, the steric arrangement within each domain. The types of connection possible between each domain and its neighbour can be fairly closely specified chemically, even though in all other respects the way in which adjacent domains are related within the whole structure is quite indeterminate. Since the chemical properties of the polymer are likely to be determined very largely by the local pattern of bonds, even though the physical properties are representative of the whole completely irregular structure, we can really know a great deal, in the chemical sense, about highly condensed structures. For our knowledge to be reliable, we need to relate our very generalized structural models to the wider context of inorganic chemical fact and theory.

In one sense inorganic chemistry is, *par excellence*, the chemistry of high polymers, since so many compounds exist only in the solid state, as crystals: three-dimensional infinite polymers, or layer lattice structures in two dimensions. These are, however, polymers of a very special type—almost perfectly stereoregular in three dimensions. It is worth mentioning them on two counts. The first is to suggest to the crystal chemists that the termination of the crystal pattern, at surface or edge, may have some useful analogies with the termination of a

chain or net (the existence and function of end groups) in a random polymer. The second is to point out that (as with complex organic macromolecules) we know rather little about the conditions in which macromolecular structures are laid down in the ordered pattern of a regular crystal. Almost the whole of the chemistry of silicate minerals is concerned with ordered and often complex polymer networks. When the silicates are melted, and depending on the silicon: oxygen ratio, there is good evidence that polysilicic anions are present in the melt. When monosilicic acid polymerizes in solution it forms an amorphous gel. Both the polymer breakdown in the fused state and the polymer aggregation from the monodisperse state in solution represent conditions that convert only with relatively great difficulty into the typical polysilicate or aluminosilicate crystals; indeed, the range of complex silicate mineral structures that have been produced in the laboratory is rather small. There is a field of interest here where the inorganic polymer chemist could shed light on the problems of the mineralogist.

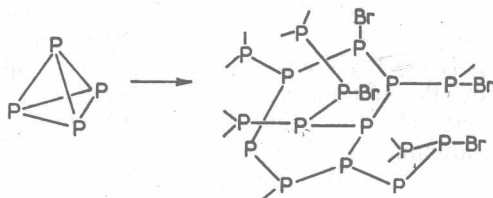
The principles of macromolecular chemistry can fruitfully be applied to much of inorganic chemistry and may, indeed, help us to interpret much that remains in a rather unsatisfactory state from the work of earlier investigators. We now know that whenever we have reactions between polyfunctional units we are liable to get cross-linked macromolecular products; rather special conditions may need to be fulfilled to yield either simple molecular complexes or the ordered state of a crystal. Where random polymer structures are built up, we can see that the backbones of linear polymers, or the side branches and fringes of two- or three-dimensional structures, are likely to be terminated by the attachment of some kind of end groups, which may have little effect on the overall properties and may be only vaguely revealed by the analytical figures. It is not surprising, therefore, that the literature has recorded numerous examples of ill-defined and genuinely amorphous substances which defied characterization.

Thus, a few years ago Krebs discussed some peculiar features of the allotropy of the semi-metallic elements from this standpoint. The general mobility inherent in metallic structures enables the metallic elements to achieve their true crystalline order. By contrast, the covalent binding between the atoms of the non-metallic elements may freeze in a bond pattern and an atomic arrangement that reflects the fortuitous features of the process by which the specimen was formed, rather than any equilibrium crystalline arrangement. We are familiar with this in the case of carbon—never obtained by direct chemical action with the diamond structure; formed by solid-state pyrolyses with an inherently random structure, and recrystallizing to form anything more than microdomains of the graphite structure only at high temperature. The

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Group V elements, phosphorus, arsenic, and antimony, have to form three  $\sigma$ -bonds per atom. They can do this in their highly strained tetrahedral tetratomic molecules, or as infinite polymers; the unique crystal structures of the metallic forms of antimony and bismuth are determined largely by this need to form three strong bonds per atom. Phosphorus, in particular, is liable to build up random cross-

FIG. 1.



Polymerisat		Mischpolymerisat	
$P_4$ fest flüss. gasf.	$\xrightarrow{200^\circ}$ amorph. rot $\downarrow >400^\circ$ krist. rot $\uparrow >550^\circ$ krist. schw.	$P_4 + PBr_3 \longrightarrow$ rot, Schenck $P_4 + H_2O \longrightarrow$ rot-violett $P_4 + H_2O + \text{Licht} \longrightarrow$ weiss-gelb- braun-rot Phosphorsuboxyd ( $P_2O$ ) Phosphorwasserstoff, fest	
$As_4$ fest gasf.	$\xrightarrow{20^\circ}$ amorph. schw. $\xrightarrow{200^\circ}$ krist. schw.	$As_4 + I_2, Br_2 \longrightarrow$ rot-braun $As_4 + CS_2 + \text{Licht} \longrightarrow$ rot-braun $As^{III} \xrightarrow{\text{Red.}}$ aq. $\longrightarrow$ braun	Hitze
$Sb_4$ — — gasf.	amorph $\xrightarrow{-180 \text{ bis } -20^\circ}$ krist. schw.	$SbH_3 + O_2, Cl_2 \xrightarrow{-90^\circ}$ gelb $\xrightarrow{-80^\circ}$ schwarz $Sb^{III} \xrightarrow{\text{Red.}}$ aq. $\longrightarrow$ schwarz $SbCl_3 \xrightarrow{\text{Elektrol.}}$ explosiv	
$Bi_4$ — — — gasf.	$\xrightarrow{-180^\circ}$ krist. schw.		

Übersicht der Phasen in der fünften Gruppe

TABLE 1.



linked networks that undergo conversion only with great difficulty into the properly-ordered black crystalline allotrope; red phosphorus is the inherently amorphous material formed as the first random product of bond cleavage and rearrangement of the  $P_4$  molecule. It is notoriously ill characterized, and is recorded as retaining variable amounts of the halogens, the elements of water, etc., depending on the conditions of its formation and the catalyst used to accelerate the allotropic transformation. Krebs has shown how the varieties of red phosphorus, the ill-defined suboxide, and supposed solid hydrides fall into a coherent and related system as a polymer network plus end groups, and that the thermal transformation of the materials arises from the elimination of volatile products and increased cross linking. (See Table 1.) With the other Group V elements, the polymer becomes progressively more labile with increase in metallic character, but the essential point is that we get the analytically ill-defined and variable polymer whenever the covalent network is laid down at a temperature too low for mobility and rearrangement. Thus, even with the more nearly metallic antimony this condition can be fulfilled in electro-deposition; the so-called "explosive antimony" can be interpreted as a random polymer terminated with  $>SbCl$  or  $-SbCl_2$  groups.

Amongst the compounds of the non-metallic elements there are many systems that need to be re-examined with these ideas in mind. It is possible to mention only one or two. The nitrides of the non-metals can be regarded as derivatives of polyfunctional reaction centres. A

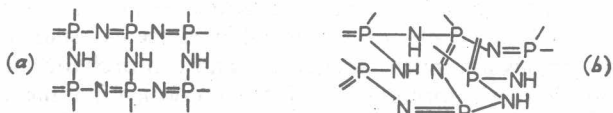


FIG. 2. (a) *Formal polymer network.*  
(b) *Typical real random structure.*

start has been made by Steger in interpreting the rather intractable amorphous phosphorus and phosphorus nitride systems from this point of view. The silicon-nitrogen system is obviously of similar complexity and we are to hear something of a systematic attack upon it during this meeting. There is, however, a dearth of work on some other topics. For example, there is much to be done about the substances formerly regarded as analogues of the typical organic compounds—the so-called silicoformic and silico-oxalic acids, etc., obtained by hydrolysis of the higher silicon halides. Wiberg and Simmler, a few years ago, showed that there was some most interesting chemistry here, involving sheet structures that were very closely parallel to the con-

stitution of the layer silicates, and with possibilities of cross-linking

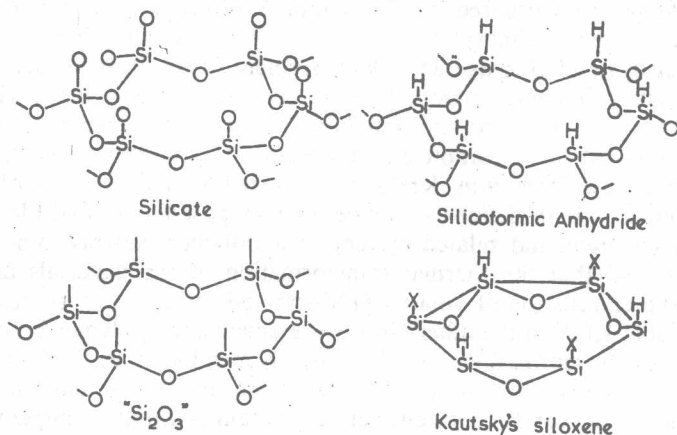


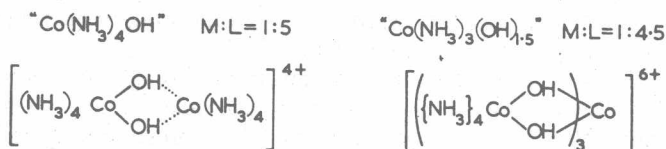
FIG. 3. *Two-dimensional siloxane sheets.*

to build up "lower oxides" with silicon-silicon bonds. Kautsky's interesting siloxene compounds, which he formulated as discrete molecular polymers, almost certainly fit into the same concept of infinite sheet polymers. However, little has been done in all this field, since we have been in a position to apply modern experimental methods and modern interpretations.

Ideas about molecular structure have been current and respectable in organic chemistry for about a hundred years. As applied to inorganic chemistry, and especially to the metallic elements, soundly based structural notions are much more recent and can probably be said to date from Werner's formulation of the co-ordination theory. It is familiar to us all that, through the work arising out of his predictions, and his controversies, he established quite rigorously the stereochemistry of the transition metals in their co-ordination compounds. Since about the 1930s we have come to accept (as Werner maintained from the outset) that the stereochemical and other implications of the co-ordination theory could be taken as a reliable working hypothesis in treating the chemistry of the metals generally, and especially the chemistry of ions in solution. The evidence of crystal structures and the development of valence theory have contributed to this outlook. Werner's favoured co-ordination numbers and favoured steric arrangements of ligands around a metal atom have found their natural interpretation in modern valency theory. The general applicability of the co-ordination theory has made it a guiding principle in every part of inorganic chemistry. It is just as applicable in discussing the structure

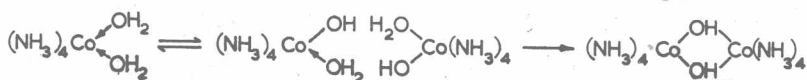
and the reactions of polymeric material involving the metals. This is a point to which I may return in a moment.

In addition to furnishing general structural principles, Werner's work on the constitution and formation of polynuclear complexes gave an insight into the nature of the condensation processes involved in polycations and polyamines. From the cardinal principle of the preservation of the characteristic co-ordination number and steric arrangements, he was led to formulate what we might term *ligand-deficient* compounds (*i.e.*, those in which the stoichiometric ratio of ligands to metal is less than would be required to give discrete complexes of maximum co-ordination number) as polynuclear complexes, with one or more ligand groups serving as bridges between two co-ordination centres, *e.g.*,

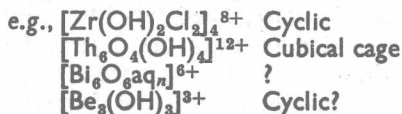


The ability to act as a bridging group in polynuclear amines was restricted to ligands of certain types, *e.g.*, to the hydroxo-group  $\text{OH}$  but not the aquogroup-group  $\leftarrow \text{OH}_2$ , to the amido-group  $\text{NH}_2$  but not the ammino-group  $\rightarrow \text{HN}_3$ , to the peroxo-group  $\text{O}_2$ , nitro-group  $\text{NO}_2$  and a few others.

Werner showed, in fact, that (expressed in modern terms) the condensation step involved the conjugate base of a potentially acidic complex, which was a sufficiently strong nucleophil to displace some more labile ligand from another co-ordination centre: *e.g.*,



One fruitful influence in inorganic chemistry in recent years has been the increasing emphasis on metal cations in solution as aquocomplexes which are typical Brönsted acids—indeed, in the case of cations of high charge, very strong acids. Reactions between their conjugate bases can lead to the same kind of condensation into polynuclear complexes as was recognized by Werner. We thus find polycation formation to be the logical extension of co-ordination theory. It can lead either to the formation of finite polycondensed species:

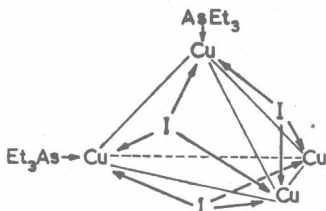
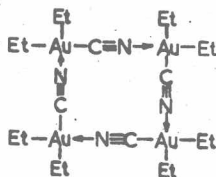


or, by repeated operation on, *e.g.*, the aquo-complex, to the formation of highly condensed basic compounds, or ill-defined hydroxo-complexes. These are substances which, as obtained, can well have a highly randomized structure even though many may, in some circumstances, order themselves into layer lattice crystals. Thus the almost inherently amorphous "basic" compounds frequently encountered in the chemistry of the polyvalent metals come naturally within the scope of a process (ligand displacement by an unsatisfied nucleophilic ligand) which is of recurrent importance in inorganic macromolecular chemistry. At the Copenhagen Conference on Co-ordination Chemistry some years ago, Professor Schmitz-Dumont showed how, on this basis, it was possible to interpret the structures and the reactions of amorphous alkoxy- and amido-compounds of the transition metals in a rational manner. We look forward, in this symposium, to hearing from him again on new developments in this field.

The requisite condition for polymerization through the formation of polynuclear complexes is—as in macromolecular organic chemistry—reaction between polyfunctional units. There must be a ligand with unused co-ordinating capacity and a metallic atom which is either co-ordinatively unsaturated or can be involved in a ligand displacement reaction. Polymerization to finite polymers is familiar in the case of some transition-metal complexes:



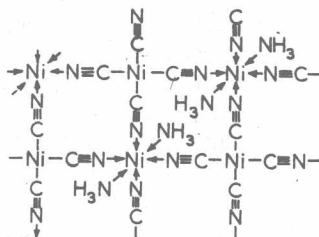
In other cases—*e.g.*, the alkoxides of the metals—it has been known for a long time that co-ordinative saturation is achieved by a limited degree of polymerization, and both cage structures and other structures



have been advanced. There are still some gaps in our knowledge of these substances, however, as regards their degree of polymerization, the structure of the polymers, and their depolymerization by donor molecules. In the issue of *Nature*, dated July 14th, 1961, is an exchange of correspondence that demonstrates the divergent conclusions that can permissibly be drawn from the evidence at present available. It may be that papers to be presented at this Symposium will remedy

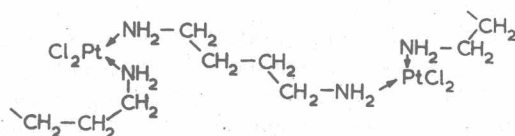
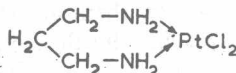
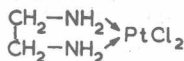
the deficiencies. Carried to its extreme, the attainment of co-ordinative saturation can lead to the formation of infinite polymers. The infinite strings of square-co-ordinated palladium atoms in crystalline palladium dichloride, or of tetrahedrally co-ordinated atoms in dimethylberyllium, or in silicon disulphide, can legitimately be regarded as stereoregular infinite linear polymers. The transition-metal ferrocyanides, or the clathrate-type complexes formed by nickel(II) cyanide, exemplify the regular infinite three-dimensional polymers arising from the double-ended ligand properties of the cyano- and similar groups (Fig. 4).

FIG. 4.



We ought, perhaps, to enquire why high-molecular polynuclear complex compounds are not formed more frequently than they are, for example, in reactions which actually furnish crystalline chelated compounds, since they might arise with almost any polyfunctional, flexible ligand molecule. As is well recognized, the stereochemical conditions for the formation of a chelate ring are rather exacting. As long ago as 1933, Drew and Tress in their critical examination of the stereochemistry of platinum, observed that, with the polymethylenediamines as ligands, only ethylenediamine and propylene-1,3-diamine yielded crystalline platinous complexes; with any longer chain interposed between the donor groups, reaction still occurred, but the products were ill-defined in composition and amorphous in nature. Drew rightly inferred that the amino-groups in these must be linked to different platinum atoms. In modern phraseology, the possibilities of cross linking are obviously great, and random polymers inevitable:

A great deal of the work that has been done on inorganic polymers



—and no doubt much that will be discussed at this meeting—is concerned primarily with their structure. This is by no means the whole story. The chemistry of a system is known when we know, also, its thermodynamic properties and equilibria, its reactions and their mechanism. Several of the Symposium papers deal with the condensed oxyacids, and the interest here is very largely in the reactions and equilibria.

Thus, there are now few uncertainties about the constitution of the finite polyanions formed by molybdenum and tungsten, as they exist in crystalline derivatives; we have a growing, but less complete, knowledge of the oxyacids of vanadium and niobium. They can all be described in terms of polynuclear complexes or cage structures. The variety of different structures is rather remarkable, and so are the highly specific differences between metals, such as molybdenum and tungsten. However, the reactions by which they are formed, or are converted into one another, or even the species that exist in solutions, are still not settled.

The range of different polyanion structures, each involving a very high degree of ordering, which can be obtained from molybdate and tungstate solutions under not very different conditions (for example, the paramolybdate  $\text{Mo}_7\text{O}_{24}^{6-}$ , octamolybdate  $\text{Mo}_8\text{O}_{26}^{4-}$ , phosphomolybdate  $\text{PMo}_{12}\text{O}_{40}^{3-}$ , and telluromolybdate  $\text{TeMo}_6\text{O}_{24}^{6-}$  anions, each with its distinctive cage structure) strongly suggests that what exists in solution is not identical with what is built into the crystal. The final stage of condensation and ordering may take place at the little known interface between crystal and solution.

Studies of polyanion condensation and hydrolytic degradation in solutions owe much to the pioneering work of Jander, and the range of experimental attack that he brought to the study of solutions—the stoichiometry of the condensation process, attempts to compare ionic weights from diffusion measurements, spectrophotometric assay of the species present—has been supplemented since by others, notably by Souhay and the other French workers. We have in our programme two further contributions to the study of tungstate and molybdate solutions, which extend the range of experimental methods applied to the problem. However, there are still substantial differences between the conclusions reached by different means and different workers, and I see little prospect yet of reaching an agreed interpretation of all the facts. One notable feature of the poly-acid condensations is that the first detectable condensation product of the mono-anions is already complex: a  $\text{W}_6$  polyanion in tungstate solutions, a  $\text{Mo}_7$  anion (as usually interpreted) in molybdate solutions. These first detectable species cannot represent the primary reaction; they must be the stable products of

a succession of unit steps. There is clearly a wide disparity in the stability and the reactivity of successive stages of condensations as well as—for some reason—very substantial differences in the reaction routes of monomolybdates and monotungstate anions.

A similar problem concerns the mechanism of polycondensation processes involving cations and the detectable stages of condensation in the formation of polycations. A few years ago, Sillen advanced a very attractive hypothesis—his “core and links” model—for describing condensation equilibria in solution in terms of the occurrence of a succession of similar unit steps. Mechanistically these unit steps would have to involve just the sort of ligand displacement (substitution in an aquo-cation) by a hydroxo-cation that we referred to earlier, to build up linear or two-dimensional polymeric species. In terms of Sillen’s “core and links” hypothesis, a solution in the pH range where hydrolysis occurs should attain an equilibrium population of all the stages in this condensation process and, by a very elegant and skilful analysis in terms of the equilibrium law, he showed how to evaluate the alternative descriptions of the condensation equilibria from hydrogen ion titration data. It is notoriously difficult to attain a guaranteed equilibrium condition in condensation reactions; moreover, where the quantitative treatment has to be pushed to the limits of precision, it encounters all the uncertainties attaching to ionic activities in relatively concentrated solutions. It is striking that as Sillen’s theory has been put to increasingly rigorous test, in his own laboratories, it has become increasingly clear that the products of polycation condensation do not cover a continuous spectrum of complexity; only a few discrete stages can be discerned between the monocation and the colloidal particle. The first detected stage of condensation may be either a binuclear species or one of such complexity that it must be regarded as the product of a succession of reaction steps. The requisite reactions must take place in kinetically probable steps and this implies that the polymers are built up unit by unit; nevertheless, the formation constants for different polymeric species must differ greatly. Why should there be such significant disparities in the free energy of reaction for successive, chemically analogous stages?

Additional point is lent to this question by what we know of the linear polyanions of the oxyacids. Between sulphuric acid, for which we can examine the equilibrium formation of only the first two or three stages of polyacid condensation in conditions of sufficiently low water activity, and orthosilicic acid, which rapidly condenses to a high and indefinite degree in aqueous solution, we have a wide range of behaviour. The properties of the polyphosphoric acid system fall usefully between these limits, and in his admirable studies of the

polymetaphosphates, Professor Thilo has done much to untangle for us the chemistry of polyacid condensation. It is noteworthy that, in addition to the true finite polymers of metaphosphoric acid, the existence of every successive distinguishable step of polyphosphate—Thilo's oligophosphates—should have been proved, in both condensation reactions and in hydrolytic degradation. It is to be hoped that, at some time, it will be found possible to make equilibrium measurements on systems of this kind; in conjunction with the quantitative information we already have for polysulphuric acids they would furnish, by extrapolation, interesting and useful data for the chemistry of silicic acid.

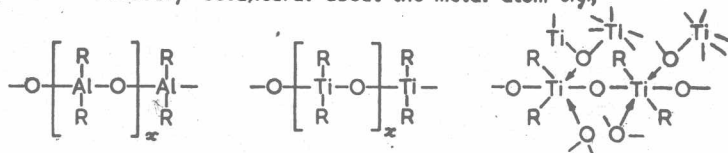
In addition to the purely scientific motives for investigating inorganic polymers, we must recognize that much of the support for work of this kind arises from the hope that it may be possible to produce new materials with desirable properties—and especially with useful properties at rather higher temperatures than are withstood by ordinary organic compounds. It was, no doubt, the discovery and the development of the silicones that drew attention to the technological possibilities of linear and cross-linked polymers with skeletons based on other elements than carbon. In the silicones the skeleton of the polymer is based on silicon-oxygen binding and, in principle, one may hope to get the same sort of condensation process, if silicon is replaced by other elements with a high affinity for oxygen—that is, with a strong covalent component in the metal-oxygen bond. Our Russian colleagues, in particular, have greatly extended our knowledge of what may be called the *metalo*xane polymers, and we are to hear Professor Andrianov during this symposium. It appears that, in passing from the polysiloxane chain to the polymetaloxanes, we encounter several questions that are very relevant for the possible applications of the materials. The first concerns the stereochemistry of the chains, and its consequent influence on the properties of the substances. In the silicones, silicon has its usual co-ordination number 4; it is linked through [ $sp^3$ ] bonds and thus acts as a bifunctional centre of combination. In going from silicon to aluminium, titanium, etc., we recognize that, as a result of atomic size and the availability of higher orbitals for bonding, we encounter an increasing tendency to form six [ $d^2sp^3$ ] bonds—i.e., to adopt the co-ordination number 6. This is typical of the oxide chemistry and co-ordination chemistry of these elements, and we must enquire whether it determines also their polymer chemistry. If so, any centre in a typical metaloxane chain may need to achieve co-ordinative saturation by forming additional bonds—for example, with oxygen atoms belonging to different chains, as a result of either cross-linking or multiple-strand formation.



## Tetrahedral about Si



Probably octahedral about the metal atom e.g.,



The legitimate technological objective of discovering new materials has been the stimulus for a great deal of work on inorganic and what is sometimes described as organometallic polymer systems, and is the origin of some important contributions to this symposium. It has been a natural consequence of this stimulus that a great deal of work has been essentially of a preparative and empirical kind; this may be an occasion to take stock and to enquire whether the general pattern of development is adequate either to round off our scientific knowledge or to answer the technological questions. My own suspicion is that it is not: that there is too much attention to preparative chemistry and not enough to physicochemical properties, thermochemistry, thermodynamics, and the study of reactions.

Consider the implications of the interest in materials that are stable at high temperatures. The term stability has reference to some kind of change, and even so is used in two distinct senses. It may refer either to the driving force behind a particular reaction—the free energy change in going from the original state to the reaction products—or to kinetic stability. A chemical reaction may be energetically possible as a spontaneous process, but may not occur because the energy or—very important—the entropy of the transition state makes the process too slow.

Thermal stability in the strict sense refers to the possibility and probability of rupturing skeletal bonds of the main polymer structure—to split off finite molecular fragments, thereby changing the average degree of polymerization, or to bring about elimination reactions between different segments, so increasing the cross linking. A good deal of empiricism could be replaced by sensible prediction, in researches which have the applied objective as part of their aim, if more studies were made of the chemistry of thermal instability, and if steps were taken to enlarge our thermochemical knowledge.