RATES AND MECHANISMS OF SUBSTITUTION IN INORGANIC COMPLEXES IN SOLUTION

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CONTENTS

I. INTRODUCTION

The experience gained in general chemistry or qualitative analysis with reactions in which metal-ion complexes are formed or dissociated is limited in scope, and often leaves the impression that all reactions of this type proceed very rapidly. Probably because no systems of contrasting behavior are ordinarily studied, the kinetic aspects of the systems have not excited a great deal of interest. Greater experience in the chemistry of the complex ions, such as is gained in the preparation of a variety of Werner complexes, does expose a large number of reactions which proceed slowly and many, in fact, which proceed very slowly. Although some careful rate studies on the systems have been completed, the

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field has not received attention commensurate with its importance. The importance of the systems becomes apparent as soon as it is recognized that they are analogs of the class of substitution reactions with carbon as the central atom which have been the subject of much careful and productive study by investigators interested in the behavior of organic compounds. In the inorganic complexes, as in the organic compounds, wide variations in the properties of the group being replaced, of that entering, and of residual groups in the complex can be realized, and the effect of these variations on the rate of substitution studied. In addition, the inorganic field presents the important possibility of comparing rates of substitution for complexes containing central ions of widely differing electronic structure, and of studying the influence of this parameter on the rate.

The present paper is an attempt to systematize the general observations which have been made on the rates of substitution reactions for inorganic complexes in water, undertaken in the hope that this address to the field may stimulate new interest by exposing some of the many significant problems which remain unsolved. In addition to reviewing the work which has been done, an effort has been made to correlate and rationalize the observations, laying particular emphasis on the aspect peculiar to the inorganic field: the effect of variation in the properties of the central ion on the rate of substitution.

The reactions in which metal ions associate with coördinating groups have already been referred to as substitution reactions. As used in this paper, "substitution" will refer to a net process in which one group coördinated to the central ion is replaced by another, without change in oxidation state for any of the atoms participating. The description as substitution reactions obviously fits the examples represented by the two equations:

$$\mathrm{py} + \mathrm{IrCl_6^{---}} = \mathrm{Cl^-} + \mathrm{IrCl_5py^{--}}$$

$$\mathrm{CNS^-} + \mathrm{Coen_2NH_3CNS^{++}} = \mathrm{Coen_2(CNS)_2^+} + \mathrm{NH_3}$$

Less obvious from their formulation is the fact of substitution in reactions such as:

$$\mathrm{Fe^{+++}aq.} + \mathrm{Cl^-} = \mathrm{FeCl^{++}aq.}$$

and

$$\mathrm{Ag(NH_3)_2^+} + 2\mathrm{H^+} = \mathrm{Ag^+aq.} + 2\mathrm{NH_4^+}$$

However, in these cases also substitution is involved, since water presumably completes the coördinative valence for the ions marked by the subscript "aq." In general, the number of the water molecules in the first sphere for each ion is not known (124). This situation prevails for ions such as $\mathrm{Fe^{+++}aq.}$, which have no groups besides water attached, and also for ions such as $\mathrm{Ag(NH_3)_2^+}$, the coördinative valence for which may be, but is not known with certainty to be, satisfied. In the present paper, the subscript "aq." will be omitted, since it is understood that most of the reactions discussed proceed in water as the medium.

When a reaction in a solvent other than water is discussed, special mention will be made of the fact.

It is evident that the field embraced by the substitution reactions under review includes the many examples of complex-ion formation and dissociation applied in qualitative analysis, as well as the reactions encountered in the preparation and transformation of the amino complexes of chromium(III), cobalt(III), rhodium(III), platinum(IV), and others. The differences in rates of substitution in inorganic complexes are extreme. A familiar example of a system of great lability is the complex formed by ferric and chloride ions. When chloride ion is added to a solution containing ferric nitrate in dilute nitric acid, the yellow color of the Fe(III)-Cl^- complexes develops at once, and the system adjusts without noticeable delay to stresses applied by dilution, change in temperature, or the addition of new reagents. By contrast, the reaction of chromic ion and chloride ion, particularly in acid solution, is very slow, so slow in fact that violet $Cr(H_2O)_6Cl_3$ (which contains $Cr(H_2O)_6^{+++}$ rather than any of the various chloride complexes) can be precipitated by passing hydrogen chloride into a solution containing the aquo-chromic ion (21). Examples of enormous differences in rate also appear in the chemistry of ammonia complexes. Thus, equilibrium between cupric ion, ammonia, and the various complexes in aqueous solution is established without noticeable delay, and when a strong acid is added, the complex Cu(II)–NH_3 ions rapidly yield ammonia to the acid. By contrast, the removal by acid of ammonia from $Co(NH_3)_6^{+++}$ to form $Co(NH_3)_5H_2O^{+++}$ and NH_4^+ is a very slow reaction, and $Co(NH_3)_6^{+++}$ will continue in 1 *M* hydrochloric acid without noticeable change almost indefinitely, although it is unstable (*vide infra*) with respect to the products mentioned, as well as other substitution products.

Some numerical values for the ranges in rate of substitution which have been observed may be of interest. None of the "rapid" reactions have been investigated kinetically, but a lower limit for the rate of one can be estimated. Schmid (255) studied the affinity of Fe^{+++} and $S_2O_3^{--}$, using a flow method. A flow technique is required, since a fairly rapid oxidation–reduction reaction takes place in addition to the association reaction. A by-product of his experiments is the conclusion that with $S_2O_3^{--}$ in excess at 0.4 *M*, the formation of $FeS_2O_3^+$ is complete within 0.03 sec. at 17°C. This leads to *ca.* 2×10^4 l. mole^{-1} min.$^{-1}$ as the lower limit for the bimolecular reaction between Fe^{+++} and $S_2O_3^{--}$. As an example of a slow reaction the rate of which has been measured, we may consider the aquotization of $Rh(NH_3)_5Br^{++}$, which proceeds as a first-order reaction with the specific rate 3×10^{-3} min.$^{-1}$ at 84°C. (157). Using the measured temperature coefficient, the specific rate at 20°C. is estimated to be about 10^{-6} min.$^{-1}$ The two examples chosen thus present a range of 10^{10} in specific rate, which corresponds (assuming identical *a* factors) to a difference in activation energies of about 14 kcal. Many substitution reactions are known to proceed less rapidly than does the aquotization of $Rh(NH_3)_5Br^{++}$, and many probably proceed more rapidly than the reaction between Fe^{+++} and $S_2O_3^{--}$. The range in specific rates encountered in the field therefore exceeds considerably the factor 10^{10} derived by comparing the two examples discussed.

II. CLASSIFICATION OF COMPLEX IONS ON THE BASIS OF RATE BEHAVIOR

A factor of great importance in determining the behavior of complex ions is the rate at which substitution reactions for them take place. It is, in fact, of greater importance for many of the observations which are made than is the factor of stability. A useful classification of complex ions can be based on the differences in the speed at which they adjust to equilibrium with respect to substitution reactions. It is the purpose of this section to discuss the implications of the differences in rate and to emphasize, by citing examples, that a slower rate for substitution does not necessarily mean greater stability. While it may seem superfluous to stress that there is no necessary connection between slow rate and stability, considerable confusion in understanding the behavior of complex ions has resulted because of the failure to distinguish between the rate and the equilibrium aspects.

As one extreme in respect to rate of substitution will be considered complexes for which these changes are consummated very rapidly. These complexes will be referred to as "labile." At the other extreme in respect to rate of substitution are the complexes which for want of a better word will be described as "inert."[2] Rates of substitution varying over the entire range may be expected, and many systems can therefore not be classified uniquely. The terms are useful, however, since the differences in rate behavior imply differences with respect to observations which can be made on the systems and in the methods of investigating them.

For labile complexes, when the composition, the environment, and other conditions are fixed, the properties of the system are fixed for any measurements made after a reasonable time; for inert complexes, the properties will depend on previous history, as well as on the prevailing conditions, and will change more or less rapidly with time. The Fe(III)–Cl^- and Cr(III)–Cl^- systems are examples of this contrasting behavior. It has already been mentioned that the Fe(III)–Cl^- system adjusts very rapidly to the equilibrium state; the properties of the system when measured even a short time after the components are mixed are independent of the way in which they are generated. By contrast, the solution which results when chromic nitrate is dissolved in 1 *M* hydrochloric acid continues different in properties for a long time from that obtained when dichromate ion is reduced in the same environment. In the former case, the purple color of $Cr(H_2O)_6^{+++}$ persists; the latter solution is green, owing to the presence of various chloro complexes. Neither solution is at equilibrium with respect to formation of the chloride complexes.

Although pure isomers can be isolated in the solid state for labile complexes, all forms rapidly yield the equilibrium mixture when dissolved. For complexes of the inert class, isomeric forms which may be unstable persist in solution. This property has been of great help in establishing the structures of inert complexes, many of the conclusions about which have been arrived at by the classical method of isomer counting. This method is applicable only when the different forms can

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[2] J. Bjerrum has used the word "robust" to describe complexes of this type. This does not seem to be a particularly good choice, since it carries the suggestion of stability.

be separately characterized, and is relatively easy to apply only when they can be obtained in a fairly pure state.

Complexes of the inert kind may be transferred to a new phase without change in composition. The solid form of a salt such as $Co(NH_3)_5Cl_3$ may be shown by x-ray diffraction studies to consist of $Co(NH_3)_5Cl^{++}$ and Cl^-. Chemical tests, and physicochemical measurements (such as conductance) on the solutions, show that the ions preserve their identity also in the liquid environment. This property has been of very great importance in the classical investigations of the structures of the cobaltammines, for example. For labile complexes, only infrequently does the constitution in the solid phase, or a new liquid phase, correspond to that of the principal species in solution. This is illustrated by the behavior of the manganese(III)-pyrophosphate system. At sufficiently high concentration of pyrophosphate ion, tripyrophosphate manganate(III) exists (150); under no conditions, however, has a solid phase containing three pyrophosphate ions for each manganic ion been formed. The method commonly used for investigating inert complexes of separating a solid phase and determining its composition often leads to erroneous conclusions when applied to labile complexes.

While it is true that some of the most stable complexes are of the inert kind, it is by no means true that all of this class are particularly stable. Very many, in fact, are less stable than analogous complexes in the labile class containing a different central ion. The dissociation quotients $((MCl^{++})/(M^{+++})(Cl^-))$ for $CrCl^{++}$ (21) and $FeCl^{++}$ (227) at $\mu = 0.3$ and 25°C. are 0.2 and 5, respectively. In spite of its lower stability, the rate at which $CrCl^{++}$ dissociates in acid solution is enormously less than the corresponding rate for $FeCl^{++}$. An analogous comparison can be made for CrF^{++} (287) and FeF^{++} (62), and for numerous other pairs. Even for the inert complexes commonly regarded as stable—the ammino complexes of cobalt(III) may be taken as examples—slight changes in environment suffice to make them unstable with respect to some substitution reactions. The important common feature of their behavior is that they persist in an environment in which they are unstable. A few examples will illustrate the instability of familiar "stable" complexes of the inert class under rather ordinary conditions.

Using data reported by J. Bjerrum (19), it may be shown that at 25°C. in 1 *M* hydrogen ion and 1 *M* ammonium ion, the reaction

$$Co(NH_3)_6^{+++} + H^+ + H_2O = Co(NH_3)_5H_2O^{+++} + NH_4^+$$

would be almost complete at equilibrium, and only 0.01 per cent or so of the luteo ion would remain unchanged. The driving force for further replacement of ammonia is even greater (19). In spite of this great driving force for conversion to the aquo ion in acid, the reaction is almost immeasurably slow. Considering the reaction in basic solution

$$Co(NH_3)_6^{+++} + 3OH^- = Co(OH)_3 + 6NH_3$$

and using, in addition to the data of Bjerrum for the stability of $Co(NH_3)_6^{+++}$, the value recorded by Latimer (164) for the solubility product of cobaltic hydroxide, a value of 10^{-7} *M* is calculated for the concentration of $Co(NH_3)_6^{+++}$

in equilibrium with $Co(OH)_3$ when hydroxide ion and ammonia are each 1 *M*. The change proceeds quite slowly, however, although more rapidly than for the ion in acid solution. As a final example, the system

$$Fe(CN)_6^{---} + 6H^+ = Fe^{+++} + 6HCN$$

is cited. At equilibrium in 1 *M* hydrogen ion and 1 *M* hydrocyanic acid, the concentration of ferricyanide ion is only 10^{-12} that of ferric ion (165). In spite of this instability ferricyanide ion persists for a long period of time under these conditions if the solution is shielded from light.

In connection with the discussion of affinity in relation to the division of complex ions into the two classes, it should be pointed out that in both classes there is usually a stepwise decrease in affinity for a particular group on progressive substitution by this group. This type of behavior has been demonstrated by quantitative measurements in a number of systems of the labile type: Al^{+++}–F^- (33), Fe^{+++}–F^- (62), Fe^{+++}–Cl^- (227), Mn^{+++}–$C_2O_4^{--}$ (263), for many ammonia complexes (19, 41), and for at least two systems of the inert class: Cr^{+++}–CNS^- (25) and Cr^{+++}–F^- (287). It is indicated by a few quantitative (19) and many qualitative observations for other systems of both types. Exceptions to this behavior do occur and have been observed for both classes. An example in the labile class is the Cd^{++}–I^- system (168); examples in the inert class are the Fe^{++}–ophen (169) and Fe^{++}–dipy (15, 155) systems. In the Fe^{++}–dipy system the association constant

$$(MX_n^p)/(MX_{n-1}^{p-q})(X^q)$$

for the first molecule of dipyridyl is 2.7×10^4 at 25°C.; for the second it is $<10^5$. Since the overall equilibrium quotient is 3.8×10^{17}, the association constant for the last step is therefore $>1.4 \times 10^8$. An explanation for the behavior of the Cd^{++}–I^- system is not immediately obvious. The behavior of the Fe^{++}–ophen and Fe^{++}–dipy systems, however, can be correlated with the change in electron structure as the amine replaces the water associated with the cation. Fe^{++} has a magnetic moment corresponding to four unpaired electrons, while $Fe(dipy)_3^{++}$ is diamagnetic. The Fe^{++}–dipy complexes in the states in which Fe^{++} retains four unpaired electrons may reasonably be expected to show the normal stepwise progression of affinities. However, the electron rearrangement gives $Fe(dipy)_3^{++}$ a greater stability than would otherwise be expected for it, thus accounting for the instability of intermediate forms. The instability of intermediate complexes with respect to disproportionation into extreme forms can be expected for other systems in which electron rearrangement takes place at some stage in the series formed by successive substitution.

A discussion of the possible reasons for the differences in the rate behavior of complex ions will be deferred until a survey of the rate behavior has been completed in the next section. It may help, however, in reading the succeeding section to have anticipated the conclusions which are eventually reached about the properties of the ions affecting the rates of substitution. While the radius of the central ion, its charge, the nature of the attached groups, and the bond type are all important factors in determining the rate of substitution, fixing only these (and the experimental conditions) does not fix the rate. A remaining significant parameter, which perhaps has the most important influence, is the electronic structure of the complex ion. Complex ions of similar electronic structure tolerate fairly wide variations in the other parameters without exhibiting strikingly different rates of substitution.

III. SURVEY OF OBSERVATIONS ON THE LABILITY OF INORGANIC COMPLEXES

In discussing the lability of various complex ions, their classification as "inert" or "labile" will sometimes be attempted. The point has already been made that a sharp dividing line between the two classes does not exist, but that there is a continuous gradation in lability from one extreme of rate behavior to the other. For the purposes of sharpening the use of the terms "inert" and "labile," an arbitrary division between the classes, consistent with the discussion of Section II, is chosen as follows: If no delay is noted in the substitution reaction under ordinary conditions (i.e., room temperature, *ca.* 0.1 M solutions) the system will be described as labile. As defined in this way, reactions in "labile" systems are complete in the time of mixing—i.e., in about 1 min. The ranges in rates of substitution are enormous, so that most of the systems will lie far outside the range of rates constituting the division and in only a few cases is there any doubt as to the classification of the systems.

Since most of the observations on the speed at which the systems under discussion reach equilibrium are qualitative, a qualitative definition of the term "lability" suffices for the purposes of this paper. Efforts to define "lability" as a useful quantitative property meet with great difficulty. In special cases, quantitative meaning can perhaps be attached to the term. Thus, for example, in systems undergoing isotopic exchange, the specific rates for forward and reverse processes are almost identical, and the single specific rate (for fixed standard conditions) is characteristic for the system and can be taken as a measure of lability. Usually the specific rates forward and reverse are not equal and the situation becomes more complicated. However, a meaningful quantitative definition is sometimes still possible. Thus, for a system in which forward and reverse reactions proceed by first-order paths, the sum of the corresponding specific rates, $k_1 + k_1'$, can serve as a measure of lability—the time to proceed a given fraction of the way to the equilibrium state is the same for forward and reverse processes, and is governed by the specific rate sum, $k_1 + k_1'$, which is therefore characteristic for the system. But, in general, considering systems in which forward and reverse rates differ in order and making comparisons for reactions of differing order, it is not obvious what function of specific rates will serve as a useful quantitative measure of lability or whether such a function exists.

Comparisons of lability will be made for systems under approximately standard (i.e., "ordinary") conditions, the conclusions being based on observations of the time required to reach equilibrium. Although complexes will be classified according to their degree of lability, the term should properly be applied only to a system as a whole, since the rate of substitution depends not only on the complex undergoing substitution but also on the substituting group. As the survey of the data will show, no great confusion is introduced by the improper usage, since the rate of substitution seems to a first approximation to be fixed by the electronic structure of the complex ion: e.g., all the substitution reactions of Cr^{+++} are slow and are slower, with little if any overlap, than all those of V^{+++}. The most meaningful comparisons are made, however, by considering a common process for various metal ions, and it is on such comparisons that the conclusions reached in a later section are based.

In reviewing data relating to the lability of complexes in solution, three types of processes have been considered: isotope-exchange reactions, substitution reactions involving net chemical change, and isomerization reactions. The relation of observations for each type of process to the property of lability is considered, and a review of the data made. Since not enough work has been done on the exchange reactions to justify systematization with respect to the periodic table, the results obtained by particular experimenters are reviewed as units. In considering the chemical substitution reactions, the observations are systematized with respect to the periodic groups, the different oxidation states for each element being discussed separately. A review of the qualitative observations on rates of substitution is given in Section IX. A summary of the conclusions which can be drawn from exchange and orthodox substitution reactions is made in Section IV.

A. Exchange reactions

The measurement of the rate of exchange for a reaction of the type

$$MA_6 + A^* = MA_5A^* + A$$

is in many cases the simplest, most direct, and least ambiguous test of lability with respect to substitution. The equilibrium state is known, corresponding as it does to an almost statistical distribution of the groups A. Hence failure to observe redistribution of the isotopes in a specified time at once means that the change is slow, since the equilibrium is favorable for exchange. Furthermore, in these systems forward and reverse specific rates are (almost) the same and can characterize the lability of the system. In view of the direct implications of observations on systems of this type, it is regrettable that so little systematic work has been done on them.

For reactions in water solution, perhaps the most fundamental in this class of exchange reactions are those between hydrated cations and solvent. They have been studied for a number of cations (76, 124, 125), using O^{18} as a tracer for water. With aluminum, ferric, and gallic ions at room temperature, both in 0.1 M and 1 M perchloric acid, the exchange is complete in 2 min. Thorium(IV) in nitrate solution, cobaltic ion (with Co^{++} present), and cobaltous ion in *ca.* 2 M perchloric acid also exchange completely in 2 min. With chromic ion the exchange is measurably slow, and the half-time in the range of acidity *ca.* 0.01–1 M perchloric acid is about 40 hr.

Crandall (55) has shown that uranium(VI) exists in water solution as the oxycation UO_2^{++}, and that the contained oxygen exchanges only very slowly with the solvent.

The exchange of water between anions and the solvent has been given study over a wide area (111, 193, 289), although a satisfactory intensive study of only a single system, the CO_3^{--}–H_2O exchange (194), has been completed. Perchlorate, sulfate, phosphate, chlorate, nitrate, and a number of other anions exchange oxygen with water very slowly in neutral or alkaline solution. Fairly generally, the rate becomes more rapid as the acidity is increased. There is an increase in rate of exchange as the size of the central ion increases in a group (arsenate compared to phosphate, selenate compared to sulfate). Permanganate and chromate ions are more labile than their analogs perchlorate and sulfate (or selenate) in the comparison groups of the periodic table.

Adamson, Welker, and Volpe (7) have studied the exchange of CN^-aq. with cyanide ion bound in various complex ions. For solutions about 0.05 *M* in the cyanide complex ion, at 25°C. and at pH = 10, they observed that $Ni(CN)_4^{--}$, $Pd(CN)_4^{--}$, and $Hg(CN)_4^{--}$ exchange completely in less than 5 min., $Mn(CN)_6^{---}$ is about 40 per cent exchanged in 4 min., while $Co(CN)_6^{---}$, $Fe(CN)_6^{---}$, $Fe(CN)_6^{----}$, $Cr(CN)_6^{---}$, and $Mo(CN)_8^{----}$ exchange less than 2 per cent in 100 hr.

Long (179) reported that at 25°C. and in 0.03 *M* solution, $Fe(C_2O_4)_3^{---}$ and $Al(C_2O_4)_3^{---}$ exchange completely with free oxalate in less than 1 min., but $Cr(C_2O_4)_3^{---}$ and $Co(C_2O_4)_3^{---}$ exchange very slightly, if at all, in 20 min. at 35°C.

Ettle and Johnson (69) noted that the exchange between Cl^- and $Co(NH_3)_4Cl_2^+$ is slow, and concluded that it proceeds by the known slow processes of aquotization and anation.

Harris (114) has shown that the exchange between CO_3^{--} and $Co(NH_3)_4CO_3^+$ proceeds slowly.

A number of observations have been made on the rate of exchange of halide complexes with halide ions in solution. Grunberg and Filanov (106) studied the exchange of $PtBr_4^{--}$ and $PtBr_6^{--}$ with bromide ion. For the former complex ion, at 3×10^{-3} *M*, the exchange is *ca.* 80 per cent complete in 20 min. at 16°C. The observations which were made with $PtBr_6^{--}$ show that exchange is complete under rather drastic conditions and are of limited usefulness for making comparisons. $PtCl_6^{--}$ and Cl^- exchange slowly in the dark with a half-time of about half a day at room temperature at concentrations of *ca.* 10^{-3} *M* (232). Iodide ion exchanges completely with HgI_4^{--} in 10 min. on boiling, over a range of concentrations (224).

A type of exchange reaction which has a less direct relation to rate of simple substitution than the simple type discussed above is that involving exchange of the central ion between two complexes (one of which may be the aquo ion). Rapid exchange in this type of reaction is a convincing demonstration of the lability of the pair of complexes in question. A slow exchange, however, does not necessarily mean that simple substitution of one ligand by another in the complexes is a slow process. Analysis of a simple system will serve to illustrate this point. Consider the equilibria:

$$\mathrm{AX_2} \underset{k'_2}{\overset{k_2}{\rightleftarrows}} \mathrm{AX} + \mathrm{X}$$

$$\mathrm{AX} \underset{k_1}{\overset{k_1}{\rightleftarrows}} \mathrm{A} + \mathrm{X}$$

which function as the path for exchange of A and X between $\mathrm{AX_2}$ and A + X. Exchange of X between $\mathrm{AX_2}$ and solution will be at least as rapid as that resulting from the operation of the first equilibrium above. Since the specific rate of an exchange reaction is proportional to the rate of the chemical change producing it (65, 181), this specific rate is proportional to $k_2(\mathrm{AX_2})$. The rate of the chemical change producing the exchange between $\mathrm{AX_2}$ and A is

$$k_2(\mathrm{AX_2})\,\frac{k_1(\mathrm{AX})}{k_1(\mathrm{AX}) + k'_2(\mathrm{AX})(\mathrm{X})}$$

and this in turn is proportional to the specific rate of the exchange reaction. If, now, $k'_2(\mathrm{AX})(\mathrm{X}) \gg k_1(\mathrm{AX})$, the rate reduces to $k_1(\mathrm{AX})$, since at equilibrium $k_2(\mathrm{AX_2}) = k'_2(\mathrm{AX})(\mathrm{X})$. $k_1(\mathrm{AX})$ may be very small compared to $k_2(\mathrm{AX_2})$; thus the rate of exchange of A for $\mathrm{AX_2}$ may be small, although the exchange of X for $\mathrm{AX_2}$ is rapid; or the system may have a high lability with respect to substitution of X for X without necessarily having a high lability for the substitution of A for A. The condition that $k_1(\mathrm{AX})$ be relatively small can be met even when k_1 is relatively large, if (AX) is very small, as is the case when the equilibrium

$$\mathrm{AX_2} + \mathrm{A} = 2\mathrm{AX}$$

is far to the left. Usually, however, the intermediate complex is stable with respect to the extremes, and therefore usually a slow rate of exchange for A for $\mathrm{AX_2}$ will mean that one or more of the steps involved is slow.

The following are among the exchange reactions of the second type which have been studied.

$\mathrm{PtCl_6^{--}}$ and *cis*-$\mathrm{Pt(NH_3)_2Cl_4}$; $\mathrm{IrCl_6^{--}}$ and $\mathrm{Irpy_2Cl_4}$ (107): At concentrations *ca.* 5×10^{-3} *M* and at room temperature, no exchange of the central atoms is observed in 2 hr.

$\mathrm{Fe^{++}}$ and $\mathrm{Fe(ophen)_3^{++}}$ as well as $\mathrm{Fe^{++}}$ and $\mathrm{Fe(dipy)_3^{++}}$ undergo a slow exchange. For the latter system in a solution containing 0.016 *M* $\mathrm{Fe^{++}}$, 0.008 *M* $\mathrm{Fe(dipy)_3^{++}}$, and 0.04 *M* hydrochloric acid, the exchange is *ca.* 23 per cent complete in 2 hr. (241).

Exchange of $\mathrm{Fe^{+++}}$ and $\mathrm{Fe(CN)_6^{---}}$, $\mathrm{Fe^{++}}$ and $\mathrm{Fe(CN)_6^{---}}$, $\mathrm{Fe^{+++}}$ and $\mathrm{Fe(CN)_6^{----}}$ is slow (140).

The exchange of $\mathrm{Ni^{++}}$ and $\mathrm{Nien_3^{++}}$ is complete in 5 min.; for $\mathrm{Ni^{++}}$ and $\mathrm{Ni(dipy)_3^{++}}$ it is 25 per cent complete in 5 min. (132).

The exchanges $\mathrm{Cr(H_2O)_6^{+++}}$ and $\mathrm{Cr(SCN)_6^{---}}$, $\mathrm{CrCl_2(H_2O)_4^{+}}$ and $\mathrm{Cr(SCN)_6^{---}}$, $\mathrm{CrCl_2(H_2O)_4^{+}}$ and $\mathrm{Cr(CN)_6^{---}}$, $\mathrm{Cr(H_2O)_6^{+++}}$ and $\mathrm{Cr(C_2O_4)_3^{---}}$,

$CrCl_2(H_2O)_4^+$ and $Cr(C_2O_4)_3^{---}$ with the ions *ca.* 0.01 M and in slightly acid solution are less than 2 per cent complete in 24 hr. The exchange of $Cr(H_2O)_6^{+++}$ and $Cr(CN)_6^{---}$ under the same conditions takes place somewhat more rapidly (190).

A number of exchange reactions of the second type have been studied in nonaqueous solutions. A brief review of this work is included, since it seems likely that the general rate relationships are not greatly altered by the changes to solvents such as pyridine, ethyl alcohol, or acetone and water.

The exchanges of magnesium ion with chlorophyll a or b in 80 per cent acetone (240), of ferric ion and ferriprotoporphyrin in 95 per cent ethanol, and of ferric and cupric ions with the corresponding pheophytins in 80 per cent acetone are all very slow. The exchanges between manganous chloride and the complex with acetylacetone or benzoylacetone in methyl alcohol over the concentration range 1×10^{-3} M to 0.02 M are complete in times of the order of 30 min. (63). The rates of exchange in pyridine of cupric acetate with complexes of cupric ion and derivatives of salicylaldehyde at concentrations of *ca.* 0.015 M vary from fast to slow (65). With the salicylaldehyde complex or the methylimine derivative of it at concentrations of the order of *ca.* 0.013 M, $t_{1/2} < 15$ sec., but with the ethylenediimine derivative, $t_{1/2}$ is 2.1 hr. The rates of exchange of nickel perchlorate with various chelate complexes in acetone, ethyl cellosolve, or methyl cellosolve solution (132) range from rapid to very slow; in the complex with salicylaldehyde, salicylaldoxime, or salicylaldimine the exchange is complete in 5 min., but in complexes with methylbenzylglyoxime, *N*,*N*-di-*n*-propyldithiocarbamate, and salicylaldehyde-ethylenediamine the extent of exchange is only 3 per cent or less in 60 min. $Znpy_2(OCOCH_3)_2$ exchanges completely in 30 sec. or less with zinc acetylacetone, zinc acetylacetoneëthylenediamine, zinc benzoylacetone, or dipyridine zinc thiocyanate at concentrations of 0.01 M in pyridine (170).

B. Substitution reactions involving a net chemical change

Although the question of lability is of primary interest for systems in which a net chemical change takes place (as contrasted to the exchange of groups which differ only in isotopic composition), it is more difficult to reach conclusions from the observations made in these systems than for simple exchange reactions. Aside from the difficulty already discussed of defining lability for a system in which the equilibrium constant differs from unity are the difficulties encountered in interpreting the observations. Some of these difficulties are considered in the following paragraphs.

Many of the experiments in which it is noted that appreciable substitution does not take place in a specified time are without significance for the present purpose because the equilibrium state is not known. Failure to react may be due to an unfavorable equilibrium, or a slow rate, or both. The simple test for distinguishing between stability and slowness by mixing the anticipated reaction products would resolve the ambiguity but has in general not been applied, often because there has been no particular interest in separating the rate and the equilibrium aspects.

Frequently the observations are made for processes in which the overall changes are complex and involve, in addition to simple substitution, changes in the groups entering or leaving. An example of the more complex type of process is the reaction:

$$PtCl_6^{--} + H_2O = PtCl_5OH^{--} + H^+ + Cl^-$$

Without further analysis, observations on such systems do not lead to conclusions about the lability with respect to simple substitution, since the changes in the ligands themselves may be partly rate determining. In some cases, however, they can lead to useful definite conclusions. The rate of simple substitution will be at least as rapid as the overall rate, if, as seems likely for a case such as the above, simple substitution is a part of the overall process. Thus, if the overall change is rapid, the system can be considered to be labile with respect to simple substitution. However, if it is slow, no definite conclusion can be reached. Considerations similar to the above apply if the net change involves multiple replacement. When oxidation–reduction takes place, the reactions are useful for the present inquiry only if it can be shown that substitution is rate determining in the overall change.

The substitution reactions most generally observed in water solution involve water, or the derivative ions OH^- or O^{--}, as replacing groups or the groups being replaced. Even when the net change does not involve water, substitution reactions often proceed through an aquo-ion or hydroxy-ion stage. This is the case in many preparative reactions: for example, $Co(NH_3)_5Cl^{++}$ or $Co(NH_3)_5CO_3^+$ is easily converted to $Co(NH_3)_5H_2O^{+++}$, and water is in turn readily replaced from this aquo ion by other anions. Direct replacement of one anion by another in water solution may in fact be a rather rare occurrence and has in no case been proven to take place. In view of the importance of hydrolytic reactions, it seems in order to discuss the general phenomena observed in further detail.

Relatively few of the hydrolytic reactions involve simple substitution of the type represented by the example:

$$Cr(H_2O)_5Cl^{++} + H_2O = Cr(H_2O)_6^{+++} + Cl^-$$

A complication which is often present is that the net change observed involves formation of a solid hydroxide or hydrated oxide. Net changes of this type may be slow, even though simple substitution on the aquo ion is rapid. For example, the Fe^{+++}–Cl^- system is very labile with respect to formation or dissociation of the ferric chloride complexes. Nevertheless, slow changes continue in a solution of ferric chloride, resulting in an increase in the acidity and in the eventual formation of a precipitate (159). It is evident that a conclusion about the lability of the ferric chloride complex cannot be based on the observations of the rate of formation of the solid, since the dissociation of the complex is not rate determining for the overall process. The reason for the slow rate of formation of the precipitate may be that it proceeds *via* such intermediates as $Fe(OH)_2^+$ and $Fe(OH)_3$, which are present at low concentration in the solution of the salt. Consistent with this view, but not proof of it, is the observation that for the systems the rate behavior of which is illustrated by the Fe^{+++}–Cl^- example, the rate of hydrolysis, as measured by the rate of formation of precipitate, is very sensitive to the acidity. However, in many hydrolytic reactions leading to eventual formation of a precipitate, the rate-determining role of the actual replacement of the ligand can be recognized, and in these cases useful inferences can be drawn from the observations. When substitution of a ligand by water is rate determining for hydrolysis, the change usually proceeds through recognizable stages, and only in the later stages may the precipitate appear. Sometimes, too, the rate of hydrolysis is independent of the acidity, over a considerable range, as in the case with $PtCl_6^{--}$ (12), $Cr(CNS)_6^{---}$ (25), and SiF_6^{--} (230).

In many hydrolytic reactions the products appear not as precipitates but as soluble (or colloidal) polynuclear species. Among the cations forming such species are Zr^{++++}, Cr^{+++}, and Ga^{+++}; among the anions, vanadate, chromate, niobate, and molybdate. Equilibrium with respect to the formation of these species is often quite slow, and may determine the rate of the overall change. For these reactions, therefore, considerations similar to those outlined for the formation of solid hydrolysis products apply, and an effort must be made to discern whether substitution, or formation of the polynuclear species, is rate determining.

In addition to the difficulties encountered in interpreting the complex systems (as described) are those met in interpreting the descriptions offered by the investigators. Usually, particularly in the more recent literature, no direct record is made of the rate of change, and one must rely on inferences drawn from preparative and other procedures, in reaching conclusions about the rate. Even when a qualitative statement about the rate is made, there remains the problem of converting adjectives such as "slow" and "rapid" as used by different authors to some common standard, in order to make comparisons between systems possible.

The review of the literature on rates of substitution for the various complex ions is given in Section IX. The conclusions about the rates of simple substitution reactions which can be derived from a critical examination of these data, as well as from those on isotopic exchange reactions, are summarized in Section IV.

C. Isomerization reactions

Although a relation between lability with respect to substitution of ligands and rates of isomerization can be expected, a consideration of existing observations shows that the relationship is not always very direct. When *cis–trans* isomerization is involved, a simple generalization is possible: the isomeric forms persist in nonequilibrium concentrations in solution only for complexes which undergo substitution at measurably slow rates. As the following examples will show, a similar generalization is not possible when interconversion of *d*- and *l*-forms for hexacoördinated complexes is considered. This field is further complicated because there are important disagreements about the observations, at least for complex ions which interchange groups rapidly in simple substitution reactions. For example, Wahl (270) and Burrows and Lauder (39) have reported resolution of $Al(C_2O_4)_3^{---}$ and Thomas (265) of $Fe(C_2O_4)_3^{---}$, but Johnson

(131) has been unable to repeat the resolution of either of these complex ions. As noted before, Long (179) has shown that both of these complex ions exchange oxalate ion rapidly with oxalate ion in solution. Neogi and Dutt (201) have reported resolution of $Ga(C_2O_4)_3^{---}$; however, the general rate behavior of gallic ion with respect to substitution makes it seem almost certain that the ion would exchange oxalate rapidly with the solvent. Resolution of $Znen_3^{++}$ and of $Cden_3^{++}$ has been reported by Neogi and Mukherjee (203). Equilibrium with respect to formation and dissociation of the complex ions appears, however, to be established rapidly. If the observations on the resolution of the complex ions are not in error, the conclusion follows that interconversion of *d*- and *l*-forms can be slow, even though the attached groups undergo rapid substitution or exchange. Substitution may be involved as a step in the racemization, but may not be the only kind of step involved. While slow *d–l* interconversion may not necessarily imply slow substitution, slow substitution in general implies that *dl*-forms of appropriate complexes can be resolved, and that racemization will be slow. Thus, hexacoördinated complexes of Cr^{+++}, Co^{+++}, Ru^{++}, Rh^{+++}, Os^{++}, Ir^{+++}, and Pt^{++++} are inert; in all these cases, optically active forms of ions of composition MC_3 (C being a bidentate chelating agent) have been resolved.

IV. SUMMARY OF OBSERVATIONS ON THE LABILITY OF COMPLEX IONS

A summary of conclusions as to the lability of various systems or complex ions with respect to simple substitution is made in this section. The basis for this summary is chiefly the observations on exchange reactions and on rates of formation or dissociation of complex ions. These observations have been examined critically; whenever possible, definite or probable conclusions have been drawn from them.

The summary presented in table 1 deals mainly with hexacoördinated ions, or ions which may reasonably be presumed to be hexacoördinated. Some discussion will be made later of the ions of coördination numbers 4 and 8, but the chief emphasis in the remainder of the paper is on the rate behavior of the hexacoördinated complexes.

V. LABILITY WITH RESPECT TO SUBSTITUTION AND ELECTRONIC STRUCTURE

In this section, a correlation is made for ions of coördination number 6 of the observations on rates of substitution with the electronic structure of the complex ions. Pursuing this point of view does not imply that other properties of the system are not also important; thus, the influence on these rates of variation in the nature of the ligand and of variations in charge and radius of the central ion is in part discussed. However, when comparisons are made for a common type of reaction (e.g., chloride or fluoride ion being replaced by water) within series in which the charge on the central ion is held constant, and the radius approximately so, it becomes evident that these factors by no means fix the rate, and that an important parameter remains to be considered. A series of this type with tripositive ions of approximately the same radius is: Al^{+++}, Ti^{+++}, V^{+++}, Cr^{+++}, Mn^{+++}, Fe^{+++}, Co^{+++}, and Ga^{+++}. When comparisons of rates of sub-

TABLE 1

Lability of hexacoördinated complex ions

Complex ions of the following are labile with respect to simple substitution: aluminum(III), scandium(III), yttrium(III), tripositive rare earth ions, titanium(III), titanium(IV), zirconium(IV), thorium(IV), UO_2^{++}, plutonium(III), plutonium(IV), PuO_2^{++}

ELEMENT	LABILITY OF COMPLEX IONS
V(II)	$V(CN)_6^{----}$ is inert; no definite evidence on other complex ions
V(III)	F^-, CNS^-, CN^-, SO_4^{--}, $C_2O_4^{--}$, citrate, and pyrophosphate complex ions are "labile"; $V(CN)_6^{---}$ appears to be more labile than $V(CN)_6^{----}$
Nb(II)	Only polynuclear complexes known in solution
Nb(III)	SO_4^{--} complex probably labile
Nb(V)	Cl^-, Br^-, and H_2O complexes labile
Ta(II)	Only polynuclear complexes known in solution
Ta(III)	No definite information; CN^- complex probably labile
Ta(V)	CN^- complex labile; F^- and $C_2O_4^{--}$ complexes probably labile
Cr(II)	Cl^- complex reported inert
Cr(III)	H_2O, F^-, Cl^-, CN^-, CNS^-, NH_3, etc. complexes inert
Mo(II)	Only polynuclear complexes known in solution
Mo(III)	Cl^-, Br^-, and CNS^- complexes inert; replacement of NH_3 slow in acid
Mo(IV)	$Mo(CN)_8^{----}$ inert
Mo(V)	Cl^- and Br^- complexes labile; CNS^- complex may be measurably slow in substitution; $Mo(CN)_8^{---}$ inert
Mo(VI)	F^-, Cl^-, and HOO^- complexes labile
W(II)	Only polynuclear complexes in solution
W(III)	$W_2Cl_9^{---}$ characterized as inert
W(IV)	Cl^- complex probably labile; $W(CN)_8^{----}$ inert
W(V)	Cl^- and $C_2O_4^{--}$ complexes probably labile; $W(CN)_8^{---}$ inert
W(VI)	F^- and Br^- complexes labile; Cl^- complex doubtful
Mn(II)	En and pyrophosphate complexes labile; $Mn(CN)_6^{---}$ inert
Mn(III)	F^-, Cl^-, $C_2O_4^{--}$, and pyrophosphate complexes labile; $Mn(CN)_6^{---}$ inert
Mn(IV)	F^- and $C_2O_4^{--}$ complexes inert
Re(III)	Cl^- complex inert; NH_3 complex probably inert
Re(IV)	Cl^-, Br^-, and I^- complexes inert
Re(V)	Cl^- and CNS^- complexes labile; $ReO_2(CN)_4^{---}$ indeterminate, may be inert
Re(VI)	F^- complex labile
Fe(II)	En and $C_2O_4^{--}$ complexes labile; $Fe(CN)_6^{----}$ (and substitution derivatives), Fe $(ophen)_3^{++}$, and $Fe(dipy)_3^{++}$ inert
Fe(III)	F^-, Cl^-, Br^-, CNS^-, NH_3, $S_2O_3^{--}$, SO_3^{--}, and $C_2O_4^{--}$ complexes labile; $Fe(CN)_6^{---}$ (and substitution derivatives) and $Fe(ophen)_3^{+++}$ inert
Ru(II)	Cl^-, CN^-, and NH_3 complexes inert
Ru(III)	Cl^-, Br^-, and $C_2O_4^{--}$ complexes inert; complex ammines and derivatives inert
Ru(IV)	Cl^- complex inert
Ru(VI)	Cl^- complex labile

TABLE 1—*Concluded*

ELEMENT	LABILITY OF COMPLEX IONS
Os(II)	Cl^- complex inert; CN^- complex probably inert
Os(III)	Cl^- complex inert
Os(IV)	Cl^- complex inert
Os(VI)	F^- complex labile; $C_2O_4^{--}$, NO_2^-, and Cl^- complexes on OsO_2^{++} undergo rapid substitution
Co(II)	Cl^-, Br^-, I^-, CNS^-, and NH_3 complexes labile; $Co(CN)_6^{----}$ may be inert
Co(III)	H_2O in presence of Co^{++} labile; CN^-, SO_3^{--}, NO_2^-, and $C_2O_4^{--}$ complexes inert; complex ammines and derivatives inert
Rh(II)	Br^- in $Rhpy_5Br^+$ slow in substitution
Rh(III)	Cl^-, CN^-, SO_4^{--}, and NH_3 complexes inert
Ir(III)	Cl^-, Br^- probably, and CN^- complexes inert; complex ammines and derivatives inert; SO_4^{--} and $C_2O_4^{--}$ complexes inert
Ir(IV)	Cl^- and py complexes inert
Ni(II)	NH_3, en, $C_2O_4^{--}$, tartrate, and CN^- complexes labile; dipyridyl complex inert
Pd(II)	Coördination number 4 only in complex ions and derivatives; some reactions measurably slow
Pd(IV)	No definite conclusions
Pt(II)	Coördination number 4 only; Cl^- and NO_2^- complexes inert; ammines and derivatives inert; complexes less labile than those of palladium(II)
Pt(IV)	Halide and CNS^- complexes inert; ammines and derivatives inert
Cu(I), Cu(II)	Cl^-, Br^-, NH_3, and SO_3^{--} complexes labile
Ag(I)	NH_3, CN^-, and SO_3^{--} complexes labile
Au(I)	Cl^-, Br^-, CN^- and CNS^- complexes probably labile
Au(III)	SO_4^{--}, Cl^-, and NH_3 complexes inert; NO_3^- complex hydrolyzed rapidly
Zn(II), Cd(II), Hg(II)	Labile
Ga(III)	F^-, Cl^-, and $C_2O_4^{--}$ complexes labile
In(III)	Probably labile
Tl(III)	$C_2O_4^{--}$ complex labile; Cl^- and Br^- complexes not certain
Si(IV)	F^- in SiF_6^{--} measurably slow in substitution
Ge(IV)	No conclusions for coördination number 6
Sn(IV)	No conclusions for coördination number 6
P(V)	PF_6^- inert
As(V)	AsF_6^- and $As(C_6H_4O_2)_3^-$ inert
Sb(V)	SbF_6^- and $SbCl_6^-$ inert
SF_6, SeF_6, TeF_6	Inert

stitution for various reactions are considered within this series, and others similarly composed, certain electronic structures stand out as resulting in slower rates than do others, no matter what reaction is being considered for all. In fact, the influence of the electron structure appears to be so profound that the same general order of lability is maintained whatever be the reactions compared, or the properties of the central ion, if only the electronic structure is specified. Certain types of electron structure almost invariably produce ions of the inert class, while others form ions of the labile class.

It is assumed in discussing the electronic structure of the complex ions that, for all beyond the alkaline earth ions, there is an important covalent contribution to the bonding,[3] and that, for the octahedral complexes considered, the electron density absorbed from the ligands is accepted into the orbital set $D^{2}\,S\,P^{3}$ (215) of the central ion. Electron structures for complex ions of the first transition series have been arrived at by taking account of data on the magnetic moments, these data having been interpreted to yield the number of unpaired electrons. When, after assigning the unshared electrons consistently with the results of the magnetic measurements to the most stable atomic orbitals, a pair or more of inner *d* orbitals is left vacant, it is assumed that the covalent contribution to the binding is made with an orbital set $(n - 1)D^{2}\,nS\,nP^{3}$ of the central ion: i.e., relatively stable *d* orbitals of lower quantum number are hybridized with *s* and *p* orbitals of higher quantum number. When no inner *d* orbitals are available, it is assumed that the electron density contributing to the covalent bonds is fed in to the set $S\,P^{3}\,D^{2}$: in these cases, relatively unstable *d* orbitals are hybridized with *s* and *p* of the same quantum number. For ions of the second and third transition series, it is assumed that the set $(n - 1)D^{2}\,nS\,nP^{3}$ is always used for bond formation if the number of unshared *d* electrons is 6 or less (i.e., up to palladium(IV) and platinum(IV) in these series), the unshared *d* electrons being distributed with maximum unpairing in the remaining *d* orbitals. With ten unshared *d* electrons present, the orbital set $S\,P^{3}\,D^{2}$, as before, is assumed to be used for the covalent contribution to the bonding. The assignments of electron structure in the second and third transition series are consistent in a number of cases (e.g., molydenum(III), molybdenum(V), ruthenium(II), ruthenium(III), palladium(IV), rhenium(IV), osmium(II), iridium(III), platinum(IV), etc.) with the magnetic data, when these are interpreted as they are for ions of the first transition series. There seems to be little reason for doubting the conclusions in these cases, and others in which the configurations[4] $d^{1}\,d^{1}\,d^{1}\,D^{2}\,S\,P^{3}$, $d^{2}\,d^{2}\,d^{1}\,D^{2}\,S\,P^{3}$, $d^{2}\,d^{2}\,d^{2}\,D^{2}\,S\,P^{3}$, have been assigned. A greater degree of doubt exists about the configuration $d^{2}\,d^{1}\,d^{1}\,D^{2}\,S\,P^{3}$, which has been assigned to ruthenium(IV) and rhenium(III). If Hund's rule of maximum multiplicity does not apply to these ions, the structure $d^{2}\,d^{2}\,d^{0}\,D^{2}\,S\,P^{3}$ is also a possibility which must be considered. The magnetic data for rhenium(III) are inconclusive in deciding between the two. Measurements have been made on $RbReCl_4$ and $Re(NH_3)_6Cl_3$ (146), which give for the magnetic moments (as determined by measurements of susceptibility at a single temperature!) a value of *ca.* 0.5 Bohr magneton. For the compound K_2RuCl_6 a magnetic moment of 3.04 Bohr magnetons has been observed, but $K_2[RuOHCl_5]$ was observed to be diamagnetic (189).

The electron structures for the complexes of coördination number 6 fall quite naturally into two classes: in one class, which will be designated as the "inner

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[3] This assumption is discussed in relation to the usual classification of complex ions as "ionic" or "covalent" in Section VI.

[4] Orbitals occupied by unshared electrons are represented by italic type, and the superscript denotes the number of electrons in each. The binding orbitals represented by capital letters are doubly occupied; for these the superscript (italicized) denotes the number of orbitals involved in binding.

orbital" type, relatively stable *d* orbitals of lower principal quantum number are combined with the set $S\,P^3$ of unit higher quantum number; in the other, designated as the "outer orbital" type, the *d* orbitals have a considerably lower stability, since they are of the same principal quantum number group as the *s* and *p* orbitals with which they are hybridized. It will be convenient to consider the two types separately in presenting the correlation of lability with electron structure, which is attempted immediately below.

A. "Inner orbital" complex ions

(*a*) The electronic structures characteristic of the labile members, and representatives of each type of electronic structure, are as follows:

(1) $d^0d^0d^0\ D^2\ S\ P^3$: Sc(III), Y(III), tripositive rare earth ions, Ti(IV), Zr(IV), Hf(IV), Ce(IV), Th(IV), Nb(V), Ta(V), Mo(VI), W(VI), Np(III), Np(IV), Pu(III), Pu(IV)
(2) $d^1d^0d^0\ D^2\ S\ P^3$: Ti(III), V(IV), Mo(V), W(V), Re(VI)
(3) $d^1d^1d^0\ D^2\ S\ P^3$: Ti(II), V(III), Nb(III), Ta(III), W(IV), Re(V), Ru(VI)

(*b*) The electronic structures characteristic of the inert complexes, and examples for each, are as follows:

(1) $d^1d^1d^1\ D^2\ S\ P^3$: V(II), Cr(III), Mo(III), W(III), Mn(IV), Re(IV)
(2) $d^2d^1d^1\ D^2\ S\ P^3$: Cr(CN)$_6^{---}$, Mn(CN)$_6^{---}$, Re(III), Ru(IV), Os(IV)
(3) $d^2d^2d^1\ D^2\ S\ P^3$: Mn(CN)$_6^{---}$, Re(II), Fe(CN)$_6^{---}$, Fe(ophen)$_3^{+++}$, Fe(dipy)$_3^{+++}$, Ru(III), Os(III), Ir(IV)
(4) $d^2d^2d^2\ D^2\ S\ P^3$: Fe(CN)$_6^{----}$, Fe(ophen)$_3^{++}$, Fe(dipy)$_3^{++}$, Ru(II), Os(II), Co(III) in all but F$^-$ complexes, Rh(III), Ir(III), Pd(IV), Pt(IV)

One of the most striking features pointed up by the classification is the discontinuity in rates between the inert and labile classes, which appears at the point at which the last available inner *d* orbital is occupied by an unshared electron. This discontinuity can be demonstrated by a number of comparisons.

V(III) and Cr(III): The simple substitution reactions of vanadium(III) are all rapid; those of chromium(III) are all slow.
Mo(V) and Mo(III): The complexes of molybdenum(III) are in general less labile than those of molybdenum(V).
Re(V) and Re(IV): The complex ions of rhenium(IV) reach equilibrium very slowly with respect to substitution; those of rhenium(V) much more rapidly.

These examples show that the discontinuity in rates which appears at this point as the series of regularly changing electron structure develops is maintained for comparisons with ions of the same charge, with ions of different charge, for ions of the same or different periods, and for reactions involving a variety of ligands.

B. "Outer orbital" complex ions

For this class, the distinction between labile and inert complexes on the basis of electron structure is not nearly as sharp as for the previous class. With central ions of low charge, the complex ions are labile. There is a general decrease in lability in an isoelectronic series as the charge on the central ion increases. An example of such a series is constituted by the hexafluoro complexes of aluminum(III), silicon(IV), phosphorus(V), and sulfur(VI). The fluoro complex ions for aluminum(III) are still quite labile, SiF_6^{--} hydrolyzes at a rapid but measurable rate, PF_6^- hydrolyzes slowly, and SF_6 hydrolyzes exceedingly slowly.

Among the cations forming labile complex ions having electron structures of the "outer orbital" type are: Al^{+++}, Mn^{++}, Fe^{++}, Fe^{+++}, Co^{++}, Ni^{++}, Zn^{++}, Cd^{++}, Hg^{++}, Ga^{+++}, In^{+++}, and Tl^{+++}. Among the complexes which reach equilibrium measurably slowly are: SiF_6^{--}, PF_6^-, AsF_6^-, $SbCl_6^-$, SF_6, SeF_6, and TeF_6.

Comparison of the results of classifying the complex ions in respect to their electron structures with the conclusions reached in the previous section on the basis of a survey of the experimental data shows that there is a close correspondence. In a number of cases, the observations for the ions included in the classification of the present section are still inconclusive, but in few cases is there a definite disagreement with the correlation. However, it should be emphasized again that the differences in lability indicated can have very reliable meaning only when a common reaction under common conditions is considered, although in a general way the difference of lability between two cations of two electronic structure types (Cr^{+++} and Ga^{+++}, for example) is maintained even when different reactions under common conditions are compared for the two.

VI. RATIONALIZATION OF THE RELATION OF LABILITY TO ELECTRON STRUCTURE

If the assumptions which were made in the assignments of the particular electron structures to complex ions are adopted, the correlation of the previous section can be regarded as an empirical effort, the value of which is determined by its validity and the usefulness of its consequences. It seems of interest now to enquire into reasons for the relation which exists between lability and electron structure. In embarking on this task, two points of view suggest themselves: (*1*) that the electron structure affects the rate by affecting the type of binding (i.e., degree of covalent character); (*2*) that the influence of electron structure on lability is directly felt and may therefore not be a simple function of type of binding. At the outset, the conclusion of the inquiry will be stated: the degree of covalent binding alone does not determine the rate, but the electronic structure appears to have a most important influence *per se*.

Attempts to account for the differences in rate simply in terms of degree of ionic or covalent character of the bonds meet with immediate difficulties. Thus, it seems likely that because of the higher charge and smaller radius for the first member of each of the pairs: molybdenum(V) and molybdenum(III), tungsten(V) and tungsten(III), rhenium(V) and rhenium(IV), the bonds in the various complexes of the first members would be more covalent than for similar complexes of the second members. However, the rates of substitution are more rapid for the first members of each pair. Considering now the series of ions of equal charge and similar radii: Al^{+++}, V^{+++}, Cr^{+++}, Fe^{+++} (in the "outer orbital" type of complexes), and Ga^{+++}, it is observed that only Cr^{+++} is exceptional in its rate behavior, all of its substitution reactions being slow. However, on applying a variety of tests (125), no evidence appears that the binding in chromic-ion complexes is more covalent than that obtaining in all the others. The most satisfactory discussion of this point can be based on the behavior of the aquo complexes. It can reasonably be supposed that, other things being equal, the acidity of the aquo ions will increase as the covalent contribution to the bonds with water increases, since a greater covalent contribution will mean stronger polarization of the water molecules. The dissociation constants for the aquo acids Al^{+++} aq. (22), V^{+++} aq. (77), $Cr(H_2O)_6^{+++}$ (23), Fe^{+++} aq. (27), and Ga^{+++} aq. (197) are 1.4×10^{-5}, 1×10^{-3}, 1×10^{-4}, 6×10^{-3}, and 4×10^{-4}, respectively. The aquo-chromic ion does not occupy an exceptional position in this series. In fact, the data indicate that the quality of the interaction of cation and water is nearly the same for all in the series, since each of the cations enhances the acidity constant of water from $10^{-14}/55$ to a value of the order of 10^{-4}. As a second test of the interaction between these cations and water, the hydration energies can be considered. It can reasonably be supposed that, other things being equal, a peculiarly strong covalent contribution to the binding between the cations and water would result in a hydration energy of abnormal magnitude. The hydration energies ($-\Delta H_{\text{hyd}}$) which are calculated from the data in *Tables of Selected Values of Chemical Thermodynamic Properties* (261), using for chloride ion the common value $\Delta H_{\text{hyd}} = -88.7$ (166), are 1109, 1048, 1038, and 1115 kcal. for Al^{+++}, Cr^{+++}, Fe^{+++}, and Ga^{+++}, respectively. Again, there is no evidence that there is a peculiar interaction for chromic ion and water. Lastly, data on the stability of complex ions can be considered as a test of the type of interaction between the central ions and the ligands. Here it seems a plausible argument that central ions tending to make covalent bonds will form complex ions which are relatively more stable with polarizable ligands. Thus, the stability of the chloride complex relative to the fluoride complex might be expected to increase, the greater the tendency of the central ion to form covalent bonds. The data on the stability of halide complexes are unfortunately still too incomplete to apply a satisfactory test based on these ideas. Such data as there are, however, do not place Cr^{+++} in an exceptional position relative to Al^{+++}, Fe^{+++}, and Ga^{+++}. The constants governing the reaction

$$M^{+++} + HF = MF^{++} + H^+$$

at 25°C. and $\mu = 0.5$ are 1570, 26, 189, and 120 for Al^{+++} (33), Cr^{+++} (287), Fe^{+++} (62), and Ga^{+++} (287), respectively. While there are differences in the stabilities of these complexes, it is not obvious how they might be considered to point to a strikingly more covalent type of binding on the part of chromic ion. Nor does this view receive any support when ratios of stability are compared. The ratio of the stability constants of ferric ion and chromic ion in the fluoride complexes is 8; in the chloride complexes it is *ca.* 16. If the data on affinities indicate anything about the type of binding, they suggest that it is remarkably similar for the four cations considered, aluminum ion perhaps being the most "ionic."

It should be pointed out that the arguments of the previous section are not invalidated if allowance is made for the slight variation in ionic radius among the ions which were compared. The value of the ionic radius for chromic ion is bracketted by those for aluminum ion and ferric ion and is very nearly the same as that for gallium ion. The conclusion seems unavoidable that the differences in rate observed for ions of differing electron structure cannot be attributed solely to differences in type of binding in the complex ions. Although reactivity with respect to substitution has sometimes (14, 70) been taken as a measure of the degree of covalent character of the bonds, it is evident that dependable conclusions cannot be arrived at in this way without further qualification.

While variations in the degree of covalent character of bonds in complex ions do not account directly for the main features of the correlation of lability with electron structure, this parameter nevertheless is a factor of importance. Thus, the decrease in lability observed for an isoelectronic series of complexes of the "outer orbital" type—e.g., AlF_6^{---}, SiF_6^{--}, PF_6^-, and SF_6—can, in part at least, be attributed to the increasing covalent character of the bonds in the complex ions. This factor also makes itself evident, in an indirect way, by influencing the electronic structure of certain complex ions of the first-row transition elements. Some of these ions, notably Mn^{++}, Mn^{+++}, Fe^{++}, Fe^{+++}, Co^{++}, and Co^{+++}, form complexes of both the "outer orbital" and the "inner orbital" type. The complexes of the "outer orbital" type for these ions are invariably labile with respect to simple substitution, and those of the "inner orbital" type are inert. The factors determining the electronic structure type of the complex ion are therefore important in understanding the lability of the various complexes. Of these factors, an important one appears to be the extent of the covalent contribution to the binding in the complex. In general, considering a particular cation, as the associated ligands become more polarizable (i.e., as the covalent contribution to the bonds increases), the electronic structure of the ground state of the complex ion changes from that of the "outer orbital" type to that of the "inner orbital" type. This can be illustrated by the behavior of cobaltic ion with the ligands fluoride ion, water, and ammonia. The polarizability of these ligands increases from fluoride ion to ammonia. The complex of cobaltic ion with fluoride ion has four unpaired electrons and is therefore of the "outer orbital" type. The aquo complex (26, 75) and the hexammino complex have no unpaired electrons and are therefore of the "inner orbital" type. Qualitatively, the change in electronic structure can be understood fairly readily. The driving force for the formation of the "inner orbital" complex in preference to the "outer orbital" complex is presumably the possibility of stronger polarization of the ligands when the relatively stable pair of inner d orbitals is used for binding rather than the less stable outer pair. Opposing it is the energy required to raise the cation to a state in which a pair of inner d orbitals is left vacant by pairing unshared d electrons. The second factor remains constant as ligands become more polarizable, but the first one becomes more important; hence, at a certain stage, a complex of the "inner orbital" type can eventually be expected to become more stable than the corresponding one of the "outer orbital" type. The relations obtaining as the central ion is varied are considerably more complex than those for a series with a common cation and varying ligands. A change in the central ion changes both the energy required to produce the excited state and the difference in energy produced by substituting inner *d* orbitals for outer *d* orbitals in the binding of the ligands, and it is difficult to estimate the balance between these factors as a function of electron structure. It is of interest, however, to direct attention to some features of the observations. One noteworthy point is that in the transition elements of the second and third rows, if inner orbitals can be made available without promoting electrons, the complexes are always of the "inner orbital" rather than the "outer orbital" type, whatever the nature of the ligands. Consideration of data on the acidity of ammino (31) complexes (using the arguments developed earlier for the aquo complexes) suggests that the bonds in these complexes are not strikingly more covalent for the heavier transition elements, and that the differences in electron structure can presumably be attributed more to differences in the energy required to produce the excited states by pairing unshared *d* electrons. Another observation of interest is that "inner orbital" complexes for cobaltous and nickelous ions, although formed in a few cases, are not as abundant as they are for cobaltic and ferric ions. With cobaltous and nickelous ions, formation of "inner orbital" complexes requires the promotion of one and two electrons, respectively, from inner orbitals to outer, less stable orbitals, and the expenditure of energy for this process limits the possibilities. With cuprous and zinc ions, four electrons would have to be promoted to form "inner orbital" complexes. There is no evidence that complexes of this type are formed with these cations.

The discussion of the previous paragraph has shown that variation in the bond type exercises an influence on the rate. In an important set of cases this influence is indirect, the variation in degree of covalent character being an important factor in determining, for those ions for which both possibilities exist, whether the complex ion will be of the "inner orbital" or the "outer orbital" electronic type. Earlier discussion has emphasized that the differences in electronic structure are responsible, *per se*, for the gross features of the variations in lability as the central ion is changed.

It seems appropriate to digress from the principal thesis of this section to discuss the classification of complex ions. This digression is particularly appropriate at this point, since the discussion just preceding has a direct bearing on the practice of classifying complex ions as "ionic" or "covalent." These terms have been used to distinguish the complex ions described in this report as of the "outer orbital" type from those of the "inner orbital" type for cations which form both types of complexes. In this limited sphere the terms have some applicability, since for the same cation the complexes of the "outer orbital" type do appear to have less covalent bonds than those of the "inner orbital" type. However, the practice of describing others by these terms has also become prevalent, and the criteria upon which the classification is based in other cases have never been clearly defined. One of them appears to be that lability is taken as a measure of ionic character. The dangers of such an oversimplified approach have been set forth at some length in the preceding paragraphs. The terms do appear to be quite inappropriate in general, since all of the complex ions must reasonably be supposed to make bonds which are partially covalent, and there is no reason whatever to suppose that there is a sharp transition from complexes with essentially covalent bonds to those with essentially ionic bonds. Furthermore, it seems probable that some complexes of the "outer orbital" type which are described as "ionic" have more covalent bonds than some of the "inner orbital" type which are described by the term "covalent." A comparison illustrating this paradox in the use of the terms "ionic" and "covalent" is that between Ga^{+++} aq. and Cr^{+++} aq. Of these, it is not unlikely that Ga^{+++} makes slightly more covalent bonds with ligands than does Cr^{+++}, although Ga^{+++} aq., but not Cr^{+++} aq., would be classified as "ionic." No particular brief will be made for the names which have been attached to the various classes of complex ions suggested in this paper. The classifications which have been proposed do, however, pretend to merit. Of these, the empirical classification as "inert" and "labile" is based on an important aspect of the behavior of the complex ions—the differences in lability of the ions with respect to substitution. The theoretical classification focusses attention on an important feature of the electron structure of the complex ions. Its significance in considering lability has already been suggested and will be further amplified when the mechanism of substitution is considered. It may be noted that the "inert" complexes of the "inner orbital" type correspond to the class of *Durchdringungscomplexe* described by Klemm (143).

In rationalizing the correlation of lability with the electronic structure, it must be borne in mind that an explanation is demanded which can account for extreme differences in rate without requiring extreme differences in the type of binding, stability, or other equilibrium properties of the complex ions. With this in mind, the idea suggests itself to look for an explanation by examining the properties of the transition states which can reasonably be expected for the substitution processes. On this basis, important features of the observations can readily be rationalized.

Considering first the complex ions which have electronic structures of the "inner orbital" type, the most striking observation presented for explanation is that there is a sharp difference in rate of substitution for complexes which have one or more vacant inner *d* orbitals, and those for which the inner *d* orbitals are completely occupied. Since for the whole series consisting of ions of the same row inner *d* orbitals are being used for binding, a sharp discontinuity in bond type or stability of the complexes will not be expected. In spite of this similarity in properties and stability for the complex ions, a sharp discontinuity in the energy required to generate the activated intermediate complex can be expected. When one or more stable inner *d* orbitals[5] is available, it can reasonably be expected that substitution proceeds by an intermediate complex of coördination number 7. The incoming group can make use of a stable orbital and this additional interaction helps to stabilize the intermediate complex, providing a path of low activation energy for the reaction. If, however, the inner *d* orbitals are

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[5] These vacant orbitals correspond to the metallic orbitals postulated by Pauling (217) to explain the properties of metals.

completely occupied, the activation energy by this path will be considerably higher, since unshared electrons must be promoted to higher orbitals or must be paired to make a useful orbital available. The alternative path, in which a ligand is lost in the rate-determining step, can also be supposed to require a high activation energy, since there is no factor which compensates effectively for the energy required to remove the group.

Considering ions with electronic structures of the "outer orbital" type, the observation which needs explanation is that the complex ions are labile when the charge on the central cation is small (1, 2, or 3) but become inert when the charge builds up to high values. It seems not unlikely that complex ions of the "outer orbital" type undergo substitution by a dissociation mechanism, at least when the charge on the central ion is low. In such a dissociation for these ions, while there is an expenditure of energy to remove one of the groups, there is a compensating influence; for in removing one or two ligands, the average stability of the orbitals responsible for the covalent contribution to the binding is increased by the removal from hybridization of one or two of the relatively unstable outer *d* orbitals. The observation that many of the cations of complex ions belonging to the "outer orbital" type fairly readily assume coördination number 4 supports the suggestion about mechanism and the explanation offered. Thus, aluminum and ferric ions have a coördination number of 6 toward chloride ion in the solid chlorides. With a relatively small uptake of energy, 13.4 kcal. per mole of aluminum chloride (261), the solid is transformed to a vapor in which the coördination number of aluminum ion to chloride ion is 4. By contrast, chromic ion, a typical ion forming complexes of the "inner orbital" type only, has not been observed in a complex of coördination number 4, and very great energies are required to convert the solid chloride to vapor. As the charge on the central ion increases for complexes of the "outer orbital" type, several factors will contribute to the decrease in lability. The bonds will presumably become more covalent as the charge increases, and this will contribute to a higher activation energy, whatever be the mechanism of substitution. It seems probable that the difference of energy between the state of coördination 6 and a state of lower coördination number becomes greater as the charge on the central ion increases, at least up to the point at which the central ion becomes so small that steric interferences between the ligands begin to limit stability.

VII. COMPLEXES OF COÖRDINATION NUMBER OTHER THAN SIX

Considerations of the type which have been applied in correlating the observations for complexes of coördination number 6 apply directly to those of coördination number 8. Among the ions for which the coördination number in solution is almost certainly 8 are $\mathrm{Mo(CN)_8^{----}}$, $\mathrm{Mo(CN)_8^{---}}$, $\mathrm{W(CN)_8^{----}}$, and $\mathrm{W(CN)_8^{---}}$. Of these complexes, those having the central ion in oxidation state +4 are diamagnetic (146), while $\mathrm{Mo(CN)_8^{---}}$ (228) has a magnetic moment corresponding to one unpaired electron. Electronic structures consistent with these data are:

$$d^2\ D^4\ S\ P^3 \text{ for } \mathrm{Mo(CN)_8^{----}} \text{ and } \mathrm{W(CN)_8^{----}}$$

and

$$d^1 D^4 S P^3 \text{ for } Mo(CN)_8^{---} \text{ and } W(CN)_8^{---}$$

Since inner stable orbitals are completely occupied, slow rates of substitution are expected for these ions, as is observed to be the case.

Among complex ions which probably have coördination number 4 in solution and, if so, undoubtedly have a tetrahedral arrangement are those of Hg^{++} with Cl^-, Br^-, I^-, NH_3, CN^-, and CdI_4^{--}, all of which are relatively labile. It seems fairly certain that net substitution in these complexes proceeds by a substitution mechanism. Even for a carbon atom, which because of its small size would offer less favorable geometry, this type of mechanism is possible. The substitution mechanism is relatively favored for the metal ions also because outer orbitals (d) are available for interaction with the incoming group. With carbon as the central atom, the only vacant orbitals are those of higher principal quantum number. A special class of complexes of coördination number 4 with tetrahedral symmetry are oxy-anions such as perchlorate, sulfate, and chromate. Within this class, a general increase in lability as the size of the central ion increases and its charge decreases can be noted. In a comparison of results for these ions with complexes such as those of Hg^{++} referred to above, it must be recognized that exchange of the oxygen of the oxy-ions with the solvent is not a simple substitution process of the type defined. The exchange process requires, in addition to the formation and release of bonds between oxygen and the central atom, formation and release of H^+–O^{--} bonds. An electronic interpretation of the observations on the exchange phenomena for the oxy-ions must admit the possibility that the bonds to the central ion are not simply single bonds occupying $S P^3$ orbitals for the central ion, but that the shared electron density may correspond to double bonds (221).

A particularly interesting class of complex ions of coördination number 4 consists of those with the coplanar arrangement of the central ion and the four ligands. The electron density contributed by the attached groups is presumably accepted into the orbital set $D S P^2$ of the central ion. These ions range in lability from very labile [$Ni(CN)_4^{--}$] to inert (Pt^{++} complexes). Consideration of electron structure alone would suggest that substitution in all cases should be rather rapid, since a relatively stable orbital (p) is available for interaction with the incoming group. Considerable activation energy may be required, however, to form the activated complex of appropriate geometry. A possibility for the reaction intermediate is a trigonal bipyramidal arrangement with the five attached groups making use of the orbital set $D S P^3$. Net exchange is completed when one of the apical groups is lost, and the resulting complex resumes the stable planar configuration.

The rate behavior of a large number of compounds of coördination number 4 remains essentially unexplored. An important group of this type includes organic derivatives of the elements of Groups IV, V, and VI. A beginning in this field has been made by Swain, Estese, and Jones (260), who have studied the hydrolysis of fluorotriphenylsilane, $(C_6H_5)_3SiF$. The points of view which have stimulated so much important work in studying the rates of substitution on carbon apply directly to the compounds with silicon, germanium, etc. as central atoms, and there is little doubt that exploration of the inorganic compounds would reveal interesting relations. The conclusion reached by Swain and coworkers is that in the silicon compound studied the substitution takes place by a mechanism involving a transition state of coördination number 5 for the silicon atom. This mechanism is favored for silicon in comparison with carbon because of the larger size of the silicon atom, and because orbitals (*d*) relatively more stable are available for interaction with the incoming group. A similar mechanism is expected therefore for substitution on corresponding germanium, tin, and lead compounds. In some cases, however, a dissociation mechanism can be anticipated for inorganic complexes of coördination number 4. A system in which this type of mechanism would not be surprising is BF_4^-. Exchange of F^- with BF_4^- can conceivably occur by operation of the equilibrium: $BF_4^- \rightleftarrows BF_3 + F^-$. An important difference between boron on the one hand, and carbon, silicon, etc. on the other, is the greater stability of complexes of coördination number 3 for boron.

The importance of the role which electronic structure can play in affecting mechanism for ions of coördination number 4 is evident from the few comparisons offered. An important influence of electronic structure on the rate can also be expected. Its role in influencing this property may, however, be difficult to isolate, since no extensive series of complexes with this as the only important variable can be separated for discussion.

VIII. GENERAL CONSIDERATIONS

Any success which the correlation of rate of substitution with electronic structure attempted for complex ions of coördination number 6 has depends on the condition that rearrangement of electrons for complex ions having inner relatively stable orbitals completely occupied requires a considerable input of energy. For free gaseous ions, this condition would in general be realized; for complex ions, however, the situation is complicated by the contribution to the total energy furnished by the interaction of the ligands with the central ion. Exceptions to the simple empirical conclusions can be expected, and are in fact observed.

A system which is probably an exception to direct application of the empirical rule is Co^{+++}aq. It has been shown that exchange of water with the hydrated ion is rapid (76), very much more rapid than replacement of ammonia in an ion such as $Co(NH_3)_6^{+++}$ by water. It has also been shown that the magnetic moment of the ion is very nearly the same as that of Ga^{+++} (75). Hence, the electronic structure of most of Co^{+++}aq. is: $d^2\ d^2\ d^2\ D^2\ S\ P^3$, a structure which is expected to lead to a slow rate of substitution. It seems fairly likely, however, that the paramagnetic labile state ($d^2\ d^1\ d^1\ d^1\ d^1\ S\ P^3\ D^2$) for Co^{+++}aq. is only slightly above the diamagnetic ground state in energy. This relation can be expected from the known facts that in the complex with fluoride ion, the paramagnetic state is the more stable (42), while for ammonia the diamagnetic state is more stable. Water is intermediate in polarizability between fluoride ion and ammonia; hence the diamagnetic state is not stabilized as much relative to the paramagnetic state as when ammonia is the ligand. A difference of only a few kilocalories in energy between the two states would result in a system in which most of the complex ion could be in a diamagnetic state but still fairly labile with respect to substitution.

A similarly close balance between the energies of "inner orbital" and "outer orbital" complexes for a given central ion can be expected in other systems. It is apparently encountered in Fe^{++}– and Fe^{+++}–porphyrin systems. Thus hemoglobin, in which four of the octahedral positions about Fe^{+++} are occupied by porphyrin nitrogen, one by a group contributed by the protein, and the sixth presumably by water, has a magnetic moment of 5.80 Bohr magnetons and the complex is obviously of the "outer orbital" type. The magnetic moment of hemoglobin fluoride is 5.90 Bohr magnetons. The polarizable groups CN^- and HS^- convert the complex to the "inner orbital" type and reduce the magnetic moment to values corresponding nearly to one unpaired electron. Hydroxide ion, which is intermediate in polarizability between water and hydrosulfide ion, produces a complex in which the magnetic moment of ferric ion is 4.47 Bohr magnetons (54). A possibility in explaining the intermediate value of magnetic moment for hemoglobin hydroxide is that the system contains the "inner orbital" and "outer orbital" forms in equilibrium with each other. A system in which the "outer orbital" and "inner orbital" states have nearly the same energy would combine the virtue that an attached group is strongly polarized (this results from interaction with stable inner orbitals) and thereby activated for certain reactions with the high lability with respect to substitution characteristic of many outer orbital complexes. These conditions would appear to be favorable for some types of enzyme action.

Adopting the view that for them a rearrangement of electrons takes place on the formation of the activated intermediate complex, important differences in rates of substitution can be expected among the complex ions of the "inner orbital" type, having the inner orbitals completely occupied. For the purpose of simplifying the discussion immediately following, it will be assumed that the mechanism is one of substitution, involving an activated complex of coördination number 7. Since the observations are for the most part qualitative, significance can be attached only to striking differences in rate. One type of electron structure which does stand out as being associated with more labile systems than others of the inert, inner orbital class is that shared by manganese(III) in the cyanide complex, and ruthenium(IV) in its complex ions. Although exchange of cyanide ion with $Mn(CN)_6^{---}$ is measurably slow, the rate is considerably greater than for any of the other cyanide complexes of the class under discussion. Ruthenium(IV), in its turn, appears to undergo substitution in complex ions more rapidly than other ions of its class in the same period. The complex ions under discussion presumably have the electronic structure $d^2\ d^1\ d^1\ D^2\ S\ P^3$. It seems not unlikely that relatively little energy is required to go from this state, which may be considered to be relatively unstable, because it is derived from the stable $d^1\ d^1\ d^1\ D^2\ S\ P^3$ state by the addition of an electron, to the state $d^2\ d^2\ D^3\ S\ P^3$ for the activated complex of coördination number 7, thus accounting for a fairly rapid rate of substitution. On this basis, $Cr(CN)_6^{----}$ is expected to be more labile than the analogous complexes $Fe(CN)_6^{----}$ or $Mn(CN)_6^{----}$.

A number of complex ions do not fit the electronic structure types which have been proposed. An important class is that constituted by polynuclear complexes having metal–metal interactions. The metal–metal separations in the polynuclear complex halides of molybdenum(II), tungsten(II), niobium(II), tantalum(II), and in $W_2Cl_9^{---}$ (32, 34, 268) are such that metal–metal bonds can reasonably be postulated (216). Such interactions would tend to fill inner orbitals more completely, and in general result in low rates of substitution for attached groups. In all the cases mentioned, there is evidence for measurably slow rates in certain stages of substitution. The situation, particularly for the polynuclear complexes of the dipositive ions mentioned, is complicated, since the bonds which any particular metal ion makes with associated ligands may not all be equivalent.

In some complex ions, ambiguity exists about the description of the electronic structure in terms of the language adopted. This is true of hexacoördinated Ni^{++} complexes. The ion $Ni(NH_3)_6^{++}$ can be formulated as: $d^2\ d^2\ d^2\ d^1\ d^1\ S\ P^3\ D^2$ or $d^2\ d^2\ d^2\ D^2\ S\ P^3\ d^1\ d^1$. Both formulations are consistent with measurements of the magnetic moment. For an ion in which the two states have nearly equal energy, or with the former as the more stable type, a labile system with respect to substitution can be expected, but with the second as the more stable configuration, a slower rate of substitution should result. On this basis the complex ion $Ni(NH_3)_6^{++}$ or $Nien_3^{++}$ would be formulated as of the "outer orbital" electronic type but $Ni(dipy)_3^{++}$ as of the "inner orbital" type.

The electronic structure type which has four inner *d* orbitals singly occupied by unpaired electrons has been omitted completely from the preceding discussion. With central ions of this electronic type, an ambiguity exists as to the coördination number. If the coördination number of the corresponding ions (Cr^{++}aq. and Mn^{+++}aq. are examples) is 6, the electronic structures $d^1\ d^1\ d^1\ d^1\ D\ S\ P^3\ D$ or $d^1\ d^1\ d^1\ D^2\ S\ P^3\ d^1$ are to be expected, and in these systems labile or inert complexes may result, depending on the energy of interaction of the central ion with the associated groups (the case is similar to that discussed for nickel(II)). However, another reasonable formulation would appear to be as a complex ion with coördination number 4, the electron structure being $d^1\ d^1\ d^1\ d^1\ D\ S\ P^2$. At present, there are no data which establish the coördination number for these complex ions.

The coördination number comes into question in other cases as well, including such ions as Al^{+++}aq., Fe^{+++}aq., and Ga^{+++}aq. The point has already been made that these ions display variable coördination number when chloride ion is the associated group. In the earlier discussion it was assumed that the coördination number for water is 6 in solution, but the possibility that a part, or even the major part, of the hydrated cations is tetraaquated is not excluded. The determination of the coördination number remains an important problem for aquo cations, as well as for partly substituted aquo ions (e.g., $FeCl^{++}$ and $FeCl_2^{+}$). Two particular cases appear worthy of mention: $ReO_2(CN)_4^{---}$ and $OsO_2(CN)_4^{--}$. From the positions of rhenium and osmium in the periodic table, and their behavior, it does not seem unreasonable to suppose that these ions may have coördination number 8 in solution and could therefore be represented as $Re(OH)_4(CN)_4^{---}$ and $Os(OH)_4(CN)_4^{--}$. The electronic structures would then correspond to that of $Mo(CN)_8^{----}$ and $W(CN)_8^{----}$: namely, $d^2 D^4 S P^3$.

IX. QUALITATIVE OBSERVATIONS RELATING TO THE LABILITY OF COMPLEX IONS

A. Miscellaneous ions

Aluminum(III): Under most conditions, the system Al^{+++}–F^- reaches equilibrium without noticeable delay. Brosset and Orring (35) note, however, that the electrode potential for the equilibrium Fe^{++}–Fe^{+++} is established measurably slowly in a system containing also aluminum ion and fluoride ion, if fluoride ion is less than equivalent to the trivalent ions. This behavior may be due to a measurably slow reaction of aluminum ion and fluoride ion when the latter is maintained at very low concentrations. The $Al(III)$–$C_2O_4^{--}$ complex ions decompose in acid without noticeable delay.

Scandium(III), titanium(III), ytterbium(III), rare earth ions of valence + 3, plutonium(III), neptunium(III), titanium(IV), zirconium(IV), hafnium(IV), cerium(IV), thorium(IV), neptunium(IV), plutonium(IV): No cases of slow complex-ion formation or dissociation, involving simple substitution, have been reported for these ions. Even reactions involving bidentate chelating groups such as tartrate or acetylacetonate reach equilibrium rapidly—e.g., with titanium(IV), zirconium(IV), plutonium(IV). Under some conditions, the observations with many of the cations are complicated by the existence in solution of polynuclear species, which may reach equilibrium only slowly.

Some specific examples of reactions involving the formation of complex ions are the following:

Scandium(III) is extracted without delay from aqueous solution as the thiocyanate by ether (72).

A color change takes place rapidly when fluoride ion or thiocyanate ion is added to a solution of titanium trichloride (214).

A number of complex ions of zirconium(IV) have been studied by Connick and McVey (53), among them the complexes with fluoride, sulfate, nitrate, and chloride ions. No evidence was obtained that the reactions are slow.

When chloride is added to a solution containing cerium(IV) in perchlorate solution, a color change takes place at once.

The fluoride complex of thorium(IV) reaches equilibrium without noticeable delay (62).

No mention of slowness is made by the various authors in describing the formation in aqueous solution of the chloride (116), fluoride (182), or oxalate (229) complex ions of plutonium(IV).

B. Ions of elements of Group V B

Vanadium(II): There is very little literature on the chemistry of complex ions formed by dipositive vanadium in aqueous solution. The complex ions with ligands such as halides or thiocyanate ion are probably not stable, unless the associating groups are present at very high concentration. The ion $V(CN)_6^{----}$ has been reported (218), but the description in the literature leads to no conclusions about its lability. Roscoe (234) has conducted some experiments on the rate of decomposition of this ion in acid. A solution containing $V(CN)_6^{----}$ is originally red but changes gradually, over about a 2-min. interval, to the blue color characteristic of V^{++}aq. when sulfuric acid is added in amount equivalent to the cyanide ion.

Vanadium(III): Complex ions of vanadium(III) with fluoride, thiocyanate, pyrophosphate, and citrate ions have distinctive colors. Simple mixing experiments show that color changes indicating reaction take place very rapidly. $V(CN)_6^{---}$ in solution decomposes at once, yielding V^{+++}, when treated with dilute sulfuric acid or even a weaker acid such as acetic acid (234). The cyanide complex is described in the literature (178). When ammonia or calcium ion is added to a solution of $K_3V(C_2O_4)_3 \cdot 3H_2O$ in water, precipitation of vanadium trihydroxide and calcium oxalate, respectively, is rapid and complete (222). $V(NH_3)_6Cl_3$ dissolves in dilute hydrochloric acid, forming a solution which has the green color characteristic of V^{+++}aq. (191).

Vanadium(IV) and vanadium(V): These oxidation states in aqueous solution have not been well characterized, and the chemistry is complicated by the formation of polynuclear species. No complex ions inert to substitution, as are those of chromium(III), for example, have been reported.

Niobium(II): Only polynuclear complex ions of this oxidation state are known in solution. The complex chloride described by Harned (113), by analogy with similar tantalum and molybdenum compounds, probably has the formula $H_2Nb_6Cl_{14} \cdot 7H_2O$. A recent investigation of the ion in solution by x-ray (268) diffraction reveals a fundamental structural unit of the formula $[Nb_6Cl_{12}]$. On warming a solution of the complex chloride, only one-seventh of the chloride ion is released (113). The polynuclear structure persists, even in an environment in which it is unstable. Thus, decomposition with ammonia requires continued boiling.

Niobium(III): The ion of +3 oxidation state exists in solutions prepared by electrolytic reduction of niobate in acid. Color changes take place when the concentration of acid in the reduced solution is changed. A solution 3 M in sulfuric acid is blue, while one 6–10 M in sulfuric acid is red. No mention is made in the report on this system of slowness in these color changes (141).

Niobium(V): The aqueous chemistry of this oxidation state is complicated by the formation of condensed species. A number of groups form complexes in solution, among them fluoride ion, hydrogen peroxide, and oxalate ion. There is no evidence for slowness in these association reactions. Solid compounds of the type Cs_2NbOCl_5 and the corresponding compounds with bromide ion in place of chloride ion are hydrolyzed at once in contact with water (285).

Tantalum(II): The compound of formula $H_2Ta_6Cl_{14} \cdot 8H_2O$ dissolves to some extent in water. The chemical behavior (174) suggests that a polynuclear form persists in solution. This conclusion is supported by x-ray diffraction data, which show that the structural unit Ta_6Cl_{12} is present (268) in solution. Chloride is released only slowly and only partially; on boiling, one-seventh of it appears as free chloride ion. Analogous compounds with bromine in place of chlorine are known (173).

Tantalum(III): When tantalum pentoxide is heated with aluminum and aluminum chloride at 300°C. and the product is extracted with water, part dissolves forming a green solution which apparently contains tantalum in the oxidation state +3. The solutions have been little investigated. Among the few experiments reported, one is of present interest. A complex cyanide develops when excess cyanide ion is added, but decomposes on being acidified (248). No mention of delay in this reaction was made.

Tantalum(V): Fluoride ion and oxalate ion associate with tantalum(V). There is no evidence of slowness in these reactions. The compound $(C_5H_6N)_2TaOCl_5$ hydrolyzes rapidly in water, precipitating tantalic acid (285). The chemistry of tantalum(V) is also complicated by the formation of polynuclear ions.

C. Ions of elements of Group VI B

Chromium(II): Chromium of oxidation state +2 in solution can reduce water. This side reaction complicates the observations on the behavior of the complex ions. The complex ions with ammonia, ethylenediamine, and thiocyanate ion are formed when these substances are added at high concentrations to solutions of chromous chloride (123). A test of lability would be to acidify solutions containing the complex ions, but no conclusive observations on experiments of this type have been reported. When $Cr(CN)_6^{----}$ is acidified, oxidation to chromium(III) takes place (123). Anthranilate ion precipitates chromous anthranilate, apparently without delay (123). Isomers of chromous chloride, which persist in acid solution, have been reported (147). A green variety releases one chloride ion per chromous ion to the solution, while the blue variety releases two. The green changes to the blue, very rapidly in neutral solution but only slowly in acid. The report on these observations leaves no room for doubting the conclusions. In view, however, of the difficulties of working with solutions of chromium(II), and of the importance of the observations for correlation of lability with electronic structure, the system merits reinvestigation.

Chromium(III): The chemistry of chromium in the +3 state offers many interesting examples of slow rate of substitution. Polynuclear complexes are formed even by the aquo ion; however, freshly prepared solutions of violet hexaquo salts contain $Cr(H_2O)_6^{+++}$ (124), and at room temperature a period of time of the order of weeks is required before the bridging reactions reach equilibrium (112). The rate of bridge formation is diminished by acid, as is the stability of the bridge structures. Phenomena due to condensation are not determining for the observations on rate which are cited in the following survey.

With chromic ion and hydrofluoric acid, each in concentration of about 10^{-2} *M*, in 0.01 *M* acid the time to reach equilibrium is of the order of weeks. It can reasonably be supposed that all stages of the stepwise association of chromic ion and fluoride ion would take place at measurable rates (287).

N. Bjerrum (21) has studied the equilibrium relationships for systems containing chromic ion and chloride ion. The affinity of chromic ion for chloride ion in solution is quite low. Thus, for a solution 1.06 *M* in chromic chloride at 25°C., 85 per cent of the chromic ion at equilibrium is present as $Cr(H_2O)_6^{+++}$, about 13 per cent as $CrCl^{++}$, and 2 per cent as $CrCl_2^+$. Much higher activities of chloride ion would be required to build up the higher complexes in solution. Bjerrum has also studied the rates of transformation of the green forms $CrCl_2^+$ and $CrCl^{++}$ to Cr^{+++} and Cl^-. The changes are slow, and for the solution described above, the time necessary to reach equilibrium is of the order of weeks. The reactions increase in speed, however, as the solutions become less acidic. Solids of composition K_3CrCl_6 (1) and $K_2CrCl_5H_2O$ (204) can be prepared. Werner and Gubser (283) have shown that when silver nitrate is added to a freshly prepared solution of $K_2CrCl_5 \cdot 5H_2O$, a precipitate of silver chloride does not form at once. The replacement of chloride ion by water, even from the highly unstable ion $CrCl_5H_2O^{--}$, thus takes place at a measurably slow rate.

The affinity of chromic ion in solution for bromide is even less than it is for chloride. The rate of replacement of bromide ion by water is greater than the rate of replacement of chloride ion, but is by no means instantaneous. The ion $CrBr_2^+$ is known in solution (24), and the ion $CrBr^{++}$ presumably also exists. The solid of composition $Rb_2CrBr_5H_2O$ (1) and others of similar composition have been prepared. These substances dissolve, forming solutions which are initially red but which rapidly turn green.

The trend in affinity noted in the series fluoride ion, chloride ion, bromide ion presumably continues to iodide. In any event, no complexes of aquo-chromic ion with iodide ion have been reported.

N. Bjerrum (25) has studied the equilibrium aspects of the system Cr(III)–CNS^- very thoroughly, and has recorded a number of semiquantitative observations on the rate of change. In somewhat acidic solutions, the rates of change for all of the steps are slow; under ordinary conditions at room temperature, the changes are not complete even after a week. The lability of thiocyanate ion in the ions in which replacement of water by thiocyanate ion is not yet complete decreases as the acidity rises, but for $Cr(CNS)_6^{---}$ it is not affected by acidity.

$Cr(CN)_6^{---}$ is decomposed by hydroxide ion and sulfide ion, but only on prolonged boiling. Acid solutions are also unstable, and decompose at a measurable rate.

Observations with sulfate (2), oxalate (3), and tartrate (187) show that these groups associate with chromic ion or are released from chromic ion at slow measurable rates under ordinary circumstances.

The chromammines constitute a large class of complex ions based on coördination number 6 for chromium. Complexes exist in which the positions left vacant by ammonia may be filled by other neutral species or by ions. Thus, in the series $Cr(NH_3)_6^{+++}$. . .$Cr(H_2O)_6^{+++}$ and $Cr(NH_3)_6^{+++}$. . .$Cr(CNS)_6^{---}$ only the species $Cr(NH_3)(H_2O)_5^{+++}$ and $Cr(NH_3)(CNS)_5^{--}$, respectively, have thus far not been prepared. As is true for the aquo complexes, replacement of anions by water (or ammonia or other anions) is a slow process also in the ammine series. A few examples will be cited to demonstrate that the Cr(III)-NH_3 bond itself is not labile to substitution. A solution of $Cr(NH_3)_6(NO_3)_3$ decomposes slowly on standing at room temperature, with the formation of chromic hydroxide. This change is accelerated on boiling, or when hydroxide ion is added, but the rate is diminished when acid is added. In concentrated hydrochloric acid the luteo ion is slowly converted to $Cr(NH_3)_5Cl^{++}$ (134). It is noteworthy that the chromammines are essentially unstable in water, at ordinary low concentrations of ammonia. This is demonstrated by the decomposition of $Cr(NH_3)_6^{+++}$ recorded above, and by the additional observation that when ammonia is added to a solution of $Cr(NH_3)_5H_2O^{+++}$, $Cr(OH)_3$ is formed rather than $Cr(NH_3)_6^{+++}$ (48). $Cren_3^{+++}$ in water at room temperature also persists for long periods of time, but on heating, the solution becomes red (roseo complex?), then green, and eventually chromic hydroxide is precipitated (219). *Cis* and *trans* forms of $Cren_2(H_2O)_2^{+++}$ persist in water, but unless the solution is acid, the *trans* species changes to the *cis* in a matter of days (220). *Cis* and *trans* forms of $Cren_2Cl_2^{++}$ etc. persist in solution.

Molybdenum(II): The simple ion of this oxidation state is not known in water solutions. While solids of simple composition, corresponding to this oxidation state, exist (e.g., $MoCl_2$, $MoBr_2$, MoI_2), they are not soluble in water. However, when molybdous chloride is treated with concentrated hydrochloric acid, the compound of formula $HMo_3Cl_7 \cdot 4H_2O$ may be obtained. Aqueous solutions are unstable; after a few seconds a precipitate forms which contains all the molybdenum, while the solution contains part of the chloride ion. At maximum, three out of seven chloride ions are released to the solution. Solvolysis does not take place in alcohol, and in this medium, three out of seven chloride ions (175) can be precipitated at once by silver ion. Chemical evidence (87) suggests that this and related compounds contain a polynuclear unit as a fundamental structural unit. Brosset (34) has shown by analysis of x-ray diffraction data for the solid $Mo_3Cl_4(OH)_2(H_2O)_8$ that the polynuclear $Mo_6Cl_8^{+4}$ is present. An analogous unit presumably functions in the chemistry of the corresponding complex bromine compounds (176).

Molybdenum(III): Complex fluorides containing the ion MoF_6^{---} have not been reported. The compounds $KMoF_4 \cdot H_2O$ and $NH_4MoF_4 \cdot H_2O$ have, however, been prepared (236). The potassium compound is not very soluble in water. On long standing at room temperature, $Mo_2O_3 \cdot nH_2O$ is formed. No definite conclusions about the lability of the Mo(III)–F^- bond can be drawn from the published observations.

The affinity of chloride ion for Mo^{+++} in solution is quite small. Thus each of the compounds K_3MoCl_6, $(NH_4)_2MoCl_5H_2O$, $KMoOCl_2 \cdot 3H_2O$ (36), and $MoOCl \cdot 4H_2O$ (273) undergoes replacement of chloride ion by water (or hydroxide ion) when dissolved in water. The existence of this series of compounds with varying Mo(III)/Cl^- ratios suggests a stepwise decrease in affinity as the ratio decreases. All of the reactions proceed at measurable speeds. Measurements of osmotic coefficients and conductivities of the solutions show that all dissolve initially without dissociation of chloride ion. For a solution of K_3MoCl_6, only after 50 min. does the osmotic coefficient increase to the extent expected for the release of an average of one chloride ion for each Mo^{+++}. Color changes are produced when salicylate or oxalate ion is added to a solution of K_3MoCl_6. These changes proceed gradually even when the solutions are heated to 70°C. (36). The inertia to substitution of the $Mo(III)-Cl^-$ bond is demonstrated also by the fact that red and green forms of $Mo(III)-Cl^-$ complexes can be formed by the electrolytic reduction of molybdate in hydrochloric acid (47). The red form is obtained when the acidity is high, of the order of 8 *N*, while the green form results at *ca.* 2–4 *N* acid and is the less stable of the two, changing gradually to the red form on standing (73). The change is more rapid at higher acid and is accelerated by molybdenum(V). Wardlaw and Wormell (273) have succeeded in isolating a brown solid of composition $MoOCl\cdot 4H_2O$ from the red solutions, and a green solid of the same composition from the green. These solids dissolve initially with little dissociation, but undergo hydrolysis fairly rapidly, the green the more rapidly of the two.

Complex bromides of composition corresponding to the chloro complexes cited above have been prepared. $MoOBr\cdot 4H_2O$ dissolves initially with incomplete dissociation, but bromide ion is released, more rapidly than for the analogous chloro complex under similar conditions (271).

The conductance of a solution of $K_3Mo(CNS)_6\cdot 4H_2O$ indicates that it contains K^+ and $Mo(CNS)_6^{---}$, and that the complex ion does not undergo appreciable dissociation over the time interval of the measurements (180). This behavior is to be attributed to inertia rather than stability, since $Mo(CNS)_6^{---}$ is converted to ions of the type $Mo(CNS)_5OH^{---}$ if the solution is warmed to 50–60°C. for several days (250).

Under most conditions, the reaction of cyanide ion with molybdenum(III) yields a cyanide complex which contains octacoördinated molybdenum(IV). However, Young (295) has succeeded in preparing a compound of formula $K_4Mo(CN)_7(H_2O)_2$ which presumably contains cyanide ion coördinated to molybdenum(III). This substance is soluble in water, forming a solution which is brown when concentrated but becomes pink on dilution. On the addition of hydroxide ion, $Mo_2O_3\cdot nH_2O$ is precipitated. There is no indication in the report that these changes are slow.

Sulfate ion associates with molybdenum(III) but does not form a simple trisulfato ion. Observations have been recorded for solutions of solids of the type $M'_2SO_4\cdot 2Mo_2O(SO_4)_2\cdot 6H_2O$ (205) and for $Mo_2O(SO_4)_2\cdot 5H_2O$ (272), but do not lead to definite conclusions about the lability of the $Mo(III)-SO_4^{--}$ bond.

Examples of complexes containing $Mo(III)-NH_3$ bonds are fewer in number than they are for chromium(III). It is not certain whether this difference is due to a lower stability, or only because hydrolysis takes place more rapidly. The difference in inertia seems to be an important aspect, since even the chromammines are unstable in solution under ordinary conditions. A few complexes are known in which Mo(III)–N bonds persist in water solution. When molybdenum trichloride is treated with liquid ammonia, a product of formula $Mo(NH_3)_6Cl_3$ is formed. In moist air, ammonia is evolved from the compound. When it is heated with concentrated hydrochloric acid, one of the products obtained is $Mo(NH_3)_4(H_2O)_2Cl_3$ (235). As is the case also with chromium(III), the Mo(III)–N bonds are much more sensitive to alkali than to acid. Thus $Mo(NH_3)_4(H_2O)_2^{+++}$ has been shown to persist in acid solution, as does $Mo(CH_3NH_2)_4Cl_2^+$. Both ions are much more rapidly hydrolyzed in water. With pyridine in place of ammonia the complexes better resist hydrolysis; for example, compounds containing the ion $Mo(CNS)_4py_2^-$ can be crystallized from warm water (235).

Molybdenum(IV): No simple complex ions of coördination number 6 are known for this oxidation state. Solids of the type $M'_2Mo_3O_4(C_2O_4)_3 \cdot 5H_2O$, which contain molybdenum in the average oxidation state +4, have been prepared. These dissolve to give polynuclear species (trimers) which yield oxalate ion only at very low concentration (259). Definite conclusions about the lability of $Mo(IV)–C_2O_4^{--}$ with respect to simple substitution cannot be drawn from the data. In the complex cyanide of oxidation state +4, molybdenum has coördination number 8. From its behavior, the conclusion can definitely be drawn that substitution of cyanide ion is slow. Thus, a solution of $H_4Mo(CN)_6$ at room temperature persists for long periods of time without change but does decompose on prolonged boiling (237). Similarly, the ion $Mo(OH)_4(CN)_4^{----}$ persists in dilute acid at room temperature but loses hydrogen cyanide in strong acid at 50°C.

Molybdenum(V): The affinity of molybdenum(V) for chloride ion is apparently not very great. Measurements (127) of the conductances and freezing points of solutions of solids of the types M'_2MoOCl_5, $M'MoOCl_4 \cdot H_2O$, and $M'MoO_2X_2 \cdot 2H_2O$ show that the $Mo(V)–Cl^-$ complex ions are extensively dissociated at concentrations as high as 0.05 *M*. The dissociation apparently proceeds without delay. The color of Mo(V)aq. in the presence of hydrochloric acid depends markedly on the concentration of the acid, changing from emerald green at 8 *M* hydrochloric acid to shades of brown in the range 7–4 *M* hydrochloric acid, and then to amber at lower acid concentration (117). These color changes, which can also be produced by neutral halide and can therefore be attributed to changes in the extent of dissociation of molybdenum(V) and chloride ion, proceed without time lag (118).

Solutions of compounds of the type M'_2MoOBr_5 and $M'MoOBr_4$ behave similarly to those of the analogous chloro compounds (9).

Compounds of the type $M'_2MoO(CNS)_5$ and $M'_2MoO_2(CNS)_3$ dissociate almost completely on passing into dilute solution (128). James and Wardlaw made no mention of delay with respect to dissociation, and it may be presumed that the changes proceed fairly rapidly. When thiocyanate ion is added to a solution of molybdenum(V) in hydrochloric acid a red color is produced at once. Hiskey and Meloche (117) have shown the color change to be reversible, the color fading as the solution is diluted. The system does show a time lag in reaching final equilibrium. In view of the rapid initial color changes, it seems reasonable to attribute the lag to changes in extent of condensation of molybdenum(V) species, rather than to inertia in the $Mo(V)–CNS^-$ bond.

Molybdenum(V) in association with cyanide ion forms complexes of coördination number 8 only. Cyanide ion resists removal from $Mo(CN)_8^{---}$, but yields when heated with mercuric chloride in solution. Under these conditions, mercuric cyanide is gradually formed (50).

Molybdenum(VI): MoF_6 is hydrolyzed rapidly in water (243).

Silver chloride is precipitated rapidly when silver nitrate is added to a solution of $MoCl_3(OH)_3 \cdot 6H_2O$. The compound $Cs_2MoO_2Cl_4$ hydrolyzes at once in contact with water (276).

Equilibrium with respect to association of hydrogen peroxide with molybdates is reached very rapidly (149).

Tungsten(II): The complex-ion chemistry of tungsten in the oxidation state +2 resembles that of molybdenum(II). The compound of simplest formula, $HW_3Cl_7 \cdot 4H_2O$ (177), is soluble in water, but hydrolysis gradually takes place and a precipitate forms. Only one-seventh of the chloride is released to silver benzoate when the reaction is carried out in alcohol solution. By reaction with sulfuric acid, three out of seven chloride ions are replaced. The observations suggest that a polynuclear unit is preserved in many of the transformations.

Tungsten(III): The only well-defined ion of this oxidation state in solution is $W_2Cl_9^{---}$. The binuclear formulation is supported by conductance measurements in solution (52) and by x-ray structure analysis of the solid $K_3W_2Cl_9$ (32). Substitutions on this ion are slow. It persists in water solution for considerable periods of time but hydrolysis eventually takes place (52). With thiocyanate ion, a color change from green to red takes place gradually (211). A red unstable form of tungsten(III) in chloride solution also exists. The change from the red to the more stable green form is slow (51).

Tungsten(IV): Dilute alkali and ammonia form precipitates immediately when added to a solution of K_2WOHCl_5 (211).

Replacement of cyanide ion from $W(CN)_8^{----}$ in solution at room temperature is a slow process, and the complex ion continues without change for long periods of time. Addition of dilute hydrochloric acid at room temperature has no observable immediate effect, but if the solution is warmed, hydrogen cyanide is removed (86).

Tungsten(V): Solid compounds of the type M'_2WOCl_5 and $M'WOCl_4$ hydrolyze at once in water. Solutions in concentrated hydrochloric acid are blue, on dilution change through green to brown, and eventually form a precipitate (49). Complex oxalates are formed in solution by the reduction of tungstate in acid solutions by oxalate. These complexes also appear to be labile. Concentrated solutions are red, but change to yellow on dilution. They react with hydrochloric acid to form blue solutions, which presumably contain $W(V)\text{–}Cl^-$ complexes.

Tungsten(V) forms the ion $W(CN)_8^{---}$ with cyanide ion. Olsson (212) states that a solution of $K_3W(CN)_8$ is fairly stable toward dilute acid.

Tungsten(VI): Tungsten hexafluoride is very sensitive to water and hydrolyzes readily (244). Solid tungsten hexachloride persists in contact with water. The inertia may be peculiar to the crystal, rather than to the molecule WCl_6. Fischer states that the solubility in water cannot be measured because the substance is readily decomposed in water (71). Tungsten hexabromide is decomposed by water, forming a precipitate. The fact that it fumes in air implies that the reaction with water takes place readily (252). The association of peroxide with tungsten(VI) in tungstate takes place rapidly.

D. Ions of elements of Group VII B

Manganese(II): Few stable complexes of manganous ion with simple ligands are known. The complex ion $Mn(CN)_4^{----}$ exists in solution, and its chemical behavior suggests that substitution of cyanide ion is a slow process. The most definite evidence is that, although the ion is unstable in acid solution, $H_4Mn(CN)_6$ can be prepared and persists (61). Contributing evidence is that the reactions with sulfide ion and hydroxide ion are slow (68). The complexes of manganous ion with the chelating groups ethylenediamine, pyrophosphate ion (274), and oxalate ion (115) are fairly stable and apparently reach equilibrium rapidly.

Manganese(III): Equilibrium with respect to the formation of complexes between manganic ion and the ligands chloride ion (262), fluoride ion (262), sulfate ion (262), oxalate ion (167, 262), malonate ion (44), and pyrophosphate ion (262, 274) is established rapidly. $Mn(CN)_6^{---}$ hydrolyzes at a measurable rate, forming manganese trihydroxide and hydrochloric acid. The reaction with sulfide ion is also measurably slow (68).

Manganese(IV): A solution of the compound K_2MnF_6 in water hydrolyzes slowly; even in the presence of hydroxide or carbonate ion, the reaction takes place at a measurable rate (277). Replacement of oxalate ion from $Mn(C_2O_4)_2(OH)_2^{--}$ also appears to take place at a measurable rate. A cold solution of the potassium salt remains green for a reasonable length of time, and the behavior is not appreciably altered by the addition of small amounts of acid or alkali (43).

Rhenium(III): Rhenium trichloride dissolves in water, forming a solution which initially contains little chloride ion. Chloride ion is progressively released however, and eventually a precipitate is formed (78). Acid inhibits the hydrolysis (207). Recognizable early stages of the hydrolysis do not involve formation of precipitate, and it can therefore be concluded that the substitution of chloride ion by water is a slow process. The reaction of $ReCl_3$aq. with thiocyanate ion also takes place at a measurable rate (207). The behavior of the ions resulting from solids of the types $MReCl_4$ (294) and M'_3ReCl_6 (152, 208) bears out the conclusion that the Re(III)–Cl^- bond is not labile to substitution.

From the description of rhenium tribromide, no definite conclusions can be drawn about the lability of the Re(III)–Br^- bond (208).

When rhenium trichloride or tribromide is treated with liquid ammonia, a product $[Re(NH_3)_{6+n}X_3]$ is obtained which in dilute hydrochloric acid forms a brown solution. Since the color of the solution differs from that of the parent ReX_3, it is likely that ammonia complexes of rhenium(III) are present, and the observations suggest that the Re(III)–NH_3 bond persists in acid aqueous solution (144).

Rhenium(IV): The compound K_2ReF_6 dissolves in water without apparent hydrolysis at room temperature, but if the solution is warmed to 35–40°C., a precipitate forms gradually (247).

Solids of composition M'_2ReCl_6, $M'_2ReOHCl_5$, and $M'_4Re_2OCl_{10}$ are known. The latter two form yellowish brown solutions on dissolving, and the first a green solution. Conductance measurements indicate that solutions resulting from the latter two compounds contain the ion $ReOHCl_5^{--}$. Numerous observations show that substitution of chloride ion on rhenium(IV) is a slow process. None of the salts mentioned above release chloride ion on being freshly dissolved, but all undergo hydrolysis slowly. When a solution of K_2ReCl_6 is allowed to undergo partial hydrolysis and is filtered, and concentrated hydrochloric acid is then added to the resulting brownish solution, the color changes slowly to the green color of $ReCl_6^{--}$ (206). The reverse reaction presumably involves converting species such as $ReOHCl_5^{--}$, $Re(OH)_2Cl_4^{--}$, etc. to $ReCl_6^{--}$. It should be noted that $ReCl_6^{--}$ is not a particularly stable ion. The hydrolysis occurs, although slowly, in 5 per cent hydrochloric acid solution (206). Jakob and Jezowska (126) and Maun and Davidson (188) have noted that the properties of rhenium(IV) in hydrochloric acid solution vary markedly with the method of preparation. The reaction between $ReCl_6^{--}$ and thiocyanate ion takes place slowly (119); the rate is increased by stannous ion or hydrazine.

Compounds of the type M_2ReBr_6 and M_2ReI_6 hydrolyze at measurable rates in solution (102).

Rhenium(V): Solids of composition corresponding to the type formula M'_2ReOCl_5 have been prepared. The solution in 2 *M* hydrochloric acid hydrolyzes rapidly, forming a precipitate. In more concentrated hydrochloric acid rhenium-(V) remains in solution, in a form which depends on the concentration of the acid. The color is greenish blue in less concentrated acid. Similarly colored solutions result when ReO_4^- is reduced to the +5 state in solution. In contrast to the behavior of complexes of rhenium(IV) chloride, those of rhenium(V) appear to adjust rapidly to the environment. A color change takes place, apparently rapidly, when thiocyanate ion is added to a solution containing rhenium(V) in hydrochloric acid (126).

The compound $K_3ReO_2(CN)_4$ dissolves in water, forming an orange solution which turns violet on being made strongly acid. No apparent change in the orange solution is produced by the addition of hydroxide ion. From the latter observation, it is not certain whether the affinity of cyanide ion for rhenium(V) is too great for replacement of this ion by hydroxide ion, or whether the rate is slow. It should be pointed out that the color change on adding acid may be due to the addition of a proton to the ion, rather than to release of cyanide ion (144).

Rhenium(VI): Rhenium hexafluoride is hydrolyzed readily in water (246). A compound of composition K_2ReOCl_6 has been prepared, but it is so unstable with respect to disproportionation that no conclusion about the lability of the Re(VI)–Cl^- bonds can be reached from the observations (209).

E. Ions of elements of the iron group

Iron(II): Few complexes of ferrous ion with simple ligands are stable enough to make them accessible to study in dilute solution. The complexes with the bidentate groups ethylenediamine and oxalate ion (251) are sufficiently stable for study and are apparently labile.

For $Fe(CN)_6^{----}$, and derivatives, changes involving substitution are slow. The complex ion in 1 *M* hydrogen ion is unstable with respect to ferrous ion and hydrocyanic acid but persists under these conditions for fairly long periods of time. The initial change is the replacement of cyanide ion by water (129). Cyanide ion is also replaced by nitrite ion:

$$Fe(CN)_6^{----} + NO_2^- + H_2O = Fe(CN)_5NO^{--} + CN^- + 2OH^-$$

The reaction is very slow at room temperature, and reaches equilibrium at small percentage conversion. The rate is increased and the equilibrium is shifted to the right by mercuric ion (257). A considerable number of complexes of the type $Fe(CN)_5^{---}\cdot X$ persist in water solution (X may be H_2O, NH_3, CO, NO^+, NO_2^-, SO_3^{--}, or AsO_2^-). The reactions involving replacement of one of these groups by another are in general slow. Some of the examples of this behavior are: cyanide ion replaces sulfite ion or arsenite ion very slowly at room temperature, considerably more rapidly on warming the solution (257). Replacement of ammonia by nitrite ion (ca. 2 *M*) at room temperature takes about 30 min. for completion (257). Replacement of water by ammonia, sulfite ion, nitrite ion, or cyanide ion also takes place at a measurable rate.

The rate and equilibrium relations for $Fe(ophen)_3^{++}$ (169) and for $Fe(dipy)_3^{++}$ (15, 155) have been studied thoroughly. Both ions dissociate at measurable rates in acid.

Iron(III): Equilibrium is established rapidly in the reactions involving association of ferric ion with fluoride ion, chloride ion, bromide ion, thiocyanate ion, thiosulfate ion, sulfite ion, and oxalate ion. The compound $Fe(NH_3)_6Cl_3$ is hydrolyzed rapidly in contact with water (4).

Substitution by other groups of cyanide ion attached to ferric ion is usually slow. $Fe(CN)_6^{---}$ is unstable in 1 *M* hydrogen ion with respect to hydrocyanic acid and ferric ion as products, but the change takes place only slowly. In a solution 0.5 *M* in $Fe(CN)_6^{---}$ and 0.42 *M* in hydrochloric acid, only a few per cent of the complex ion is changed to $Fe(CN)_5H_2O^{--}$ after 48 hr. at room temperature. Complex ions are known in which one cyanide ion has been replaced by water, ammonia, or nitrite ion. Many of the substitution reactions in the pentacyanoferrate(III) series are accompanied by reduction of ferric ion to ferrous ion (5).

$Fe(ophen)_3^{+++}$ dissociates measurably slowly (169) in acid.

Ruthenium(II): A number of substances have been studied which contain chloride ion associated with ruthenium(II). For all, the evidence is strong that substitution in the Ru(II)–Cl^- complexes is a slow process. The solid of composition $RuCl_2$ dissolves in alcohol–water mixtures (although not in either solvent separately), forming a solution which is initially reddish purple but which changes to azure blue. The solutions are very little ionized, and while reactions with hydroxide ion, hydrogen sulfide, and silver ion do take place, they are slow (121). The blue solutions of $HRuCl_3$ form silver chloride slowly when silver nitrate is added (231). Blue solutions are also obtained when ruthenium trichloride is reduced in hydrochloric acid and resemble in properties those obtained by adding hydrochloric acid to ruthenium dichloride in water. Chloride ion is not readily released from compounds of the type $(pyH)_2RuCl_4$ in solution (103). The ions Ag^+, Tl^+, and Pb^{++} do not yield chlorides, but dark green products which may contain the ion $RuCl_4^{--}$. Ruthenium may be considered to be in the oxidation state +2 in compounds of the type K_2RuCl_5NO. The ion $RuCl_5NO^{--}$ continues in water without change for long periods of time, and although reactions with cyanide, thiocyanate, nitrite, and hydroxide ions do take place, they are very slow at room temperature (91).

Replacement of cyanide ion from $Ru(CN)_6^{----}$ is a slow process. From a cooled solution containing the complex ion and hydrogen ion, $H_4Ru(CN)_6$ can be prepared, but if the solution is warmed it liberates hydrogen cyanide (120).

Several complex ammines with ruthenium in oxidation state +2 are known, among them $Ru(NH_3)_5SO_2^{++}$ (79), $Ru(NH_3)_4(SO_3H)_2$ (82), $Ru(NH_3)_4 \cdot H_2O \cdot SO_2^{++}$ (82), and $Ru(NH_3)_4Cl \cdot SO_2^+$ (82). The Ru(II)–NH_3 bonds persist in acid solution. Since the stability relations are not known, the conclusion that these bonds are inert rather than stable is not certain. It is, however, indicated by the fact that only a limited number of Ru(II)–NH_3 complexes have been prepared, and they do not appear to possess extraordinary stability. The replacement of residual groups on Ru(II)–NH_3 radicals takes place with varying rates, some rapidly (e.g., chloride ion by ammonia in $Ru(NH_3)_4SO_2Cl^+$) (79), others measurably slowly (e.g., bisulfite ion by bromide ion in $Ru(NH_3)_4(SO_3H)_2$). The ion $Ru(dipy)_3^{++}$ is not attacked by boiling concentrated hydrochloric acid or concentrated alkali (40). It is not known whether the failure to react is due to a slow rate or to great stability of the complex ion.

Ruthenium(III): Complexes involving ruthenium(III) and chloride ion at various degrees of association are known. The behavior of all shows that substitution of chloride ion by other groups attached to ruthenium(III) is slow. $RuCl_3 \cdot H_2O$ (105) in water forms a solution which is initially brown, but which changes on standing to emerald-green and then to yellowish brown, and eventually deposits a precipitate. Accompanying these color changes there is a gradual increase in the concentration of free chloride ion in solution. Initially little is present, but at the green stage, which is complete in ca. 1 hr. at 0°C., one chloride ion has been released for each Ru^{+++} present. The liberation of chloride ion is very slow beyond the stage at which two have been released for each Ru^{+++}. In dilute hydrochloric acid the changes take place less rapidly than in water (104). The compounds $NH_4RuCl_4 \cdot 2H_2O$, $RbRuCl_4 \cdot 4H_2O$, and $CsRuCl_4 \cdot 4H_2O$ in water yield reddish brown solutions which continue for months without change. When hydroxide ion is added, an olive-green color develops gradually (38). $K_2RuCl_5 \cdot H_2O$ forms in water a red solution which hydrolyzes slowly (172).

The compound $K_3RuCl_6 \cdot H_2O$ has been prepared, but no conclusion about the lability of chloride ion in the complex ion can be drawn from the published observations (45).

A number of bromide complexes of ruthenium(III) have been prepared, among them $RuBr_3$, $NH_4RuBr_4 \cdot 2H_2O$, and $K_2RuBr_5 \cdot H_2O$. Only in the case of ruthenium tribromide do the published observations point to a conclusion about the lability of the Ru(III)–Br^- bond. Ruthenium tribromide hydrolyzes slowly (90).

The complex ammines (88) of ruthenium(III) include the species $Ru(NH_3)_6^{+++}$, $Ru(III)(NH_3)_5X$ (where X may be water, chloride ion, bromide ion, or hydroxide ion), $Ru(III)(NH_3)_4XY$ (where XY may be Cl^-Cl^-, Br^-Br^-, OH^-Cl^-, OH^-Br^-, OH^-I^-, or $C_2O_4^{--}$), and $Ru(NH_3)_3Cl_3$. Complex ions containing pyridine or ethylenediamine in place of ammonia have also been prepared. A large number contain NO replacing NH_3 (e.g., $Ru(NH_3)_4H_2O \cdot NO)^{+++}$. These may, however, be regarded as derivatives of ruthenium(II), since NO^+ is isoelectronic with CN^- or CO. Replacement of ammonia from ruthenium(III) is possible, but takes place slowly with most reagents. When a solution containing $Ru(NH_3)_6^{+++}$ in concentrated hydrochloric acid is refluxed for 5 or 6 hr., $Ru(NH_3)_5Cl^{++}$ is formed (83). The Ru(III)–NH_3 bond is in general more sensitive to alkali than to acid. Dilute alkali at room temperature produces a yellow color in a solution of $Ru(NH_3)_6^{+++}$, and boiling soda solution converts it to ruthenium red. $Ru(NH_3)_5Cl^{++}$ resists the effects of boiling hydrochloric acid, but warming with weak alkali produces ruthenium red. Substitutions involving groups attached to the Ru(III)–NH_3 nucleus usually take place at slow measurable rates. Thus, chloride ion is removed by silver nitrate from *trans*-$Ru(NH_3)_4Cl_2^+$ only slowly even on warming (81) and the removal of bromide ion by silver ion from $Ru(NH_3)_4Br_2^+$ is likewise slow (80).

Changes involving replacement of oxalate ion from $Ru(C_2O_4)_3^{---}$ are slow (46). The complex reacts with hydroxide ion, but only on heating, and the reaction with hydrochloric acid is slow in the cold. The reaction of oxalate ion with $Ru(H_2O)Cl_5^{--}$ is measurably slow at room temperature.

Ruthenium(IV): A summary of the evidence accumulated for Ru(IV)–Cl^- complexes is that while substitutions of chloride ion are not instantaneous, the changes are more rapid than they are for Ru(III)–Cl^-. A solution of $K_2RuOHCl_5$ hydrolyzes fairly rapidly—less rapidly in acid—to a solution of different color, containing ruthenium(IV) halide species in solution (171). The hydrolysis of $RuCl_4 \cdot 5H_2O$ in water proceeds at a measurable rate, to $RuOHCl_3$ as a recognizable succeeding stage (89).

Ruthenium(VI): Dilute solutions of $H_2RuO_2Cl_4 \cdot 3H_2O$ undergo hydrolysis very rapidly (10).

Osmium(II): The oxidation state of osmium in $K_2OsNOCl_5$ may be considered to be +2. A solution of the compound in water reacts slowly with ammonia, releasing chloride ion from the complex ion (292). The fact that $H_4Os(CN)_6$ can readily be prepared suggests that replacement of cyanide ion is a slow process. However, since the stability of the ion is not known, the conclusion can not be considered as being certain (95).

Osmium(III): Osmium trichloride is readily soluble in water. With silver ion, there is no precipitation of chloride ion from a fresh solution, but a precipitate develops after about 30 min. at room temperature. When ammonium sulfide is added, a precipitate develops slowly on heating (242). Hydrolysis of the ion $OsCl_6^{---}$ is measurably slow, but is more rapid than for osmium trichloride. A number of other compounds containing complex ions of osmium(III) have been prepared (e.g., $K_2Os(NO_2)_5$ (96), K_3OsBr_6 (242), $(NH_4)_2(OsCl_5)\cdot 1.5H_2O$ (96)), but the observations published for their behavior lead to no certain conclusions about lability.

Osmium(IV): Solutions containing $OsCl_6^{--}$ undergo hydrolysis slowly at room temperature. Initially yellow, they gradually become green, and eventually a precipitate forms. With ammonia a slow reaction takes place, leading to eventual formation of a precipitate (94). The description of the preparation of $OsCl_6^{--}$ and $OsCl_5Br^{--}$ from $OsCl_5OH^{--}$ and hydrochloric or hydrobromic acid includes boiling with concentrated acid as a step. This implies that the reactions are slow at room temperature. The reaction of chloride or bromide ion in more nearly neutral solution with $OsOHCl_3$ to produce $OsCl_5OH^{--}$ and $OsCl_3Br_2OH^{--}$, respectively, appears, however, to be rapid (154).

$OsBr_6^{--}$ in solution hydrolyzes gradually (109), while OsI_6^{--} undergoes hydrolysis rapidly (291).

NH_2 is replaced in $K_2OsNH_2Cl_5$ by chloride ion, but only on boiling with hydrochloric acid (30).

Osmium(VI): Osmium hexafluoride is attacked very rapidly by water (249). A number of compounds of osmium in the +6 state contain the radical OsO_2^{++}. The compounds $K_2OsO_2(NO_2)_4$, $K_2OsO_2(C_2O_4)_2$, $K_2OsO_2Cl_4$, and $K_2OsO_2Br_4$ and some aspects of their behavior in solution have been described by Wintrebert (290). In general, replacement of groups attached to OsO_2^{++} is rapid. Thus, $K_2OsO_2(C_2O_4)_2$ forms at once when oxalic acid is added to $K_2OsO_2(NO_2)_4$ in solution. A precipitate forms at once when hydroxide ion is added to a solution of $K_2OsO_2(C_2O_4)_2$ or of $K_2OsO_2Cl_4$.

No hydrocyanic acid is formed when $K_2OsO_2(CN)_4$ in solution is heated with hydrochloric acid (151). This may be due to a slow rate of reaction, or to great stability of the ion $OsO_2(CN)_4^{--}$.

The observations published for K_2OsNCl_5 (281) and $KOsNBr_4$ (282) do not lead to definite conclusions about the lability of the complex ions in these compounds. Substitution of chloride ion may, however, be measurably slow.

F. Ions of elements of the cobalt group

Cobalt(II): Solutions containing cobaltous ion undergo color change when ions such as chloride, bromide, iodide, or thiocyanate are added at high concentration. The changes are presumably due in part at least to the formation of complex ions and reach equilibrium rapidly. Equilibrium is established rapidly also for the complexes of cobaltous ion with ammonia, ethylenediamine, and oxalate ion. The complex ions of cobaltous and cyanide ions appear, however, to be less labile. The acid $H_4Co(CN)_6$ can be prepared and persists for a time in water, although it is unstable (60). The solution is initially red but changes color on standing. When cyanide ion, even in excess, is added to $CoCl_2$aq. at room temperature, $Co(CN)_5H_2O^{---}$ rather than $Co(CN)_6^{----}$ is formed (122, 200). Solutions containing the pentacyano ion are yellow-green in color.

Cobalt(III):[6] Co^{+++}aq. can be preserved for reasonable lengths of time only in solutions of high acidity. At lower acidity, the rate of oxidation of water becomes rapid, and as neutrality is approached cobalt trihydroxide precipitates. This behavior limits the possibilities for the study of reactions involving the formation of complex ions, and none have been described involving cobaltic ion as reactant.

K_3CoF_6 has been mentioned in the literature (42), but its chemical properties have not been described. Solid $CoF_3 \cdot 3.5H_2O$ (17) is hydrolyzed at once by water. This would seem to indicate that the Co(III)–F^- bond is very labile when only fluoride ion and water are coördinated to cobalt(III).

Most other substitution reactions recorded for complexes of cobalt(III) are slow.

The decomposition of $Co(NO_2)_6^{---}$ in both acid and alkali is slow at room temperature. Cyanide ion or carbonate ion converts it to the cyano or carbonate complexes, but these changes are slow.

Cyanide ion can be removed from $Co(CN)_6^{---}$ by mineral acid on boiling.

$Co(CO_3)_3^{---}$ is decomposed at a measurable rate by alkali and by acid. The reactions with ammonia and cyanide ion are also measurably slow (264).

$Co(C_2O_4)_3^{---}$ is decomposed by hydroxide ion at room temperature at a slow rate, and reacts with ammonia also at a slow rate at room temperature.

Almost all substitution reactions in the cobaltammine series of complex ions are measurably slow, whether they involve removal of ammonia, or of some group attached to the cobaltammine residue. In general, the cobaltammines are more sensitive to change in alkali than they are in acid. The ion $Co(NH_3)_6^{+++}$ is thermodynamically unstable in 1 *M* hydroxide ion and in 1 *M* hydrogen ion. It yields to hydroxide in solution even at room temperature, but resists boiling in concentrated hydrochloric acid (135). It is of interest to note that the luteo ion reacts fairly rapidly with sulfide ion at room temperature, forming Co_2S_3 and other products (74). $Coen_3^{+++}$ is more stable than $Co(NH_3)_6^{+++}$ (19) and more resistant to substitution reactions. It is unaffected by boiling alkali, and the reaction with sulfide ion is slow at room temperature (136). In general, removal of succeeding ammonia molecules takes place more rapidly, once the first one has been replaced. Thus, the ion $Co(NH_3)_5H_2O^{+++}$ decomposes to cobalt trihydroxide and ammonia fairly rapidly on boiling in water. Since most pentammino complexes with anions yield the corresponding aquo complex fairly readily in water, their behavior is similar.

Anions attached to the cobaltammine nucleus are in general replaced but slowly, and many reactions of this type have been the subject of detailed kinetic studies.

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[6] Unless an original reference is given, reference 6 has been the source of the information summarized.

Numerous examples of *cis–trans* isomerism are known in the cobaltammine series.

Rhodium(II): A number of complex compounds of rhodium(II) have been described which dissolve in water. $Rhpy_6Br_2$ reacts with concentrated hydrobromic acid at 0°C. to yield $Rhpy_5Br_2$. The latter compound yields bromide ion to silver ion, but only on boiling, indicating that the substitution is slow (67). Reduction of rhodium trichloride by hypophosphorous acid in the presence of substituted arsines yields a complex of rhodium(II) containing the arsine. The complex is not formed, however, when arsine is added to a reduced solution. This indicates that the substitution is a slow process (66).

Rhodium(III): The aquo ion of this oxidation state probably exists in solutions of rhodium(III) nitrate, in solutions of rhodium alums, and in the yellow solutions of rhodium chloride. Hydrated rhodium sulfate exists in two forms. Barium ion rapidly precipitated sulfate from a solution of the yellow form, but only very slowly from the red. The red form presumably contains sulfate ion associated with rhodium(III) in a complex ion; the other contains hydrated rhodium(III) ion. The transformations between the two forms are slow (153).

A solution of yellow rhodium chloride immediately releases all the chloride to silver ion, and $Rh_2O_3 \cdot nH_2O$ is precipitated at once by hydroxide ion. A reddish brown solution is obtained by dissolving $RhCl_3 \cdot xH_2O$ in water. Silver ion gives no immediate precipitate of silver chloride. Higher complexes of rhodium(III) are formed slowly when hydrochloric acid is added to either the yellow or the brown solution. These complexes do not yield an immediate precipitate of Rh_2O_3 when hydroxide ion is added, but slowly become yellow and then form a precipitate Solutions of Na_3RhCl_6 behave similarly (92).

$RhBr_6^{---}$, $Rh(CN)_6^{---}$, and $Rh(CNS)_6^{---}$ have been described. The data reported do not lead to certain conclusions about lability. It is very unlikely, judging from their behavior, that they are labile.

The existence of *cis* and *trans* forms of $Rh(C_2O_4)_2Cl_2^{---}$ suggests that substitution in this complex ion is slow (93).

The chemistry of the ammino complexes of rhodium(III) resembles that of the ammino complexes of cobalt(III). Substitution reactions are slow, whether rupture of Rh(III)–NH_3 or of some other bond in the complexes is considered. Only a few reactions of either type will be mentioned. $Rh(NH_3)_5Cl^{++}$ can be converted to $Rh(NH_3)_6^{+++}$ by concentrated ammonia, but the reaction requires about a day at 100°C. for its completion (137). The luteo ion resists attack by boiling hydrochloric acid. Although the equilibrium state is not known, it seems fairly likely that the ion is unstable in this environment and that failure to react is due to slowness. The rhodium ammines appear to be less reactive in alkali than are those of cobalt(III). $Rh(NH_3)_5Cl^{++}$ does not liberate ammonia on boiling with alkali (133). Chloride ion is replaced by water in $Rh(NH_3)_5Cl^{++}$ very slowly even in the presence of silver ion.

Iridium(II): No water-soluble complex of this oxidation state is known.

Iridium(III): The properties of the aquo ion of iridium(III) are not well established, and it is not known in fact whether an ion of charge +3 exists in solution. An iridium cation probably exists in solutions of iridium nitrate, and in the yellow solutions of hydrated iridium sulfate (184).

Solutions of hydrated iridium chloride give tests for chloride ion only after a time. Reaction takes place with concentrated chloride ion, but the reaction is slow at room temperature (57). Higher complexes presumably exist in solutions of salts such as $K_2IrCl_5H_2O$ and K_3IrCl_6. Solutions containing $IrCl_6^{---}$ react slowly with dilute alkali solution.

Complex bromides similar to the complex chlorides exist. The reaction of dilute hydroxide ion with a solution of $K_3IrBr_6 \cdot 3(4)H_2O$ is slow at room temperature (18). $IrBr_6^{---}$ is formed from $IrBr_4^-$ $[IrBr_4(H_2O)_2^-]$ when a solution of the tetrabromo ion is heated at 130°C.

$Ir(CN)_6^{---}$ is transformed by hydrochloric acid, but very slowly, to iridium tricyanide and hydrocyanic acid (186).

$Ir(NO_2)_6^{---}$ is transformed to $IrCl_6^{---}$ by repeated addition and evaporation of hydrochloric acid (97).

Substitution reactions in the ammino complexes of iridium(III) are in general slow. Only a few examples will be presented for illustration. $Ir(NH_3)_6^{+++}$ persists in hot concentrated acid, although slow formation of $IrCl_6^{---}$ does take place (213). $Ir(NH_3)_5Cl^{++}$ is converted to $Ir(NH_3)_6^{+++}$ in concentrated ammonia at 140°C. after a number of hours. *Cis* and *trans* forms of $Irpy_3Cl_3$ (59) and of other complex ammines are known. Replacement of groups attached to complex ammine radicals is also slow: e.g., replacement of X^- by H_2O in $Ir(NH_3)_5X^{++}$, and the reverse (158).

$Ir_2O_3 \cdot xH_2O$ dissolves in dilute sulfuric acid to form a yellow solution. This solution readily yields alums on being treated with the appropriate alkali sulfate (185). The solution turns green when it is warmed. The behavior resembles that of rhodium(III) sulfates, and suggests a change from the aquo complex (yellow) to a sulfate complex (green) (233).

Oxalate ion can be replaced from $Ir(C_2O_4)_3^{---}$, but reaction is in general slow at ordinary concentrations and temperature. Concentrated hydrochloric acid transforms the ion to $IrCl_6^{---}$. With dilute chloride, on continued refluxing, the equilibrium

$$Ir(C_2O_4)_3^{---} + 2Cl^- = Ir(C_2O_4)_2Cl_2^{---} + C_2O_4^{--}$$

is established. Mixed oxalate complexes also exist: e.g.,

$$Ir(C_2O_4)_2(H_2O)_2^-, \quad Ir(C_2O_4)_2Cl_2^{---}, \quad IrC_2O_4Cl_4^{---}, \quad Ir(C_2O_4)(NO_2)_2Cl_2^{---}$$

and others (98). Substitutions in these ions appear to proceed slowly in general.

Iridium(IV): Observations on solutions of sodium chloroiridate (210) suggest that the ion $IrCl_6^{--}$ undergoes stepwise hydrolysis in water solution. The changes are measurably slow and are catalyzed by light.

Cis and *trans* forms of $Irpy_2Cl_4$ are known (99). Replacement of pyridine by chloride ion in $IrpyCl_5^-$ is slow, but can be accomplished by heating $IrpyCl_5^-$ with hydrochloric acid at 150–160°C. (56).

Iridium(VI): Iridium hexafluoride reacts rapidly with water (245). The reaction is complicated, however, and reduction as well as hydrolysis takes place.

G. *Ions of elements of the nickel group*

Nickel(II): There is no evidence for slowness in the formation and dissociation of complex ions of ammonia, ethylenediamine, oxalate, and tartrate with nickelous ion. $Ni(CN)_4^{--}$ is rapidly dissociated by acid or silver ion. The reaction of nickel dimethylglyoxime with ammonium sulfide is slow, and is measurably slow with cyanide ion (267). The complexes $Ni(dipy)_3^{++}$ and $Ni(ophen)_3^{++}$ are decomposed by ammonium sulfide only on repeated treatment in hot solution.

Palladium(II): Substitution reactions involving complexes of this oxidation state vary in speed from quite rapid to slow. A considerable number appear to proceed at measurable rates.

A solution of $K_2Pd(NO_2)_4$ containing carbonate ion forms a precipitate on continued boiling. With ammonia, a precipitate appears after a time. The ion $Pd(NO_2)_4^{--}$ is decomposed very slowly by acids (161).

The reaction of $Pd(NH_3)_2Cl_2$ with oxalate or nitrite ion is apparently slow at room temperature, but is rapid with cyanide ion (183).

Redistributions in the $Pd(II)$–NH_3–Cl^- systems take place at measurable rates. $Pd(NH_3)_4PdCl_4$ changes to yellow $Pd(NH_3)_2Cl_2$ on boiling with water, or on long contact with water (64). Yellow $Pd(NH_3)_2Cl_2$ is formed from $Pd(NH_3)_4Cl_2$ when the latter compound in water is boiled (64). A convincing demonstration of slowness in substitution for $Pd(II)$–NH_3 bonds is the observation that exchange of ammino hydrogen with that of the solvent water is slow (8). Since free ammonia and water exchange hydrogen rapidly, the release of ammonia from the $Pd(II)$–NH_3 complexes must be at least as slow as the measured exchange. It is in fact considerably slower, since the hydrogen exchange proceeds mainly by dissociation of hydrogen ion from $Pd(II)$–NH_3.

$Pd(NH_2CH_2COO)_2$ reacts rapidly with thiourea at room temperature, but with hydrochloric acid or ethylenediamine the system must be heated to bring about rapid reaction (223).

A number of examples of *cis–trans* isomers have been reported among palladium(II) complexes. Some are $Pd(NH_3)_2Cl_2$, $Pd(NH_3)_2Br_2$, $Pdpy_2Cl_2$, $Pdpy_2Br_2$ (108), $Pd(NH_3)_2(NO_2)_2$ (161), and $Pd(NH_2CH_2COO)_2$ (223).

Palladium(IV): A number of complexes of this oxidation state are known, among them $PdCl_6^{--}$, $PdBr_6^{--}$, $Pd(NH_3)_2Cl_4$, and $Pdpy_2Cl_4$ (238). No definite conclusions about lability with respect to substitution can be drawn from published observations. A complication is introduced by the fact that some of the complexes are readily reduced. The equilibrium $PdCl_4^{--} + Cl_2 = PdCl_6^{--}$ has been studied (280).

Platinum(II): The aquo ion does not exist in appreciable concentration at ordinary acidity. Platinous oxide or hydrated forms of this oxide are only slightly soluble in dilute nitric acid. The solubility in concentrated nitric acid is appreciable, but it is not known whether platinum(II) in this environment exists as the aquo ion or as a nitrate complex.

A fresh solution of K_2PtCl_4 has the conductance expected for dissociation to potassium ion and chloroplatinate ion. Hydrolysis does take place after a time (139). The hydrolysis is undoubtedly stepwise; the compounds of composition $H[PtCl_3H_2O]\cdot H_2O$ and K_2PtCl_3OH exist and presumably contain the complex ions indicated. Replacement of chloride ion by nitrite or sulfite ion is slow at room temperature (161); replacement by ammonia also takes place at a measurable rate (138).

No definite conclusions can be drawn about the lability of bromide ion in $PtBr_4^{--}$.

A definite conclusion about the lability of cyanide ion in $Pt(CN)_4^{--}$ is not possible. The complex ion is known to be of very great stability. Cyanide ion can transform $PtO\cdot nH_2O$ and the dimethylglyoxime compound to $Pt(CN)_4^{--}$. $K_2Pt(CN)_4$ dissolves in concentrated sulfuric acid without change, but on heating $Pt(CN)_2$ is formed (148).

The fact that the unstable acid $H_2Pt(NO_2)_4$ can be isolated suggests that $Pt(II)–NO_2^-$ bonds are not labile. Nitrite ion is replaced by chloride, bromide, or iodide ion (269) in the presence of hydrogen ion. The changes are rapid only when the solutions are heated. Mixed complexes containing nitrite ion as one of the ligands are known: e.g., $PtCl(NO_2)_3^{--}$, $PtCl_2(NO_2)_2^{--}$, $PtCl_3(NO_2)^{--}$, and $PtBr_2(NO_2)_2^{--}$. These can be prepared by mixing the isocomplexes, but equilibrium is established slowly (101).

The affinity of ammonia for platinum(II) is very great. $PtO\cdot nH_2O$ dissolves in aqueous ammonia, and $Pt(NH_3)_4^{++}$ is not affected by hydroxide ion even on boiling (84). Ammonia is removed by acid but the change is much slower than it is for the palladium(II) compounds. A preparative procedure for $Pt(NH_3)_2Cl_2$ calls for the reaction of $Pt(NH_3)_4Cl_2$ with an equimolar amount of hydrochloric acid at 108°C. The ions $PtCl_4^{--}$ and $Pt(NH_3)_4^{++}$ exchange groups in solution, but the reactions take place at measurable speed only on warming. *Cis–trans* isomers of $Pt(NH_3)_2py_2^{++}$ are known, as are numerous examples of the type $Pt(NH_3)_2X_2$. A direct demonstration of the slow rate of rupture of $Pt(II)–NH_3$ bonds is furnished by observations on the rate of exchange of hydrogen between $Pt(NH_3)_4^{++}$ and water (8). Dissociation of anions attached to $Pt(II)–NH_3$ radicals is usually also slow. The conductance of $Pt(NH_3)_2Cl_2$ in water increases slowly with time (284), and that of $Pt(NH_3)_2SO_4$ also increases with time (142). With $Pt(NH_3)_2(NO_3)_2$ dissociation is complete during the process of dissolution (142). This is itself a slow process, in which aquotization of the salt may be rate determining.

The reaction of ammonia in water with $Pt(C_2O_4)_2^{--}$ is slow (258).

Platinum(IV): Replacement of fluoride ion from PtF_6^{--} is a slow process. The substitution reaction with iodide ion does take place, but is not complete after weeks at room temperature (253, 254).

$PtCl_6^{--}$ in water undergoes slow hydrolysis, which is accelerated by light and by platinum black (11). The reaction is undoubtedly stepwise, since compounds corresponding to all but one of the intermediate stages between $PtCl_6^{--}$ and $Pt(OH)_6^{--}$ are known (100). For each stage, replacement of chloride ion by hydroxide ion (or water) or addition of chloride ion is a reaction proceeding at a measurable rate. For example, H_2PtCl_5OH (195) in water shows a slow increase of conductance with time, which can be referred to increasing hydrolysis; it reacts with chloride ion forming $PtCl_6^{--}$ but at a measurable rate. The reaction of $PtCl_6^{--}$ with bromide ion (253) and with hydroxide ion (293) is slow at room temperature.

The hydrolysis of $PtBr_6^{--}$ is measurably slow and is accelerated by light (13). When iodide ion is added to a solution of $PtBr_6^{--}$, or bromide ion to PtI_6^{--}, equilibrium is established fairly rapidly—in about 1 hr. at room temperature (253).

The ion $Pt(CN)_6^{--}$ does not appear to exist. Mixed cyanide-ion complexes can be formed however: e.g., $Pt(CN)_4Cl_2^{--}$ and $Pt(CN)_4Br_2^{--}$. No definite conclusions can be drawn from the published data about the lability of cyanide ion in these groups.

The observation that $Pt(CNS)_6^{--}$ in the presence of hydrogen ion persists without noticeable change at room temperature but does react at higher temperatures suggests that rupture of the $Pt(IV)–CNS^-$ bond is a slow process (37).

Platinum(IV) forms a large class of ammino complexes based on coördination number 6. $Pt(NH_3)_6^{+4}$ persists in the presence of dilute hydroxide ion even when the solution is warm. Others of the substituted ions, $Pt(NH_3)_4SO_4^{++}$ and $Pt(NH_3)_4Cl_2^{++}$, for example, lose ammonia slowly when heated in potassium hydroxide (85). At least some of the complexes resist attack by concentrated hydrochloric acid. Thus, $Pt(NH_3)_4Cl_2Cl_2$ can be prepared by evaporating a solution of the corresponding nitrate in concentrated hydrochloric acid. It seems unlikely that the $Pt(IV)–NH_3$ bond is stable in concentrated hydrochloric acid with respect to the product $PtCl_6^{--}$ and NH_4^+, and the observation suggests that rupture is slow. The lack of lability of the ammine complexes is indicated also by the existence of *cis–trans* isomers in the series $Pt(NH_3)_4X_2$.

H. Ions of elements of the copper group

Copper(I): There is no evidence for slowness in establishing equilibrium with respect to complexes of cuprous ion with ammonia, chloride ion, bromide ion, iodide ion, sulfite ion, and cyanide ion.

Copper(II): There is no evidence for slowness in establishing equilibrium with respect to complexes of cupric ion with ammonia, chloride ion, bromide ion, or nitrite ion.

Silver(I): Equilibrium in the formation of complexes of silver(I) with ammonia, cyanide ion, nitrate ion, sulfite ion, and thiosulfate ion is established rapidly.

Gold(I): Complex ions of gold(I) with chloride, bromide, cyanide, thiocyanate, sulfite, thiosulfate, and other ions are known. The complexes with chloride and bromide ion are unstable with respect to disproportionation. Some of the complexes are very stable—with cyanide and thiosulfate ion, for example. There is no evidence, however, which suggests that equilibrium is established slowly for them.

Gold(III): $Au_2O_3 \cdot nH_2O$ has a low solubility even in fairly concentrated acid (130); hence Au^{+++} as an aquo ion is not stable at any reasonable acidities.

The solid $KAu(NO_3)_4$ presumably contains the ion $Au(NO_3)_4^-$. It is decomposed at once by water (256). The sulfate $KAu(SO_4)_2$ is decomposed much more slowly.

When hydroxide ion is added to a solution of $HAuCl_4$, equilibrium is reached rapidly if one equivalent of base at most is added. Succeeding increments of hydroxide ion bring about replacement of chloride ion. These changes are not instantaneous, and become slower with succeeding stages of replacement (20, 28). Cyanide ion replaces chloride ion from $AuCl_4^-$. In this case also, equilibrium may be established slowly (29). Ammonia reacts rapidly with $HAuCl_4$, forming a mixture of water-insoluble products, $Au_2O_3 \cdot 3NH_3$ and $Au_2NH(NH_2)_2Cl_2$ (279).

No definite conclusion can be reached from published data about the lability of Br^- in $AuBr_4^-$, I^- in AuI_4^-, CN^- in $Au(CN)_4^-$, and CNS^- in $Au(CNS)_4^-$. Indications are that some substitution reactions may proceed measurably slowly; none, however, appear to be extremely slow.

When auric halides or certain other auric compounds are treated with ammonia, solid substances are formed, some of which contain nitrogen in the -3 oxidation state. However, when chloroauric acid is treated with ammonia in the presence of concentrated ammonium nitrate, the substance $Au(NH_3)_4(NO_3)_3$ precipitates. This compound presumably contains the ion $Au(NH_3)_4^{+++}$, since a number of double decomposition reactions can be carried out in which the unit is carried along. The ion is rather inert with respect to substitution, and it persists in concentrated acid, although slow changes do occur. In the presence of hydroxide ion, a yellow color slowly develops, and eventually a precipitate forms. $Au(NH_3)_4(NO_3)_3$ in hydrochloric acid changes color slowly, and eventually a precipitate forms. The change brought about by chloride ion is more rapid in less acidic solutions (279).

I. Ions of elements of the zinc group

There is no evidence for marked delay in establishing equilibrium in solution with respect to complexes of zinc, cadmium, and mercuric ions with chloride, bromide, iodide, cyanide, or thiocyanate ions or with ammonia.

J. Ions of elements of the gallium group

Gallium(III): Little is known quantitatively about the behavior of gallium(III) in complex-ion solutions. Equilibrium in the system Ga(III)–HF (156, 287) and Ga(III)–Cl^- (287) is apparently reached rapidly. The Ga(III)–F^- complex ion is more stable than that formed by chromium(III). High concentrations of chloride ion are required to obtain appreciable concentrations of $GaCl^{++}$. Solid ammines of gallium trichloride are known; there is no evidence that Ga(III)–NH_3 bonds persist when these substances are added to water. Equilibrium in the system Ga(III)–$C_2O_4^{--}$ is apparently reached rapidly (156). It should be noted, however, that Neogi and Dutt (202) have reported that $Ga(C_2O_4)_3^{---}$ can be resolved and that racemization in water solution is not complete in a number of hours.

LaCroix (156) has reported that the properties of $GaCl_3aq.$ are changed when the solution is boiled. He concluded that condensation takes place, since the acidity increases markedly. Equilibrium is reëstablished only slowly.

Indium(III): A variety of solid compounds containing complex ions of indium(III) have been prepared: examples are $(NH_4)_3InF_6$, $K_3InCl_6 \cdot 2H_2O$, $(NH_4)_2InCl_5 \cdot H_2O$, and $K_3InBr_6 \cdot 2H_2O$. Equilibria in solution have been little investigated, and few definite conclusions about lability can be drawn from published observations. Indium(III) in solution forms a cyanide complex of reasonable stability (192). There is no evidence for slowness in the establishment of equilibrium in the system $In(III)–C_2O_4^{--}$ (196).

Thallium(III): Observations from which conclusions about the speed at which thallic ion reaches equilibrium in complex-ion reactions may be drawn are very limited. In most systems in which association can be expected, reduction of thallium(III) also takes place.

In a description of studies on the stability of $Tl(III)–Cl^-$ and $Tl(III)–Br^-$ complex ions (16), mention is made of the fact that it was necessary to wait in order to reach equilibrium. This delay, however, may have been due to slowness in the silver–silver bromide and silver–silver chloride electrodes used in the study. Hydroxide ion rapidly precipitates $Tl_2O_3 \cdot nH_2O$ from solutions containing the chloride and bromide complexes. $TlCl_3 \cdot 3NH_3$ is decomposed at once by water (286). Thallic hydroxide is precipitated at once from a solution of $KTl(C_2O_4)_2 \cdot 2H_2O$ (226).

For elements of Groups IV, V, and VI, only the observations for complexes of coördination number 6, with the central atoms in the states of highest oxidation, will be reviewed. These observations have the closest relation to the major thesis of the paper. Inclusion of the observations for all oxidation states and coördination numbers would result in an unduly long presentation of material, only part of which forms the basis for discussion in the present paper.

K. Ions of elements of Group IV

Silicon(IV): The compounds formed by the reaction of a base such as pyridine with the acids silicon tetrafluoride or silicon tetrachloride may result in compounds of coördination number 6. A complex ion of proven coördination number 6 is SiF_6^{--}. This ion is stable in acid, but in neutral or alkaline solution it decomposes according to the reaction:

$$4OH^- + SiF_6^{--} \rightarrow SiO_2 \text{ (hydrous)} + 6F^- + 2H_2O$$

The reaction is measurably slow at 20°C., and the rate is independent of hydroxide ion (230) provided enough is present to suppress the reverse reaction. The coördination number of silicon(IV) is almost certainly 6 also in $(NH_4)_2Si(O_2C_6H_4)_3$ (239). No conclusions as to lability can be drawn from the published observations on this compound.

Germanium(IV): Among complexes of coördination number 6 for germanium(IV) the following are known: GeF_6^{--} (in K_2GeF_6) (288), $Ge(C_2O_4)_3^{--}$ (266) (in $M'_2Ge(C_2O_4)_3$), $Ge(OCOCH_3)_3^+$ (in the compound with $CuCl_2^-$, for example) (199). No definite conclusions as to lability of the ligands can be drawn from the observations which have been published. Mention is made of the fact that $Ge(OCOCH_3)_3^+$ is hydrolyzed by water or OH^-aq., but the rate is not discussed.

Tin(IV): Hydrolysis of $SnCl_6^{--}$ is reported as being slow (110). It is not known, however, whether the rate-determining step is replacement of chloride ion. Morgan and Drew noted that silver bromide is formed slowly when aqueous silver nitrate is added to an alcoholic solution of $Sn(OCOCH_3)_2Br_2$ (198).

Lead(IV): Among the complex compounds known are K_2PbCl_6, K_3HPbF_8, and Na_2PbF_6. These are hydrolyzed by water. No conclusions as to lability can be reached from the observations.

L. Ions of elements of Group V

Phosphorus(V): PF_6^- is unstable with respect to hydrolysis. The reaction is very slow (162), but does take place in acid solution on boiling. The initial attack by water on phosphorus pentafluoride is rapid. PF_6^- is the only ion of coördination number 6 for phosphorus(V) known in solution.

Arsenic(V): AsF_6^- hydrolyzes slowly, although more rapidly than does PF_6^- (163). Complexes are known in which arsenic(V) is coördinated to six oxygen atoms. Among them is the ion $As(O_2C_6H_4)_3^-$. This ion is hydrolyzed slowly in water, more rapidly if the solution is acidified (275).

Antimony(V): SbF_6^- is hydrolyzed measurably slowly in water, and the system reaches equilibrium before the hydrolysis is complete (163). In alkali, the reaction is complete and is much more rapid. $SbCl_6^-$ is unstable in dilute solution, and the hydrolysis proceeds at a measurable rate. The rate is greatly decreased by hydrogen ion (278).

M. Ions of elements of Group VI

Application of thermodynamic data (261) shows that the hexafluorides of sulfur, selenium, and tellurium are unstable in acid and in alkaline solution with respect to the hydrolysis products. Sulfur hexafluoride is extraordinarily inert; selenium hexafluoride may undergo very slow hydrolysis (225); tellurium hexafluoride is hydrolyzed fairly readily in alkali (145).

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