

THE STABILIZATION OF VALENCES BY COÖRDINATION¹

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Through the formation of complex ions of varying stability, the oxidation-reduction potentials of metal ions can be altered greatly. This often leads to a "stabilization of the valence" of the element in either higher or lower states of oxidation. Many factors which may have a bearing upon this phenomenon are considered, but it is pointed out that no theory of structure of complex compounds has yet been projected which adequately explains all of the very numerous examples of stabilization.

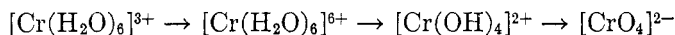
I. INTRODUCTION

The phrase "stabilization of valences by coördination" is used frequently in reference to the formation of ions in states of oxidation not ordinarily met in everyday laboratory practice. For example, silver salts may be oxidized to the divalent and trivalent states when coördinated with pyridine and analogous compounds (3, 13, 15, 19, 25), and iron may be carried to states of oxidation of 4+ and 6+ by anodic oxidation in alkaline solution (19). Cobalt ions exist ordinarily in aqueous solution in the divalent state, but in the well-known and stable amines, cobalt is more stable in oxidation states of 3+ and perhaps 4+ (46). On the other hand, in the nitrosyl and carbonyl derivatives cobalt appears to exhibit oxidation numbers of -1 and 0 (5). Several studies have indicated that nickel (4, 6) and manganese (22) form complex cyanides in which the metals show quite unusual oxidation states. Coördination of the thermally unstable lead tetrachloride with two additional chloride ions, in hydrochloric acid solution, produces the much more stable hexachloroplumbate(IV) ion.

The hydroxide ion coördinates strongly with many metallic ions, especially those of higher valence. Consequently, we usually achieve the higher valence

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states in alkaline solution (2). This tendency is doubtless furthered by the fact that the hydroxo complexes so formed lose water and are acidic, thus generating oxo complexes:

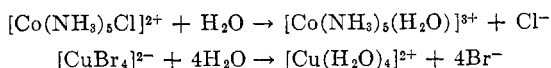


Carbon monoxide and nitric oxide always seem to stabilize the lower valences, and in the nitrosyls and carbonyls the metals appear in very low states of oxidation; in the volatile carbonyls and nitrosyls, in fact, the uncharged elements themselves combine with carbon monoxide and nitric oxide to form compounds in which their state of oxidation is zero. The non-volatile carbonyls are for the most part coördination compounds of carbon monoxide with salts in which the metal ion shows a low valence. Thus we have $\text{PtCl}_2 \cdot (\text{CO})_2$, $\text{RuI}_2 \cdot (\text{CO})_2$, $\text{IrCl}_2(\text{CO})_2$, $\text{PdCl}_2(\text{CO})$, and $\text{OsCl}_2(\text{CO})_3$. Hieber and Marin (12) have even reported the preparation of $\text{Co}(\text{NO})_2\text{I}$, in which cobalt shows a valence of 1. It is conceivable, of course, that the carbon monoxide or nitric oxide in these compounds assumes a negative charge from the metal, thus raising the formal charge of the latter beyond its apparent value. This idea was first suggested by Werner and Karrer (47), and has been developed by Reihlen (31, 32, 33, 34, 35). Manchot (21), however, has maintained that the carbon monoxide and nitric oxide retain their neutral character. Certainly the nitrosyls do not exhibit saltlike properties, and it is generally agreed that the metal shows an abnormally low valence.

II. OXIDATION-REDUCTION POTENTIALS

These are but striking manifestations of a completely general phenomenon. Uncoördinated metallic ions exist only in the gaseous phase; in solution, they at once coördinate with the solvent or with some other solute, and the coördinated ions thus generated have entirely different physical and chemical properties from the parent ions. As Emeléus and Anderson have pointed out (7b), "stabilization of valence" is simply a modification of the oxidation-reduction potential of the element or ion, induced by the specific influence of different coördinating groups. By coördination with water or ammonia or with chloride or bromide ion, the cupric ion forms complexes of greatly different color, and these complexes vary simultaneously in their resistance to reduction to the cuprous state or to the metal. This is a general phenomenon; coördination will nearly always (if not always) alter the tendency of an ion to undergo oxidation or reduction. When we say that coördination *stabilizes* an ion, we really mean (though we may not realize it) that the type of coördination in question produces a greater degree of stabilization than does *aquation*.² It should also be

² *Hydration* means combination with water, but not necessarily to form hydrates; *aquation* refers to the formation of aquo ions; *aquotization* is more specific and refers to the expulsion of negative groups, from a complex ion, by the entrance of water molecules: e.g.,



In this review, however, the more general term *aquation* will be used exclusively.

borne in mind that coördination may stabilize a valence state against reduction, but not against oxidation, or *vice versa*. In some cases, an ion is protected to some extent against a change in valence in either direction. Consideration of tables 1 and 2 will make these points clear.

It is evident from table 1 that ammoniation stabilizes the cobaltous state against reduction to the metallic condition more than does aquation but offers much less protection against oxidation to the cobaltic condition. Because we are accustomed to thinking in terms of aquated ions, the latter part of this

TABLE 1
Electrode potentials of some Co/Co²⁺ and Co²⁺/Co³⁺ couples (19)

| COUPLES | POTENTIALS |
|---|----------------|
| $[\text{Co}(\text{CN})_6]^{4-} = [\text{Co}(\text{CN})_6]^{3-} + e^-$ | $E^0 = +0.83$ |
| $\text{Co} + \text{NH}_3(\text{aq}) = [\text{Co}(\text{NH}_3)_6]^{2+} + 2e^-$ | $E^0 = +0.422$ |
| $\text{Co} + x\text{H}_2\text{O} = [\text{Co}(\text{H}_2\text{O})_x]^{2+} + 2e^-$ | $E^0 = +0.277$ |
| $[\text{Co}(\text{NH}_3)_6]^{2+} = [\text{Co}(\text{NH}_3)_6]^{3+} + e^-$ | $E^0 = -0.1$ |
| $[\text{Co}(\text{H}_2\text{O})_6]^{2+} = [\text{Co}(\text{H}_2\text{O})_6]^{3+} + e^-$ | $E^0 = -1.842$ |

TABLE 2
Electrode potentials of some Cu/Cu¹⁺ and Cu¹⁺/Cu²⁺ couples (19)

| COUPLES | POTENTIALS |
|---|---------------------------|
| $\text{Cu} + 2\text{CN}^- = [\text{Cu}(\text{CN})_2]^{1-} + e^-$ | $E^0 = \text{ca. } +0.43$ |
| $[\text{Cu}(\text{H}_2\text{O})_x]^{1+} = [\text{Cu}(\text{H}_2\text{O})_x]^{2+} + e^-$ | $E^0 = -0.167$ |
| $\text{Cu} + \text{H}_2\text{O} = \text{Cu}(\text{H}_2\text{O})_x^{1+} + e^-$ | $E^0 = -0.522$ |
| $[\text{Cu}(\text{CN})_2]^{1-} = [\text{Cu}(\text{H}_2\text{O})_x]^{2+} + 2\text{CN}^- + e^-$ | $E_B^0 = -1.12$ |

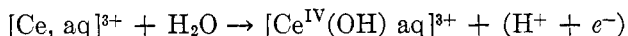
TABLE 3
Electrode potentials of coördination Fe²⁺/Fe³⁺ couples (19)

| COUPLES | POTENTIALS |
|---|--------------------------|
| $[\text{Fe}(\text{CN})_6]^{4-} = [\text{Fe}(\text{CN})_6]^{3-} + e^-$ | $E^0 = -0.36$ |
| $[\text{Fe}(\text{H}_2\text{O})_6]^{2+} = [\text{Fe}(\text{H}_2\text{O})_6]^{3+} + e^-$ | $E^0 = -0.771$ |
| $[\text{Fe}(\text{dipy})_3]^{2+} = [\text{Fe}(\text{dipy})_3]^{3+} + e^-$ | $E^0 = \text{ca. } -1.1$ |
| $[\text{Fe}(o\text{-phen})_3]^{2+} = [\text{Fe}(o\text{-phen})_3]^{3+} + e^-$ | $E^0 = -1.14$ |
| $[\text{Fe}(\text{NO}_2\text{-}o\text{-phen})_3]^{2+} = [\text{Fe}(\text{NO}_2\text{-}o\text{-phen})_3]^{3+} + e^-$ | $E^0 = -1.25$ |

statement is usually worded in the converse: "Coördination with ammonia stabilizes the trivalence of cobalt against reduction (more than coördination with water does)." Coördination with the cyanide ion produces such a great change in the potential of the Co²⁺/Co³⁺ couple that the hexacyano cobaltate (II) ion liberates hydrogen from water.

Table 2 illustrates the point that a donor group may protect an ion from both oxidation and reduction. In this case, coördination with the cyanide ion protects the cuprous ion against change in the oxidation state either way more than aquation does. Tables 3 and 4 show some similar relations for iron and

cerium. It is evident that by varying the anion (since all of the acids are highly dissociated), it is possible to alter the composition and the stability of the complex which contains the cerium. Unpublished work done by Mr. R. C. Spooner in the laboratory of Professor Sherrill of the Massachusetts Institute of Technology (40) seems to indicate that the effect of the acid is possibly even more complex, owing to hydrolysis of the ceric ion, as shown by the half-cell reaction based entirely upon physicochemical data:



Smith, Frank, and Getz, however, have chemical evidence to show that in the tetravalent condition cerium is present in a complex anion, such as $[\text{Ce}(\text{NO}_3)_6]^{2-}$ (42).

A valence state may seem to be stabilized, even though it is thermodynamically unstable, because it changes to another very slowly. We usually think that coördination with the cyanide ion protects the ferrous ion from oxidation, but the data of table 2 show that this is not the case; the tendency of ferrocyanide to undergo oxidation to ferricyanide is greater than that of the aquated ferrous ion to undergo oxidation to the aquated ferric ion. Many cases of

TABLE 4
Electrode potentials for the Ce³⁺/Ce⁴⁺ couple in the presence of different acids 1 M in concentration (43)

| | | | | |
|------------|-------------------|------------------|--------------------------------|-------|
| Acid..... | HClO ₄ | HNO ₃ | H ₂ SO ₄ | HCl |
| E.M.F..... | -1.70 | -1.61 | -1.44 | -1.28 |

“stabilization” should probably be explained as “decrease of oxidation (or reduction) rate.” One cannot be certain until the electrode potential of the couple in question is known.

A. Metal-ion couples

In every consideration of the problem of stabilization it must be borne in mind that we seldom deal with ions which are *not* coördinated; simple ions do not exist in solution, but only in the gaseous or solid phases. Ions in solution are stabilized relative to the solid metal by solvation, thus in an aqueous solution by *hydration* or *aquation*. It is impossible to measure the absolute value of the energy difference between a solvated ion and the metal; however, the energy relative to the standard hydrogen couple is known for most of the metallic elements. The standard oxidation-reduction potential, as usually defined, is a measure of this relative energy difference for a couple comprised of the metal and the aquated ion at unit activity. For smaller *activities* of the aquated ion, the oxidation-reduction potential has a larger positive (or smaller negative) value, and when the *activity* is increased, the potential becomes less positive (or more negative), in accordance with the equation:

$$E = E^0 - \frac{0.05914}{n} \log_{10} Q$$

where Q has the same general form as the equilibrium constant but refers to the actual activities of the reaction substances and their products (19). If a coordinating group—ion or molecule—is added to a solution containing the aquated ions, with the result that the water of aquation is largely replaced, the *activity* of the hydrated ion is reduced, and the new complex ion is more stable relative to the metal than the aquated ion. The standard oxidation–reduction potential for the new couple has a larger positive (or less negative) value; that is, the new complex ion formed is a poorer oxidizing agent than the aquated ion. This is illustrated in the behavior of copper with hydrochloric, hydrobromic, and hydriodic acids, as shown in table 5. The oxidation–reduction potential of the metallic copper–cuprous couple is raised sufficiently by the more strongly coordinated bromide and iodide ions to permit the displacement of hydrogen from the concentrated acids, but not with hydrochloric acid under ordinary conditions of temperature and concentration.

Similar changes in electrode potentials are observed with all the other elements and must be taken into account in predicting the course of chemical reactions (19).

TABLE 5
Electrode potential for the Cu/Cu⁺ couple in the presence of halide ions (19)

| COUPLES | POTENTIALS |
|--|--------------------|
| $\text{aq} + \text{Cu} = [\text{Cu}, \text{aq}]^+ + e^-$ | $E^\circ = -0.522$ |
| $2\text{Cl}^- + \text{Cu} = [\text{CuCl}_2]^- + e^-$ | $E^\circ = -0.19$ |
| $2\text{Br}^- + \text{Cu} = [\text{CuBr}_2]^- + e^-$ | $E^\circ = -0.05$ |
| $2\text{I}^- + \text{Cu} = [\text{CuI}_2]^- + e^-$ | $E^\circ = 0.00$ |

B. Polarographic determination of oxidation–reduction potentials

The polarographic method of analysis gives a measure of oxidation–reduction potentials, and has brought to light many examples of valence stabilization through complex-ion formation. The half-wave potential of the ferric ion found by this method is -1.32 volts, but addition of excess oxalate ion converts this to a value so strongly negative that it cannot be measured. Addition of fluoride ion produces a similar effect. The complex ions formed are apparently $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ and $[\text{FeF}_6]^{3-}$ (44). The aquated cupric ion gives only one polarographic wave, which corresponds to reduction to the metal, but cupric solutions containing ammonia or chloride ion show two distinct waves, the first corresponding to reduction to a stabilized cuprous state (44). Pines, using the polarographic technic in the study of the deposition of zinc from cyanide solutions, has found that if the ratio of potassium cyanide to zinc cyanide is less than 4:1, zinc will deposit. Larger amounts of potassium cyanide cause the formation of $\text{K}_4\text{Zn}(\text{CN})_6$, from which potassium, rather than zinc, is electrodeposited (28). Cadmium, on the other hand, is deposited from cyanide solutions, no matter how great the excess of cyanide ion (29).

Considerations of this sort have found practical application in the polarographic estimation of related ions. The half-wave potentials of the aquated zinc

and nickel ions are so close together that the simultaneous determination of these ions, as such, is impossible. The addition of a large excess of ammonium oxalate, however, causes the formation of complex oxalato ions which differ greatly in their resistance to reduction, and can be readily estimated (30). The data of Lingane and Kerlinger (20) on the similar case of nickel and cobalt are interesting in this connection (see table 6). The solutions used were 0.001 *M* in nickel(II) chloride and 0.002 *M* in cobalt(II) chloride and contained 0.01 per cent of gelatin. Half-wave potentials are given with respect to the calomel electrode at 25°C. It is interesting to observe that the addition of pyridine or thiocyanate ion, both of which are coordinated strongly, increases the ease with which the nickel and cobalt ions are reduced (but not equally). It is well known that the presence of these substances also increases the ease with which the cobalt(II) ion is oxidized.

Heyrovsky and Ilkovič (11) assume that reduction of a complex ion takes place in two steps: (1) formation of the simple ion and (2) its subsequent reduc-

TABLE 6
Half-wave potential differences due to coordination (20)

| ELECTROLYTE ADDED | CONCENTRATION | HALF-WAVE POTENTIALS | | |
|--|---------------|----------------------|------------------|------------|
| | | Ni ²⁺ | Co ²⁺ | Difference |
| KCl | <i>M</i> 1 | -1.1 | -1.2 | 0.1 |
| NH ₄ Cl NH ₄ OH | 1 1 | -1.12 | -1.30 | 0.18 |
| KCl C ₅ H ₅ N | 1 0.5 | -0.78 | -1.07 | 0.29 |
| KCNS | 1 | -0.70 | -1.03 | 0.33 |

tion. This is doubtless an oversimplification of the process, for the relationships between the oxidized and reduced forms of the metal ion, the coordinating group, and the solvent (which in most cases can also form complexes with both forms of the metallic ion) must be extremely complex. If their assumption is correct, stabilization of the ion against reduction takes place only because the concentration of reducible ion is greatly decreased. Kolthoff and Lingane (18), in a review of this field, have suggested that "the reduction of very stable complex metal ions may take place by the direct capture of electrons from the electrode".

Ion stabilization is thus directly connected with the equilibrium constant for the aquation of the complex ion. The smaller the value of this constant, the more stable the ion is relative to the metal.

C. Ionic oxidation-reduction couples

When we come to a comparison of the stability in solution of two different valence states of a metal, we may still use oxidation-reduction potentials as criteria. The oxidation-reduction potential of a couple comprised of the ions

in the two valence states, each at unit activity and presumably aquated, in contact with an inert electrode, is used as a standard. Addition of another coördinating group will in general produce *unequal* changes in the concentration or activities of the aquated ions in the two oxidation states. If the displacement of the water of aquation proceeds nearer to completion for the higher state of oxidation—thus, if in the higher state of oxidation the newly coördinated ion is more stable than in the lower state—then the oxidation–reduction potential of the new couple will have a higher positive (or less negative) value. As has been shown in table 1, the oxidation–reduction potential of the couple $[\text{Co}(\text{H}_2\text{O})_6]^{2+}/[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ is -1.842 volts and, as a result, the aquated cobalt(III) ion is a powerful oxidizing agent; on the other hand, the oxidation–reduction potential of the complex cyanide couple $[\text{Co}(\text{CN})_6]^{4-}/[\text{Co}(\text{CN})_6]^{3-}$ is $+0.83$ volt. The hexacyanocobaltate(II) complex is thus a powerful reducing agent and even reduces water with the evolution of hydrogen. Contrariwise, the couple $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}/[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ has an oxidation–reduction potential of -0.771 volt, compared to that of -1.14 volts for the couple comprised of the ferrous and ferric ions coördinated with *o*-phenanthroline, $[\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3]^{2+}/[\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3]^{3+}$. Evidently the *o*-phenanthroline forms a more stable complex with divalent than with trivalent iron. The trivalent state, however, is stabilized by coördination with α -pyridylhydrazine (9) and α -(α' -pyridyl)pyrrole (8). It is of interest to note that all good oxidation–reduction indicators for the titration of ferrous ion are examples of coördination in which stabilization of low valences is achieved.

Hence the equilibrium constants for the aquation of the corresponding complexes of an element in two states of oxidation give us a measure of the resistance to change in valence. If the equilibrium constant for the higher valence state is smaller than that for the lower valence state, stabilization of the higher valence state results, since this involves a greater decrease in the concentration of the aquated ion in the higher valence. This line of reasoning suggests that certain predictions as to the ease of oxidation or reduction can be made. Thus, we should expect the chloropentammine cobalt(III) ion to be reduced more readily than the nitropentammine or the hexammine, for it is readily aquated while the others are not.

An interesting application of these concepts has been made by Reinders and his coworkers (36, 37, 38). They have shown that the oxidation–reduction potential of an equimolar mixture of ferrous and ferric sulfates can be varied from $+0.64$ volt to zero by the addition of salts of hydroxy- or poly-carboxylic organic acids. The salts which they studied were sodium citrate, malonate, oxalate, tartrate, lactate, and succinate, of which the first three were the most satisfactory. The anions of these salts coördinate with both the ferrous and ferric ions and give solutions which show a considerable buffer action toward oxidation and reduction. These systems were used in studying the process of photographic development.

III. TYPES OF BONDS FOUND IN COÖRDINATION COMPLEXES

In a complex, each atom loses its individual properties, including its characteristic state of oxidation, and becomes simply a part of the whole. The re-

sultant electrical charge of a complex ion is determined by the coördinating groups as well as by the central metal ion. It is quite possible that any metal could be carried through a wide range of stable oxidation states if it were coördinated with the proper groups. Conversely, it is evident that with many elements the realization of different states of oxidation is possible only through coördination with certain atoms or groups of atoms. A most important question arises: "Why do different coördinating groups, apparently sharing the same number of electrons with a metallic ion, give rise to complexes of such varying electron affinities?" No complete answer to this question has yet been offered—indeed, none seems possible in our present state of knowledge. It is the purpose of this review to discuss certain aspects of the problem with the hope of stimulating further study of it.

Sidgwick (41) has suggested that stable valence groups are formed when the *effective atomic number* of the metallic ion is equal to that of an inert gas. On this basis, the stability of the hexammine cobaltic salts is attributed to the fact that the twenty-four electrons of the metal ion, with the twelve furnished by the coördinated nitrogen atoms, give the stable inert-gas configuration of krypton. The stability of $\text{Co}(\text{CO})_5\text{NO}$, in which the cobalt atom seems to have no charge, is explained in the same way [$27 + (3 \times 2) + 3 = 36$]. This theory may appear to explain the formation of many coördination compounds, but there are numerous exceptions to it. We cannot hope to use it to explain the stabilization of oxidation states by coördination when different groups, which apparently furnish the same number of electrons, do not stabilize the same valence state. Thus, coördination with *o*-phenanthroline stabilizes the divalency of iron (in this case the *E.A.N.* becomes that of krypton) but coördination with water, cyanide, or hydroxyl groups stabilizes the trivalency, even though the resultant complex has one electron fewer than the inert gas.

Fajans has attempted to explain the instability of cupric iodide on the basis of *ion-deformation* (10). The deepening in color of the silver and cupric halides with increasing atomic weight of the halogen indicates an increasing deformation of the electron shells of the halogen. The iodide ion is so greatly deformed by its proximity to the cupric ion that it completely loses one of its electrons, with consequent reduction of the cupric ion. This explanation implies that the cupric condition will be more stable if the metallic ion is kept from close proximity to the iodide ion, by surrounding it, say, with coördinated neutral groups. The diethylenediamine copper(II) ion, $[\text{Cuen}_2]^{2+}$, in contrast to the aquated cupric ion, indeed forms a stable iodide, and is not reduced by hyposulfites (23). On the other hand, the cuprous condition of copper is stabilized by coördination with acetonitrile (26) and derivatives of thiourea and thiocarbamide (17, 24, 39).

One of the common pitfalls in the consideration of the problem of stabilization of valences should perhaps be mentioned here. It must be borne in mind that the *apparent* oxidation state of an element is not always a true measure of its condition. Thus, the supposed divalency of gallium, indium, and thallium is very doubtful, the dichlorides probably being auto-complexes of the type $\text{Ga}^{\text{I}}[\text{Ga}^{\text{III}}\text{Cl}_4]$, $\text{In}^{\text{I}}[\text{In}^{\text{III}}\text{Cl}_4]$, and $\text{Tl}^{\text{I}}[\text{Tl}^{\text{III}}\text{Cl}_4]$ (7a). The diamagnetic nature of these dihalides (16) is in agreement with such a formulation. We can safely

draw conclusions only when it is clearly demonstrated that the complex in question has a known structure and contains only one ion or atom of variable valence,—conditions frequently not fulfilled.

Coördinating groups, presumably, must have an atom present with at least one pair of unshared electrons, but the type of bond formed is not at once apparent. The attraction of the field around a positive ion for the pair of electrons might be considered to be largely responsible for the formation of a coördinate bond. The intensity of this field surrounding the ion depends on its charge and is obviously always greater for the more highly charged valence state. If the bond between the coördinating group and the ion were of ionic character, that is, only so-called Coulombic forces were operative, then the stronger bond would always be formed by the more highly charged ion. This would lead to a uniformly smaller value for the aquation constant in the higher valence state and thus stabilization of the higher valence state. The numerous examples of stabilization of low valences contradict the assumption of a purely ionic bond and suggest that, in general, the coördinate link is covalent in character. Evidence for the existence of covalent bonds in many coördination complexes has been obtained from the measurement of the magnetic moments of ions in solution (27a). On the basis of the available information practically the only coördinating groups which form bonds of ionic character are water, fluoride ion, and occasionally the oxalate ion. Very few quantitative data are available on fluoride and oxalate complexes; these are, however, sufficient to allow the conclusion to be drawn that in the fluoroferrate and oxalatoferrate ions the trivalent state is stabilized. The resolution of many coördinated ions into optical isomers suggests, in addition, that covalent bonds occur frequently, since if ionic bonds were present it is less likely that definite orientation in space relative to the central ion would exist.

An excellent discussion of the type of bonds involved in the formation of complex ions is given in a recent treatise by Pauling (27b), in which he elaborates the idea that "atoms in the transitional groups are not restricted to the formation of single covalent bonds but can form multiple covalent bonds with electron-accepting groups by making use of the electrons and orbitals of the shell within the valence shell". Because of this it is difficult to postulate the formal charge or state of oxidation of the central atom. It would not seem possible at present, however, to explain on the basis of multiple bonds why zinc forms complexes with cyanide ions while aluminum and gallium do not. The specific and individual behavior of many of the elements still lacks clarification.³

³ *Note added in proof:* J. E. B. Randles (J. Chem. Soc. 1941, 802) has investigated the factors governing the stability of cuprous and cupric complexes and claims that, "The chief controlling factor appears to be the degree of covalency or electrovalency of the bonding between the copper ions and neighbouring ions or molecules, which is mainly dependent on the polarizability of the latter." This concept does not appear to be of general application, however, since hydration does not invariably form the higher state of oxidation, nor does combination with ammonia or pyridine invariably lead to stabilization of the lower state, as has been emphasized in the body of this review. Randles' conclusions, while in agreement with the experimental data he presents, cannot be extended to other systems.

IV. CONCLUSIONS

When the element in two states of oxidation forms covalent bonds with the coördinating groups, our present knowledge of the factors which govern this type of bond formation does not permit the prediction of bond strengths; hence no theoretical estimate of the relative magnitudes of the aquation constants for different valence states can be made. The experimental evidence from aquation constants and from oxidation-reduction potentials leads to the following conclusions:

1. *If, for an element in a particular state of oxidation, its complexes with coördinating groups are listed in the order of increasing stability, it is probable that the same order will not hold for other valence states of the element.* There seem to be no definite examples of actual changes in order, but there are many examples of large changes in stability, so it is logical to assume that the order may be altered. There is need for more data on this point.

It may be difficult to obtain such data, however, for any great change in stability may make the ion so unstable that it will not exist under ordinary conditions. In other words, the difference between "stability" and "instability" is not great, and any large change in conditions may forbid an oxidation state completely, thus making it impossible to obtain some of the complexes which it would be desirable to study. An example of this is afforded by the triethylenediamine chromium(II) ion, which apparently cannot exist in water solution but changes rapidly to the corresponding chromium(III) ion (1) with the evolution of hydrogen. Hydrazine, however, gives fairly stable complex chromium(II) ions (45).

2. *Different ions in the same state of oxidation do not exhibit the same order of stability with coördinating groups. Thus, it is impossible to arrange coördinating groups in a definite series, in the order of their ability to form stable bonds, which will apply to all metallic ions.* However, certain rough generalizations may be made from available data. Familiar coördinating groups, such as hydroxyl ion, cyanide ion, nitrite ion, and ammonia, ordinarily stabilize the higher valence state. There seem to be some exceptions to this, such as the compounds $K_4Ni^0(CN)_4$ and $K_2Ni^I(CN)_3$, recently discussed by Burgess (6), and $K_5Mn^I(CN)_6$, reported by Manchot (22). These compounds, however, have not been completely studied, and when their structure has been determined it is possible that the apparent discrepancies will disappear. If they are real exceptions, it must be admitted that at present there is no explanation for them.

A survey of the various types of stabilization groups seems to substantiate a rule which has been suggested by Professor John P. Howe of Brown University (14): *Coördinating groups of higher negativity stabilize the higher valences, and large groups containing resonating structures stabilize the lower valence states;* thus, divalent oxide ions stabilize chromium, iron, and nickel with an oxidation number of 6, as in $[CrO_4]^{2-}$, $[FeO_4]^{2-}$, and $[NiO_4]^{2-}$, and, as previously noted, other negative ions in general stabilize higher valences. Neutral molecules like *o*-phenanthroline, with conjugated double bond structures, stabilize the lower valences. This might be summarized by stating "that the greater the electron

affinity of the group itself for additional electrons, the more the lower valence state is stabilized".

V. SUMMARY

Valence stabilization by coördination is a real phenomenon, but the term signifies a relatively large change in the oxidation-reduction potential of a couple, rather than a sudden and unexpected jump in valence. The phenomenon is a very general one, but at present no adequate theory of structure of complex compounds is able to explain much of the data. Experimenters who measure electrode potentials are cautioned to ascertain and to report *all* of the components of their solution, as frequently the obscure variations in potentials observed are due to the formation of complexes which have been overlooked. Many of the data on electrode potentials recorded in the literature are worthless because of this oversight.

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