THE STABILIZATION OF OXIDATION STATES OF THE TRANSITION METALS

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I. Introduction and Scope

A number of reviews (*39*, *40*, *41*, *66*) have been written on the stabilization of unusual oxidation states of transition metals, but, as time goes by, it becomes more and more apparent that, in this context, the word "unusual" is purely relative and sometimes meaningless. A transition metal atom, when examined in chemical combination, will be in an oxidation state that is stabilized by its chemical environment in the compound under examination. This stability may be either thermodynamic, i.e., due to an unfavorable free energy change associated with the most probable decompositions, or kinetic, i.e., due to an unfavorable free energy of activation associated with the most probable decompositions, generally an electron-transfer process between the metal and the ligand. The definition of a usual oxidation state refers to oxidation states that are stable in environments made up of those chemical species that were common in classical inorganic compounds, e.g., oxides, water and other simple oxygen donors, the halogens, excluding fluorine, and sulfur. Nowadays, however, such species constitute only a minority of the vast number of donor atoms and ligands that can be attached to metals, so that such a definition of normality has historical, but not chemical, significance. On the occasions, in this article, when it will be convenient, for the sake of brevity, to make use of the term "unusual oxidation state," it will be with this definition in mind.

This article will discuss the ways in which the chemical environment may stabilize a particular oxidation state and will attempt to rationalize the dependence of the oxidation state upon the various electronic promotion energies of the transition metal atom or ion and the pertinent properties of the chemical environment.

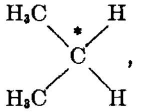
The concept of an oxidation state also requires some clarification. In ionic compounds, where there is little sharing of electrons between the metal and its environment, it is easy to give the term "oxidation state" a definition that has chemical significance, but as soon as the covalent contribution towards the bonding becomes significant, the concept of oxidation states becomes less precise and the discussion of the oxidation states of atoms in essentially covalent compounds has little physical reality.

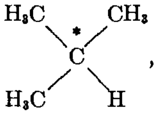
One of the basic empirical concepts that has been applied to coordination compounds is the Principle of Electroneutrality as propounded by Pauling (*58*). It is pointed out that, on the formation of a compound, charge is transferred wherever possible, to maintain the electroneutrality of each atom. Variations of up to $\pm\frac{1}{2}$ of an electronic charge (ϵ), depending on the electronegativities of the atoms constituting the bond, are considered permissible, but any charge separation greatly in excess of this will lead to instability provided no other factors become important. Although difficulties arise in quantitatively defining an envelope for each atom within which the charge balance between the positive nucleus and the negative electrons can be assessed, it would appear that, if this electroneutrality principle is accepted, the physical reality of oxidation state vanishes unless one believes that in all complexes the metal atom strives to achieve a true oxidation state between -1 and $+1$ and that any deficiency or excess of electronic charge is spread as much as possible over the whole complex ion or molecule.

Provided that it is realized that the concept of an oxidation state can often have little chemical reality when applied to an atom engaged in bonding, there is no doubt that, as a working hypothesis to discuss the stoichiometry of compounds and to systematize the teaching of descriptive inorganic chemistry, the concept is extremely useful.

For the purposes of *this* article the term "oxidation state" will be defined formally in the usual way, e.g., as the charge left on the metal atom after all the attached ligands have been removed in their closed shell configurations, e.g., chlorine as Cl^-.

The definition of oxidation state by an analytical procedure works well when one can decide unambiguously which electron configuration to confer on the ligand when it is withdrawn. The outstanding cases that present difficulty are hydrogen which can be withdrawn as H^+ or H^-, nitric oxide which can be withdrawn as NO^-, NO^+, or even NO (*43*), and the many important new complexes that contain metal-metal bonds. The former cases can often be resolved by applying chemical knowledge of the way in which the ligand is behaving in the compound in question, i.e., in $HCo(CO)_4$, the ability to form the sodium salt of the anion $Co(CO)_4^-$ suggests that the hydrogen is protonic in character. In nitric oxide complexes the problem is more difficult to resolve unless one can determine the extent to which an odd electron is transferred to or from the nitric oxide molecule. The case of metal-metal bonding is of interest with respect to the parallel that it presents with the carbon-carbon bond in organic compounds. When the two atoms forming the bond have virtually identical electronegativities one must assume equal sharing of the bonding electrons with a result that the analytical definition of oxidation state splits bonds between like atoms homolytically, these bonds, therefore, being ignored in the computation of the oxidation state. This, unfortunately, gives rise to the paradox that in methane CH_4 the oxidation state of carbon is IV, whereas in ethane $H_3C—CH_3$ it is III, and the oxidation state of the asterisked C atoms in the compounds





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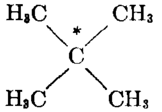

are II, I, and O, respectively. Chemically, all these carbon atoms resemble one another far more than do the carbon atoms in CH_4 and CCl_4 to which are both formally ascribed the oxidation state IV. Also, in the complexes $Co_2(CO)_8$ or $Mn_2(CO)_{10}$, where there is a metal-metal bond, the metals are in zero oxidation state. The discovery of compounds containing heteronuclear metal-metal bonds present difficulties that are less easily resolved (*1, 13, 18, 37, 54, 65*). It is proposed that these bonds be treated computationally as if they were homonuclear, unless there is a clear chemical reason for doing otherwise. It might be thought that the valency of the metal atom would be a more reliable concept to use than its oxidation state. The oxidation state of the atom is often, but by no means always, equal to the valency of the atom. The differences always arise in the cases that have just been discussed, i.e., those compounds whose electronic interactions are not self-evident from their composition. In order to assign a valency to an atom in a particular environment it is necessary to have some prior information about the mode of bonding. When applied to the case of carbon, the ambiguities that arise in the assignment of an oxidation state in the above compounds do not appear in the assignment of a valency, which is always 4.

It should be realized that, since the concept of an oxidation state is only an artificial aid to the systematization of inorganic chemistry, effort should not be wasted in attempting to reconcile those areas of chemistry where the concept breaks down with the main mass of inorganic chemistry where it holds and is usefully applicable.

It has often been thought that magnetic and spectroscopic studies of transition metal complexes can give information about the oxidation state of the metal atom. These properties, however, arise mainly from the electrons *not* involved in chemical bonding and give little information about the electrons whose loss, or gain determines the oxidation state. An exception might be made of studies of characteristic infrared frequencies assigned to the metal-ligand bond or diagnostic bonds in the ligand itself which, in favorable circumstances, will provide information about the way in which the ambiguous ligands, e.g., H, NO, O_2, etc., are bound in the compound under examination.

It is necessary, finally, to define what will be meant, in this article, by a stable oxidation state. Stability that arises from kinetic considerations can lead to compounds that possess a whole spectrum of lifetimes ranging from those that are capable of existing indefinitely under suitable conditions to those which have only a transient existence and can only be demonstrated by an interpretation of kinetic data in *redox* reactions. The modern view of chemistry does not insist that isolation is a prerequisite of identification and, since modern techniques allow analysis and identification of transient molecules in a very short space of time, it is difficult to know where to draw the line. Rather than be forced, for the sake of consistency, to ignore all compounds that are thermodynamically unstable but kinetically stable, it is proposed to consider only those compounds that exist long enough for them to be isolated and characterized.

II. The Effect of the Environment upon the Stability of the Oxidation State of the Metal

A. GENERAL

The study of isolated atoms in high oxidation states simply requires the provision of sufficient energy to remove electrons from the atom and a means of observing the result before recombination can take place. The oxidation states produced will depend entirely on the ionization potentials of the atoms and the strength of the applied field. Such conditions obtain in high energy discharges, and arc and spark spectra show contributions from oxidation states far greater than those encountered in chemical combination. Although the data obtained from these studies greatly assist our understanding of inorganic chemistry and will be drawn on extensively in the later part of this article, it is not necessary, in inorganic chemistry, to consider the chemical properties of isolated atoms or ions, in fact, an isolated atom does not have chemical properties (*15*). In an element or compound the atom under examination is always surrounded by chemical environment of like or unlike atoms. The atom and the environment interact and the stability of the possible oxidation states will depend upon the nuclear charge and electronic configuration of the atom and the properties of the environment.

The factors that determine the contribution of the metal to the stabilization of a particular oxidation state will be discussed in the next section and it is now necessary to examine the ways in which the environment interacts with the metal ion.

In general, the main influence of the environment will come from the nearest neighbors. The interaction can vary from the essentially electrostatic forces between ions to the complete electron exchange of the covalent bond. If the interaction is to remain essentially electrostatic it is necessary both for the anion to have minimum polarizability and for the cation to have minimum polarizing power. Polarization interaction will lead, either to significant covalent contributions to the bonding, which while not decreasing the formal oxidation state of the cation, reduces the positive charge in its vicinity, or to complete transfer of an electron from the anion to the cation, leading to a redox reaction. If the latter change takes place, the metal must have been not only in an oxidation state that is unstable with respect to its environment but also able to react with it. Such a situation is of interest to this discussion only when we consider the effect of a substitutionally labile environment. While realizing that a description of the interaction with the environment in terms of purely electrostatic or purely covalent bonds would be inadequate and probably misleading, it is convenient to discuss the extreme cases and to interpolate to achieve reality.

B. THE ELECTROVALENT COMPOUND

The first limiting type of compound to be discussed is that in which positively and negatively charged components of finite size are held together by a combination of electrostatic and repulsive forces in a crystalline lattice. The stability of a particular oxidation state of a cation in such a solid can be assessed by calculating the free energy of formation ($\Delta G^0_{\mathrm{form}}$) of the compound from its elements in their standard states. If ($\Delta G^0_{\mathrm{form}}$) is large and negative then the product will be very stable. This consideration, however, does not take into account the possibility of disproportionation into compounds other than the elements and this will be discussed separately. Whereas it is not always easy to measure or calculate free energy charges, sufficient data are available to calculate the enthalpy of formation (ΔH_{form}). The two quantities are related by the expression

$$\Delta G = \Delta H - T\Delta S$$

and provided that $T\Delta S$ is small compared to ΔH it can be ignored. It should be noted that at 298°K $T\Delta S_{\text{form}}$ of sodium chloride is -6.45 kcal/mole, (7% of ΔH_{form}) and is mainly due to the entropy loss of the gaseous chlorine ($T\Delta S = 7.94$ for $\frac{1}{2}\mathrm{Cl}_2$ at 298°K) (*36*). If the heat of formation of a salt is large, >50 kcal/mole, then this compound will be thermodynamically stable. When the heat of formation is small (either positive or negative), the stability may very well be controlled by the entropy of formation. Large positive enthalpies of formation indicate that the compound has little chance of existence.

It is possible to calculate a value for the heat of formation of an electrovalent compound by means of the well known Born-Haber cycle as follows:

$$\begin{tikzcd}
\underset{\text{Standard state}}{a[\mathrm{M}]} + \underset{\text{Standard state}}{b[\mathrm{X}]} \arrow[r, "+b[\Delta H_{\mathrm{at}}]_{\mathrm{X}}", "+a[\Delta H_{\mathrm{at}}]_{\mathrm{M}}"'] \arrow[d, "-\Delta H_{\mathrm{form}}"] & \underset{\text{gas}}{a\mathrm{M}} + \underset{\text{gas}}{b\mathrm{X}} \arrow[d, "+a[I_b]_{\mathrm{M}}"', "-b[E_a]_{\mathrm{X}}"] \\
\underset{\text{crystalline}}{\mathrm{M}_a\mathrm{X}_b} & \underset{\text{gas}}{a\mathrm{M}^{b+}} + \underset{\text{gas}}{b\mathrm{X}^{a-}} \arrow[l, "-\mathrm{U}_{\mathrm{M}_a\mathrm{X}_b}"']
\end{tikzcd}$$

The processes involved in this cycle are, (1) the conversion of the elements in their standard states to gaseous atoms and the provision of the appropriate heats of atomization [ΔH_{at}], (2) the conversion of the atoms to ions, processes involving the appropriate ionization potential of the metal $[I_b]_{\mathrm{M}}$ and electron affinity of the nonmetallic element $[E_a]_{\mathrm{X}}$, and, (3) the combination of these ions to form the crystalline solid which is accompanied by the release of the lattice energy U. Thus, if the heats of these individual reactions can be calculated independently, an approximate value can be obtained for the enthalpy of formation of the compound. The agreement between this value and the experimentally determined heat of formation will depend, not only upon the accuracy of the data used in the calculation, but also upon the validity of the simple electrostatic picture. The quantities are related by the simple expression:

$$-[\Delta H]_{\mathrm{M}_a\mathrm{X}_b} = -a[\Delta H_{\mathrm{at}}]_{\mathrm{M}} - b[\Delta H_{\mathrm{at}}]_{\mathrm{X}} - a[\mathrm{I}_b]_{\mathrm{M}} + b[E_a]_{\mathrm{X}} + U_{\mathrm{M}_a\mathrm{X}_b}$$

The heats of atomization are often known accurately, the ionization potentials of the metals are known from spectroscopic measurements and the electron affinities of the nonmetallic elements can sometimes be measured and often estimated. The lattice energy cannot be measured directly by an independent method but can be calculated in favorable circumstances. As it depends upon ionic charges and lattice geometry it can be evaluated approximately by comparison with other isomorphous compounds or by the various computational approximations that are available. Of all the thermal quantities used in the Born-Haber cycle, that most amenable to experimental measurement when the compound in question is known is the heat of formation. Thus one usually finds that electron affinities and lattice energies are often calculated using the Born-Haber cycle. Using the concept of the electrostatic bond and the Born-Haber cycle it is proposed now to see how the various properties of the environment affect the stability of a particular oxidation state when the bonding is essentially ionic. It will be convenient to limit this discussion to the monatomic ions of group V, VI, and VII and the B subgroups which are isoelectronic with the inert gases.

1. Heats of Atomization

The heats of atomization of many elements are known with reasonable accuracy. For elements that are gaseous and diatomic in their standard state, the heat of atomization is equal to one half of the bond dissociation energy. The heats of vaporization of liquid elements and the heats of melting or sublimation of solid elements must also be taken into account. Difficulties may sometimes arise when the electronic configuration of the element in its ground state requires some change during the process of atomization, e.g., the triplet-singlet transition of oxygen. Selected values of heats of atomization are given in Table I.

TABLE I
HEATS OF ATOMIZATION OF SOME ELEMENTS FROM THEIR STANDARD STATES AT 298° (kcal/mole) (*20*)

F	Cl	Br	I
18.5	28.9	26.7	25.4
O	S		
59	57		
N	P	As	
113	75	60	
C	Si		
171	<105		

An important point is that the heats of atomization of anions will make only a small contribution to the stabilizing effects of the environments produced by these elements.* Apart from carbon, and to a lesser extent nitrogen, which require more than the average amount of energy, each need between 20–30 kcal/gm ion when compared on equal terms, i.e., one oxygen atom is equivalent to two fluorine atoms, etc.

2. Electron Affinities

In recent years many independently evaluated electron affinities have been published and discussed in review articles. Although it is possible to evaluate single electron affinities for reactions of the type $X + \epsilon^- - X^-$, it is still not possible experimentally to determine values for the addition of more than one electron. In general, the values quoted for reactions of the type

$$X + n\epsilon^- \rightarrow X^{n-} \qquad \text{where } n > 1,$$

are obtained from the Born-Haber cycle assuming wholly ionic bonding. It is, therefore, not strictly correct to feed these data back into any other Born-Haber cycle. However, comparable values can be found for the electron affinity of oxygen $O + 2\epsilon^- \rightarrow O^{2-}$, from many oxides of the types M_2O and MO (*47*) and so it is not unreasonable to believe that the value is reasonably correct and that the original assumption that the bonding is essentially ionic does not depart significantly from the truth. Calculations based on extrapolation techniques also yield values similar to those found from heats of formation (*48*), but it should always be remembered that a

TABLE II

ELECTRON AFFINITIES, I.E., EXOTHERMICITY OF THE REACTION $X + \epsilon^- \rightarrow X^{a-}$ IN KCAL/MOLE (*60*)

	F	Cl	Br	I	O	N
(i) $X + \epsilon^- \rightarrow X^-$	83	88	82	75	54	−16
	O	S	Se			
(ii) $X + 2\epsilon^- \rightarrow X^{2-}$	−156	−80	−97			
	N					
(iii) $X + 3\epsilon \rightarrow X^{3-}$	−547					
	C					
(iv) $X + 4\epsilon \rightarrow X^{4-}$	−708					

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* For metals in the early transition series, the heat of atomization is so large (e.g., W, 200 kcal/mole) that compounds are formed in lower oxidation states which involve metal–metal binding as well as covalent metal–halogen and ionic bonds. (See $MoCl_2$, p. 32.)

"theoretical" calculation can always approach the "right answer" provided that this is known beforehand.

Some accepted values are given in Table II. It is immediately apparent from Table II that the halogens possess an overwhelming advantage over all the other elements in the energetics of ionization. The addition of extra electrons to a negatively charged ion is energetically unfavorable in spite of the approach to a closed shell configuration because of the repulsion between the negative charges on the ion and on the electron. Thus, oxygen and nitrogen require a considerable amount of energy to form the O^{2-} and N^{3-} ions and were it not for the other compensating factor which will be discussed below, ionic oxides and nitrides would not be thermodynamically stable.

3. Lattice Energies

Continuing the purely electrostatic description of ionic compounds, it is necessary to consider the energy that is released when the ions are assembled in the crystalline lattice. This lattice energy makes a major contribution to the heat of formation of the compound. The calculation of lattice energies has been the subject of many reviews (*21, 64*) and it is not necessary to discuss the topic in great detail in this article. The "experimental" lattice energy is a quantity that can be calculated by means of the Born-Haber cycle provided the other data are known or can be estimated satisfactorily. In principle, it is possible to calculate the lattice energy in terms of a summation of the individual electrostatic interactions between lattice points, but it is necessary to know the charges, the lattice geometry and internuclear distances for the compound in question. A comparison of the "experimental" and calculated lattice energy will give some indication of the extent to which the electrostatic model is correct and significant differences in the values obtained may indicate the extent to which covalent bonding is present.

It is possible to express the lattice energy in terms of the formula,

$$U = A \frac{N\epsilon^2}{r} Z_1 Z_2 \left(1 - \frac{1}{n}\right)$$

where ϵ, Z_1, and Z_2 are the electronic and the ionic charges, N is Avogadro's number, r is a characteristic interionic distance, n the electron shell repulsion coefficient, and A is the Madelung constant (a structural coefficient that depends, amongst other things, upon the characteristic interionic distance, r used, and the relative number of anions to cations). The expression is not exact and more elaborate expressions have been derived to account for some of the other factors, e.g., Van der Waals's forces and zero point energy, that are involved but discussion of these refinements is not pertinent to the subject of this article. For other than simple structures all these expressions are not easy to apply and when it is necessary to predict the lattice energy without knowing the structure of the crystal they are useless.

Kapustinskii (*35a*) has developed an expression,

$$U = 287.2 \frac{\Sigma n Z_1 Z_2}{r_c + r_a} \left\{ 1 - \frac{0.345}{r_c + r_a} \right\}$$

where Σ_n is the number of ions per "molecule" of the compound and r_c and r_a are the Goldschmidt radii, referred to a coordination number of six.

While realizing the very approximate character of this treatment, it is possible to use it, in a crude quantitative fashion, to show how the various properties of the anion affect the lattice energy. It is clear, by inspection, that the smaller the radius of the anion, the greater will be the lattice energy. The charge of the anion makes a major contribution to the lattice energy.

Comparing M^+X^- with $M_2{}^+Y^{2-}$ and $M_3{}^+Z^{3-}$, if X, Y, and Z had identical radii the lattice energies for equivalent amounts of M would be in the ratio, 2:6/2:12/3, i.e., 2:3:4. In a similar way for a bivalent metal, $M^{2+}X_2{}^-$, $M^{2+}Y^{2-}$, and $M_3{}^{2+}Z_2{}^{3-}$ the ratios are 6:8:30/3 or 6:8:10 for a tervalent metal, $M^{3+}X_3$, $M_2{}^{3+}Y_3{}^{2-}$, and $M^{3+}Z^{3-}$ the ratios are 12:30/2:18, i.e., 12:15:18. Taking ionic radii into account it would appear that, from their charge alone, oxides benefit by about 150 kcal/equivalent of metal, and nitrides by 300 kcal/equivalent for univalent metals; 300 and 600 kcal/equivalent for bivalent metals; and 450 and 900 kcal/equivalent for tervalent metals with respect to fluorine. Thus, in spite of the extremely unfavorable energetics involved in the formation of anions that are isoelectronic with the inert gases, oxygen and nitrogen are able to compete adequately with fluorine in the formation of ionic compounds as a result of the increased lattice energy due to the increased anionic charge. That this compensation is inadequate can be seen by comparing the heats of formation of some ionic fluorides and oxides (kcal/mole).

NaF	BaF_2
136	286.9
$\frac{1}{2}Na_2O$	BaO
49.7	133.4

4. Stabilization of High Oxidation States in Electrovalent Compounds

The simple Born-Haber cycle can be used to show why compounds such as NaNe or NeCl or even NaF_2 are too unstable to exist.* These calculations

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* See note added in proof on page 39.

have often appeared in textbooks and review articles and need not be repeated here (*26*, *62*). In general, they show that the lattice energy of the product is insufficient to compensate for the adverse ionization potentials or electron affinities. When such a treatment is applied to the problem of which environment is most suitable for the stabilization of the high oxidation states of the transition metals, the simplicity is lost. It is of interest to see why this should be so.

At first sight, it might appear that the halogens, since they are the only elements that take electrons exothermically to form anions with an inert gas configuration, should be most effective in stabilizing a high oxidation state in an ionic environment. In particular fluorine, because of the small size of its anion and its low heat of atomization, should be the most effective halogen. Since, however, the halide ions can only possess unit charge, the relative number of anions to cations will be large for a high oxidation state. Thus, for every M^{n+} cation that is present, n halide ions are required to maintain electrical neutrality, whereas the same function can be performed by $n/2$ divalent or $n/3$ trivalent anions. It is not unreasonable to expect that, since electrostatic forces are isotropic, they will function most effectively when the charge distribution around a particular ion is spherically symmetrical. This is possible only with 8:8, 6:6, 4:4, and 8:4 coordination and with any other arrangement the asymmetry of the electrostatic environment must lead to some directional polarization which may be sufficient, in certain cases, to lead to a significant departure from purely electrostatic bonding. The use of polyvalent anions brings its own drawback since the polarizability of the anion increases markedly with the charge, and unless prevented by the geometry of its environment and the orbitals available on the metal, the multiply charged anion will assume some covalent character in its bond with a cation possessing a high polarizing power. It would appear, therefore, that the highest oxidation state that can be stabilized in an essentially electrovalent compound is rarely greater than two, an observation that is in accordance with the Electroneutrality Principle.

5. Stabilization of Intermediate Oxidation States in Electrovalent Compounds

Up to this point the discussion has hinged on whether the compound of the metal in a particular oxidation state is thermodynamically stable with respect to its elements but such a consideration is inadequate because it is necessary, in addition, for the compound to be stable towards other modes of decomposition, e.g., disproportionation. Calculation shows that the heats of formation of all the fluorides of the first row transition elements in oxidation state I are negative and that these are therefore stable with respect to their elements. However, it is also possible to show that the heat of disproportionation into the metal and a higher fluoride is also negative.

$$\text{e.g., } 2CrF \rightarrow CrF_2 + Cr, \qquad \Delta H = -110 \text{ kcal/mole}$$

A similar situation obtains for TiF_2 which disproportionates as follows:

$$3TiF_2 \rightarrow 2TiF_3 + Ti, \qquad \Delta H = -40 \text{ kcal/mole}$$

These considerations, while showing why it is not possible to produce pure crystalline specimens of univalent transition metal fluorides by direct reaction of the elements, also indicate how it might be possible to isolate the metal in oxidation state (I) in an ionic environment. In order for disproportionation to succeed it is necessary for the electrons to be transferred from one metal ion to another and this can be avoided if the ions are prevented from approaching one another too closely. If, therefore, the ions can be held in dilute solid solution they should be kinetically stable and observable. The production of detectable quantities of Fe^I in an ionic environment can be achieved by irradiating a solid solution of FeF_2 in NaF (*29*). The Fe^+ ion produced by electron capture is partly stabilized by interaction with the solvent environment since FeF might be expected to be isomorphous with NaF. There is no reason why, in favorable circumstances, the disproportionation should not be reversed as a result of isomorphic replacement in the solid solution. If the free energy of disproportionation is small, it is possible that it may be compensated by the free energy of solution of the lower oxidation state compound in the isomorphic solvent. This could be achieved by taking equivalent amounts of a suitable metal difluoride and the free metal and fluxing them with a large excess of sodium fluoride. If the above conditions are satisfied it is possible that a solid solution of the monofluoride in NaF may separate out as a stable phase on cooling.

6. *Complex Ions with Essentially Ionic Binding*

In previous sections the discussion has been concerned mainly with ionic lattice compounds in which it is not possible to pick out discrete chemical units other than the individual ions. However, one of the foundations of transition metal chemistry is the concept that the metal ion is surrounded by a fixed number of ligands. Since this coordination number is often not equal to the charge on the free ion and since it can be satisfied equally well by neutral molecules and charged ions, the resultant complex can be positively or negatively charged or even be uncharged. It remains however a chemical entity which is identifiable in the crystal and may, in favorable circumstances, retain its identity on going into solution. The lattice energy will still make a significant contribution towards the heat of formation but much of the energy release will be due to the formation of the complex. The packing of complex ions in the lattice will be controlled almost entirely by the minimization of their mutual repulsion since the much smaller noncomplex anion, or cation will fit in suitable "holes" in the lattice. The coordination number of the metal will not be controlled by the desire to minimize the potential energy of the lattice and two other factors become of major importance. The first is the electronic configuration of the metal and the interactions between the ligands and the nonbonding electrons. The second is the extent to which the ligands displace charge towards or away from the metal.

The interaction between the ligands and the nonbonding electrons is only significant when these electrons are in a partly filled shell, especially a *d*-shell. The *d*-orbitals of a free transition metal ion are energetically degenerate, but on coordination the ligands approach sufficiently close to the ion for this degeneracy to be removed and solely by electrostatic interaction those orbitals which "point towards" the ligands are destabilized with respect to those which do not. The energy separation will depend upon the symmetry of the field and the effective field strength of the ligands and may be sufficient to change the spin multiplicity of the ion. This purely electrostatic picture is embodied in Crystal-Field theory and explains many of the properties of the complex that arise from these nonbonding electrons, i.e., visible absorption spectra and magnetism. This orientation of the ligands around the metal, apart from providing an optimum coordination number and geometry, places the ligands in a position where there is the possibility of overlap between filled orbitals on the donor atom and suitable empty orbitals on the metal. This produces a covalent contribution towards the bonding and the covalent-electrostatic picture is embodied in Ligand Field Theory but for essentially ionic complexes this latter refinement is unnecessary.

C. Covalent Binding in Coordination Compounds

When we come to consider this other extreme picture of the metal-ligand bond, we find that it is no longer easy to separate the role of the metal from the role of the environment. The reciprocative character of covalent binding requires that the atoms attached to the metal will alter its bonding properties and will be altered themselves in return. Thus, when considering the factors which control the stability of a particular oxidation state of the metal, it is necessary to know something of the nature of the attached groups.

The ionization potential of the metal and electron affinity of the donor atom play only a minor role. It is still desirable to consider the promotion energies of electrons in both atoms forming the bond because it is often necessary for electrons in the ground state of the atom to be promoted to higher levels in order to make way for covalent bonding. One well known case is that of carbon which has a ground state configuration $1s^22s^22p^2$ that must be changed, by promoting an electron to $1s^22s2p^3$ in order to make four orbitals available for bonding. A knowledge of the appropriate promotion energies for both the metal and the donor atom enables us to understand some of the factors controlling the stability of the system. This aspect is considered in more detail later on in this article (*54*). If this picture is taken as the start of our concept of covalent coordination the next process is to bring up to the free metal atom in its correct electron configuration, the appropriate number of ligands, each, one electron short of the closed shell configuration. The delocalization of the bonding electrons in the appropriate molecular orbitals provides the bonding energy and the strength and polarity of the resultant bond will depend upon the extent to which the bonding electrons experience the positive charge of the nuclei through the other shielding electrons. However close this representation may be to reality and however useful it may be in its application, it cannot be used in any discussion concerning the stabilization of oxidation states because at no stage is the metal ion oxidized. The concept of oxidation states as applied to covalent compounds was dealt with in the introduction to this article and the discussion need not be repeated here. If we wish to retain the concept of oxidation state as a useful method of correlating facts then it is necessary to picture the covalent bond as forming in a different way. We must take the free metal ion in the appropriate oxidation state and bring up to it the required number of ligands, each in their closed shell configuration, the bonds being formed by pairs of electrons originally located on the donor atoms. Not only is this the classical representation of the coordinate bond, but it is also the reverse of the process whereby the oxidation state of the metal is defined. The formation of the bond in this way leads to a transfer of charge from the ligand to the metal of up to one electron per ligand, if the electron pairs are equally shared, and therefore reduces its positive charge. The stabilization behavior can be understood relatively well if we apply the electroneutrality principle and expect to find instability when the charge on any one atom greatly exceeds $\pm\frac{1}{2}\epsilon$. The principle is less applicable to the electrovalent compounds that we have already discussed, since there, a greater charge separation is acceptable if the resultant increase in lattice energy provides adequate compensation. The transfer of charge towards the metal explains how coordination can stabilize a metal whose formal oxidation state is high. Often, the coordination number of the metal is greater than, or equal to, its formal oxidation state so that there is always an availability of electronic charge. However, with a metal ion in a high oxidation state it is also important that the donor atom should have a strong enough hold on the shared electrons, i.e., a high electronegativity, in order to prevent the process being too efficient and leading to oxidation of the ligand. Only a few ligands are suitable for the stabilization of the very highest oxidation states. Neutral molecules in general are unsuitable because too much positive charge is transferred to them. A ligand such as water might be suitable but the transfer of positive charge to the hydrogen atom makes it too acidic to remain attached. Of the uninegative anions, the halides are the most important, but in most cases fluorine is the only one possessing sufficient electronegativity to prevent oxidation-reduction. The doubly charged anions can provide even more negative charge and the complex anion formed with a high coordination number would have a very high negative charge even when the metal is in its highest oxidation state. Of the monatomic divalent anions, oxygen is by far the best in stabilizing high oxidation states, partly because of the high electronegativity of oxygen. In general, four O^{2-} ligands are used, leading to a tetrahedral arrangement. In addition to the transfer of charge by the σ type coordinate bond, the oxygen has the capacity to donate more charge to the metal by way of a π-donor bond involving another pair of electrons. The stabilization of the highest oxidation states of transition metals as their complex oxyanion is well known, e.g., TiO_3^{2-}, VO_4^{3-}, CrO_4^{2-}, MnO_4^-, FeO_4^{2-}, as well as the neutral RuO_4 and OsO_4. The ability of oxygen to form double bonds is paralleled by the other first row elements, carbon and nitrogen, and is ascribed in part to the size of the second quantum shell which is only separated from the nucleus by a 2-electron shell. The second row elements have an 8-electron penultimate shell and are unable to form double bonds as efficiently. Thus, sulfur is not as effective as oxygen in stabilizing high oxidation states so that although thiovanadates and thiomolybdates exist, any attempt to replace the oxygen in the chromate or permanganate ion results in oxidation of the sulfide to sulfur.

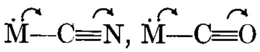
The ability of oxygen to form a donor π bond decreases to some extent down any group of the periodic table, and whereas the lighter members form oxyanion complexes the heavier members form hydroxyanions in the same oxidation state. Many examples are known in the *p* block elements e.g., $HClO_4$ and H_5IO_6, $\{ClO_3OH, IO(OH)_5\}$; H_2SO_4 and $Te(OH)_6$. With transition metals in their highest oxidation states, the effect is shown in the increased tendency towards the formation of polyanions (cf., chromates and molybdates) where the polymerization is the result of oxygen acting as a bridging group.

As the bonding assumes a more covalent character, so the coordination of the metal tends to be controlled by the inert gas or nine orbital rule. Stability can be achieved by giving the metal the same electronic configuration in its complex as that of the next inert gas atom, i.e., $nd^{10}(n + 1)s^2$-

$(n + 1)p^6$, and these electrons can be derived from nonbonding lone pairs on the metal or bonding pairs shared with the ligands. The rule can be extended to paramagnetic complexes if occupancy of an orbital by one electron is accepted as sufficient under the circumstances.

Intermediate oxidation states require less transfer of charge to and from the metal so that the bonding can be more electrovalent in character. Such complexes are amenable to ligand field treatments that require no great departure from the simple electrostatic picture.

The provision of an environment that will stabilize low oxidation states presents a new problem. As has already been shown, the ionic compounds of transition metals in their lowest positive oxidation state (+I), will usually disproportionate to gain stability. Covalent binding between the metal, in a low oxidation state, and the ligand will lead to excess negative charge being on the metal, a situation that would make the resulting complex unstable unless there were means whereby this excess charge could be returned to the ligands, usually by way of orbitals different from those used for the σ bonding. Therefore donor atoms which possess empty orbitals of suitable size and symmetry, e.g., the empty d orbitals of P, As, S, Se, or which are attached to a system that is able to conjugate with the metal, e.g.,



$$\dot{\mathrm{M}}\text{—C}\equiv\text{N},\ \dot{\mathrm{M}}\text{—C}\equiv\text{O}$$

etc., should form stable complexes with the transition metals in their lowest oxidation states, provided they can form a sufficiently covalent σ bond.

D. THE STABILIZATION OF OXIDATION STATES IN SOLUTION

Consideration of the stabilization of a particular oxidation state in solution will introduce factors which have not, as yet, been discussed, and all of which derive from competition between the ligands and the solvent molecules for a place within the most important part of the environment of the metal, namely the first coordination sphere. The important contribution made by lattice energy in the solid compounds is now replaced by the equally important contribution made by the free energy of solvation. It should be noted that, because the entropy change now makes a very significant contribution to the free energy of the process, it can no longer be ignored as it was in the case of the solid compound and so we have to change from considering an enthalpy (lattice energy) to a free energy. Interaction between the metal and the solvent will produce new possibilities of destabilization and redox reactions between the metal and the solvent will have to be avoided. It is reasonable to believe that the high oxidation states are stabilized in solvents that are not readily oxidized, e.g., water, liquid HF, and that low oxidation states are best stabilized in solvents not readily reduced, e.g., liquid ammonia. However, even when the complex is thermodynamically unstable with respect to its solvent environment, there may not be a suitable path for the electron transfer to take place and so kinetic metastability is achieved. This can arise, in inert complexes, because the solvent cannot readily displace a ligand and become directly bound to the metal. If, however, the complex is labile, there will be a rapid equilibration between the ligands and the solvent molecules for a place in the coordination sphere and, if the equilibrium products are unstable, redox processes will rapidly follow. For instance, iridium(VI) is stabilized as the volatile IrF_6, (as also is Pt^{VI}), but with excess water, hydrolysis is instantaneous and the hydrolyzed species give oxygen, ozone, and $Ir(OH)_4$. However, as we have already seen, oxygen can stabilize high oxidation states very well, and the normal behavior of a high oxidation state fluoride in water is to hydrolyze to give the oxide or oxyanion of the metal in the same oxidation state. When one considers the cases in which a particular oxidation state is stabilized thermodynamically by its immediate environment (i.e., coordination) the cobalt(II)–cobalt(III) system presents a classical example. The reduction potential for $[Co^{III}(H_2O)_6]^{3+}$ is greater than the oxidation potential of water and so the simple hydrated Co^{III} ion is unstable with respect to its aqueous environment and is reduced, albeit slowly in the absence of catalysts, to Co^{II}. However, on coordination with other ligands, e.g., ammonia, amines, cyanide etc., the situation is reversed and the higher oxidation state is stabilized with respect to the lower, since the reduction potential is less than that required for the oxidation of water. Looking at this from the point of view of the Co^{II} species, we find that, although the oxidation potential of $Co(NH_3)_6{}^{3+}$ is more positive than the reduction potential of water to give hydrogen, it is less positive than the reduction potential of oxygen in water to give hydroxide. Therefore an aqueous cobalt(II) ammine solution is stable in the absence of oxygen, but in its presence will be oxidized to cobalt(III). The problem can be restated in terms of the oxidation-reduction potential of the solvated metal ion and the relative magnitude of the stability constants of the complexes of the metal in its various oxidation states with the ligand under examination.

If K_n and K_{n+1} are the over-all stability constants for the complex of the metal in oxidation states n and $(n + 1)$ then the change in oxidation potential of the metal caused by the addition of sufficient of the ligand is given by

$$E^{\circ}_{\text{complex}} = E^{\circ}_{\text{hydrate}} - \frac{RT}{F} \ln \frac{K_n}{K_{n+1}}$$

Thus the argument now turns on what factors determine the relative stability constants of the same ligand with the various oxidation states of the metal.

As a generalization one can say that if the ligand uses only σ bonding then, if it is more polarizable than the solvent, it will favor the higher oxidation states. If the ligand requires π bonding in addition, e.g., CO, then it will favor a low oxidation state, because here the effective nuclear charge of the metal will be lower and so draw on the d_ϵ electrons less and leave them free to engage in π bonding.

The electron configuration of the metal ion is also of supreme importance. The stability of the d^6 spin-paired configuration will destabilize adjacent oxidation states making oxidation, or reduction easy in the presence of a ligand whose field is sufficient to cause spin pairing. This is seen in the stabilization of Ni^{IV} by arsine chelates. These factors can be demonstrated in the case of iron. The oxidation potential of the $Fe_{aq}^{2+} \rightarrow Fe_{aq}^{3+} + \epsilon$ couple is -0.74 volts, inadequate to cause an oxidation of ferrous to ferric by the reduction of water but sufficient for the couple to reduce oxygen in the presence of water. One of the factors involved in this couple is the high acidity (p$K \sim 2$) of the hydrated ferric species and its subsequent stabilization contribution to the higher oxidation state. The oxidation potential for $Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-} + \epsilon^-$ is -0.36 volts, i.e., more in favor of the ferric complex, since the cyanide is acting essentially as a strong σ bonder. However, with ligands that derive much of their stability from π bonding the situation is reversed. Dipyridyl and phenanthroline stabilize the Fe^{II} state in aqueous solution even in the presence of oxygen, the oxidation potential being now in the order of -1.1 volts. Thus the larger number of d_ϵ electrons in the lower oxidation state and the smaller effective nuclear charge they experience increases the stability of the lower oxidation state complex. It is of interest to note that the stabilization of the ferrous phenanthroline complex with respect to the ferric complex is greatly decreased by increasing the acidity of the solution. With sulfuric acid the equilibrium constant for the reaction

$$Fe^{2+} + Fe(phen)_3^{3+} \rightleftarrows Fe^{3+} + Fe(phen)_3^{2+}$$

changes from 1.6×10^7 in 0.05 M H_2SO_4 to 15 in 8 M sulfuric acid (*42*). This change is said to be due to the increase in the stability of the ferric complex in high acid solution although no independent assessment of the behavior of the ferrous complex appears to have been made in this acid range.

An interesting sidelight to the stabilization of oxidation states in solution is the effect of ionic strength. $K_2Ir^{IV}Br_6$ is stable in aqueous solution with respect to $K_3Ir^{III}Br_6$ but if sufficient potassium nitrate added the Ir^{IV}

is completely reduced to Ir^{III} with the liberation of bromine (*22*). This effect is caused by the different effects of ionic strength upon the two redox couples involved.

For the $IrBr_6^{3-}/IrBr_6^{2-}$ couple $E^0 = -0.99$ volts at zero ionic strength whereas for the $Br^-/\frac{1}{2}Br_2^0$ couple $E^0 = -1.08$ volts. Because of the greater ionic charge of the lower oxidation state complex the oxidation-reduction potential of the Ir^{III}–Ir^{IV} system will increase with increasing ionic strength. This will not be matched by the bromine-bromide couple which in fact is affected in the opposite direction and a stage is reached where the redox potentials cross and $IrBr_6^{2-}$ is able to oxidize bromide to bromine.

III. Survey of Oxidation States of Various Electron Configurations

A. GENERAL

We shall discuss the various nonbonding configurations starting with the $(n-1)d^{10}ns^2$ arrangement working back to the $(n-1)d^0$ in turn. When comparing the properties of chemical compounds in which the binding is essentially electrostatic it is most convenient to think in terms of isovalent sequences, e.g., the similarity of the bivalent transition series (excepting Cr^{II} and Cu^{II}). On the other hand when comparing compounds in which the binding is essentially covalent, and most of the compounds which we consider fall into this category, one finds much closer similarity if one thinks in terms of isoelectronic sequences. As an example, the d^6 arrangement is specially favorable for the formation of spin paired d_ϵ^6 complexes. Thus we find, in the first transition series, oxidation states extending all the way from $-$I, in the $[V(CO)_6]^-$ ion, to +IV, in the $[NiF_6]^{2-}$ ion.

In the discussion of each configuration no attempt will be made to list a large number of examples of the oxidation states but suitable examples are given in each case and special attention is directed towards oxidation states which have been established recently.

B. DISCUSSION OF NONBONDING CONFIGURATIONS

1. Oxidation States with a $(n-1)d^{10}ns^2$ Configuration

This survey starts most conveniently with a discussion of an electron configuration which is trivial so far as transition elements are concerned, but it provides a necessary background to the detailed examination of the transition metals. In the following table are shown the oxidation states of the transition metals, and of some nearby elements for comparison, which possess the $d^{10}s^2$ configuration and which, at least formally, could arise.

Those shown in heavy type [i.e., **Zn^{II}**] have been observed experimentally while those in light type are, as yet, unknown. It should be emphasized, however, that some of the "unknown" oxidation states to which we shall refer are unknown probably because of the lack of purposeful attempts to obtain them.

The $(n-1)d^{10}ns^2$ Configuration

Cu^{-I}	**Zn^0** (Metal)	**Ga^I** ($Ga^+(GaCl_4)^-$)	**Ge^{II}** $GeCl_2$	**As^{III}** ($AsCl_3$)
Ag^{-I}	**Cd^0** (Metal)	**In^I** ($In^+(AlCl_4)^-$)	**Sn^{II}** ($SnCl_2$)	**Sb^{III}** ($SbCl_3$)
Au^{-1}	**Hg^0** (Metal)	**Tl^I** ($TlCl$)	**Pb^{II}** ($PbSO_4$)	**Bi^{III}** ($BiCl_3$)

The oxidation states III for the elements As, Sb, and Bi and II for Ge, Sn, and Pb are well known; the I state occurs for each of the elements Ga (*24*), In (*16*) and Tl but is much more stable for Tl than for the two lighter elements of the triad. The *relative* ease with which the $d^{10}s^2$ goes to the d^{10} configuration for these three series of elements is illustrated by the following table which shows the ionization potentials for the process $(n-1)d^{10}ns^2 \rightarrow (n-1)d^{10}$ (of relevance in ionic compounds) and also the energy required to effect the promotion $ns^2 \rightarrow ns^1np^1$, a measure of the separation between the ns and np levels; this gives an idea of the ease of forming covalent compounds which use all the electrons in the outermost valency shell.

	Zn	Cd	Hg
Sum of 1st and 2nd ionization potentials (volts)	27.35	25.90	29.19
$ns^2 \rightarrow ns^1np^1$ Promotion energy (volts)	4.01	3.74	4.67

Of particular relevance for us are the data for the triads Zn^0, Cd^0, Hg^0 and Cu^{-I}, Ag^{-I}, Au^{-I}. For the first of these triads the ns^2 configuration for the ground state of the atom represents a quasi-inert gas (cf. He); hence these elements show a definite tendency to pass to the monatomic state. This is, of course, correlated with their relatively low boiling points, with a minimum at mercury for which the energy required to reach the valence state ($6s^16p^1$) is a maximum. No *compounds* of zerovalent Zn, Cd, and Hg have been reported; it seems unlikely that the use of ligands requiring d_π-p_π or d_π-d_π bonds will effect this stabilization because, in this case, the donation of d electron pairs by the metal for the necessary π bond formation with the ligand is difficult owing to the high ionization potential of an electron from the d^{10} shell (*54*). If such complexes are isolated, however, it is likely that ligands having highly polarizable electron pairs will be required, e.g., a complex of the type $K_4[HgL_4]$. The relatively high (estimated) electron affinities of Cu(1.4 ev), Ag(1.2 ev) and Au(2.4 ev) suggest that, in some ways, these could behave like halogen atoms and become negatively charged, forming Cu^{-I}, Ag^{-I}, and Au^{-I} ions, respectively. Given the right cation A^+ with an appropriate lattice energy for the resulting salt, there seems no reason why compounds of the type $[A^+][Au^-]$ might not be prepared; thus the salt-like properties of Cs^+Au^- support this (*67*).

2. Oxidation States with an $(n - 1)d^{10}ns^1$ *Configuration*

This configuration, involving an unpaired *s* electron is commonly unstable, having the properties of a free radical. However, the existence of apparent s^1 compounds is common, stability being achieved, either by disproportionation to produce two different ions with s^0 and s^2 configurations, e.g., as in $Ga^I[Ga^{III}Cl_4]$, or by metal-metal bond formation (e.g., as in Ga_2S_2 (*27*), Hg_2Cl_2 or in Au_2 in the gas phase). There do not appear to be any known examples of paramagnetic s^1 compounds in the 1st, 2nd, and 3rd long periods.

The *formal* $d^{10}s^1$ configuration is expected to arise in the cases shown in the table below:

The $d^{10}s^1$ Configuration

Ni^{-I} $[Ni_2(CO)_6]^{2-}$	**Cu^0** (Metal)	Zn^I	**Ga^{II}** Ga_2S_2	**Ge^{III}** $R_3Ge—GeR_3$	As^{IV}
Pd^{-I}	**Ag^0** (Metal)	Cd^I	In^{II}	**Sn^{III}** $R_3Sn—SnR_3$	Sb^{IV}
Pt^{-I}	**Au^0** (Metal)	**Hg^I** Hg_2Cl_2	Tl^{II}	**Pb^{III}** $R_3Pb—PbR_3$	Bi^{IV}

In the As, Sb, and Bi triad so-called quadrivalent compounds, e.g., $SbCl_4$ (*35*), are known but these are now considered to involve a mixture of Sb^{III} and Sb^V. In the Ge, Sn, and Pb triad examples of both mixed (+II and +IV) oxidation states (e.g., in plumbous plumbate Pb_3O_4) and metal-metal bonding (e.g., in Ph_3Pb-$PbPh_3$) are known. As pointed out above, for Ga, In, and Tl, mixed (+I and +III) (see Fig. 1) oxidation states arise (e.g., in $Ga^I[Ga^{III}Cl_4]$) and also metal-metal bonding (e.g., Ga_2S_2). Coming to the Zn, Cd, and Hg triad, metal-metal bonding is well known in the mercurous halides but no similar derivatives of zinc or cadmium have been described. Also, no *complex* compounds of any of these elements in the oxidation state +I have been reported. Recently, several complexes have been prepared in which gold has an oxidation state of zero, the gold atom being attached to a different metal atom in the same oxidation state. The combination of Au^0 with metals having d^9 and d^7 configurations, for example, has been effected (*18*). Thus, the following reaction involving a

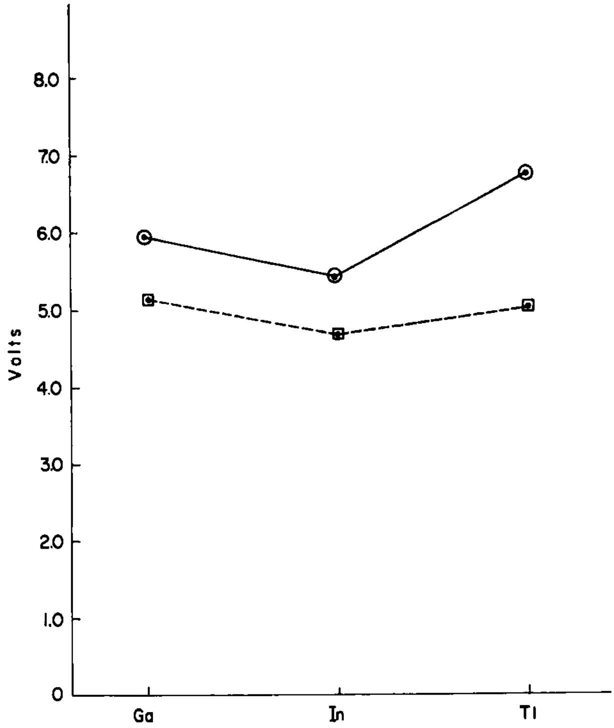


FIG. 1. ○——○ Promotion energy $ns^2 \rightarrow nsnp$ of M^+ ion; □- - - - -□ $IP_2 + IP_3$: scale to be multiplied by 10 (second and third ionization potentials). (From Nyholm *Proc. Chem. Soc.* pp. 286, 287, 288, 1961).

d^9 atom, $Ph_3P \rightarrow Au\text{-}Cl + Na^+[Co(CO)_4]^- \rightarrow Ph_3P \rightarrow Au\text{-}Co(CO)_4$ takes place readily in alcohol solution, the yellow gold cobalt complex being precipitated. Similarly the reaction $Ph_3P \rightarrow AuCl + Na^+[Mn(CO)_5]^- \rightarrow Ph_3P \rightarrow Au\text{-}Mn(CO)_5 + NaCl$ gives rise to a complex involving a d^7, Mn^0 atom. Iron gives rise to a similar derivative having the formula $(Ph_3P \rightarrow Au)_2Fe(CO)_4$.

Finally, the only example of the oxidation state −I for the triad Ni, Pd, and Pt seems to be the carbonyl hydride $H_2[Ni_2(CO)_6]$, (*32*) it being assumed that the hydrogen atom in this compound is essentially cationic.

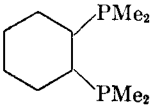
3. Oxidation States with the d^{10} Configuration

This is one of the commonest arrangements and gives rise to stable oxidation states from +VII of the halogens to −II for iron as in $Na_2Fe(CO)_4$.

The d^{10} Configuration

Fe^{-II}	**Co^{-I}**	**Ni^0**	**Cu^I**	**Zn^{II}**
$[Fe(CO_4]^{2-}$	$[Co(CO)_4]^-$	$Ni(CO)_4$	CuCl	$ZnCl_2$
Ru^{-II}	**Rh^{-I}**	**Pd^0**	**Ag^I**	**Cd^{II}**
$[Ru(CO)_4]^{2-}$	$[Rh(CO)_4]^-$	$[Pd(CN)_4]^{4-}$	AgCl	$CdCl_2$
Os^{-II}	**Ir^{-I}**	**Pt^0**	**Au^I**	**Hg^{II}**
$[Os(CO)_4]^{2-}$	$[Ir(CO)_4]^-$	$[Pt(Diphosphine)_2]$	AuCl	$HgCl_2$

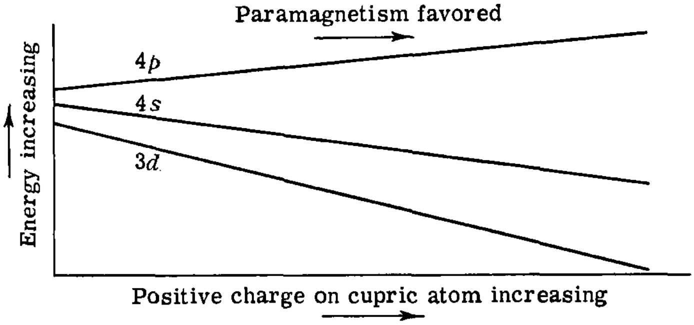
Perhaps the only problem calling for comment is the relative rarity of compounds of Pd and Pt of oxidation state zero. Thus it has been shown recently (*14*) that certain triphenylphosphine complexes in which the Pt atom appeared to have an oxidation state of zero are in fact dihydrides of Pt^{II}. Nevertheless Chatt and co-workers (*11a*) have prepared Pd^0 and Pt^0 derivatives of the diphosphine



of the type $[Pt(chelate)_2]^0$. Where strong double bonding appears to be an essential feature necessary for the attachment of the ligand (e.g., with CO), the isolation of complexes of Pd^0 and Pt^0 seems to be much more difficult. Thus, all attempts to prepare the carbonyls $Pd(CO)_4$ and $Pt(CO)_4$ have so far proven unsuccessful. It is suggested that if $d\pi$ bonding from the metal to the ligand is important for the stability of metal carbonyls, then the instability of $Pd(CO)_4$ and $Pt(CO)_4$ might be explained by the reluctance of the d^{10} Pd^0 and Pt^0 atoms to donate electrons to the ligand for $d\pi$ bond formation; the ionization potentials of the spin paired free atom configurations $Cr^0(d_\epsilon^6)$, (as in $Cr(CO)_6$); $Fe^0(d^8)$, (as in $Fe(CO)_5$); $Ni^0(d^{10})$, (as in $Ni(CO)_4$) are respectively 4.1, 3.9, and 5.7 volts (*3*). However, in marked contrast, the ionization potentials for the d^{10} atoms Pd^0 and Pt^0 are respectively 8.1 and 8.3 volts. It is suggested that, as with Cu^0, Ag^0, and Au^0, the stabilization of Ni, Pd, and Pt in the oxidation state 0 is most likely to be effected by using a negatively charged ligand; thus, Nast (*49*) has succeeded in preparing acetylides of the type $K_4M(C{\equiv}C{-}Ph)_4$ (M=Ni, Pd). These are similar to the corresponding cyano complexes $K_4Ni(CN)_4$ and $K_4Pd(CN)_4$.

4. Oxidation States with the d^9 Configuration

This is the first case where an unpaired *d* electron is involved and hence paramagnetism is to be expected. As we shall emphasize, however, this d^9 configuration shows a marked tendency to reach the d^{10} configuration, especially in covalent compounds. In passing, it is of interest to ask why atoms containing unpaired *d* electrons are fairly common but those with unpaired *s* and *p* electrons are relatively rare. A pointer to the reason for this is obtained by noting that the d^9 configuration becomes progressively less stable as the binding becomes more covalent, e.g., in the hypothetical ion $[Cu(CN)_4]^{2-}$, or as the negative charge on the atom increases. Conversely, paramagnetism is most pronounced in essentially ionic d^9 compounds, e.g., salts like cupric fluoride. It is suggested that the unpaired *d* electron becomes progressively less stable as its energy approaches that of the bonding orbitals. The higher the positive charge on the cupric atom the more the *d* orbitals is "drawn in" away from the sphere of the bonding electrons.



The d^9 configuration can reach the stable diamagnetic d^{10} arrangement in several ways: (1) by metal-metal bonding as in $Co_2(CO)_8$; (2) by oxidation of the ligand as when the cupric ion and the cyanide ion come into contact in aqueous media; (3) by disproportionation, e.g., $3Au^{2+} \rightarrow 2Au^{3+} + Au^0$. There are several factors which decide which of these will occur; of special importance are the relative values of the lattice energy of the salts produced as compared with the promotion energy required to reach the tervalent state.

The following data are of interest in order to understand the relative stabilities of the oxidation states of Cu, Ag, and Au.

IONIZATION POTENTIALS IN VOLTS

	Cu	Ag	Au
1st I. P. (Ionization potential)	7.72	7.57	9.22
2nd I. P.	20.29	21.48	20.45
Sum of 1st and 2nd I. P.	28.01	29.05	29.67
3rd I. P.	37.08	34.82	30.5
Sum of 2nd and 3rd I. P.	57.37	56.30	50.95
Promotion energy for $d^{10} \rightarrow d^9s^1$ $(^1S \rightarrow {^3D})\ J = 3$	2.72	4.85	1.86

These data show that to reach the tervalent state gold requires less energy than do copper or silver. Also, the energy required to form an M^{+3} ion starting from the M^{+} ion is considerably less for gold than it is for the other two elements. However, more energy is required to reach the Au^{2+} ion starting from the uncharged atom than for either copper or silver; hence it is not difficult to understand why the oxidation state +II in gold so readily passes to a mixture of +III and +I.

The d^9 Configuration

Fe^{-I} $[Fe_2(CO)_8]^{2-}$	**Co^0** $Co_2(CO)_8$	**Ni^I** $[Ni_2(CN)_6]^{4-}$	**Cu^{II}** $CuCl_2$
Ru^{-I}	**Rh^0** $Rh_2(CO)_8$	Pd^I	**Ag^{II}** $[AgPy_4]^{2+}$
Os^{-I}	**Ir^0** $Ir_2(CO)_8$	Pt^I	Au^{II}

Only in the cases of Cu^{II} and Ag^{II} and in the compound $K_3Ni^I(CN)_4$ has paramagnetism been observed. In all other cases diamagnetism is the rule, with metal-metal bonding. The way in which this arises in the $[Fe_2{}^{-I}(CO)_8]^{2-}$ ion, $Co_2{}^0(CO)_8$, the $[Ni_2{}^I(CN)_6]^{4-}$ ion and in cupric acetate is shown in Fig. 2.

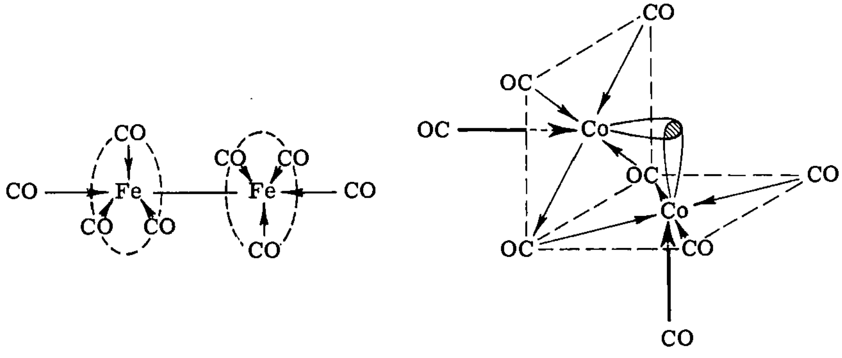
(A) $[Fe_2(CO)_8]^{2-}$ (B) $Co_2(CO)_8$

(D) $[Ni_2{}^I(CN)_6]^{4-}$ (C) $[Cu(OAc)_2 \cdot H_2O]_2$

It is of interest to note that, whereas metal-metal bond formation in $Co_2(CO)_8$ was once generally believed to be a consequence of the proximity of the two Co atoms which were bound by bridging CO groups, it is now considered likely that it is the metal-metal bond formation which causes the CO bridging. Dahl (*20a*) has shown recently that the structure of rhodium carbonyl involves a metal-metal bond without any bridging CO groups. He suggests that when the radius on the metal atom becomes small enough this enables the CO groups to come close enough together to act as a bond between the metal atoms in addition to the metal-metal bond. Obviously, in cobalt carbonyl there is then some rearrangement of the stereochemistry since the metal-metal bond is a bent one.

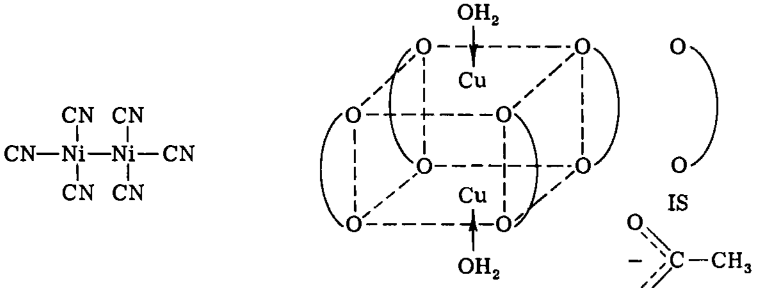
5. Oxidation States with the d^8 Configuration

The d^8 configuration gives rise to a wide range of oxidation states varying from Cr^{-II} to Cu^{III}. Paramagnetism, with two unpaired electrons, is very uncommon, having been observed only in the cases of Cu^{III} (K_3CuF_6),



$[Fe_2(CO)_8]^{2-}$
(A)

$Co_2(CO)_8$
(B)



$[Ni^{I}_2(CN)_6]^{4-}$
(D)

$[Cu(OAc)_2 \cdot H_2O]_2$
(C)

FIG. 2. Diamagnetism in metal-metal bonding.

The d^8 Spin-Paired Configuration

Cr^{-II} $[Cr(CO)_5]^{2-}$	**Mn^{-I}** $[Mn(CO)_5]^{-}$	**Fe^{0}** $Fe(CO)_5$	**Co^{I}** $[Co(RNC)_5]^{+}$	**Ni^{II}** $[NiDiars._2]^{2+}$	**Cu^{III}** $[CuO_2]_n^{n-}$
Mo^{-II} $[Mo(CO)_5]^{2-}$	Tc^{-I}	**Ru^{0}** $Ru(CO)_5$	**Rh^{I}** $[Rh(RNC)_4]^{+}$	**Pd^{II}** $[PdCl_4]^{2-}$	**Ag^{III}** $[AgF_4]^{-}$
W^{-II} $[W(CO)_5]^{2-}$	**Re^{-I}** $[Re(CO)_5]^{-}$	**Os^{0}** $Os(CO)_5$	**Ir^{I}** $[Ir(RNC)_4]^{+}$	**Pt^{II}** $[PtCl_4]^{2-}$	**Au^{III}** $[AuCl_4]^{-}$

in the well known octahedral (e.g., $[Ni(NH_3)_6]^{2+}$) and tetrahedral (e.g., $[NiCl_4]^{2-}$ nickel(II) compounds and in palladium difluoride (*6*).

The diamagnetic spin paired configuration gives rise to square four-coordinate or tetragonal six-coordinate, arrangements. More recently, it has been recognized that five-coordination is also very common for the d^8 spin paired configuration. As discussed elsewhere (*5*), five-coordination arises most readily when the $(n - 1)d \rightarrow np$ separation is a minimum. This state of affairs is favored if (1) the formal charge (oxidation state) of the metal atom is a minimum and (2) the effective nuclear charge is as small as possible. The first of these clearly increases as we pass along the sequence. $[Cr^{-II}(CO)_5]^{2-}$, $[Mn^{-I}(CO)_5]^-$, $Fe^0(CO)_5$, $[Co^I(PhNC)_5]^+$, $[Ni^{II}Cl_2{\cdot}2Et_3P]$ leading to the frequent occurrence of square-four coordination with Ni^{II}. With regard to the second item, we find that shielding decreases as we go down the periodic table in any vertical triad e.g., $Co^I \rightarrow Rh^I \rightarrow Ir^I$. As an illustration of this it is found that Co^I forms a penta-isocyanide cobalt complex whereas the Rh^I and Ir^I complexes are *four*-coordinate. Little work has been done on $Ru(CO)_5$ and $Os(CO)_5$ and it is of interest to note that in the light of the above, Os^0 is quite likely to give rise to square four coordinate complexes.

Perhaps the most interesting new oxidation states which have been stabilized recently are those in which the metal atom is in the −I or −II state. The −I state for Mn and Re are known in the ions $[Mn(CO)_5]^-$ and $[Re(CO)_5]$.[22] Recently, Kaesz (*33*) has isolated certain carbonyls and carbonyl halides of technetium, namely $Tc_2(CO)_{10}$, $Tc(CO)_5I$ and $[Tc(CO)_4I_2]_2$. There is little doubt that the corresponding $[Tc(CO)_5]^-$ ion will be obtained in due course. The −II oxidation state occurs in ions of the type $[M(CO)_5]^{2-}$ where M = Cr, Mo, and W. They are formed from the hexacarbonyls by reduction with sodium in liquid NH_3 (*8, 9*).

6. *Oxidation States with a d^7 Configuration*

We have here an odd number of electrons, and when it is borne in mind that this configuration is one electron short of the stable d^8 arrangement, it is not surprising that oxidation states with a d^7 configuration are not widespread, particularly in spin-paired complexes. Spin-free complexes with 3 unpaired electrons are formed by Co^{II} (e.g., octahedral $[Co(H_2O)_6]^{2+}$ and tetrahedral $[CoCl_4]^{2-}$) and Ni^{III} (e.g., octahedral K_3NiF_6). No spin-free Fe^I compounds are known but possibly this spin-free oxidation state may be stabilized by inclusion in a suitable host lattice which favors a tetrahedral arrangement, e.g., in a lattice of the type $K_3M^ICl_4$.

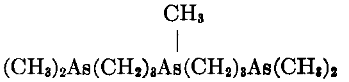
The known oxidation states having spin-paired d^7 configurations are given in the following table:

The d^7 Spin-Paired Configuration

Cr^{-I} $[Cr_2(CO)_{10}]^{2-}$	**Mn^0** $Mn_2(CO)_{10}$	**Fe^I** [Fe Diars.$(CO)_2$I]^0	**Co^{II}**[a] [Co Diars.$_2$]$^{2+}$	**Ni^{III}** K_3NiF_6
Mo^{-I} $[Mo_2(CO)_{10}]^{2-}$	**Tc^0** $Tc_2(CO)_{10}$	Ru^I	Rh^{II}	**Pd^{III}** PdF_3
W^{-I} $[W_2(CO)_{10}]^{2-}$	**Re^0** $Re_2(CO)_{10}$	Os^I	Ir^{II}	Pt^{III}

[a] Compounds with three unpaired electrons, e.g., $CoSO_4.7H_2O$ are, of course very common.

This configuration, if paramagnetic, is expected to favor square planar four-coordination or tetragonal six-coordination. The latter occurs in compounds of the type $[Ni^{III}(Diarsine)_2Cl_2]Cl$ (*53*) and the former in certain Co^{II} complexes of which the simplest example is Co^{II} protoporphyrin. It should also be emphasized that five-coordination is by no means uncommon, the arrangement being presumably square pyramidal. Examples include $NiBr_3{\cdot}2Et_3P$ (*34*) and CoI_2·Triarsine (*4*), where Triarsine has the formula



$$(CH_3)_2As(CH_2)_3\overset{\overset{\displaystyle CH_3}{|}}{As}(CH_2)_3As(CH_3)_2$$

In the case of Fe^I, a d^7 spin-paired paramagnetic complex $[Fe^I(Diarsine)(CO)_2I]^0$ has been prepared (*51*). However, as with the d^9 configuration, the tendency towards metal-metal bonding increases as the oxidation state decreases and thus the carbonyl of Mn^0 is dimeric as in $Mn_2(CO)_{10}$; replacement of one CO group by Ph_3P leads to rupture of the metal-metal bond, the monomeric paramagnetic $[Mn(CO)_4Ph_3P]^0$ being formed (*31*). If, however, one uses $(PhO)_3P$ the metal-metal bond is retained. It is not easy to decide just what is the major influence in effecting rupture of the Mn-Mn bond. A study (*18*) of the compounds produced using a variety of donors suggests that stability of the Mn-Mn bond is enhanced by using ligands which do not leave too high a positive charge on the metal atom, i.e., have polarizable donor σ pairs of electrons but which have little capacity for π bond formation. Both of these factors tend to minimize contraction of the d orbital containing the unpaired electron and hence favor overlap. The carbonyl compounds of Re^0 and Tc^0 (*33*) are now known and have properties similar to those of $Mn_2(CO)_{10}$. Lastly, we come to the $-$I oxidation state, which occurs in the dimeric complex ion $[Cr_2(CO)_{10}]^{2-}$. Similar derivatives of Mo and W are known (*8, 9*).

Before leaving the d^7 configuration it is important to note that caution is required when assigning oxidation states if metal-hydride formation is possible. Thus, certain diamagnetic rhodium compounds originally believed to have the formula $[Rh(hal)_2 \cdot 3Ph_2AsMe]_2$ with a metal-metal bond, have since been shown to owe their diamagnetism to the fact that the Rh atom is tervalent, the formula being actually $HRh(hal)_2 \cdot 3Ph_2AsMe$ (*44*).

7. *Oxidation States with the d^6 Configuration*

This is a very common arrangement for spin-paired complexes, but the only spin-free d^6 oxidation states are those of Co^{III} in octahedral K_3CoF_6, of Fe^{II} in octahedral $[Fe(NH_3)_6]Cl_2$ and of Fe^{II} in tetrahedral complexes, e.g., $[Ph_3MeAs]_2FeCl_4$ (*25*). No spin-free Mn^I complexes are known but as with Fe^I it is possible that this oxidation state can be stabilized in a suitable host lattice.

The known oxidation states having a spin-paired d^6 configuration are very extensive, the d_ϵ^6 arrangement being specially favorable for a regular octahedral arrangement.

The d^6 Spin-Paired Configuration

V^{-I} $[V(CO)_6]^-$	**Cr^0** $Cr(CO)_6$	**Mn^I** $Mn(CO)_5I$	**Fe^{II}** $[Fe(CN)_6]^{4-}$	**Co^{III}** $[Co(NH_3)_6]^{3+}$	**Ni^{IV}** $[NiF_6]^{2-}$
Nb^{-I} $[Nb(CO)_6]^-$	**Mo^0** $Mo(CO)_6$	**Tc^I** $Tc(CO)_5I$	**Ru^{II}** $[Ru(CN)_6]^{4-}$	**Rh^{III}** $[RhCl_6]^{3-}$	**Pd^{IV}** $[PdCl_6]^{2-}$
Ta^{-I} $[Ta(CO)_6]^-$	**W^0** $W(CO)_6$	**Re^I** $Re(CO)_5I$	**Os^{II}** $[Os(CN)_6]^{4-}$	**Ir^{III}** $[IrCl_6]^{3-}$	**Pt^{IV}** $[PtCl_6]^{2-}$

The octahedral spin paired complexes of Ni^{IV}, Pd^{IV} and Pt^{IV}; of Co^{III}, Rh^{III}, and Ir^{III}; and of Fe^{II}, Ru^{II}, and Os^{II} are well known but one point of interest calls for comment. The IV state for Ni is now well known but no facile generalization can be made as to relative stabilities of Ni^{IV} and Pd^{IV} unless the ligand used be specified. Thus using Cl^-, $[PtCl_6]^{2-}$ is much more stable than the readily reduced $[PdCl_6]^{2-}$ and the $[NiCl_6]^{2-}$ ion is unknown. However, for ions of the type $[M^{IV}(Diarsine)_2Cl_2]^{2+}$ the stability appears to be $Pt^{IV} \gg Ni^{IV} > Pd^{IV}$ (*28*). Presumably the relative order of the promotion energies involved changes with the residual charge on the metal atom.

The oxidation state −I appears to occur in the $[V(Dipyridyl)_3]^-$ ion but the location of the electrons is uncertain (*30*).

8. *Oxidation States with the d^5 Configuration*

The spin-free arrangement, even though it involves a half-filled *d*-shell is limited in its occurrence to Fe^{III} and Mn^{II}. The spin-paired d^5 arrangement is expected to be associated with an octahedral stereochemistry; indeed, stable d_ϵ^5 octahedral complexes are known for oxidation states from +IV (in $K_2Ir^{IV}F_6$) to O (in $V(CO)_6$) and perhaps −I (in the $[Ti(Dipyridyl)_3]^-$ ion).

The d^5 Spin-Paired Configuration

Ti^{-I} $[TiDipy_3]^{-1}$	**V^0** $V(CO)_6$	**Cr^I** $[CrDipy_3]^+$	**Mn^{II}** $Mn(CN)_6^{4-}$	**Fe^{III}** $[Fe(CN)_6]^{3-}$	**Co^{IV}** $[CoF_6]^{2-}$
Zr^{-I}	Nb^0	Mo^I	**Tc^{II}** $[Tc\ Diars._2I_2]^0$	**Ru^{III}** $[Ru(CN)_6]^{3-}$	**Rh^{IV}** $[RhCl_6]^{2-}$
Hf^{-I}	Ta^0	W^I	**Re^{II}** $[Re\ Diars._2Cl_2]^0$	**Os^{III}** $[Os(CN)_6]^{3-}$	**Ir^{IV}** $[IrCl_6]^{2-}$

Oxidation states which have been stabilized recently include Re^{II} and Tc^{II} as Diarsine complexes of the type $[M^{II}(Diarsine)_2Cl_2]^0$ (*23*), Cr^I as $[Cr^I(Dipyridyl)_3ClO_4$ and V^0 as the carbonyl $V(CO)_6$ (*10*, *61*). Earlier doubts as to whether this carbonyl is dimeric and diamagnetic or monomeric and paramagnetic have been resolved in favor of the latter. Thus $V(CO)_6$ is the only known carbonyl which does not obey the "nearest inert gas" rule. The absence of d^5 compounds of the remaining elements to the bottom left hand corner of this table probably reflects more the lack of purposeful work on this subject than inherent difficulties in their stabilization.

9. Oxidation States with the d^4 Configuration

The d^4 configuration is of special interest in many ways because it is known to give rise to 0, 2, or 4 unpaired electrons and to coordination numbers of 4, 6, and 7. Regarding the spin-free complexes of atoms with 4 unpaired electrons, we find that this highly paramagnetic state arises with Cr^{II} and Mn^{III} only. From simple crystal field theory one expects a square planar arrangement for *four*-coordinate spin-free d^4 complexes and a tetragonal arrangement if the coordination number is six. This is certainly true for $[CrCl_4]^{2-}$ and $CrCl_2{\cdot}2Py$. The spin-free oxidation states of $+I(V^I)$ and $+IV(Fe^{IV})$ have not been reported. The failure to prepare $K_2Fe^{IV}F_6$ is curious for although one has to break the d^5 shell of Fe^{III} to achieve this, the relative ease with which Fe^{IV} can be stabilized with diarsine and Fe^{VI} with oxygen suggests that this is not the main problem to be overcome.

The oxidation states in which the d^4 configuration has two unpaired electrons are shown in the Table below. In an octahedron this indicates a d_ϵ^4 arrangement and is observed for a wide range of oxidation states. The sole example of the +VI state (of Pt) is PtF_6 (*7*) and similarly only one example of +V, $KIrF_6$ is known. The +IV state is represented by Fe, Ru, and Os with compounds of the type $[M^{IV}(Diarsine)_2Cl_2][ClO_4]_2$

The d_ϵ^4 Configuration				
Cr^{II} $Cr(CN)_6^{4-}$	**Mn**^{III} $[Mn(CN)_6]^{3-}$	**Fe**^{IV} $[Fe\ Diars._2Cl_2]^{2+}$	Co^{V}	Ni^{VI}
Mo^{II} $[Mo\ Diars._2I_2]^0$	**Tc**^{III} $[Tc\ Diars._2Cl_2]^+$	**Ru**^{IV} $[RuCl_6]^{2-}$	Rh^{V}	Pd^{VI}
W^{II} $[W\ Diars._2I_2]^0$	**Re**^{III} $[Re\ Diars._2Cl_2]^+$	**Os**^{IV} $[Os\ Diars._2Cl_2]^{2+}$	**Ir**^{V} $K[IrF_6]$	**Pt**^{VI} PtF_6

[M^{IV} = Fe (*55*) or Os (*56*)] or $K_2M^{IV}Cl_6$ (M^{IV} = Ru or Os). As with the Ni, Pd, and Pt triad, we find that whereas the Cl^- ion will stabilize the two heavier elements, diarsine is needed to stabilize Fe^{IV}. Once again, as with Pd^{IV}, we find that the complex ion $[Ru^{IV}(Diarsine)_2Cl_2]^{2+}$ is much less stable than the corresponding complex Fe^{IV} ion. (It is of interest to note that the Co, Rh, and Ir sequence might be expected to show similar behavior. In fact Ir^{IV} is quite stable in the compound K_2IrCl_6 whereas, although Rh^{IV} can be prepared as $Cs_2Rh^{IV}Cl_6$ the compound loses chlorine rapidly if moist. It is more effectively stabilized by including it in a host lattice such as $[NH_4]_2PtCl_6$. Experience with the Fe, Ru, and Os and Ni, Pd, Pt triads suggests that the $[Co^{IV}(Diarsine)_2Cl_2]^{2+}$ should perhaps be less difficult to prepare than $[Rh^{IV}(Diarsine)_2Cl_2]^{2+}$.

Coming to the oxidation state +III, the complex cyanide $K_3Mn(CN)_6$ has been known for many years but Re^{III} and Tc^{III} in octahedral complexes have been obtained only recently (*23*). In both cases, the complex formed was of the type $[M^{III}(Diarsine)_2Cl_2]^+Cl^-$. The +II state can be stabilized in the case of Cr^{II} as the complex cyanide and recently a series of d_ϵ^4 octahedral complexes of Mo^{II} of the type $[Mo^{II}(Diarsine)_2Cl_2]^0$ (*46*) have been prepared. The assigned octahedral structure is supported by the fact that the compounds are isomorphous with the corresponding Tc^{II} and Re^{II} complexes. The spin-paired d_ϵ^4 oxidation state +I for vanadium has not yet been reported.

Finally, we come to the diamagnetic d^4 complexes. These are of three kinds (a) those in which the metal atom is (presumably) four-coordinate; (b) those in which it is definitely seven-coordinate and (c) those in which metal-metal bonding must be invoked. The best examples of the first of these types are the Re^{III} halide derivatives, e.g., Re_2Cl_6 and the $[ReCl_4]^-$ ion. Recent investigations (*2*) have indicated that Re_2Cl_6 is dimeric in a variety of solvents and this supports—but does not confirm—the generally accepted halogen bridged tetrahedral structure like anhydrous ferric

Footnote added in proof: It has now been shown by Cotton and also by Ferguson *et al.* (personal communications) that the $[ReCl_4]^-$ ion is in fact trimeric in the solid state. The $[Re_3Cl_{12}]^{3-}$ unit involves a central group of three Re atoms in a triangle.

chloride. Similarly, it has been shown that the $[ReCl_4]^-$ is apparently monomeric in solution. The hypothesis that the Re^{III} is tetrahedral with a d_γ^4 configuration would, as pointed out by Orgel, explain the diamagnetism. However, all attempts to establish this tetrahedral arrangement have so far proven unsuccessful.* One expects that Mo^{II} and W^{II} might give rise to similar d_γ^4 complexes, e.g., $K_2Mo^{II}Cl_4$ but so far all attempts to isolate these have proven fruitless. Similarly, $Os^{IV}Cl_4$ shows no evidence of the properties expected if it were in fact tetrahedral and monomeric.

The seven-coordinate diamagnetic complexes are derived from certain carbonyl compounds wherein the governing rule appears to be the desire on the part of the metal to reach the nearest inert gas configuration. Since there are four nonbonding electrons occupying two *d* orbitals only, there are clearly seven orbitals available for bond formation. Such compounds are formed by Mo^{II} and W^{II}, e.g., by the reaction (*52*). Mo^0 Diarsine$(CO)_4$ + $I_2 \rightarrow Mo^{II}$ (Diarsine)$(CO)_3I_2$ + CO. Finally, we have compounds in which metal-metal bonding is invoked. The best examples of this are the derivatives of the bivalent molybdenum halides. In general these can be looked upon as derived from a basic cation of the formula $[Mo_6Cl_8]^{4+}$. The structure of this is shown in Fig. 3. The eight Cl atoms occupy the corners of a cube and the six molybdenum atoms are in the middle of the six faces. Six groups now have to be attached, one to each Mo atom normal to the faces of the cube. In the compound $[Mo_6Cl_8]^{4+}[Cl^-]_4 \cdot 2H_2O$ there are clearly four chlorine ions and two water molecules. However, unless one invokes some kind of pairing of *d* electrons between molybdenum atoms, such a complex is expected to be paramagnetic. The symmetry of the d_ϵ orbitals permit such pairing of electrons and if one regards each Mo as having in effect a valency of six one can understand the magnetic properties and the absence of color in these derivatives (*59, 63*).

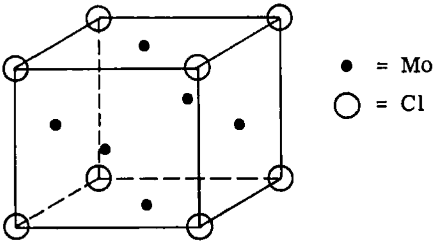


FIG. 3. Structure of $[Mo_6Cl_8]^{4+}$.

10. Oxidation States with a d^3 Configuration

Two possibilities arise in this instance, those compounds which contain *three* and those which contain only *one* unpaired electron. We discuss these

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* See note added in proof on page 40.

in turn. The spin-free d^3 configuration is specially favorable for octahedral coordination and the extent to which this d_ϵ^3 configuration is able to give rise to a wide range of oxidation states is shown in the following table:

The d^3 (Spin-Free) Configuration

V^{II} $[V(H_2O)_6]^{2+}$	**Cr**^{III} $[Cr(NH_3)_6]^{3+}$	**Mn**^{IV} $[MnF_6]^{2-}$	**Fe**^{V} $[FeO_4]^{3-}$	Co^{VI}
Nb^{II}	**Mo**^{III} $[MoCl_6]^{3-}$	**Tc**^{IV} $[TcCl_6]^{2-}$	Ru^{V} $[RuF_6]^{-}$	Rh^{VI}
Ta^{II}	**W**^{III} $[W_3Cl_9]^{3-}$	**Re**^{IV} $[ReCl_6]^{2-}$	**Os**^{V} $[OsF_6]^{-}$	**Ir**^{VI} $[IrF_6]^{0}$

Perhaps the most interesting are the compounds of Mo^{III}, W^{III}, Tc^{IV}, Re^{IV}, Os^{V}, and Ir^{VI}, since three unpaired electrons is the greatest number observed in any compounds in the second two transition series. Again, not much is known of the oxidation state +II arising with d^3 complexes of V^{II}, Nb^{II}, and Ta^{II}.

The spin-paired d^3 complexes contain only one unpaired electron and if we assume that spin pairing occurs because the third orbital is used for bond formation, seven-coordination results. This occurs in the complex cyanide of Mo^{III}, $K_4Mo(CN)_7{\cdot}2H_2O$, and in certain W^{III} complexes such as [W^{III}Diarsine$(CO)_3Br_2$]Br (*57*). Similar paramagnetic seven-coordinate derivatives are expected with Tc^{IV} and Re^{IV} and with Nb^{II} and Ta^{II} but no examples have yet been reported.

11. Oxidation States with a d^2 Configuration

We consider first the spin-free compounds, containing two unpaired electrons. These are expected to arise for the oxidation states shown in the table. The spin free d^2 configuration is of special interest in connection with the formation of tetrahedral complexes since the d_γ^2 configuration gives a half filled d_γ shell. It is no accident, therefore, that in the first transition series the oxidation states from +II to +VI are all associated with tetra-

The d^2 (Spin-Free) Configuration

Ti^{II} Na_2TiCl_4	**V**^{III} $[V(H_2O)_6]^{3+}$	**Cr**^{IV} K_2CrF_6	**Mn**^{V} K_3MnO_4	**Fe**^{VI} K_2FeO_4
Zr^{II}	Nb^{III}	Mo^{IV}	Tc^{V}	**Ru**^{VI} K_2RuO_4
Hf^{II}	Ta^{III}	W^{IV}	Re^{V}	**Os**^{VI} OsF_6

hedral complexes—although an octahedral arrangement is also possible (e.g., with $\mathrm{V^{III}}$). The isolation of $\mathrm{Na_2Ti^{II}Cl_4}$ (*45*) is a good example of the way in which an oxidation state may be stereochemically stabilized. The stability of the compound $\mathrm{K_2FeO_4}$ is presumably related to this also, $\mathrm{K_2FeO_4}$ being isomorphous with $\mathrm{K_2SO_4}$.

The d^2 Spin-Paired Configuration

$\mathrm{Ti^{II}}$	$\mathrm{V^{III}}$	$\mathrm{Cr^{IV}}$	$\mathrm{Mn^{V}}$	$\mathrm{Fe^{VI}}$
$\mathrm{Zr^{II}}$	$\mathrm{Nb^{III}}$	**Mo$^{\mathrm{IV}}$**	**Tc$^{\mathrm{V}}$**	$\mathrm{Ru^{VI}}$
		$\mathrm{[Mo(CN)_8]^{4-}}$	$\mathrm{[Tc\ Diars{\cdot}_2Cl_4]^{+}}$	
$\mathrm{Hf^{II}}$	$\mathrm{Ta^{III}}$	**W$^{\mathrm{IV}}$**	**Re$^{\mathrm{V}}$**	$\mathrm{Os^{VI}}$
		$\mathrm{[W(CN)_8]^{4-}}$	$\mathrm{[Re\ Diars{\cdot}_2Cl_4]^{+}}$	

The second possibility is, of course, diamagnetism, and this is expected to be associated with eight coordination. Running along the two heavier transition series, examples of this include: for the oxidation state +IV, $\mathrm{K_4Mo(CN)_8}$ and $\mathrm{K_4W(CN)_8}$; for the oxidation state +V, the complex cyanides $\mathrm{K_3Tc(CN)_8}$ and $\mathrm{K_3Re(CN)_8}$ (*19*) and the diarsine complexes of the type $\mathrm{[M^{V}(Diarsine)_2Cl_4]ClO_4}$, where $\mathrm{M^{V} = Tc^{V}}$ and $\mathrm{Re^{V}}$ (*23*). Surprisingly, corresponding $\mathrm{Ru^{VI}}$, $\mathrm{Os^{VI}}$ compounds have not yet been prepared and the +III state for Nb and Ta appears to have been little investigated.

12. Oxidation States with a d^1 Configuration

These are expected to arise for the elements shown in the following table and, as may be seen, it is of common occurrence.

The d^1 Configuration

Ti$^{\mathrm{III}}$	**V$^{\mathrm{IV}}$**	**Cr$^{\mathrm{V}}$**	**Mn$^{\mathrm{VI}}$**	$\mathrm{Fe^{VII}}$
$\mathrm{[Ti(H_2O)_6]^{3+}}$	$\mathrm{VCl_4}$	$\mathrm{[CrO_4]^{3-}}$	$\mathrm{[MnO_4]^{2-}}$	
Zr$^{\mathrm{III}}$	**Nb$^{\mathrm{IV}}$**	**Mo$^{\mathrm{V}}$**	**Tc$^{\mathrm{VI}}$**	**Ru$^{\mathrm{VII}}$**
$\mathrm{ZrCl_3}$	$\mathrm{NbCl_4}$	$\mathrm{MoCl_5}$	$\mathrm{TcCl_6}$	$\mathrm{[RuO_4]^{-}}$
Hf$^{\mathrm{III}}$	**Ta$^{\mathrm{IV}}$**	**W$^{\mathrm{V}}$**	**Re$^{\mathrm{VI}}$**	**Os$^{\mathrm{VII}}$**
$\mathrm{HfCl_3}$	$\mathrm{TaI_4}$	$\mathrm{WBr_5}$	$\mathrm{ReF_6}$	$\mathrm{[OsO_4]^{-}}$

A survey reveals that this configuration is associated with a wide range of coordination numbers extending from four to eight. In complexes where the binding is essentially covalent as in metal carbonyls, we expect a coordination number of eight. This observed in the case of complexes of $\mathrm{Re^{VI}}$, e.g., the $\mathrm{[Re^{VI}(CN)_8]^{2-}}$ ion, and the recently reported $\mathrm{[Tc^{VI}(CN)_8]^{2-}}$ ion. Similarly $\mathrm{Mo^{V}}$ and $\mathrm{W^{V}}$ give rise to octacyanides of the type

$[Mo^V(CN)_8]^{3-}$. These latter have a structure based on a dodecahedral arrangement which can be visualized as arising from two interlacing tetrahedra, one of which has been slightly flattened while the other is slightly elongated (cf. Fig. 4). Quadrivalent vanadium also gives rise to a structure of this type; vanadium tetrachloride and diarsine react to form the compound VCl_4·2 Diarsine (*17*) which is isomorphous with the corresponding titanium complex. The structure of this is shown in Fig. 4. No similar diarsine derivatives of niobium or tantalum have yet been prepared; in view of the greater ease with which eight coordination arises in the second two transition series one might expect eight coordinate derivatives of Nb^{IV} and Ta^{IV} to arise also. The unusual eight-coordination for quadrivalent vanadium is noteworthy. Presumably, the bonds are sufficiently ionic to ensure that bond pair-bond pair repulsions are relatively small. Six coordination is very common and is exemplified by the $[Ti(H_2O)_6]^{3+}$ ion and by compounds such as ReF_6. Four coordinate complexes of the type $[MO_4]^{2-}$ are well known for Mn^{VI} and recently the corresponding Re^{VI} and Tc^{VI} derivatives have been isolated (*38*). The single d_γ electron has practically no effect upon the regular tetrahedral stereochemistry, $BaMn^{VI}O_4$ being isomorphous with $BaSO_4$. The oxidation state V for chromium also arises in a presumably tetrahedral complex ion of the type $[Cr^VO_4]^{3-}$ described first by Klemm (*41*) and co-workers and recently investigated in more detail by Bailey and Symons (*3*).

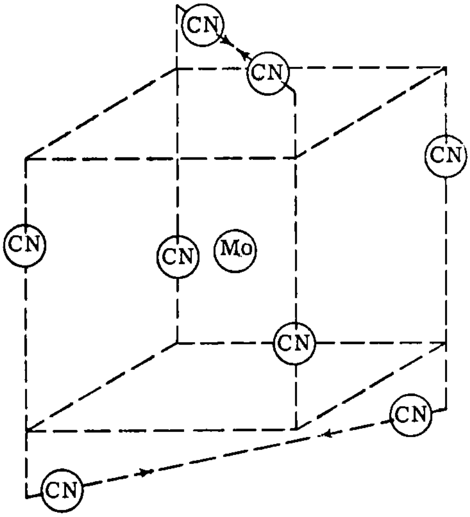

Fig. 4. Structure of $[Mo^V(CN)_8]^{3-}$.

The quadrivalent state occurs in VCl_4 which is again regular tetrahedral.

No $[Ti^{III}Cl_4]^-$ complexes have yet been reported but the ease with which the corresponding $[VCl_4]^-$ complexes can be prepared by employing a suitable solvent suggests that these should be capable of being prepared. No stable complexes of tervalent zirconium or hafnium have been reported but the tervalent halides are well known (*50*). They display only very weak paramagnetism and this appears to indicate strong antiferromagnetic interaction in the crystal.

13. Oxidation States with the d^0 Configuration

Oxidation states embodying this configuration extend all the way from the univalent K, Rb, and Cs triad to the heptavalent elements of Mn, Tc, and Re. The first break occurs at iron, no Fe^{VIII} compounds being known. Ru^{VIII} and Os^{VIII} are known as their tetroxides but the previously reported octafluoride of osmium has recently been shown to be in fact the hexafluoride. It is of interest to note that if the nine-orbital rule were obeyed, complexes having a coordination number 9 are possible. The only possible example of this is the strontium nonahydrate ion of unknown structure. Gillespie, (*25a*) however, has suggested that a 3:3:3 structure is the most likely configuration for this ion. Eight-coordination occurs in the bis-diarsine complexes of quadrivalent titanium, zirconium, and hafnium, the structure being shown in Fig. 4.

Oxidation States with a d^0 Configuration

A^{0}	**K**^{I}	**Ca**^{II}	**Sc**^{III}	**Ti**^{IV}	**V**^{V}	**Cr**^{VI}	**Mn**^{VII}	Fe^{VIII}
Element	KCl	$CaCl_2$	$ScCl_3$	$TiCl_4$	VF_5	$[CrO_4]^{2-}$	$[MnO_4]^-$	
Kr^{0}	**Rb**^{I}	**Sr**^{II}	**Y**^{III}	**Zr**^{IV}	**Nb**^{V}	**Mo**^{VI}	**Tc**^{VII}	**Ru**^{VIII}
Element	$RbCl$	$SrCl_2$	YCl_3	$ZrCl_4$	$NbCl_5$	MoF_6	$[TcO_4]^-$	RuO_4
Xe^{0}	**Cs**^{I}	**Ba**^{II}	**La**^{III}	**Hf**^{IV}	**Ta**^{V}	**W**^{VI}	**Re**^{VII}	**Os**^{VIII}
Element	$CsCl$	$BaCl_2$	$LaCl_3$	$HfCl_4$	$TaCl_5$	WCl_6	$[ReO_4]^-$	OsO_4

IV. Summary

In this article we have endeavored to show that the "formal" oxidation state adopted by transition metal in a compound depends, not only upon the nature of the metal and its electronic configuration, but also upon its environment. The fundamental controlling factor appears to be the stability of an electrically neutral situation around the metal and indeed around every atom in the system, and, although it is not possible to convert this principle of electroneutrality to a quantitative basis, it remains, nevertheless, a good working hypothesis with which to assess the stability of a particular compound. The major departure from this principle occurs in the ionic lattice compounds where the loss of stability due to the departure from electroneutrality is more than compensated by the gain in lattice energy. In these compounds the major factors influencing the stability of an oxidation state are the relevant ionization potentials of the metal and the lattice energy of the product and, to a lesser extent, the appropriate electron affinities of the nonmetallic component. In general, provided a closed electron shell on the metal is not broken into, the increase in the lattice energy due to the greater cationic charge will compensate for the increased ionization potential. The limits of stability are reached, not as a result of the energetics of the ionic system, but as a result of the increased polarizing power of the metal ion in the higher oxidation states, especially the relatively small transition metal ions. Thus no anion is sufficiently unpolarizable to resist covalent bond formation in the higher "formal" oxidation state compounds and the factors involving the stability of the covalent compounds become of major importance.

Further considerations arise when we consider the transition metals where the number and arrangement of the *nonbonding d* electrons have a considerable effect upon the stability of the compound. It was pointed out in the preceding section that certain electronic configurations were less stable than others. The stability of a more than half filled d shell is far greater when there is an even number of d electrons than when this is odd, compare d^6, d^8, and d^{10} with d^7 and d^9, whereas no similar sharp distinction exists in a shell which is half filled or less. This is attributed to the steadily increasing effective nuclear charge as the d shell nears completion, which causes the bonding to become more covalent in character, and, in doing so, draws the bonding electrons in towards the nonbonding shell. As a result it is easier for the unpaired electron on one atom to interact with one on another atom and either be shared or transferred.

Certain electron configurations favor stabilization of a regular tetrahedral or octahedral environment, e.g.,

Regular tetrahedron d^0, d^2, $d^4{}_{(\mathrm{SP})}$, $d^5{}_{(\mathrm{SF})}$, $d^7{}_{(\mathrm{SF})}$, d^{10}
Regular octahedron d^0, d^3, $d^5{}_{(\mathrm{SF})}$, $d^6{}_{(\mathrm{SP})}$, d^8, d^{10}
(SF = spin free, SP = spin paired)

and, no doubt, the provision of a suitable forced geometry by the environment might stabilize an otherwise unusual oxidation state, e.g., $\mathrm{Fe^{I}}$ in a tetrahedral environment.

Finally, it should be stressed that the absence of an example of a metal in a particular oxidation state need not reflect the inherent instability of that particular oxidation state but possibly the lack of purposeful research.

It is to be hoped that this article will make easier the task of those whose purposeful research will find examples of hitherto uncharacterized oxidation states of the transition metals.

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NOTES ADDED IN PROOF

p. 10. Note 1.

Following observations of the high electron affinity of PtF_6 (>161 kcal/mole) [Bartlett, N., and Lohmann, D. H., *J. Chem. Soc.* p. 5253 (1962)], the stabilization of Xe(I) in the compound, $Xe^+[PtF_6]^-$, was predicted and achieved [Bartlett, N., *Proc. Chem. Soc.* p. 218 (1962)]. This breaking of the "prejudice barrier" has lead very rapidly to the isolation and characterization of XeF_2, XeF_4, XeF_6, and $[XeO_4]^{2-}$, and the great interest that has been aroused in this field will lead, in a short time, to an extensive chemistry of the once "inert" gases.

p. 32. Note 2.

It has now been shown [Robinson, W. T., Fergusson, J. E., and Penfold, B. R., *Proc. Chem. Soc.* p. 116 (1963)] that the complex ion in $CsReCl_4$ is the trimeric $[Re_3Cl_{12}]^{3-}$ with each Re atom essentially seven-coordinate.