

The Connections Between Electron Configuration and the Variations of the Oxidation State*

By CHRISTIAN KLIXBÜLL JØRGENSEN

Laboratoire de Chimie Physique, Université de Genève

Summary

The ionization energy of gaseous ions, strongly increasing as a function of the charge, is compensated with a remarkable precision in compounds and aqua ions. The available oxidation states in aqueous solution correspond to actual ionization energies not below 30 kK and the electron affinity not above 50 kK (1 kK = 1000 cm⁻¹). The chemical transition groups start at a higher atomic number than the spectroscopic ones; the average oxidation number goes through a distinct maximum except in the case of the lanthanides. The effects of interelectronic repulsion, the polarisability and the back-bonding to the ligands are discussed, as well as the definition of the spectroscopic oxidation state as contrasted to fractional atomic charges.

Chemical and Spectroscopic Versions of the Periodic Table

A few metallic elements are only known in one oxidation state in solution and in non-metallic compounds. This is true for the alkali metals, the alkaline-earth metals, aluminium (III), scandium (III), zinc (II), yttrium (III), zirconium (IV), thorium (IV), and six of the lanthanides. The majority of the elements forms compounds of several oxidation states. In the five transition groups characterized by the presence of a partly filled *d*- or *f*-shell, the variation usually takes place step by step; vanadium is known in aqueous solution in the oxidation states (II), (III), (IV) and (V), and in carbonyl complexes in (-I) and (0). On the other hand, the earlier metalloids such as sulphur and chlorine, and in general

the post-transition-group elements having atomic numbers *Z* in the intervals between the transition groups and the noble gases, change their oxidation numbers by two units at a time. Actually, it is quite characteristic¹ that once iodine or xenon is oxidized, the elements arrive rather indifferently at iodine (I), (III), (V) or (VII) and at xenon (II), (IV), (VI) or (VIII). The elements situated in the Periodic Table between the noble gases and the transition groups have invariant oxidation number.

When the consecutive "Aufbau" of *nl*-shells each containing from zero to $(4l + 2)$ electrons became the accepted explanation of the Periodic Table, it became also obvious that there is not a unique and direct relation between the lowest electron configuration of a neutral atom and the chemical properties of the element. Thus, the electron configurations [Ar] 3*d*⁶ 4*s*² of the iron atom and [Kr] 4*d*⁶ 5*s*² of the ruthenium atom are strictly analogous, though the chemical behaviour differs to a larger extent than between nickel and palladium, where the groundstates of the neutral atoms belong to the configurations [Ar] 3*d*⁸ 4*s*² and [Kr] 4*d*¹⁰. On the whole, there has been far too much emphasis on the very lowest energy level, whereas frequently several configurations roughly coincide in energy, and it might be theoretically more justified to consider the baricenters, the average energies of the configurations corresponding to several

* Based on lecture given in Société Chimique de Genève the 18. April 1969: "Les raisons électroniques pour la variation de l'état d'oxydation."

¹ C. K. JØRGENSEN, in *Halogen Chemistry* (V. GUTMANN, Ed.), Vol. 1, p. 265, Academic Press, London 1967.

energy levels. Anyhow, far more serious discrepancies exist between the chemical and the spectroscopic versions of the Periodic Table. The excited levels of helium belonging to the configurations $(1s)^1(nl)^1$ are similar to those of the alkaline-earth atoms and do not at all show the complication characterizing neon and the heavier noble gases having transitions in the visible between various $(np)^5(n'l)^1$ levels and in the far ultra-violet to the ground configuration terminating $(np)^6$. What is more important for us is that the spectroscopic transition groups start earlier and in a more sharply defined fashion than the chemical groups with highly varying oxidation states. For the atomic spectroscopist, the $3d$ group starts exactly with Sc, $4d$ with Y and $5d$ with Lu, whereas the chemist notes a triangle of invariant oxidation number, at least in aqueous solution, represented by Sc(III), Y(III), Zr(IV), Lu(III), Hf(IV) and Ta(V). At the end of the d groups, wellknown oxidation states such as Cu(II), Pd(II) and Au(III) are exceptions to the behaviour Cu(I), Pd(0) and Au(I) one might expect as maximum oxidation numbers when deduced from the occurrence of closed d^{10} shells in the atoms. Also the closed-shell $4f^{14}$ Yb(II) is very readily oxidized to ytterbium(III), though the neutral atom has essentially an alkaline-earth type configuration terminating $4f^{14}6s^2$.

Standard Oxidation Potentials and Hydration Energies

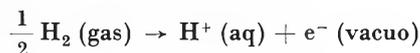
It is regrettable that the atomic spectroscopists are nearly extinct because nearly all physicists turned their interest toward nuclei and non-leptonic particles after 1931. It took some time for the chemists to take over the problems of the electronic structure of matter. The meeting between the two subjects is perhaps nowhere more surprising than in the case of the conditions for the oxidation states prevailing in chemistry. In the gaseous state, the ionization from $M^{+(z-1)}$ to M^{+z} costs an energy which, to the first approximation, is proportional to z if the two groundstates differ by the occupation of one electron in a definite nl -shell. The differences between consecutive ionization energies may be even much larger, if a closed-shell configuration occurs on the way. Seen from this point of view, the chemical stabilization going from Al(II) to Al(III) must overcompensate the large ionization energy, 229 kK of gaseous Al^{+2} to Al^{+3} because Al(II) compounds are not normally observed. The spectroscopic energy unit 1 kK = 1 kilokayser = 1000 cm^{-1} corresponds to 0.123 electron volt or 2.85 kcal/mole. In the period 1920–30, it was very fashionable to calculate MADELUNG energies of ionic crystals² and it is a good approximation (usually predicting between 95 and 105% of the observed heat of formation from gaseous ions) to use the simple model of spherically symmetric, non-over-

lapping ions, which is equiconsequential with the ionic charges concentrated on points. This treatment can be refined by evaluating a *differential ionization energy*³ which is the differential quotient of a three-term TAYLOR series going through the baricenter energies of $(nl)^z$ for a given element; and it is possible to generalize the concept of MADELUNG potentials to neutral molecules and also complex ions and to minimize the total energy of the system.⁴ Though the fractional charges (most frequently in the range from +1 to +3 for metallic elements in agreement with evidence obtained from the nephelauxetic effect in complexes containing a partly filled d shell⁵) usually are below the oxidation number, this model suggests that the total energy of fairly heteronuclear molecules is only a very moderate function of the ionicity. Consequently, the MADELUNG expression for fully electrovalent bonding is a good approximation to the total energy, though the bonding energy is slightly larger in fairly covalent cases.

The reciprocal dielectric constant of water is well below 0.1, even for interactions at a distance as short⁶ as 4 Å, and one expects the electrostatic self-energy ($z^2/2r$) to be cancelled almost completely for an ion with charge z in protonic units and radius r . It is an experimental fact that most alkali metal halides dissolve in water with very little exothermic or endothermic effect; correspondingly, the MADELUNG constant α about 1.75 for the crystal must be related roughly to the ionic radii r_M and r_X in solution

$$\frac{1.75}{R} = \frac{1}{2r_M} + \frac{1}{2r_X}$$

suggesting that the internuclear distance R in the crystal is slightly smaller than the sum of the values r_M and r_X one has to assume in the aqueous solution. However, a much more precise estimate of the *hydration energy* of the individual ions is available if one can compare with standard oxidation potentials relative to the hydrogen electrode. For the atomic spectroscopist, there is nothing indecent about requiring the ionization energy



though classical thermodynamicists argued that such a property of a single hydrated ion cannot be defined. However, in the recent years, it has been fully established (by a variety of arguments reviewed elsewhere⁷) that

³ C. K. JØRGENSEN, *Orbitals in Atoms and Molecules*, Academic Press, London 1962.

⁴ C. K. JØRGENSEN, S. M. HORNER, W. E. HATFIELD and S. Y. TYREE, *Int. J. Quantum Chem.* 1 (1967) 191.

⁵ C. K. JØRGENSEN, *Helv. Chim. Acta Fasc. extraord. Alfred Werner* (1967) 131.

⁶ T. LANDIS and G. SCHWARZENBACH, *Chimia* 23 (1969) 146.

⁷ C. K. JØRGENSEN, *Oxidation Numbers and Oxidation States*, Verlag Springer, Berlin 1969.

² E. RABINOWITCH and E. THILO, *Periodisches System, Geschichte und Theorie*, Verlag Enke, Stuttgart 1930.

Table 1. Chemical and spectroscopic ionization energies

	Standard oxidation potential		Ionization energy of gaseous ion		Hydration difference
	relative to H ₂	absolute	Groundstates	Baricenters	
Ti(III) → Ti(IV)	0 V	36 kK	350 kK	350 kK	314 kK
Ce(III) → Ce(IV)	+ 1.9	51	296	295	245
Hf(III) → Hf(IV)	< -2	< 20	270	267	> 250
Th(III) → Th(IV)	< -1	< 28	232	230	> 204
V(II) → V(III)	- 0.25	34	236	232	202
Fe(II) → Fe(III)	+ 0.77	42	247	273	205
Cu(II) → Cu(III)	> 2	> 52	297	308	< 245
Cu(I) → Cu(II)	+ 0.17	37	164	165	127
Ag(I) → Ag(II)	+ 2.0	52	173	176	121

this ionization energy is 36 kK or 4.5 eV. Admittedly, this value has an uncertainty ± 1.2 kK or ± 0.15 eV of various reasons, but for our purposes, it is entirely satisfactory for estimating the ionization energy of a species having the standard (one-electron) oxidation potential E_0 to $36 \text{ kK} + (E_0/8.06) \text{ kK}$. This quantity is called the "adiabatic" ionization energy (allowing the internuclear distances to re-arrange) in photo-electron spectroscopy of gaseous⁸ and solid⁹ compounds. If the ionization is very rapid, obeying FRANCK and CONDON's principle, one talks about the "vertical" ionization energy conserving the internuclear distances.

In Table 1, the standard oxidation potentials of aqua ions are compared with the corresponding gaseous ions. In this particular case, the energy differences between the groundstates are more appropriate than the baricenter differences. We call the difference between the ionization energy of the gaseous ion and of the aqua ion in aqueous solution the *hydration difference*. In the 3d group, the hydration difference for M(III) → M(IV) is approximately 7κ , for M(II) → M(III) 5κ and for M(I) → M(II) 3κ where the empirical parameter κ is 42 kK. Such a behaviour is compatible with a hydration energy $-\kappa z^2$ not explicitly considering the decrease of the ionic radius as a function of increasing oxidation number z . In the case of the 3d group M(II) and M(III) hexa-aqua ions, it was pointed out¹⁰ in 1956 that the "ligand field stabilization" originating in the deviations from spherical symmetry in central ions containing a partly filled shell contributes to the hydration energy and actually explains the oscillation of the standard oxidation potentials going from V(H₂O)₆³⁺ to Co(H₂O)₆²⁺. The two examples in Table 1, V(II) and Fe(II), have only a minor contribution of this kind to the hydration difference. We are not going here to discuss ligand field theory¹¹⁻¹⁴ which has changed since 1956 from a con-

sideration of the non-spherical parts of the MADELUNG potential to a more satisfactory description in terms of molecular orbitals with emphasis on the kinetic energy in the bond-region and on effects of interelectronic repulsion, as discussed below. It is seen from Table 1 that the standard oxidation potential of copper(II) aqua ions probably is well above +3 volt.

On the other hand, it is also seen that the hydration difference decreases when the ionic radii increase. Though the standard oxidation potentials for aqua ions are not too well known because of hydrolysis of M(IV), there is not the slightest doubt that Ti(III) is more readily oxidized than Ce(III) whereas, in the gaseous state, the ionization energy of Ti³⁺ is nearly 7 eV higher than of Ce³⁺. Since the chemical effects of a difference of only one volt in the standard oxidation potential are considerable, it is a regrettable fact that the theoretical prediction of the hydration difference is too uncertain at present to be of great interest to chemists, and one has to accumulate empirical evidence for the variation of the hydration difference. This is also the reason why the ionization energy of xenon being slightly below that of hydrogen and of krypton slightly above does not by itself constitute a proof that Xe and Kr form compounds, as they do in fact. Another difficulty for predicting oxidation states higher than M(IV) is that hydroxo and oxo complexes are formed by deprotonation of the less stable, hypothetical, aqua ions. With exceptions of certain linear species such as chlorine(I) and mercury(II), this tendency toward deprotonation¹⁵ is mainly determined by (z/r) , and actually, species such as ReO₄⁻, OsO₄⁻ and NO₃⁻ do not accept protons even in strongly acidic solution.

A situation where the hydration energy for a given element has the form $(-\kappa z^2)$ and where the parameter κ decreases with increasing ionic radii from 42 kK in the

⁸ D. W. TURNER, in *Physical Methods in Advanced Inorganic Chemistry* (H. A. O. HILL and P. DAY, editors) p. 74, Interscience, London 1968.

⁹ C. S. FADLEY, S. B. M. HAGSTRÖM, J. M. HOLLANDER, M. P. KLEIN and D. A. SHIRLEY, *Science* 157 (1967) 1571.

¹⁰ C. K. JØRGENSEN, *Acta Chem. Scand.* 10 (1956) 1505.

¹¹ L. E. ORGEL, *Introduction to Transition-Metal Chemistry*, Methuen, London 1960 (2. Ed. 1966).

¹² W. SCHNEIDER, *Einführung in die Koordinationschemie*, Verlag Springer, Berlin 1968.

¹³ C. K. JØRGENSEN, *Absorption Spectra and Chemical Bonding in Complexes*, Pergamon Press, Oxford 1962.

¹⁴ C. K. JØRGENSEN, *Modern Aspects of Ligand Field Theory*, North-Holland, Amsterdam 1969.

¹⁵ C. K. JØRGENSEN, *Inorganic Complexes*, Academic Press, London 1963.

3d to some 30 kK in the 5f group is the ideal case for an almost exact cancellation of the variation of the ionization energy as a function of the ionic charge z in the gaseous state. Figure 1 gives a qualitative representation of the variation of the average oxidation state as a function of the atomic number Z (from which Z_0 of the previous noble gas is subtracted) in the five transition groups. Obviously, this concept might be defined in various ways; one alternative is to consider the composition of the element in an aqueous solution of 1 molar, non-complexing acid at a definite oxidation potential¹³, say +0.5 V. Another alternative would be the most common oxidation state. However, Fig. 1 represents a reasonable *average* of oxidation numbers under normal circumstances. This average value happens to be close to 4 for chromium, though Cr(IV) is a far less frequent oxidation state than Cr(III) and Cr(VI) contributing to the weighted average.

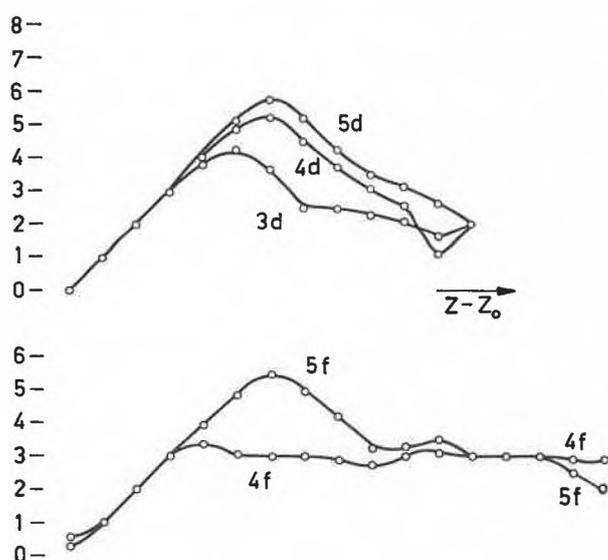


Fig. 1. The average oxidation number in the iron (3d), palladium (4d) and platinum (5d) group as well as the lanthanides (4f) and 5f group as a function of the increase of the atomic number Z above that Z_0 of the preceding noble gas (in the 5d group $Z_0 = 68$). Half-filled shell effects (due to interelectronic repulsion) are perceptible in the 3d and 4f groups

The typical behaviour outside the transition groups corresponds to straight lines with the slope 1 such as the isoelectronic series containing a noble gas, the most typical example being N(-III), O(-II), F(-I), Ne, Na(I), Mg(II) and Al(III). Such straight lines are the closest to occur in the 5d group going from Lu(III) and nearly reaching Os(VIII) and in the 5f group between Ac(III) and U(VI). On the other hand, the 4f group is very conservative, staying close to the horizontal line M(III), and the 3d group is the least varying among the three d groups. The retarded maximum of each of the d and 5f curves on the Figure represents the end of the interval of $(Z-Z_0)$ where the hydration

energy or other chemical stabilizations no longer overcompensate the ionization energy of the corresponding gaseous ions. After each such maximum, the average oxidation state drops rapidly. In particular, the 4d and the 5f group achieve relatively low values at the end, and we are going to discuss the electronic reasons for this behaviour.

Ionization Energy, Electron Affinity and Interelectronic Repulsion

When taking chemical stabilization into account, the standard oxidation potential of a given species MX_N^{+z-Na} (where z is the oxidation number of the central atom M and $-a$ is the charge of each of the N ligands X) and the standard oxidation potential of the reduced species $\text{MX}_N^{+z-Na-1}$ differ by the difference between the ionization energy and the electron affinity. Outside the transition groups, this difference is large because of the accessible one-electron orbital energies. It is quite clear-cut that Al(III) loses a very strongly bound (by 969 kK) 2p electron if Al(IV) is formed, and no known chemical stabilization can overcome this ionization, whereas the 3s electron gained in Al(II) corresponds to an electron affinity of 229 kK of gaseous Al^{+2} which happens to be slightly less than 5% in this system.

The situation is fundamentally different in the d and f groups. Here, the ionization energy of the *same*, partly filled, shell is much larger than its electron affinity. The origin is the two-electron operator of *interelectronic repulsion*. It can be shown generally^{3, 7, 16} that the average energy of the states having a given value of the total spin quantum number S and belonging to the configuration l^q (and otherwise only closed shells) contains the contribution of interelectronic repulsion

$$\frac{q(q-1)}{2} A_* + [\langle S(S+1) \rangle - S(S+1)] D$$

where the average value of $S(S+1)$ for l^q is

$$\langle S(S+1) \rangle = \frac{3}{4} q \left[1 - \frac{q-1}{4l+1} \right] = \frac{3q(4l+2-q)}{16l+4}$$

whereas it would be $\frac{3}{4} q$ in the case of non-equivalent electrons unrestricted by PAULI's exclusion principle. Both A_* and the (about ten times smaller) spin-pairing energy parameter D are inversely proportional with the average radius $\langle r \rangle$ of the partly filled shell, or more strictly speaking, directly proportional with $\langle r^{-1} \rangle$. In the case of partly filled shells, the main contribution to the difference between the ionization energy and the electron affinity is A_* .

The effects of interelectronic repulsion are very important in transition group chemistry¹⁶. Thus, the coeffi-

¹⁶ C. K. JØRGENSEN, *Bull. Soc. Chim. France* 1968, 4745.

cient to A_* would be $(q^2/2)$ in a classical description of extended charge distributions, and the decrease of this coefficient by $(-q/2)$ in quantum mechanics counteracts the tendency (mainly caused by the kinetic energy operator) of molecular orbitals to be as delocalized as possible. The stabilization of an integral number of strongly localized electrons is particularly pronounced in the $4f$ group with small average radius of the partly filled shell, and consequently, even metallic alloys¹⁷ have magnetic moments and other physical properties corresponding either to M(III) or to M(II).

It can be safely predicted that the $4f$ group prefers a constant oxidation state in aqueous solution. It is not quite easy to calculate that it is necessarily M(III). Unfortunately, the evidence for the hydration difference increasing from some 160 kK for Ce(II) to about 180 kK for Yb(II) is rather indirect⁷ but in agreement with the value $\kappa = 35$ kK for Ce(III) seen in Table I. The relative stability of the unusual oxidation states Eu(II) and Tb(IV) isoelectronic with $4f^7$ Gd(III) is frequently described as a "half-filled shell stabilization" in textbooks. This effect can be quantitatively described by the spin-pairing energy in agreement with the parameters of interelectronic repulsion known from the absorption spectra. Actually, the treatment can be refined to a considerable extent^{17, 18} and also cover the *electron transfer spectra* which are less frequently observed in the $4f$ group than in the d group complexes.^{1, 3}

Anyhow, it is beyond doubt that the lanthanides are not trivalent because they contain three valence electrons. Actually, at least ten of the neutral lanthanide atoms are known to have groundstates belonging to $[\text{Xe}] 4f^q 6s^2$ and not, as La, Ce, Gd, to $[\text{Xe}] 4f^{q-1} 5d 6s^2$. The same problem re-appears in the $5f$ group¹⁹. Though the neutral uranium atom has the groundstate originating in $[\text{Em}] 5f^3 6d 7s^2$, this does not make U(III) a common oxidation state more than the configuration $[\text{Xe}] 4f^4 6s^2$ of neodymium favours Nd(II). This is a good example of the discrepancies between the chemical and the spectroscopic versions of the Periodic Table, and in particular, it demonstrates the retardation of the chemical transition groups, as seen on Fig. 1.

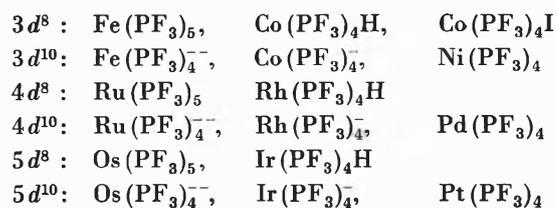
In the theory of electron transfer spectra¹⁸ occurs a parameter, $(E - A)$, which can be thought of as the difference between E , the stabilization of the one-electron energy per unit of increasing atomic number keeping the ionic charge constant, and A which is a parameter of interelectronic repulsion closely similar to A_* above. It is an experimental fact that $(E - A)$ is comparatively small in the case of partly filled shells having a small average radius, such as $4f$ and $3d$, and is larger in the $4d$, $5d$ and $5f$ groups. This behaviour can perhaps be rationalized by A varying more than E .

Anyhow, $(E - A)$ can also be determined from the variation of standard oxidation potentials when corrected for the influence of the spin-pairing energy mentioned above. One effect of the larger $(E - A)$ in the $4d$ group is that Ag(I) is more difficult to oxidize to Ag(II) than Cu(I) to Cu(II). Quite recently, mendelevium ($Z = 101$) and nobelium ($Z = 102$) have been shown²⁰ to be readily reduced to Md(II) and No(II) quite in contrast to thulium and ytterbium. This behaviour can be related²¹ to $(E - A)$ being about 5 kK in the $5f$ group but only 3 kK in the $4f$ group. The $3d$ group $M(\text{II}) \rightarrow M(\text{III})$ standard oxidation potentials for hexa-aqua ions indicate $(E - A) = 8$ kK.

Unusual Oxidation States Stabilized by Specific Ligands

We have mainly concentrated our interest on aqua ions until this point. There is much preparative evidence¹⁵ that definite ligands are able to stabilize either unusually high or unusually low oxidation numbers. The two best known ligands in the former category are fluoride and oxide. This is easy to understand in terms of the strongly oxidizing character of elemental F_2 and O_2 and of the strong MADELUNG energy of such compounds. Definite crystal structures such as fluorite PrO_2 , TbO_2 , AmO_2 , CmO_2 , and BkO_2 are more readily prepared than M(IV) in aqueous solution. Certain elements are much more stable in high oxidation states, say Cr(VI), Mn(VII), Ru(VIII), Os(VIII) and Np(VII), in oxo complexes than in the corresponding fluorides, which are in part unknown. The opposite situation occurs in IrF_6 , PtF_6 and in Nd(IV) and Dy(IV) only observed in Cs_3MF_7 . The electron transfer spectra occur at so low wavenumbers¹ in the three latter compounds that one can extrapolate that the oxides spontaneously would reduce.

It is usually argued that the stabilization of low oxidation states is connected with *back-bonding* of the loosely bound d -electrons to empty orbitals of the ligands. There is no doubt that such back-bonding occurs in carbon monoxide complexes (with the conceivable exception of mixed halides such as $\text{Pt}(\text{CO})\text{Cl}_3^-$ or $\text{Ir}(\text{CO})\text{Br}_5^{2-}$ possibly only σ -bonded) and in certain cyanide complexes such as $\text{Cr}(\text{CN})_6^{6-}$ and $\text{Pd}(\text{CN})_4^{4-}$. A most unexpected series of low oxidation states are found by KRUCK²² in phosphorus trifluoride complexes:



¹⁷ F. HULLIGER, *Helv. Physica Acta* 41 (1968) 945.

¹⁸ C. K. JØRGENSEN, *Mol. Physics* 5 (1962) 271 and 7 (1964) 417.

¹⁹ M. HAÏSSINSKY and C. K. JØRGENSEN, *J. Chim. Physique* 63 (1966) 1135.

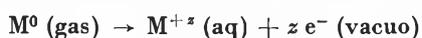
²⁰ J. MALY, T. SIKKELAND, R. SILVA and A. GHIORSO, *Science* 160 (1968) 1114.

²¹ C. K. JØRGENSEN, *Chem. Physic. Letters* 2 (1968) 549.

²² T. KRUCK, *Angew. Chem.* 79 (1967) 27.

It is worth noting that these low oxidation states differ from the monatomic entities by having all additional electrons in *d*-like and not in *s*-like orbitals. Since the time of ABEGG, it is usually argued that a given element at most can change its oxidation number by eight units, corresponding¹ to the differing occupation of one *s* and three *p* orbitals. However, ruthenium and osmium most definitely can change by ten units, from $M(-II)$ to $M(VIII)$, corresponding to the five *d* orbitals. A third, somewhat debatable case, is the green solid $Mn(NO)_3CO$ which may be considered as a $3d^{10}$ system involving $Mn(-III)$ and the ligand NO^+ isoelectronic with CO . At this point, it is an important argument⁷ that KRUCK's complexes are colourless; it is much easier to define spectroscopic oxidation states in compounds not having low-lying excited levels, whereas the difficulties are disastrous in dipyriddy complexes of apparently low oxidation numbers, which may as well contain reduced dipyriddy anion ligands.

From a spectroscopic point of view, it has been argued¹⁵ that the importance of back-bonding frequently has been overestimated. However, a compromise may consist in the back-bonding going to continuum orbitals^{7, 23} rather than to definite, discrete orbitals. GOLDSCHMIDT's concept of lithophilic and chalkophilic elements was generalized by PEARSON^{24, 25} to the idea of hard and soft anti-bases (J. BJERRUM's word for LEWIS acids) and bases. The features of the electronic structure producing the "softness" of central atoms and of ligands have been intensively discussed in recent years; a very simple and attractive proposal is made by AHLAND²⁶ suggesting that the ionization energy



divided by *z* is a measure of the softness of the element *M* in the oxidation state *z*. This quantity was introduced previously¹³ of a very different reason, and is related to the absolute potential of the hydrogen electrode discussed above.

On the other hand, the *electric polarizability* does not seem to have a unique relation with the softness. The approximate additivity of the polarizability of atomic constituents in compounds and of aqua ions has been discussed recently^{27, 28} and though the chemical deformability and back-bonding to continuum orbitals obviously is somewhat similar to the electric polarizability involving excited states belonging mainly to the continuum, there is no proportionality between the two effects.

An unexplained fact is the tendency of arsenic-containing ligands both in the form of arsine ligands¹⁵ in monomeric complexes and of crystalline poly-arsenides²⁹ to stabilize high oxidation states of certain central atoms, such as $Fe(IV)$, $Co(IV)$ and $Ni(IV)$. Apparently, the delicate balance between stronger covalent bonding of less electronegative ligands and their tendency to be oxidized and reduce the central atom can allow unexpected results, like the still unconfirmed report from 1857 of salts of IrI_6^- . Comparable problems frequently arise with sulphur-containing ligands.^{7, 30}

Fractional Atomic Charges and the Fallacy of One Electron-Pair per Bond

It is not necessary here to emphasize the lack of correspondence between the fractional atomic charges^{4, 5} in heteronuclear compounds and the integers indicating the oxidation states. In the case of a well-defined configuration of molecular orbitals each containing one or two electrons, it is quite evident that the delocalisation of the molecular orbitals produces an electronic density integrating to fractional charges on each atom. At the same time, the main constituents of the loosest bound molecular orbitals may allow an oxidation state (written with Roman numerals) to be defined⁷. Thus, the presence of five *d*-like electrons is *ipso facto* sufficient to characterize manganese(II) and three *d*-like electrons manganese(IV). It is quite conceivable that the fractional charge is lower on the central atom in MnF_6^- than in solid MnF_2 and $KMnF_3$, and arguments can be given⁵ that it is approximately 1.5 in the former and 1.85 in the two latter cases. The five *d*-like electrons in the iron(III) complex FeF_6^{3-} are sufficiently delocalized and have expanded radial functions in such a way that the fractional charge seems to be 2.2. Without the charge separation favoured by the MADELUNG potential, these charges would have been well below +1. Though the total wave-functions are not well-defined configurations the spectroscopic oxidation state can still be defined from the *preponderant configuration* classifying correctly the energy levels.⁷

A consequence of the popularity of the hybridisation hypothesis between 1931 and 1955 is the persistent feeling that *N* orbitals are needed to explain the binding of *N* ligands. This argument is entirely unreasonable for $N = 6$ in octahedral complexes¹³ and it is by no means clear whether 3*d* orbitals play any important role of the bonding in silicon, phosphorus, sulphur and chlorine compounds^{31, 32}. If they do, it is rather in the hydrides and organic compounds with low coordination number *N* and definitely not in the fluorides and oxo complexes.

²³ C. K. JØRGENSEN, *Structure & Bonding* 3 (1967) 106.

²⁴ R. G. PEARSON, *J. Amer. Chem. Soc.* 85 (1963) 3533.

²⁵ R. G. PEARSON, *J. Chem. Educ.* 45 (1968) 581 and 643.

²⁶ S. AHLAND, *Structure & Bonding* 5 (1968) 118.

²⁷ J. J. SALZMANN and C. K. JØRGENSEN, *Helv. Chim. Acta* 51 (1968) 1276.

²⁸ C. K. JØRGENSEN, *Rev. Chim. Min. (Paris)* 6 (1969) 183.

²⁹ F. HULLIGER, *Structure & Bonding* 4 (1968) 83.

³⁰ C. K. JØRGENSEN, *Inorg. Chim. Acta Rev. (Padova)* 2 (1968) 65.

³¹ E. A. C. LUCKEN, *Structure & Bonding* 6 (1969).

³² C. K. JØRGENSEN, *Structure & Bonding* 6 (1969) 94.

However, this problem is related to our subject because the relative sign of electronegativity of M and X in many molecules MX_N may determine an increase of the oxidation state of M by $2N$ units. It is possible to discuss³³ the relative *plausibility* of the distribution of oxidation states in such cases. Certain central atoms, such as tellurium (II)³⁴ and iodine (III) tend to form bent species XM which can be considered as limiting cases of *cis*-quadratic MX_2Y_2 . The quadratic species ICl_4^- and XeF_4 do not show such a distortion. These $5p^2$ -systems have a certain similarity with quadratic $4d^8$ -complexes formed by palladium (II), and actually, the absorption band

intensities³⁵ suggest comparable deviations on a instantaneous picture, as are definitely present in *cis*-Pd- $(NH_3)_2(H_2O)_2^{++}$. The plausibility of H_2Te being described as a protonic adduct of tellurium (-II) or as a hydride of Te (II) are about equivalent. In compounds containing chemical bonds between identical atoms, such as yellow $(OC)_5MnMn(CO)_5$ or perhaps even in $RSSR$ (the oxidized dimer of RS^-) it is tempting⁷ to introduce *conditional oxidation states*, reserving an electron pair for the bonding between two Mn (I) or two S (II) in the examples. However, it is far from a general rule that bonds always correspond to one electron pair, and the oxidation states may become impossible to define for this reason.

³³ C. K. JØRGENSEN, *Chem. Physic. Letters* 3 (1969) 380.

³⁴ O. FOSS, in *Selected Topics in Structure Chemistry* (P. ANDERSEN, O. BASTIANSEN and S. FURBERG, editors) p. 145, Universitetsforlaget, Oslo 1967.

³⁵ L. RASMUSSEN and C. K. JØRGENSEN, *Acta Chem. Scand.* 22 (1968) 2313.