from the study of other phenomena, for example, the volta and photoelectric effects.

The writers wish again to acknowledge their indebtedness to Professor G. N. Lewis.

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THE COLOR OF INORGANIC COMPOUNDS.

BY F. RUSSELL V. BICHOWSKY.

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In order for a substance to show selective absorption of light in any part of the visible or invisible spectrum it is necessary, according to present electromagnetic theories, that the substance contain some sort of electromagnetic mechanism capable of vibration with a free period corresponding to that of the light absorbed. The mechanism usually assumed is the constrained electron. In other words, substances capable of selective absorption in the visible or ultraviolet are supposed to contain electrons which are held by elastic or pseudo-elastic electrical constraints to some definite point of equilibrium and which are capable of vibration, given a suitable electromagnetic stimulus, with a certain definite free period determined by the magnitude of the constraining forces.

In some cases it is uncertain just what electrons are involved in the absorption. In the case of absorption in the visible and in that part of the ultraviolet extending to say 2100° A, the overwhelming evidence of organic chemistry showing that color is a function of structure proves that the electrons involved in selective absorption in this region, at least, are the same electrons that take part in chemical union, *i. e.*, are the so-called valence electrons.

Now unfortunately very little is known either about the nature or the magnitude of the forces acting on a valence electron, certainly not enough to justify a quantitative theory of light absorption. However, enough is known about the comparative stability of certain electron arrangements to be able to predict the comparative magnitude of the mean restoring forces acting on valence electrons and thus predict certain qualitative regularities of the absorption spectra of various inorganic compounds.[1]

The magnitude of the mean restoring force acting on a valence electron measures not only the period of mean free vibration of the electron but it

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[1] Compared with the vast amount of attention that has been given to the color of organic compounds very little has been given to the more fundamental problem of the color of inorganic compounds. This is probably because it is impossible to make much headway in this field without a rather definite theory of atom structure. An adequate summary of the earlier work attempting to connect color with valence or atomic weight will be found in Kayser, *Handbuch d. Spectroscopie*, III, 141 (1905).

is also the measure of the degree of stability of that particular electron arrangement, for the degree of stability of an electron arrangement is of course simply the magnitude of the force resisting small displacements from that arrangement, *i. e.*, it is the magnitude of the force which it is necessary to apply in order to start any possible change involving the destruction of the electron arrangement in question. Electron stability thus measures what the chemist means by the reactivity of a compound and is connected with the possibility of the element existing in different valence states, because with strong forces tending to restore any particular valence arrangement it is obvious that other arrangements are less likely to exist. It has, however, no direct connection with the thermodynamic stability of a compound or of a valence state, for thermodynamic stability is measured by the total work, not the initial force, necessary to separate the various parts of the molecule into some other arrangement.

Now it is known by various arguments admirably summed up by Parson[1] and by Lewis[2] that for all atoms there is one particular arrangement of electrons which has maximum electron stability. This arrangement consists, except in the case of H and He, of eight or zero electrons arranged around, or in, the positive nucleus. All other arrangements such as 2, 4, 6, or 10 electrons are very much less stable; of still less stability is the grouping of an odd number of electrons around or in the central nucleus.

Now adopting Lewis' convenient nomenclature where the heavy-typed symbols for the element represent the positive nucleus of the atom in question (supposed to have the number of charges corresponding to the ordinal number of its group in the periodic table, 1 for sodium, 2 for beryllium, etc.) and the dots represent valence electrons (no assumptions being implied as to their spacial distribution, probably except for carbon, helium and hydrogen in the corners of a cube), the chlorine atom becomes $:\overset{\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:$ and the sodium atom $\overset{\cdot}{\mathrm{Na}}$ and sodium chloride becomes $\mathrm{Na}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:$, the electrons thus forming a group of eight. NaCl therefore is a substance in which the electrons show maximum electronic stability and which would be expected to show selective absorption only for the higher frequencies. As a matter of fact the absorption bands for NaCl lie well in the ultraviolet. This argument is in no sense limited to NaCl but is perfectly general for substances of its class and it is to be expected that any compound of two or more elements which had all its electrons in groups of eight would show selective absorption at shorter wave lengths than compounds of these same elements having their electrons in groups of any other number. This expectation in the form in which we have put it can only be tested directly

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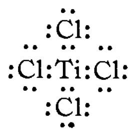
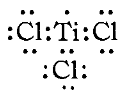
[1] Parson, "A Magneton Theory of the Structure of the Atom," Smithsonian Pub. 2371, Washington (1915).

[2] Lewis, THIS JOURNAL, 38, 762 (1916).

by comparing the color of the same salt, say the chloride, of the same element in different valence states. Thus we should expect  $\begin{array}{c} :\overset{\cdot\cdot}{\mathrm{Cl}}: \\ :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Ti}}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}: \\ :\underset{\cdot\cdot}{\mathrm{Cl}}: \end{array}$ which has all its electrons in groups of eight to have its absorption further in the ultraviolet than $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}:\overset{\cdot\cdot}{\mathrm{Ti}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}:$ which has a group of six, and we should expect both of these substances to have their absorption further towards the ultraviolet (shorter wave lengths) than  $\begin{array}{c} :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}:\underset{\cdot\cdot}{\overset{\cdot}{\mathrm{Ti}}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}: \\ :\underset{\cdot\cdot}{\mathrm{Cl}}: \end{array}$ which contains an odd number of electrons and which would hence be expected to show absorption at comparatively long wave lengths. As a matter of fact $TiCl_4$ is colorless (absorption in the ultraviolet), $TiCl_2$ yellow (absorption in the violet), and $TiCl_3$ is blue (absorption in the red and yellow). Because of the paucity of complete series of differently valenced salts of the same elements it is difficult to carry out this test in detail, nevertheless in no well-established case does it fail. That is, the order of colors of salts of the same element in differently valenced states, as the number of electrons in the groups varies from 8 to 6, 4, 2, to 1, 3, 5, 7, always follows the order: colorless, yellow, green, blue, violet, black. The color of the initial salt in the series is, however, not necessarily zero, and more than one salt may have the same color.[1]

But this test is neither the only nor the best test that can be given our theory. The color of an inorganic compound, experience has shown, can be explained, for many cases at least, by giving to each atom present a characteristic valence color, *e. g.*, blue for Cu^{++}, zero for Cu^{+}, zero for F^{-}, etc., and then adding together these valence colors to give the color of the molecule. Thus CuF_2 according to this rule is blue, CuF colorless,

[1] We have disregarded the known complexity of the absorption spectra of certain valence states and have treated all absorption spectra as if they consisted of a single band placed so as to explain the visible color. This is a somewhat broad assumption, as it is by no means evident that all the widely scattered bands lying in various parts of the visible spectra are due to any one group of causes as this assumption implies. Nevertheless, such is the lack of data, unless we made this assumption, we would have been unable to treat the greater part of the color phenomena of inorganic chemistry. Moreover, the fact that marked regularities exist in the color of inorganic compound may be taken as a justification of this assumption. Our procedure is equivalent to renouncing all attempts to explain the shape of the intensity wave-length absorption curve and restricting our attention to the comparative position of the center of gravity of that curve; in other words, it is equivalent to restricting our discussion of the forces of restitution acting on an electron to the average or mean force. To explain completely the known facts of absorption spectra a much more detailed theory of atomic structure is required.

etc. All of which means, when translated into terms of the valence theory, that the forces acting on any particular valence electron in the class of compound where this rule holds are dependent only on one particular atom nucleus and are not affected by the others. Even in the cases of compounds where the color is not the sum of its valence colors we "explain" the deviation from additivity by saying that in these cases the electrons are no longer acted on by only one nucleus but are acted on by both.

In most cases the chemist's instinct will allow him, without reference to any particular set of rules, to pick out the valence color of any particular atoms. Thus anyone would say that the valence color of Ni^{++} is green, Mo^{+++++} blue, etc., and so on for most of the valence colors given in the following table. However it is perfectly possible to reduce this feeling to certain definite rules.

(A) Since the valence color may be defined as that part of the color of a compound which is due to one nucleus alone, the color of a free ion will obviously be the valence color.

(B) In the case where the ion color is unknown, *i. e.*, in cases where the substance does not ionize, or is not stable in solution, or has its color masked by other substances present, we have to depend on more general rules. As we have said, the color of a compound depends, first, on the valence color of its atoms, and, second, on the amount of interference the forces due to one nucleus have on the stability of arrangement of the electrons belonging to another atom. Thus to find the amount of deviation in the color of compounds from the law of the additivity of valence colors of its elements, it suffices to find some means of measuring this interference. Now obviously the amount of this interatom interference with the natural period of vibration of any electron, will depend on the magnitude of the stabilizing forces normally acting on that electron. If the electron arrangement around the nucleus is very stable, as in sodium compounds, the interference due to the weaker forces from other atoms in the molecule will be very small and hence the color of these compounds will be simply the sum of the valence colors of their constituent atoms. In other words, compounds of two or more electronically stable atoms are likely to be colorless (have their absorption in the ultraviolet), compounds of one or more electronically stable atoms with one electronically less stable are likely to have a color which is the sum of the valence colors of its constituent atoms, while compounds of two or more electronically unstable atoms will in general have a color which is not the sum of the valence colors of the constituent atoms but is, because the effect of one atom on the electron stability of the other atom (on account of the slope of the potential gradient) is to decrease the restraining forces acting on the electrons, a color which corresponds to absorption in the longer wave lengths.

But now power to exist in many valenced forms is one of the tests of low electron stability. Therefore we should expect (*a*) that compounds of elements of high electron stability, that is, compounds of invariant-valence elements would be colorless; (*b*) that compounds between invariant-valence elements and elements that exist in more than one valence compound would have a color that is the sum of the valence color of their constituent atoms; (*c*) that compounds among multivariant-valence atoms would have a color which is not the sum of the valence colors of their constituent atoms.

Thus we have a means of determining the valence colors of all the elements in almost all valence states. In cases where the compound of an element of invariant valence with an element in a particular valence state is not known, the atom color we have put down in our table is but little more than a guess. It is usually based on the color of some complex salt, in which, because of the extreme polar nature of the environment in such compounds, the interference in normal electron stability is probably small. All of these cases are discussed in detail in what follows.

The atom colors as determined according to the above principles are tabulated in Table I. In this table the rare earth compounds are neglected as we do not know their normal valences. The first column gives the symbols of the elements. The elements of invariant valence, H, He, Ne, Ar, Kr, Xe, Nt, Li, Na, K, Rb, Cs, Be, Mg, Ca, Lu, Sr, Ba, Ra, B, Al, Sc, Si, Zr, F, are grouped together under the symbol Σ. The second column gives the normal valence of the element, that is, the valence which corresponds to the group in the periodic system to which the element belongs. It equals the number of positive charges on the nucleus.

It will be noted that manganese is placed in the eighth group with iron, cobalt and nickel and not in the seventh group with chlorine. If this were not done manganese would form a most striking exception to our theory. But except for the tempting gap after chlorine in the seventh group there is not the slightest reason for placing manganese with chlorine which it resembles perhaps less than any other known element. Then, too, its resemblance to the members of the iron group is quite marked and the only reason that can be urged against putting it in that group is that it would disturb the pretty though apparently quite meaningless rule of three that obtains in that group. This rule it would replace by a rule of four and indicate that the (B) section of the seventh group was fictitious and that one element was missing from the Ru and Os group. It will, of course, be seen that the proposed shift of manganese, *eka-* and *diva*-manganese into the eighth group and the accompanying abolition of the (B) section of the seventh group, makes no change in either the number or the order of the elements as known from Moseley's rule.

TABLE I.—VALENCE COLORS OF THE ELEMENTS IN THEIR DIFFERENT VALENCE STATES.

	N.	$N+2$.	$N+1$.	N.	$N-1$.	$N-$]2.	$N-3$.	$N-4$.	$N-5$.	$N-6$.
Σ	–	..	...	O_o	..	..	..	..	...	..
Cu	1	..	blue$_*$	O_*	..	..	..	..	...	..
Ag	1	..	brown$_*$	O_*	..	..	..	..	...	..
Au	1	yellow$_*$	red	O_*	..	..	..	..	...	..
Cd	2	..	...	O_*	..	..	..	..	...	..
Hg	2	..	...	O_*	..	O_*	..	..	...	..
Ga	3	..	...	O_o	..	O	..	..	...	..
In	3	..	...	O_o	..	O_*?	..	..	...	..
Tl	3	..	...	O_*	..	O_*	..	..	...	..
C	4	..	...	O_o	various	O_o	..	..	...	..
Ti	4	..	...	O_o	violet	O_*	..	..	...	..
Ge	4	..	...	O_o	..	..$_*$	..	..	...	..
Sn	4	..	...	O_o	..	O_*	..	..	...	..
Pb	4	..	...	O_*	..$_*$	O_*	..	..	...	..
N	5	..	...	O_o	..$_*$	O_o	..$_o$	..$_o$	...	..
P	5	..	...	O_o	..	O_o	..	..	...	..
V	5	yellow	...	O_*	blue$_*$	green?$_*$	violet$_*$	..	...	..
As	5	..	...	O_*	..	O_*	red?	..	...	..
Nb	5	..	...	O_o	..$_*$	..	..	..	...	..
Sb	5	..	...	O_*	brown?	O_*	..	..	...	..
Ta	5	..	...	O_o	..$_*$	..	..	..	...	..
Bi	5	..	...	..	..	O_*	dark	..	...	..
O	6	..	...	O_o	..	O_o	..	..	...	..
S	6	..	...	O_o	..	O_o	blue$_*$	..	...	..
Cr	6	..	blue?$_*$	yellow$_*$	..	..$_*$	violet$_*$	yellow$_*$	...	..
Se	6	..	...	O_o	..	O_o	..	..	...	..
Mo	6	..	...	O_o	blue$_*$	yellow$_*$	violet$_*$	yellow$_*$	...	..
Te	6	..	...	O_o	..	O_o	..	..	...	..
W	6	..	...	O_*	dark?$_*$	yellow$_*$	..$_*$	yellow	...	..
U	6	..	...	O	brown?$_*$	green$_*$	purple$_*$	yellow$_*$	...	..
Cl	7	..	...	O	..	O	yellow$_*$	O	...	O
Br	7	..	...	O	..	O	..	..	...	O
I	7	..	...	O	..	O	..	..	...	O
Mn	8	..	...	..	purple	green$_*$	..	yellow$_*$	red?$_*$	pink$_*$
Fe	8	..	...	..	..	?	..	..	purple?$_*$	yellow?$_*$
Co	8	..	...	..	..	..	..	..	various?$_*$	pink$_*$
Ni	8	..	...	..	..	..	..	..	dark?	green$_*$
Ru	8	..	...	O	..	..	..	yellow$_*$	blue	green?
Rh	8	..	...	..	..	orange	..	..	...	green?
Pd	8	..	...	..	..	..	..	yellow	...	yellow
Os	8	..	...	O	..	..	..	yellow	blue	green
Ir	8	..	...	..	..	green?	...	yellow	blue	orange
Pt	8	..	...	..	..	..	..	yellow	...	orange

The third column of the table gives the valence color of the elements that form compounds in a valence state of two higher than normal; the fourth column, the valence color of elements in valence state one higher than normal; the fifth column, the valence color in the normal valence state;

the sixth column, in one less than normal, *e. g.*, for vanadium in the tetravalent state; the seventh column $N - 2$, etc.

O in the table indicates that the substance is colorless. The subscripts refer to the color of the oxides and sulfides; (*o*) indicates that the oxide and sulfide are colorless, (*) that one or both are colored.

From this table it will be seen that the agreement between fact and theory is most striking.

I. From the theory one would expect the valence color of the N-valence elements to be more nearly zero than the valence color of any of the other valence forms of the same element. This, because substances in the N-valence state have all their electrons in groups of eight. As a matter of fact in all cases except chromium the valence color of the valence form N is actually zero. Chromium with the valence six as in the chromates has a valence color yellow and an absorption band just in the visible. It is no real exception to the rule.

II. From the theory one would expect the even electron chromopheric compounds, that is, compounds of elements with variable valence, as the oxides, sulfides and iodides, with invariant valence elements to be colorless. The only exceptions to this rule are the yellow sulfide and brown oxide of cadmium.[1] Silver is usually considered of invariant valence but a higher oxide as well as the so-called peroxynitrate[2] are known and thus the black oxide and sulfide as well as yellow iodide do not form a real exception.

III. From the theory we would expect the valence colors listed in the columns labeled $N + 1$, $N - 1$, $N - 3$, $N - 5$, to be more towards the blue than the color for the same elements given in columns N, $N + 2$, $N - 2$, $N - 4$, $N - 6$. This rule is strikingly borne out. For the $N + 1$ column the blue color of cupric compounds needs no comment. Argentic compounds are listed as brown on the somewhat dubious evidence of the peroxynitrate referred to. Our information about Au^{++} compounds is based on the existence of the chloride, bromide and sulfate, but these compounds are reported as dark red, black and brown, respectively. Probably none of them is pure, but surely the valence color of Au^{++} compounds must be more towards the blue than that of the colorless Au^{+} or yellow Au^{+++} atoms. The blue color of the seven-valence chromium atom is based on the color of the so-called perchromic acid. Whatever the true formula of this substance turns out to be, the molecule must be odd and the valence of chromium either seven or nine. In the $N + 2$ compounds the so-called true peroxides like BaO_2 have been neglected. Their formula can be interpreted either on the basis of the change of valence of the metal atom or that of the oxygen. The latter is preferred. Their in-

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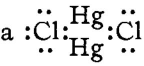
[1] ZnO is yellow at higher temperatures.

[2] Cf. Brown, *J. Phys. Chem.*, 20, 686 (1916).

clusion or exclusion could make no difference in this table except as to the membership of the group Σ. The only compounds included in $N + 2$ are the yellow auric and pervanadic ions. The fact that an atom with no valences can still form compounds should not seem strange after consideration of such compounds as H_2F_2.

Among the compounds in the $N - 1$ column the purple or blue Mn^{+++++}, Mo^{+++++}, V^{++++}, T^{+++} compounds call for no special comment. All the compounds in this column are colored except the so-called Hg^{+}, Ga^{++}, In^{++} and Ce^{+++} compounds (the last only if one insists on placing cerium in the fourth group of the periodic table). The Hg^{+}, Ga^{++} and In^{++} compounds reported, *e. g.*, the chlorides, are all probably diatomic complexes like Hg_2Cl_2 which is, on chemical evidence, a mercury-mercuric complex of the formula  $:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:\overset{Hg}{\underset{Hg}{}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:$. The brown color for Sb^{++++} is based on the brown solution that obtains when $SbCl_3$ and $SbCl_5$ are mixed, and on the double Rb and NH_4 salts which $SbCl_4$ forms.[1] The dark color for W^{+++++} and the brown color for U^{+++++} are based on the colors for impure WCl_5 and UCl_5. WCl_5 has been reported to have almost every color in the spectrum except yellow.[2]

In the case of the $N - 2$ column it will be observed that whenever the $N - 1$ compounds are not known the $N - 2$ atom color is O. This is what might be expected from the theory. The fact that there are no exceptions to this rule is a rather surprising indication of the marked difference of electronic stability between the odd and even molecular forms. Another indication of the same principle is that the only elements in this column whose atomic color is not zero, except the meagerly studied rhodium are also well known in $N - 1$, $N - 3$ or $N - 5$ valences. This rule also holds of course for the $N - 4$ column. It may perhaps be stated as an invariant rule that only compounds of those elements which can exist in odd electronic compounds will be colored. The other columns of this table will not be so carefully discussed. The color As^{++} is based on the dubious evidence of the color of As_2I_2, while that of Bi^{++} depends on that of $BiCl_2$ which as Herz[3] says, "is probably impure." The evidence for the blue color of S^{+++} compounds will be discussed fully in a paper shortly to be published. The yellow color for Cl^{++++} is based exclusively on the color ClO_2. Since Cl^{+++++} and Cl^{+++} are colorless, this color is no exception. The $N - 4$ group has higher electronic stability than either the $N - 2$ or $N - 6$ group. It is therefore not surprising that Mn^{++++} should be yellow while Mn^{+++++} is green and Mn^{++} pink. The vast number of the colors shown by the cobalt complexes makes it somewhat

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[1] Schenck, *Abegg's Handbuch*, [3] III, 609 (1907).

[2] Gmelin-Kraut, *Handbuch*, [1] III, 754 (1912).

[3] Herz, *Abegg's Handbuch*, [3] III, 648 (1907).

difficult to decide on the real atom color of Co^{+++}, but it is probably purple. The ion Co^{++} is of course pink. Why so many Co^{++} compounds should be blue is not known. It is interesting to note that the only colorless compound of chromium is $:\overset{..}{\underset{..}{\mathrm{Cl}}}:\mathrm{Cr}:\overset{..}{\underset{..}{\mathrm{Cl}}}:$. The ion is yellow. The valence color of ferric iron is based on the color of its complex salts, the so-called ferric ion, which is yellow, is the complex FeFe.

Summary.

(1) Every valence state of an element can be associated by means of purely experimental evidence with a definite "atom color."

(2) There is a marked relation between atom color thus determined and valence and valence variability.

(3) The atom color of every element in its normal valence state, that is in the valence state which corresponds to its place in the periodic system, is zero (all non-variant-valence atoms have their normal valence).

(4) The atom color of an element, in valence states where the valence is decreased or increased by an odd number from the normal valence, lies further in the blue than the atom color of the same element in any other valence state.

(5) The atom color of an element in a state whose valence is removed by an even number from normal will be zero if compounds of the element do not exist in which the valence of the element is removed by an odd number from normal; otherwise the atom color will lie further in the yellow than the atom color of the same element in a state of valence removed by an odd number from normal.

(6) Manganese *eka* and *diva* manganese belong in the eighth group with iron and the rare earths, and not in the seventh group with chlorine.

(7) Mercurous, gallous, and indous salts are double complexes. So is the ferric ion.

(8) Compounds between non-variant-valence elements will be colorless.

(9) Compounds between a non-variant-valence element and a variant-valence element will have the same color as the "atom" of variant-valence element.

(10) Compounds between other elements will have colors more to the blue than the sum of their atom colors.

(11) All these regularities can be deduced from a variation of Lewis' theory of atom structure.

(12) The almost perfect accord between the deduction and the facts indicates very strongly that Lewis' fundamental hypotheses are correct.

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