potassium, rubidium and cesium bromides, is treated as described in a previous paper, the rare alkalies being provided for by segregating them into one group along with potassium. The procedure, based on quantitative separations of the individual elements, has been tested and found satisfactory for a rapid identification of the alkali and alkaline earth metals when present in mixture.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 292]

THE NATURE OF THE CHEMICAL BOND. III. THE TRANSITION FROM ONE EXTREME BOND TYPE TO ANOTHER[1]

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A question which has been keenly argued for a number of years is the following: if it were possible continuously to vary one or more of the parameters determining the nature of a system such as a molecule or a crystal, say the effective nuclear charges, then would the transition from one extreme bond type to another take place continuously, or would it show discontinuities? For example, are there possible all intermediate bond types between the pure ionic bond and the pure electron-pair bond? With the development of our knowledge of the nature of the chemical bond it has become evident that this question and others like it cannot be answered categorically. It is necessary to define the terms used and to indicate the point of view adopted; and then it may turn out, as with this question, that no statement of universal application can be made.

In the following sections, after a discussion of the properties of ionic compounds and compounds containing electron-pair bonds, the transition from one extreme to the other is considered. It is concluded that in some cases the transition could take place continuously, whereas in others an effective discontinuity would appear.

Bond Type and Atomic Arrangement

The properties of a compound depend on two main factors, the nature of the bonds between the atoms, and the nature of the atomic arrangement. It is convenient to consider that actual bonds approach more or less closely one or another of certain postulated extreme bond types (ionic, electron-pair, ion-dipole, one-electron, three-electron, metallic, etc.), or

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[1] A part of the material of this paper was presented to the American Chemical Society at Buffalo, New York, September 2, 1931, under the title "The Structure of Crystals and the Nature of the Chemical Bond."

are intermediate between one extreme type and another, or involve two or more co-existent types. The satisfactory description of the atomic arrangement in a crystal or molecule necessitates the complete determination of the position of the atoms relative to one another. Sometimes individual details of the atomic arrangement are of interest; for example, in case the atoms are held together in part by strong bonds and in part by very weak bonds, it is instructive to mention the type of atomic aggregate formed by the strong bonds (finite molecules or complex ions, or molecules or complex ions of very great extent in one, two or three dimensions). In other cases the number of nearest neighbors of each atom (its coördination number) and their relative positions are items of interest.

There is, of course, a close relation between atomic arrangement and bond type. Thus the four single bonds of a carbon atom are directed toward the corners of a tetrahedron. But tetrahedral and octahedral configurations are also assumed in ionic compounds, so that it is by no means always possible to deduce the bond type from a knowledge of the atomic arrangement.

An abrupt change in properties in a series of compounds, as in the melting points or boiling points of halides, is often taken as indicating an abrupt change in bond type. Thus of the fluorides

	NaF	MgF_2	AlF_3	SiF_4	PF_5	SF_6
M. p.	980°	1400°	1040°	−77°	−83°	−55°

those of high melting points have been described as salts, and the others as covalent compounds. Actually the Al–F bond is no doubt closely similar to the Si–F bond. The abrupt change in properties between AlF_3 and SiF_4 is due to a change in atomic arrangement. In NaF, MgF_2 and AlF_3 the coördination number of the metal (six) is greater than the stoichiometric ratio of non-metal to metal atoms, so that each non-metal atom or ion is held jointly by two or more metal atoms or ions, resulting in high melting and boiling points. In SiF_4, PF_5 and SF_6 the coördination number is just equal to this ratio. The discrete molecules of composition given by the formulas are held only loosely together, and the substances melt and boil easily. As pointed out long ago by Kossel, this ease of fusion and volatilization would be expected for symmetrical ionic molecules, and is not sound evidence for the presence of electron-pair bonds. Volatility does not depend mainly on bond type, but on the atomic arrangement and the distribution of bonds.

The Ionic Bond

The theoretical treatment of the properties of ionic crystals and molecules has been carried farther than that of other types of atomic aggregates. The Born theory of crystal energy permits the calculation to within a few per cent. of the energy of dissociation of an ionic crystal into gaseous ions when the structure of the crystal and the equilibrium interionic distances are known. Moreover, it is now possible to predict interionic distances to within 2 or 3%, with the use either of Goldschmidt's set[2] of ionic radii, derived from the experimentally observed interionic distances in crystals of simple structure, many of which were prepared for the first time and studied with x-rays in his Mineralogical Institute in Oslo, or of a closely similar set obtained[3] by a method of treatment based on the theory of the electron distribution in atoms and ions. The screening constants[4] used in the derivation of this set were derived in part theoretically (for light ions) and in part from the experimental values of the mole refraction of atoms and ions. It has been recently found[5] that screening constants can be obtained purely from observed ionization potentials and x-ray term values. The new set of screening constants is in nearly complete agreement with the old one, which gives a feeling of confidence in this method of treating the properties of many-electron atoms and monatomic ions.

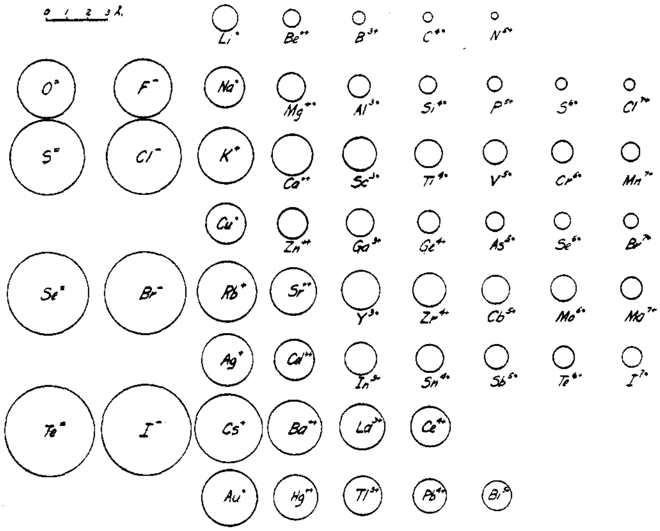

Fig. 1.—The sizes of spherically-symmetrical ions. The radii of the spheres are taken equal to the crystal radii of the ions.

The fundamental character of the understanding of ionic crystals which has been obtained is seen from the nature of the dependence of ionic radii on atomic number, shown in Fig. 3 of Ref. 3. The univalent radii lie on

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[2] V. M. Goldschmidt, "Verteilungsgesetze der Elemente." Oslo, 1926. Vol. VII.

[3] Linus Pauling, THIS JOURNAL, **49**, 765 (1927).

[4] Linus Pauling, *Proc. Roy. Soc.* (London), **A114**, 181 (1927)

[5] Linus Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

a smooth curve for each isoelectronic sequence; these are corrected in a systematic way for the effect of increasing Coulomb attraction in pulling highly charged ions more closely together to obtain the crystal radii. As is seen in Fig. 1, anions are very large, larger than all cations except those of the alkali metals. Moreover, the anions occur in pairs of nearly the same radius, $O^=$ and F^-, etc. This is the reason that hydroxyl ion and fluorine ion so often replace each other isomorphously in minerals, such as topaz, $Al_2SiO_4(OH,F)_2$. (The proton has little effect on the crystal radius.)

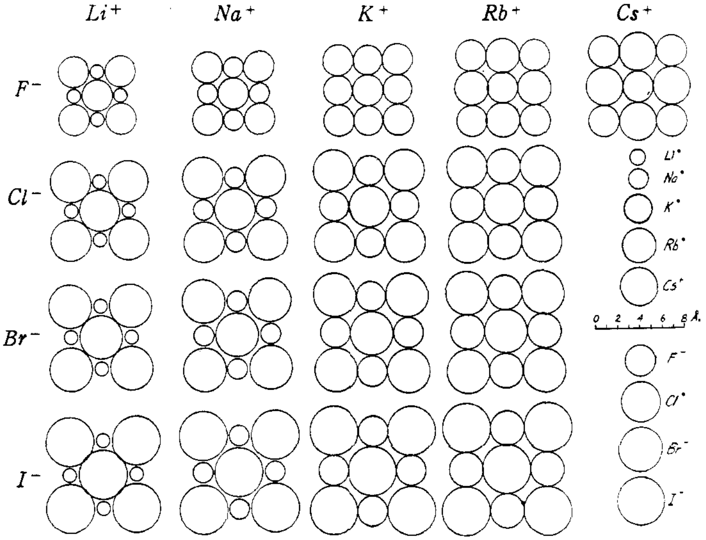

Fig. 2.—The arrangement of ions in cube-face layers of alkali halide crystals with the sodium chloride structure.

The equilibrium interionic distances and accordingly the properties of crystals are influenced not only by the sum of the radii of anion and cation, but also by their ratio, as discussed by Van Arkel and especially by Goldschmidt. This is shown in Fig. 2, representing the alkali halide crystals with the sodium chloride structure. In most of the crystals the anions and cations are in contact. In LiCl, LiBr and LiI, however, the anions are so large relative to the cations that they come into mutual contact, and the size of the unit of structure is determined by the anion radius alone, the cations being left to rattle around in the interstices. This determination of the dimensions of the units and the arrangement of the anions by the anions alone has been especially discussed by W. L. Bragg and co-workers,[6] who have utilized it extensively in studying the structures of silicate minerals. In LiF, NaCl, NaBr and NaI the phe-

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[6] W. L. Bragg and J. West. *Proc. Roy. Soc.* (London). **A114**, 450 (1927).

nomenon of *double repulsion* (anion–cation as well as anion–anion repulsion operative) causes the unit to be larger than would be expected from either the anion–cation or anion–anion radius sum. Anion contact and double repulsion have a striking effect on the course of the properties of the alkali halides, particularly the melting points and boiling points.[7]

The conception of simple ionic crystals as coördinated structures, developed by Ewald, Goldschmidt and others, has been shown to be applicable to complex crystals by W. L. Bragg's determination of the structure of a number of the silicate minerals,[8] and through the study of brookite[9] and topaz[10] led ultimately to the formulation of a set of principles governing the structure of complex ionic crystals.[11] These rules may be illustrated by the application of one of them to the question of the isomorphous replacement of OH^- by F^-. The electrostatic valence rule states that in a stable crystal each anion tends to have its charge balanced by the electrostatic bonds of adjacent cations, the strength of a bond from a cation being taken as the ratio of its charge to its coördination number; in other words, the valence of the cation is considered as evenly distributed among the anions coördinated about it. Thus Si^{4+} with coördination number 4 has bonds of strength 1, Al^{3+} with coördination number 6, bonds of strength $^1/_2$. In topaz, $Al_2SiO_4(OH,F)_2$; chondrodite, $Mg_5Si_2O_8(OH,F)_2$; etc., the OH^- ions are in positions of total strength of bonds from cations other than hydrogen equal to 1, and so they may be replaced by F^- ions. But in staurolite, $H_2FeAl_4Si_2O_{12}$, there are not two oxygens in positions of total bond strength 1, but rather four with total bond strength 3/2, suggesting strongly the presence of two $[OHO]^{=}$ groups. In consequence fluorine should not be expected to occur in this mineral, in agreement with observation.

The Electron-Pair Bond

It was shown by G. N. Lewis and Irving Langmuir that unique electronic structures involving electron-pair bonds can be assigned with considerable certainty to a great many molecules and crystals. For many others, however, decision between two or more alternative structures has been difficult; moreover, the theory has not led to predictions regarding atomic arrangements other than the postulated tetrahedral arrangement of four electron pairs. Considerable further progress has now been made possible through the deduction from the quantum mechanics of a set of rules regarding electron-pair bonds, and in particular the discovery of a simple semi-quantitative treatment of bond eigenfunctions which

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[7] Linus Pauling, This Journal, **50**, 1036 (1928).

[8] W. L. Bragg, *Z. Krist.*, **74**, 237 (1930).

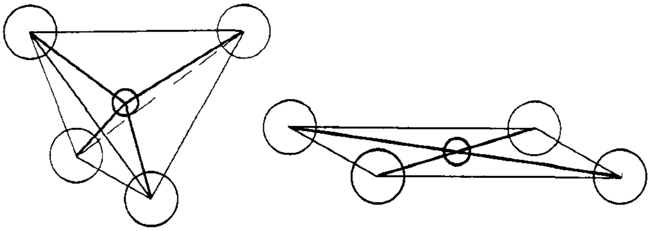
[9] Linus Pauling and J. H. Sturdivant, *ibid.*, **68**, 239 (1928).

[10] Linus Pauling, *Proc. Nat. Acad. Sci.*, **14**, 603 (1928).

[11] Linus Pauling, This Journal, **51**, 1010 (1929).

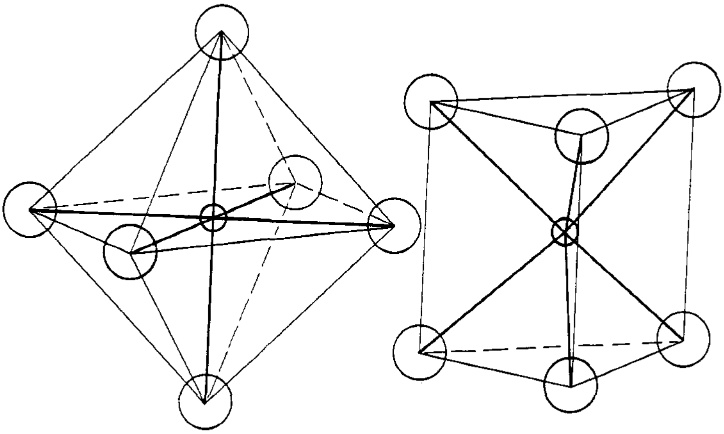
gives much information regarding the strength and mutual orientation of the bonds which can be formed by various atoms.[12]

It has been found that the strength and direction of an electron-pair bond formed by an atom are determined essentially by one electronic eigenfunction. The bond tends to be formed in the direction in which the eigenfunction has its maximum value, and the greater the concentration of the eigenfunction in the bond direction the stronger the bond will be. The spherically-symmetrical *s* eigenfunction can form a bond in any direction of strength 1 according to the semi-quantitative treatment, and a *p* eigenfunction a bond of strength 1.732 in either of two opposite directions. But in most atoms which form four or more bonds



Tetrahedral, sp^3 (2.000). C in diamond and compounds. Zn in $[Zn(CN)_4]^{=}$, etc.

Square, dsp^2 (2.694). Ni in $[Ni(CN)_4]^{=}$, Pd in $[PdCl_4]^{=}$, Pt in $[PtCl_4]^{=}$, Au in $[AuCl_4]^{-}$, etc.



Octahedral, d^2sp^3 (2.923). Co in $[Co(CN)_6]^{\equiv}$, Pd in $[PdCl_6]^{=}$, Pt in $[PtCl_6]^{=}$, etc.

Trigonal–prismatic, (2.983). Mo in MoS_2, and perhaps in $[Mo(CN)_6]^{=}$.

Fig. 3.—The relative orientations of various electron-pair bonds.

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[12] (a) Linus Pauling, *Proc. Nat. Acad. Sci.*, **14**, 359 (1928); (b) THIS JOURNAL, **53**, 1367 (1931); (c) *Phys. Rev.*, **37**, 1185 (1931); (d) J. C. Slater, *ibid.*, **37**, 481 (1931); **38**, 1109 (1931).

the *s* and *p* eigenfunctions do not retain their identity, being instead combined to form new eigenfunctions, better suited to bond formation. The best bond eigenfunction which can be formed from the one *s* and three *p* eigenfunctions in a given shell has the strength 2.000. Moreover, three other equivalent bond eigenfunctions can also be formed, and the four bonds are directed toward the corners of a regular tetrahedron (Fig. 3). This result immediately gives the quantum-mechanical justification of the chemist's tetrahedral carbon atom, with all its properties, such as free rotation about a single bond (except when restricted by steric effects) and lack of it about a double bond, and shows that many other atoms direct their bonds toward tetrahedron corners.

The nature of possible bond eigenfunctions involving *d* eigenfunctions depends on the number of *d* eigenfunctions available. Bivalent nickel contains eight unshared 3*d* electrons, which require at least four of the five 3*d* eigenfunctions, leaving only one for bond formation. When this is combined with the 4*s* and the three 4*p* eigenfunctions of nearly the same energy, it is found that not five but only four equivalent bond eigenfunctions, of strength 2.694, can be formed, and that these are directed toward the corners of a square. Thus the $[Ni(CN)_4]^{=}$ ion should have a square rather than a tetrahedral configuration. This was suggested for complexes containing bivalent palladium and platinum by Werner, and was verified by Dickinson[13] by the x-ray study of K_2PdCl_4 and K_2PtCl_4. We expect a similar configuration for complexes of trivalent copper, silver and gold.

When two *d* eigenfunctions are available, as in trivalent cobalt, quadrivalent palladium and platinum, etc., six equivalent bond eigenfunctions of strength 2.923 and directed toward the corners of a regular octahedron can be formed. These form the bonds in a great many octahedral complexes.

It is interesting to note, as pointed out to me by Mr. J. L. Hoard, that these considerations lead to an explanation of the stability of trivalent cobalt in electron-pair bond complexes as compared to ionic compounds. The formation of complexes does not change the equilibrium between bivalent and trivalent iron very much, as is seen from the electrode potentials, while a great change is produced in the equilibrium between bivalent and trivalent cobalt.

$$\begin{array}{rcll} Fe^{++} & = & Fe^{+++} + E^{-} & -0.74\text{ v.} \\ & & & \qquad\rangle\, -0.25\text{ v.} \\ [Fe(CN)_6]^{\overline{\equiv}} & = & [Fe(CN)_6]^{\equiv} + E^{-} & -0.49\text{ v.} \\ Co^{++} & = & Co^{+++} + E^{-} & -1.8\text{ v.} \\ & & & \qquad\rangle\, -2.1\text{ v.} \\ [Co(CN)_6]^{\overline{\equiv}} & = & [Co(CN)_6]^{\equiv} + E^{-} & +0.3\text{ v.} \end{array}$$

The effect is so pronounced that covalent compounds of bivalent cobalt are difficult to prepare, decomposing water with the liberation of hydro-

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[13] R. G. Dickinson, THIS JOURNAL, **44**, 2404 (1922).

gen. The explanation is contained in Fig. 4. In the ions Co^{++}, Co^{+++}, Fe^{++}, and Fe^{+++} there is room for all unshared electrons in the 3*d* subshell or inner subshells. When octahedral bonds are formed only three 3*d* eigenfunctions are left for occupancy by unshared electrons. These are enough for bivalent and trivalent iron and for trivalent cobalt, but they hold only six of the seven electrons of bivalent cobalt. The seventh electron must accordingly occupy an outer unstable orbit, causing the complex to become unstable.

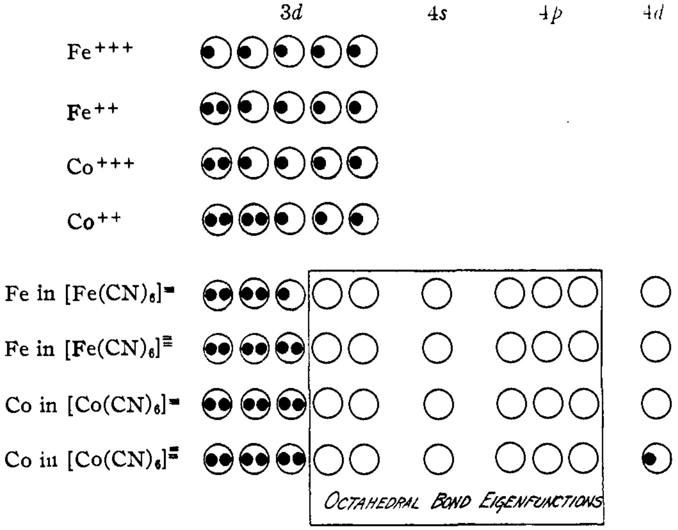

Fig. 4.—A diagram representing the electronic configurations of certain complex ions. Each circle represents a single-electron positional eigenfunction, each dot an electron.

The structure[14] of the mineral molybdenite, MoS_2, in which each molybdenum atom is surrounded by six sulfur atoms at the corners of a triangular prism, has long been puzzling, for if the crystal were composed of ions an octahedral arrangement would be more stable, and the large number of octahedral complexes containing electron-pair bonds would suggest an octahedral electron-pair bond structure also. But the molybdenum atom contains only two unshared *d* electrons, and it has been recently found by Mr. Ralph Hultgren that in this case six equivalent bonds of strength 2.983 (considerably greater than that of octahedral bond eigenfunctions) directed toward the corners of a trigonal prism may be formed. The theoretical ratio of altitude to base of the prism is 1000, while the experimental value is 1.007 ± 0.038. It would be interesting to determine whether a similar configuration holds for $[Mo(CN)_6]^{\equiv}$; a di-substituted complex such as $[Mo(CN)_4Cl_2]^{\equiv}$ should then exist in three isomeric forms.

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[14] R. G. Dickinson and Linus Pauling, THIS JOURNAL, **45**, 1466 (1923).

The Transition from One Bond Type to Another

The question as to whether or not the transition from one extreme bond type to another would take place continuously as one or more parameters determining the nature of the atoms involved were varied can now, I believe, be satisfactorily answered. The quantum mechanics shows that if, for a polyatomic system having a given atomic arrangement, there are two possible electronic states with nearly the same energy and with the same multiplicity, then it is necessary to consider mixed states, with an eigenfunction for the system formed by linear combination of the eigenfunctions for the first two states. The actual state of the system would lie somewhere between the two postulated extremes. If the states have different multiplicities, however, they cannot be combined with one another (so long as spin-orbit interactions of the electrons are negligible). So although every energy level of a system changes continuously as parameters defining the system are changed, the normal state may show a discontinuity at the crossing of two non-combining levels.

This discussion is most easily made precise by the use of the energy integral. If ψ represents an arbitrary normalized wave function for a system, then the integral

$$E = \int \psi^* H \psi d\tau$$

in which H is the Hamiltonian operator, gives a value of E which must be equal to W_0, the energy of the lowest state of the system, or be greater than W_0. For E to be equal to W_0 it is necessary that ψ be the eigenfunction for the normal state of the system, and the closer ψ approaches this eigenfunction the smaller the difference $E - W_0$ will become. Now let us set up a function ψ_1 of the coördinates of the system which represents a conceivable state of the system, for example, a state corresponding to a given Lewis electronic formula for a molecule. We can then evaluate the electronic energy E_1 as a function of the internuclear distances by substituting ψ_1 for ψ in the above equation. Similarly a function ψ_2 corresponding to an alternative electronic formula can be used to calculate E_2. If E_1 lies far below E_2, then the function ψ_1 is a much better approximation to the normal state of the system than ψ_2, and, in the absence of further alternatives, the electronic formula corresponding to ψ_1 is to be accepted. In general, if ψ_1 and ψ_2 have the same symmetry character and especially the same multiplicity (that is, the same number of unpaired electrons), values of E for a more general function $a\psi_1 + b\psi_2$ should be calculated. When E_1 and E_2 are not much different in value and when the interaction terms between ψ_1 and ψ_2 are large, it is found that the function giving the best approximation to the eigenfunction for the normal state of the system is neither ψ_1 nor ψ_2, but the combination of them, with the coefficients a and b of the same order of magnitude. In this case neither electronic formula alone can be assigned the molecule, but instead both, with one perhaps more important than the other. The molecule could be described as fluctuating rapidly between the two electronic formulas, and achieving stability greater than that of either formula through the "resonance energy" of this fluctuation.

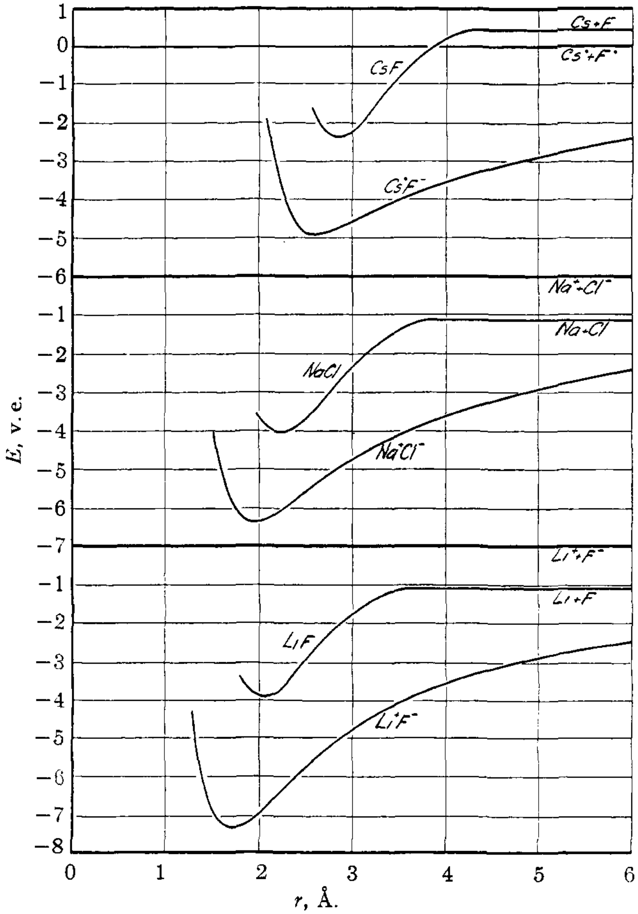

Fig. 5.—Potential energy curves for alkali halide molecules. The upper curve of each pair corresponds to electron-pair bond formation ($\text{Cs}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}}:$, etc.), the lower to an ionic structure (Cs^+F^-, etc.).

It is impossible to carry out this program of directly evaluating the energy integral except in the simplest cases; but rough energy curves for various electronic structures can often be constructed by semi-empirical methods, and the discussion outlined above carried out with them. Thus information regarding the repulsive forces between ions obtained from the observed properties of ionic crystals can be used for ionic states of molecules. In Fig. 5 the lower curve of each pair represents the electronic energy as a function of the internuclear separation for extreme ionic molecules CsF, NaCl and LiF. The attractive potential is taken as the Coulomb potential $-e^2/r$, polarization being neglected. (Polarization might lower the minimum of each curve by 1 or 2 v. e.) The repulsive potential used is b/r^9, with b given the values which lead to the observed equilibrium separations in the crystals. The upper curves, which represent shared-electron-pair structures $\mathrm{Cs:\ddot{\underset{..}{F}}:}$, etc., are Morse curves with a dissociation energy of about 3 v. e., a value found to be correct to within ±1 v. e. for most electron-pair bonds. The relative positions of the curves are determined by ionization potentials and electron affinities.[15] It is seen that the ionic structures are much more stable than the electron-pair bond structures, so that the normal states of these alkali halide molecules (and presumably of the others) can be described as essentially ionic. There is, no doubt, some contribution of the electron-pair bond structure to the function $a\,\psi_{\text{ionic}} + b\,\psi_{\text{electron-pair}}$ which best approximates the normal state; but the coefficient b is small compared with a, which is nearly unity.

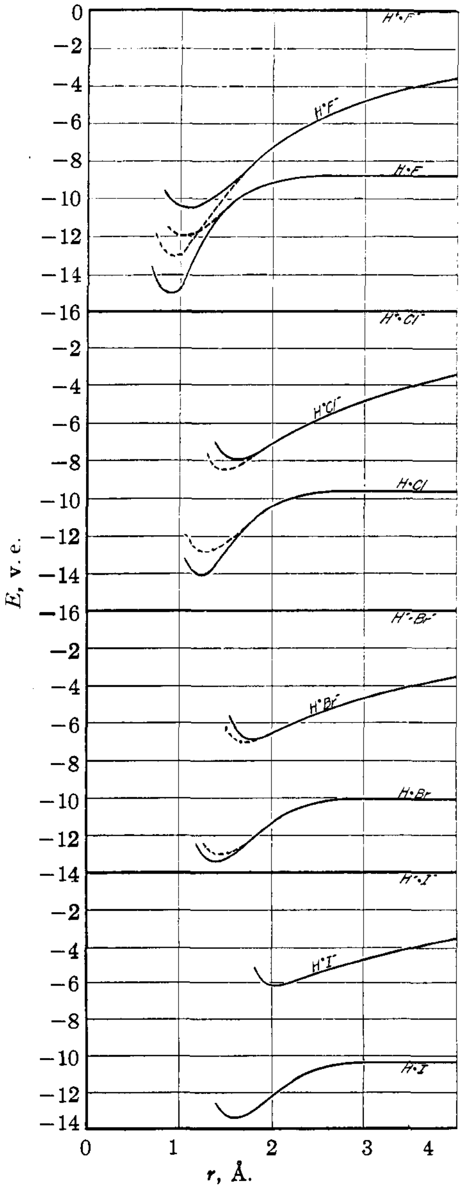

Fig. 6.—Potential energy curves for hydrogen halide molecules.

In Fig. 6 similar curves are shown for the hydrogen halide molecules. The electron-pair bond structures $\mathrm{H:\ddot{\underset{..}{F}}:}$, etc., are

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[15] The values used are from a paper by Mr. J. Sherman, which will appear early in 1932 in *Chemical Reviews*.

represented by Morse curves of about 3 v. e. dissociation energy, with their minima at distances given by electron-pair bond radii.[16] The ionic curves were calculated with the use of hydrogen-like eigenfunctions, as described in a previous paper.[4] The screening constants used are from the revised set.[5] Polarization has been neglected.

It is seen that for hydrogen fluoride the two curves intersect, the minimum for the ionic curve lying below the other. In the region around r = 1 Å. the interaction between the two assumed structures would be large, and the resonance energy would be expected to amount to 1 or 2 v. e. A potential curve representing the normal state has been drawn in, corresponding to a combination of the ionic and electron-pair bond structures. The curve is drawn so that the minimum lies at the observed equilibrium separation of the nuclei, and at the energy level given by thermochemical data. An excited state also formed by combining the two original structures is shown.[17] In the eigenfunction $a\ \psi_{\text{ionic}} + b\ \psi_{\text{electron-pair}}$ approximating that of the normal state, the coefficients a and b are of the same order of magnitude, with a somewhat larger than b. The normal HF molecule is represented by neither the formula H^+F^- nor $\mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{F}}}:$, but by both, with H^+F^- somewhat more important than $\mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{F}}}:$. The bond is largely ionic.

The curves for HCl, HBr and HI do not cross, in the main because the ionic radii of Cl^-, Br^- and I^- are much larger than that of F^-. Accordingly the normal states of these molecules are essentially of the electron-pair bond type, and the formulas $\mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}:$, $\mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{Br}}}:$, and $\mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{I}}}:$ may be used as giving a reasonably accurate picture of the state of the molecules. This conclusion had been reached before on the basis of other arguments, especially the tendency of fluorine alone of the halogens to form hydrogen bonds.

There is no doubt some interaction of the two structures for these molecules also, changing the curves by a small amount, as indicated for HCl and HBr.

It is not possible at the present time to carry out similar calculations for more complicated molecules, inasmuch as a small change in internuclear distance produces a very large change in the Coulomb energy of highly charged ions, and the equilibrium distances cannot yet be accurately predicted. Certain less specific conclusions can, however, be drawn. For example, the energy curves for a number of structures of SiF_4 (the pure ionic $Si^{4+}F^-{}_4$, and those with one, two, three or four fluorine atoms attached by electron-pair bonds) are found to have their minima

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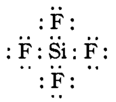
[16] Taken from a set contained in a paper by Linus Pauling and M. L. Huggins, to appear in *Z. Krist.*

[17] The values of a and b for this state must be such as to make the function orthogonal to that of the normal state.

close together. Neither the ionic extreme $Si^{4+}F^{-}_{4}$ nor the electron-pair bond extreme  $\begin{matrix} & :\ddot{F}: & \\ :\ddot{F}: & \ddot{Si} & :\ddot{F}: \\ & :\ddot{F}: & \end{matrix}$ represents the actual normal state of the molecule, which instead lies somewhere between them. There is little evidence as to which extreme is approached more closely. A tetrahedral configuration would be expected in either case.

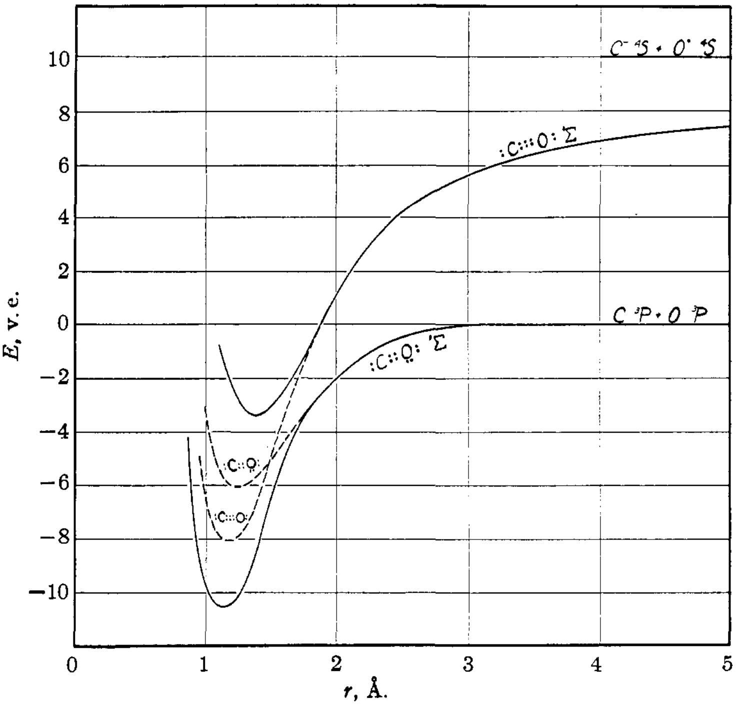


Fig. 7.—Potential energy curves for the carbon monoxide molecule.

Silica, the silicates and, in general, crystals containing oxygen or fluorine and metal atoms which can form noble-gas type cations are found to satisfy the electrostatic valence rule and the other rules for ionic crystals, which indicates that the ionic character of these substances is of greatest importance. The sulfides of metals other than the alkalies and alkaline earths, on the other hand, do not satisfy these rules; magnetic evidence further shows these substances not to be ionic.

The discussion of electronic energy curves also throws light on such questions as the structure of the carbon monoxide molecule. The empirical study of potential curves obtained from band spectral data has shown[18] that for atoms in the first row of the periodic system a double bond leads

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[18] An account of this work will be published at some future time.

to a dissociation energy of about 6 v. e. and a triple bond to 9 v. e. In Fig. 7 the Morse curve due to normal atoms C^3P and O^3P, extended by dashes to the left, corresponds to the double-bonded structure :C::Ö:. The upper curve with its dashed extension corresponds to the structure :C:::O:, formed from the ions C^- ^4S and O^+ ^4S. In drawing this curve a Coulomb curve for large r was combined with a 9 v. e. Morse curve for small r in such a way as to make the total dissociation energy 9 v. e. plus $\frac{e^2}{r_0}\left(1 - \frac{1}{n}\right)$, with n placed equal to 5 and r_0 to 1.25 Å. The electron affinity of carbon was estimated at 3.5 v. e.

It is evident that the normal state of CO is not the double-bonded state, especially since the normal molecule is found experimentally to lie 10.3 v. e. (rather than 6 v. e.) below the normal atoms. The triple-bonded ionic structure leads to a curve which crosses the other, dropping to about −8 v. e. Strong interaction between these two $^1\Sigma$ structures is to be expected for small values of r, giving rise to combined states represented by the two potential curves drawn in the figure. The normal state of CO is accordingly a combination of :C::Ö: and :C:::O:, with the latter of greater importance. On separating the nuclei the electronic structure changes, until from about 2 Å. on the double-bonded structure alone is present.[19]

The Magnetic Criterion[12b]

Many compounds of transition elements behave differently from the substances discussed above, for the reason that the lowest ionic state and the lowest electron-pair bond state may contain different numbers of unpaired electrons, so that they cannot be combined with one another. An octahedral complex $[FeX_6]^{\equiv}$ forms a good example. If the complex contained extreme ionic bonds, the singlet ions X^- and the Fe^{+++} ion (with a stable state of maximum multiplicity, in accordance with the rules of line spectra) would produce a $^6\Sigma$ complex, containing five unpaired electrons, as shown in Fig. 4. An unstable ionic $^2\Sigma$ state would also be formed by pairing four of the electrons; it would lie several volt-electrons above the normal state. With extreme electron-pair bonds the normal state, involving $3d^2$ $4s$ $4p^3$ bond eigenfunctions, would be a $^2\Sigma$ state. A $^6\Sigma$ state, with the much less stable $4s$ $4p^3$ $4d^2$ bonds, would lie much higher. The energy levels of an actual complex would lie somewhere on the curves shown in Fig. 8. The normal state would be either $^2\Sigma$, mainly the octahedral electron-pair bond state with a small contribu-

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[19] The arguments for the triple-bonded ionic structure presented by N. V. Sidgwick [*Chem. Rev.*, 9, 77 (1931)] in the main support this structure also. Thus we may expect for :C::Ö: an electric moment with oxygen negative, for :C:::O: one with oxygen positive (the electronic structure being symmetrical, and oxygen having the larger nuclear charge), so that the combined structure could well lead to the observed very small electric moment.

tion from the excited ionic extreme, or $^6\Sigma$, mainly ionic with a small contribution from the excited electron-pair bond extreme. It is accordingly convenient to designate the $^2\Sigma$ state as essentially of the electron-pair bond type, and the $^6\Sigma$ state as essentially ionic, and to take the intersection of the two curves as a discontinuity in the normal state.

The multiplicity can be determined from the experimental values of the magnetic susceptibility, the magnetic moment in Bohr magnetons being equal to $2\sqrt{S(S+1)}$, in which S is the spin quantum number. (The multiplicity is $2S + 1$.) The moments for $^2\Sigma$ and $^6\Sigma$ are 1.73 and 5.91, respectively. The experimental values for $K_3Fe(CN)_6$ and $(NH_4)_3FeF_6$ are 2.0 and 5.88, respectively, so that the bonds in the $[Fe(CN)_6]^{\equiv}$ ion are electron-pair bonds, and those in $[FeF_6]^{\equiv}$ are ionic.

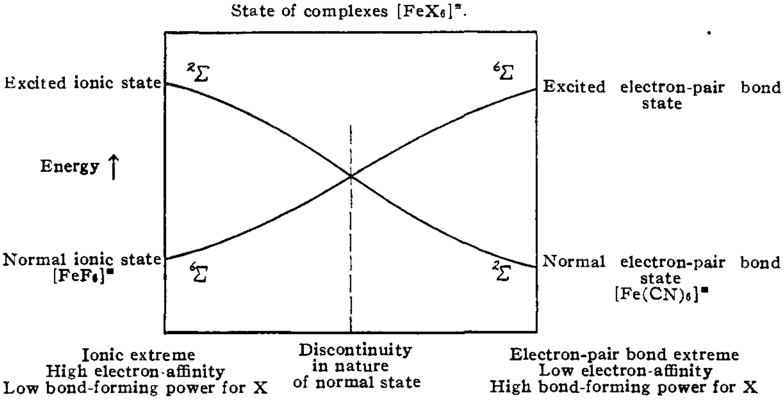

Fig. 8.—Diagram of two energy levels for complexes $[FeX_6]^{\equiv}$, showing an effective discontinuity in the normal state.

The magnetic criterion is particularly valuable because it provides a basis for differentiating sharply between essentially ionic and essentially electron-pair bonds. Experimental data have as yet been obtained for only a few of the interesting compounds, but these indicate that oxides and fluorides of most metals are ionic. Electron-pair bonds are formed by most of the transition elements with sulfur, selenium, tellurium, phosphorus, arsenic and antimony, as in the sulfide minerals (pyrite, molybdenite, skutterudite, etc.). The halogens other than fluorine form electron-pair bonds with metals of the palladium and platinum groups and sometimes, but not always, with iron-group metals.

Summary

After a discussion of the properties of substances containing ionic bonds and electron-pair bonds, it is shown that the transition from one extreme bond type to another could take place continuously in some cases (when the normal states for the two extremes have the same number of unpaired electrons), and not in others. A method of treatment of bond type based on electronic energy curves is developed. Its application shows the normal alkali halide molecules to be essentially ionic. HF is largely ionic, while HCl, HBr and HI contain electron-pair bonds. The normal state of CO corresponds to both structures :C::Ö: and :C:::O:, with the latter predominant. Some general statements based on observed magnetic moments are made relative to the types of bonds formed by metals of the transition groups.

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EXPERIMENTS ON THE RATE OF DISSOCIATION OF NITROGEN TETROXIDE

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1. **Previous Work.**—The dissociation of the colorless gas nitrogen tetroxide to form the highly colored red nitrogen dioxide has long been of interest to chemists. The equilibrium between the two gases provided one of the earliest examples for the application of thermodynamics to the calculation of the effect of temperature on chemical equilibrium;[1] and the very high rate of attainment of the equilibrium has been the subject of much speculation and experiment.

Previous to the quite different mode of attack to be described in the present article, a number of attempts have been made to determine the rate of the dissociation and recombination by measuring the velocity of sound through an equilibrium mixture of the two gases. Using high enough frequencies, one should obtain the velocity corresponding to the passage of the sound wave through the mixture of the two gases without reaction, but at low enough frequencies one should expect the equilibrium to adjust itself by reaction to the periodic compression and rarefaction, and hence should expect a decrease in the velocity of sound, which amounts theoretically to about 3.8% with gas at 25° and atmospheric pressure.[2] At intermediate frequencies one should expect a "critical region" with intermediate velocities. A theory of the effect of frequency on the velocity

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[1] Gibbs, *Trans. Connecticut Acad.*, **3**, 108, 343 (1875–6–7–8); *Am. J. Sci.*, Ser. 3, **18** (1879).

[2] See Table VII in article by Grüneisen and Goens.[8] Their calculation was made in accordance with the theory of Einstein,[3] correcting for an obvious slip as to sign in Einstein's work. Kistiakowsky and Richards,[10] apparently not correcting for the wrong sign, give a larger theoretical lowering of about 5.1%.