Chemical Bonds involving d-Orbitals. Part I.

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Overlap integrals involving $3s$-, $3p$-, $3d$-, $4s$-, and $4p$-orbitals (see Part II, following paper) have been used as criteria of bond strengths in a critical discussion of chemical bonds which may require the use of d-orbitals. Pauling's treatment of σ-bonds of this type (" Nature of the Chemical Bond," Cornell Univ. Press, 1950) has been extended by considering the effect of variations of the radial part of the wave-functions. The occurrence of π-bonds and of other types has been considered.

The values of the overlap integral between various hybrid σ-orbitals and a $3p$-orbital, all the exponents being taken as equal, lead to conclusions differing quantitatively from those obtained by Pauling, who considered the products of the maxima of the angular functions.

It is found that Slater orbitals (*Phys. Review*, 1930, **36**, 57) for the inner valency d-electrons of the transition metals are too compact to give large overlaps with ligand orbitals which are themselves compatible with the s- and the p-orbitals of the central atom. On the other hand, with elements such as phosphorus and sulphur the outer d-orbitals are much too diffuse for electrons in them to be likely to form useful bonds. In the former case the Slater functions are probably at fault; but in the latter it must be assumed that the d-orbitals on the central atom contract as a result of perturbation by the ligands.

A number of different cases of d_π–p_π- and d_π–d_π-bonding are considered. It is shown that the overlap values are often large enough to give quite strong bonds, and are rather insensitive to difference in size of the bonded orbitals. In particular, a diffuse d_π-orbital may overlap quite strongly with a compact p_π-orbital. Hybridisation between p_π- and d_π-orbitals to give strongly directed π-bonds is shown to be possible.

Bonds of types other than σ and π are considered, but the overlap values for them are found to be small.

The experimental evidence for the participation of d-orbitals in bonding is discussed in the light of these conclusions. It is shown that reasonable overlap values are found for most of the important situations in which π-bonding between d_π- and p_π- or d_π-orbitals has been postulated. The experimental facts that central atoms which could use penultimate d-orbitals do form compounds with ligands of low electronegativity, while those with ultimate d-orbitals rarely do this, save with the more electronegative ligands, are explained as previously indicated. The importance of the conditional stability of d-orbitals, both σ and π, resulting from the polar character of the bonds formed by the s- and the p-orbitals is stressed. The effect of double-bonding on the stereochemistry of the transition-metal compounds is discussed.

THE importance of d-orbitals in covalent bonding has been much discussed since Pauling's classic paper on the hybridisation of atomic orbitals in molecule formation (*J. Amer. Chem. Soc.*, 1931, **53**, 1367). That it is real is shown by the existence of peculiar spatial arrangements which can be rationalised if such d-orbital hybridisation be postulated. Examples are the square arrangement of equivalent bonds in, *e.g.*, $[ICl_4]^-$ (Mooney, *Z. Krist.*, 1938, **98**, 377) and $[Ni(CN)_4]^{--}$ (Brasseur *et al.*, *ibid.*, 1934, **88**, 210), of trigonal bipyramidal bonds in phosphorus pentachloride (Rouault, *Compt. rend.*, 1938, **207**, 620), of tetragonal pyramidal bonds in iodine pentafluoride (Lord *et al.*, *J. Amer. Chem. Soc.*, 1950, **72**, 522), of octahedral bonds in sulphur hexafluoride (Brockway and Pauling, *Proc. Nat. Acad. Sci.*, 1933, **19**, 68), and of pentagonal bipyramidal bonds in iodine heptafluoride (Lord *et al.*, *loc. cit.*). Furthermore such arrangements often occur in association with magnetic properties (Pauling, " Nature of the Chemical Bond," Cornell Univ. Press, 1950) which can be predicted from the same hypothesis.

It has been suggested that d-orbital hybridisation may account for the abnormal strength of the simple homocentric σ-bonds formed by the elements of the second short period, compared with those formed by elements of the first (Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 4493). Further, π-bonding involving d-orbitals has been shown, not only to be formally possible in certain cases, but to explain certain physical and chemical properties of transition-metal compounds with an octahedral arrangement of σ-bonds based on d^2sp^3 hybridisation or with square bonds from dsp^2 hybridisation (Pauling, *op. cit.*), of thiophen (Longuet-Higgins, *Trans. Faraday Soc.*, 1949, **45**, 173), of the sulphoxides and sulphones (Koch and Moffitt, *ibid.*, 1951, **47**, 7), and of some of the complexes formed by tertiary phosphines, arsines, and stibines, or by sulphides, selenides, or tellurides (see Chatt, *J.*, 1952, 4300, and Nyholm, *J.*, 1951, 3245, for full references). Gillespie (*J.*, 1952, 1002)

FIG. 1.

A, σ- *and* schedo-σ-*Bonding.*

B, π-*Bonding.* C, δ-*Bonding.*

D, σ-*Symbatic bonding.*
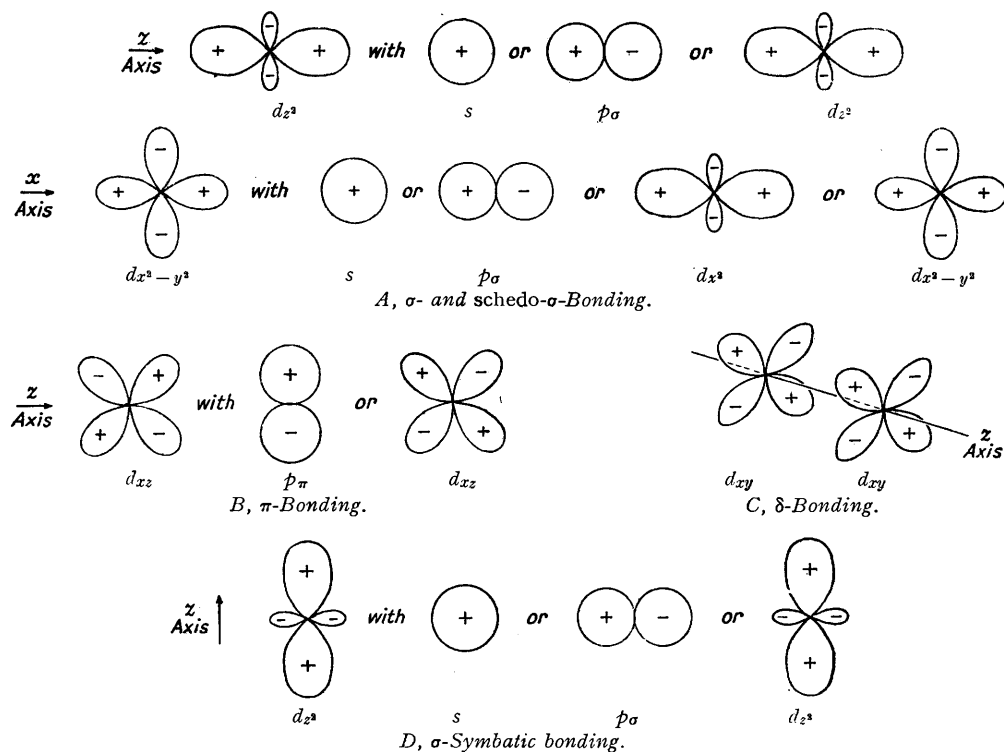
has drawn attention to the possible importance of d-orbitals in the formation of activated complexes, even for elements from the first short period. It is therefore of interest to apply new canons of criticism to the main hypothesis and its ramifications.

The present work originated in a desire to discover the dependence of bond strength on the radial part of the d-orbital involved. Pauling assumed that the difference between the radial functions for s-, p-, and d-orbitals could be ignored, and concentrated attention on the angular functions. He carried this view so far as to postulate a quantitative relation between the maximum value of the angular function and the bonding power of the orbital, *viz.*, that the strength of a bond is proportional to the product of these maxima for the two orbitals used by them (Pauling, *op. cit.*). For qualitative explanations of the facts of stereochemistry this simplification seems adequate : but it now seems inadequate for more precise discussion ; *e.g.*, Maccoll (*Trans. Faraday Soc.*, 1950, **46**, 369) and Mulliken (*J. Amer. Chem. Soc.*, 1950, **72**, 4493) have shown that conclusions based on it about the relative strengths of bonds between s, p, and sp hybrid orbitals on two centres are not supported by calculations of overlap integrals or by experimental evidence.

From a review of the observational evidence, it appears that differences of radial function might even be of major importance. It is well known that the higher valencies of the B-sub-group elements, which are considered to involve hybridisation of d-orbitals with s- and p-orbitals, are developed only by ligands of high electronegativity. On the other hand, this is not true of ligands which form strong octahedral complexes with the ions of the transition elements Cr, Mn, Fe, Co, Ni.

The whole question of the participation of d-orbitals in covalent bonds of various kinds was therefore re-examined by the best means at present available, *i.e.*, by the calculation of overlap integrals. The main conclusions were presented at a symposium on Co-ordination Chemistry (I.C.I. Report BRL/146, of 1950; see also *Nature*, 1951, **167**, 434).

Before the results are described and discussed, it is necessary to consider in more detail the formal nature of the problem and the means of attacking it. This is done in the next three sections. The detail of the calculations, and the main body of numerical results are given in Part II (following paper).

The Forms of Bonding available with d-*Orbitals.*—It is assumed in the present discussion that the angular functions of s-, p-, or d-orbitals are the same as in the free atoms, *i.e.*, that molecule formation has no serious effects on them. We then see that d-orbitals, because of their more elaborate symmetry, might form more kinds of bond than can s- or p-orbitals.

Because linear molecules have cylindrically symmetrical fields, their bonds may be classified as σ, π, δ, etc., according as the corresponding orbitals have 0, 1, 2, etc., units of angular momentum about the molecular axis. In such cases, d-orbitals can give rise to σ-, π-, or δ-bonds. The respective possibilities are shown in Figs. 1*A*—*C*.

In non-linear molecules this classification breaks down. The types of bond already mentioned may be modified, and new types may appear. Two particular points arise. First, a $d_{x^2-y^2}$ type of orbital * with a lobe directed along the line of centres (which would have to be the x- or the y-axis for the atom about which this orbital is centred) can form a very good approximation to a σ-bond since, in the essential bonding region, it has very nearly the characteristic cylindrical symmetry. Such bonds are often called σ-bonds without qualification, but they might better, perhaps, be distinguished as " *schedo-σ* " or " pretty-nearly-σ " bonds. Secondly, a d_{z^2} orbital can combine with an s, a p_x, or a p_y orbital, or a further d_{z^2} orbital with its axis parallel to the first one, on another atom (see Fig. 1*D*), the line of centres being the x or the y axis; also it may hybridise with s, p_x, or p_y orbitals on the same atom. In such circumstances a d_{z^2} orbital may be described as σ-symbatic : a bond between two such orbitals is best termed a d_{z^2}–d_{z^2}-bond.

π-Bonding arises if an orbital such as d_{xz} is oriented with its positive and negative lobes equally inclined to the line of centres, and requires a similar d-orbital or a p_π-orbital at the other centre (Fig. 1*B*); and δ-bonding arises only between two d_{xy}-, d_{xz}-, d_{yz}-, or $d_{x^2-y^2}$-orbitals oriented with their lobar planes parallel, as in Fig. 1*D*.

Symmetry conditions allow hybridisation between orbitals on the same centre, having the same symmetry about the bond axis.

Just as it has already been assumed that the angular functions of the atomic orbitals are the same in the combined as in the free atoms, so it might be assumed initially that the radial functions are not much altered. Now, in the cases which will be considered, if d-orbitals participate in σ-bonding it is through hybridisation with s- and p-orbitals. A hybrid orbital will form a strong σ-bond only if it is well concentrated along the bond direction. This means that the component functions must have their maximum values at about the

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* The notation used is that of, *e.g.*, Eyring, Walter, and Kimball (" Quantum Chemistry," Wiley, New York, 1944, p. 89) and differs from that of, *e.g.*, Pauling and Wilson (" Introduction to Quantum Mechanics," McGraw-Hill, New York, 1935, pp. 138—9). For convenience, the relation between them is given below :

Angular function	Notation of Eyring *et al.*	Notation of Pauling and Wilson
$3\cos^2\theta - 1$	d_{z^2}	d_z
$\sin\theta \cos\theta \cos\phi$	d_{xz}	d_{x+z}
$\sin\theta \cos\theta \sin\phi$	d_{yz}	d_{x+z}
$\sin^2\theta \cos 2\phi$	$d_{x^2-y^2}$	d_{xy}
$\sin^2\theta \sin 2\phi$	d_{xy}	d

same regions in space since otherwise the reinforcement and annulment of the wave function caused by hybridisation would cause little change in total electron distribution in any particular orbital and so would not cause stronger total binding. There can, for example, be useful hybridisation between 2s and 2p functions but not between 2p and 3s.

Slater radial functions have the form

$$R(r) = r^n e^{-\alpha r}$$

n being an effective principal quantum number, and $\alpha = Z^*/n$ depending on n and upon an effective atomic number Z^* assigned for a given case by Slater's rules (Slater, *Phys. Review*, 1930, **36**, 57). They have a maximum at $r_m = n/\alpha$; so r_m values may be used as a rough criterion of compatibility.

In general, for Slater functions corresponding to orbitals having the same main quantum number, or having these differing by only unity, the projection is determined mainly by α. Slater's rules assign equal exponents to s and p functions; so hybridisation between them gives strongly bonding functions. For d-orbitals, however, the exponent assigned is different : *e.g.*, in nickel, with the configuration $(3d)^9 4s$, Slater's rules give

$$\alpha(3d) = 2\cdot4, \ n = 3, \text{ whence } r_m = 1\cdot25 \text{ a.u.}$$
$$\alpha(4s, 4p) = 1\cdot0, \ n = 3\cdot7, \text{ whence } r_m = 3\cdot7 \text{ a.u.}$$

Contrariwise, for sulphur in the sexacovalent configuration $3s3p^3 3d^2$,

$$\alpha(3d) = 0\cdot55, \ n = 3, \text{ whence } r_m = 5\cdot45 \text{ a.u.}$$
$$\alpha(3s, 3p) = 2\cdot05, \ n = 3, \text{ whence } r_m = 1\cdot46 \text{ a.u.}$$

In neither case does it appear from this criterion that hybridisation between 3d and 4s or 4p functions, or 3d and 3s or 3p, will be useful, the d-orbital being much the less diffuse in the former case, and much the more diffuse in the latter. It is necessary to suppose that molecule formation reduces these differences. Pauling's criterion for bond strength requires that they vanish. As will be shown later, it is possible that they are exaggerated by the Slater rules but at least some further consideration of this problem is called for.

Since bond strength is essentially a function of two centres, and not merely of one, the simple " α-criterion " is not adequate for a fuller study. A better one is the overlap integral for the atomic functions on these centres.

The Overlap Integral as a Criterion of Bond Strength.—It is generally impracticable to calculate accurately the energy of formation of a bond between two centres, or even to attempt anything near to a formally correct procedure, so various approximate measures of bond strength have been devised. One of these, much used and discussed by Mulliken and his school (see, *e.g.*, Mulliken, *J. Phys. Chem.*, 1952, **56**, 295), is the overlap integral. If two centres A and B have atomic wave functions ψ_A and ψ_B available for bond formation, the overlap integral is $\int \psi_A \psi_B d\tau$, often called S. It gives some measure of the concentration of electronic charge between the nuclei, which is necessary for covalent bonding to occur- It is not, however, very close to the formal quantum-mechanical expression for the bind. ing energy of a system with a wave function, based on orbitals ψ_A and ψ_B.

Furthermore, there is the much more fundamental difficulty that the correct function for the system requires the combination, not merely of two, but of an indefinite number of one-centre functions of which the selected ψ_A and ψ_B can, at best, only be the most important. Nevertheless, because it is the simplest two-centre quantity of quantal significance, its value as a measure of bond strength has been carefully considered; and attempts have been made to provide more or less empirical corrections for its obvious shortcomings. Each such attempt is open to specific criticisms when measured against the ideal of a complete and rigorous calculation of binding energy : equally each may have virtues in particular problems.

Mulliken (*loc. cit.*) has proposed that for a bond between like centres the expression $\kappa IS/(1 + S)$, where κ is an arbitrary constant depending on the type of bond and I is the ionisation potential of the atoms, should be a good measure of bond strength. This takes account of the variation from one atom to another of the field effective at the region between

centres where the electron space charge has built up. Mulliken has given an approximate justification of this expression for roughly homocentric bonds. His assumptions are reasonable for such cases but break down rapidly as the difference between the centres increases. It therefore appears that Mulliken's relation is not well suited to the quantitative discussion of *d*-orbital binding which often involves very disparate α values, and that the overlap integral itself is as good and much more convenient.

Apart from the fundamental inadequacy already mentioned, which overlap treatments ordinarily contain, arising from the assumption that the simplest LCAO function $(\psi_A + \psi_B)/(2 + 2S)^{\frac{1}{2}}$ is adequate for the bonding electrons, there is the practical difficulty of choosing atomic orbitals ψ_A and ψ_B. The Slater functions used in the present work, and also by Mulliken, are not very good approximations, though they should be reasonably adequate because chemical binding is determined mainly by the nature of the atomic functions at moderate distances from the nucleus, on the atomic scale, *i.e.*, near the " periphery " of the atom If self-consistent-field (S.C.F.) functions were available for atoms and ions of all the types which we wish to consider, it would be better to use them ; but they are lacking particularly for atoms with occupied *d*-orbitals in the outer shell, so Slater functions are used throughout. Finally, in any save the simplest problems the exact hybridisation ratio for the atomic orbitals is not known.

From all this it is clear that the overlap integral is but a rough measure of the strength of the covalent part of a bond; and that the internuclear distance for maximum overlap is not necessarily that of the actual bond length : but it is, withal, the most satisfactory measure at all readily available.

In the present investigation no attempt has been made to compare actual bond strengths with overlap integrals. What has been done is to explore the conditions which the radial part of the *d*-function must satisfy in order that there may be *d*-hybridisation with *s* and *p* functions in σ-bonding, or that there may be π-bonding involving either a d_π-orbital or a d_π–p_π hybrid orbital, and to consider how far these are satisfied in actual cases.

The calculations of overlap integrals already available (Mulliken, Riecke, Orloff, and Orloff, *J. Chem. Phys.*, 1949, **17**, 1248; Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 4493) have therefore been extended to cover the following cases :

σ-*Type* $3s$–$3p$; $3p$–$3p$; $3d_{z^2}$–$3p$.
$\quad\quad\quad 4s$–$3p$; $4p$–$3p$ (equi-exponent case only).

Because of the interest of other types of bonding, the following were also calculated :

π-*Type* $3d$–$3d$; $3d$–$3p$.
δ-*Type* $3d$–$3d$, *i.e.*, $3d_{xy}$–$3d_{xy}$, the *z* axis being the internuclear axis.
σ-*Symbatic Type* $3d_{z^2}$–$3d_{z^2}$.

The method of computation is described and the values obtained are tabulated in the next paper. After these integrals had been evaluated, certain of them were independently reported by Jaffé (*J. Chem. Phys.*, 1953, **21**, 258). Points arising from the comparison are dealt with in Part II.

Save as mentioned below, these integrals were evaluated as functions of the variables $p = \frac{1}{2}(\alpha_A + \alpha_B)\rho$ (where ρ is the internuclear distance in Bohr radii), and $t = (\alpha_A - \alpha_B)/(\alpha_A + \alpha_B)$, a measure of nuclear asymmetry. The exceptions are the $4s$–$4p$ and $4p$–$4p$, which were calculated for the equi-exponent case only ($t = 0$), as functions of p.

<div style="text-align:center">THEORETICAL CONCLUSIONS</div>

(1) σ-*Bonding.*—We will first compare the overlap integral (S) values for tetrahedral sp^3 hybrid orbitals with those for some orbitals involving *d*-hybridisation. By taking the very simple case wherein the exponents for all the hybridising orbitals are equal, we can also compare S values with the bond strengths given by Pauling's simple criterion, *viz.*, that they are proportional to the products of the angular functions of the two orbitals along the bond direction. The calculations are for a $3p_\sigma$ orbital on one centre with (*a*) a $3s3p^3$ tetrahedral hybrid orbital, (*b*) a $3s3p^33d^2$ octahedral hybrid, (*c*) a $4s4p^3$ tetrahedral hybrid, (*d*) a

$3d^24s4p^3$ octahedral hybrid, and (e) a $3d4s4p^2$ square hybrid, on the other centre, these being the combinations with which we shall be largely concerned.

The results, expressed as functions of $p = \alpha\rho$ (ρ being the internuclear distance in Bohr radii) are shown graphically in Figs. 2A and B.

It will be noted, from comparing curves (a) and (b), that overlap of the octahedral bonds at p values > 6 is about 10—20% greater than that for the tetrahedral bonds, while for (c) and (d) the increase is about 10%. In both cases it is less than would be expected from Pauling's criterion which gives the ratio octahedral : tetrahedral as $2 \cdot 923 : 2 \cdot 0 = 1 \cdot 46$. The respective maximum overlaps for octahedral and tetrahedral functions are about equal. The square hybrid overlaps, case (e), are almost identical with the octahedral ones, case (d), instead of being appreciably less (Pauling's ratio for square : tetrahedral would be $2 \cdot 694 : 2 \cdot 0 = 1 \cdot 35$).

sp^3d *and* sp^3d^2 *Hybridisation.* The first specific compound to be considered will be phosphorus pentachloride. The trigonal biprismatic arrangement of bonds (Pauling,

FIG. 2
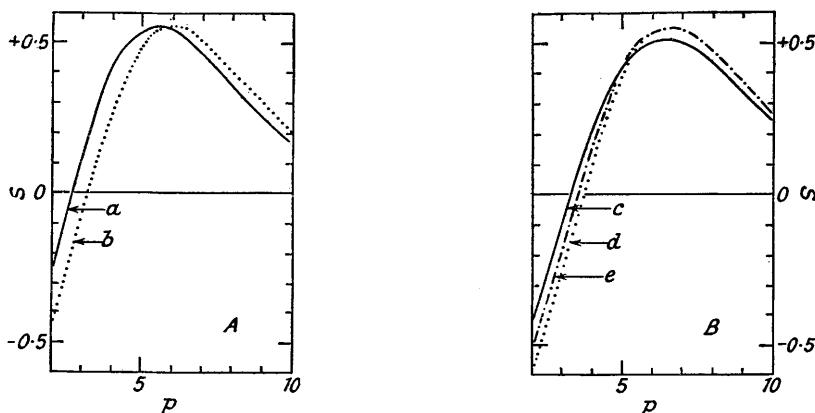
A, *Overlaps with* (a) $3s3p^3$ *hybrid orbital,*
(b) $3s3p^33d^2$ *hybrid orbital, with* $3p_\sigma$-
orbital, as functions of p.

B, *Overlaps of* (c) $4s4p^3$ *hybrid orbital,*
(d) $3d^24s4p^3$ *hybrid orbital,* (e) $3d4s4p^2$
hybrid orbital, with $3p_\sigma$-*orbital, as*
functions of p.

op. cit., p. 109) indicates sp^3d hybridisation (cf. Kimball, *J. Chem. Phys.*, 1940, **8**, 188) of the outer phosphorus orbitals. Use of Slater's rules to calculate $\alpha(S)$ [$= \alpha(p)$] for phosphorus and for chlorine gives $1 \cdot 71$ and $2 \cdot 03$ respectively; these give $t = 0 \cdot 086$, so it is a satisfactory approximation to take $t = 0$.

The bond lengths (Pauling, *loc. cit.*) are about $4a_0$ (a_0 being the Bohr radius), giving $p = ca.$ 8. Now from Tables 1—3 (Part II) or from Fig. 3A in which the σ-overlaps for $3s$–$3p$, $3p$–$3p$, and $3p_z$–$3d_{z^2}$ * are compared, it can be seen that, with $t = 0$, the $3p_z$–$3d_{z^2}$ overlap is smaller than the other two at small p values; but, as p increases, the three values, all falling, converge and at p 8—10 are not significantly different. As t for the $3p_z$–$3d_{z^2}$ overlap becomes positive [*i.e.*, as $\alpha P(d)$ becomes less than $\alpha Cl(p)$] the overlap remains large for values of p from 6 to 10 (see Fig. 3B); but it always falls rapidly as p falls below 6. As t becomes negative [*i.e.*, as $\alpha P(d)$ becomes greater than $\alpha Cl(p)$] the overlap falls off quite rapidly in the range $p = 5$—10. Now if t' is the particular value of t for the phosphorus d-orbital relative to the chlorine p-orbital, then p', the parameter for this overlap, is equal to $p_0/(1 + t')$, where p_0 is the value appropriate to the equi-exponent overlap for s–p and p–p, the exponent for Cl(p) and the value of ρ(P–Cl) both being kept constant. If t' becomes more than $0 \cdot 33$, p' is so small ($p' \ll 6$) that the $3p_z$–$3d_{z^2}$ overlap (see Fig. 3B) is insignificant compared with the s–p and p–p overlaps. Since this consideration therefore limits the

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* The change in order between the first two of these pairs and the third, although it is the central atom which may use s-, p-, or d-orbitals, while the peripheral one uses only a p-orbital, is in conformity with the convention proposed by Mulliken (*J. Amer. Chem. Soc.*, 1950, **72**, 4493).

ratio $\alpha\text{Cl}(p) : \alpha\text{P}(d)$ to be $\leqslant 2$, and since we have taken $\alpha\text{P}(s, p) = \alpha\text{Cl}(p)$ we conclude that $\alpha\text{P}(s, p)/\alpha\text{P}(d) \leqslant 2$ if spd hybridisation is to be effective. The value for $\alpha\text{P}(d)$ from Slater's rules is, however, only 0·33, giving a ratio $\alpha\text{P}(s, p) : \alpha\text{P}(d) = 1\cdot71 : 0\cdot33 = 5\cdot15$ which is much greater than the permissible limit.

We shall find other examples of this anomaly, but before considering these, or their explanation, it is convenient to consider what other information about the bonding in phosphorus pentachloride can be obtained. Accepting the trigonal structure, we may distinguish two types of phosphorus hybrid orbitals, the two axial and the three radial orbitals. The expressions for these would be :
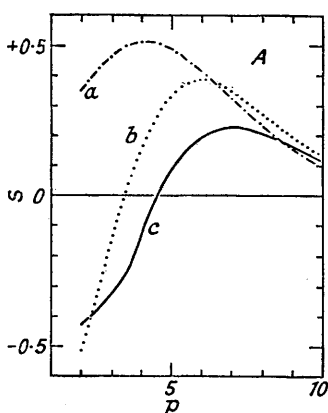
$$\psi_{\text{ax.}} = (\cos\chi/\sqrt{2})\ \psi\text{P}(s) + \psi\text{P}(p_z)/\sqrt{2} + (\sin\chi/\sqrt{2})\psi\text{P}(d_{z^2}), \text{ etc.}$$

$$\psi_{\text{rad.}} = (\sin\chi/\sqrt{3})\ \psi\text{P}(s) + \psi\text{P}(p_x)\sqrt{2/3} - (\cos\chi/\sqrt{3})\psi\text{P}(d_{z^2}), \text{ etc.}$$
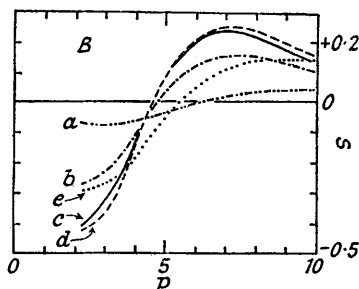
where χ is a convenient mixing parameter.

The overlaps for the axial and the radial bonds to chlorine may then be calculated as functions of p and of $\cos^2\chi$, on the assumption, first, that $t = 0$ for phosphorus s-, p-, and

FIG. 3

A, Overlaps for (a) 3s–3pσ, (b) 3pσ–3pσ, (c) 3p$_z$–3d$_{z^2}$, as functions of p, with $t = 0$.

B, Overlaps for 3p$_z$–3d$_{z^2}$ as functions of p, for $t = $ (a) $-0\cdot5$, (b) $-0\cdot2$, (c) 0, (d) $+0\cdot2$, (e) $+0\cdot5$.

d-orbitals relative to chlorine p-orbitals, then that $t = 0\cdot2$ for P(d) relative to Cl(p) [*i.e.*, $\alpha\text{P}(d) < \alpha\text{Cl}(p)$], with t remaining zero for the P(s) and the P(p) orbitals relative to Cl(p).

These results (Figs. 4A—B) indicate that even a small degree of s character markedly increases overlap in either type of bond, and hence that the s-orbital contributes to both, whence it follows that the d_{z^2}-orbital must do so too. In this connection it may be noted that the overlap of a Cl(p_σ) function with the P(d_{z^2}) function along the axial direction is exactly twice that along a radial direction (the σ-symbatic overlap) and is opposite in sign.

For $t = 0$ the best total overlap for the five bonds proves to be for $\cos^2\psi$ near to 0·25, corresponding to 0·75 of the s-orbital's being shared between the three radial bonds. For $t = 0\cdot2$, it is closer to $\cos^2\psi = 0\cdot5$. A simple interpretation of this is that the contribution of the d-orbital to the overlap has decreased so much that it is determined almost entirely by the s- and p-orbitals. This re-emphasises the previous conclusion. Furthermore, when $t = 0$, the maximum overlap for the axial bonds comes near $p = 6\cdot0$, whereas for the radial bonds it is at $p = 5\cdot5$, and the maximum overlaps for both bonds are nearly equal.* On the assumption that there is a parallel between overlap and bonding energy these results indicate that the axial bonds would be somewhat longer than the radial ones, but that all would be of approximately equal strength. The former result agrees with observation [1(P–Cl) axial $= 2\cdot11$ Å ; 1(P–Cl) radial $= 2\cdot04$ Å] (Pauling, *loc. cit.*).

The strengths of the two types of bond cannot be obtained in any such direct way. The

* Duffey (*J. Chem. Phys.*, 1949, **17**, 196) finds that for sp^3d^2 hybridisation the equatorial bonds are *weaker* than the axial ones.

most that can be obtained is a mean value for the bonds in phosphorus pentachloride, and that only if allowance is made for promotion to the quinquevalent state (cf. Gillespie, *loc. cit.*). Even if a similar allowance be made in calculating the heats of formation of the bonds in phosphorus trichloride, these are not strictly comparable with the three radial ones in the pentachloride.

The next specific compound for consideration is sulphur hexafluoride. For sulphur $(3s3p^33d^2)$ Slater's rules give $\alpha(s) = \alpha(p) = 2\cdot05$ and $\alpha(d) = 0\cdot55$, while for fluorine $(2s^22p^5)$ they give $\alpha(s) = \alpha(p) = 2\cdot60$. For the $S(s, p)$–$F(p)$ overlaps t is therefore *ca.* 0, but for the $S(d)$–$F(p)$ overlap it is $6\cdot51$. As we have previously seen, so large a t value makes the $3d_{z^2}$–$3p$ overlap insignificant, and the same can be taken as true for the $3d_{z^2}$–$2p$ overlap. Again, therefore, it is not obvious that d-hybridisation can occur.

The general position can be briefly summarised. If we could show rigorously that d-

FIG. 4
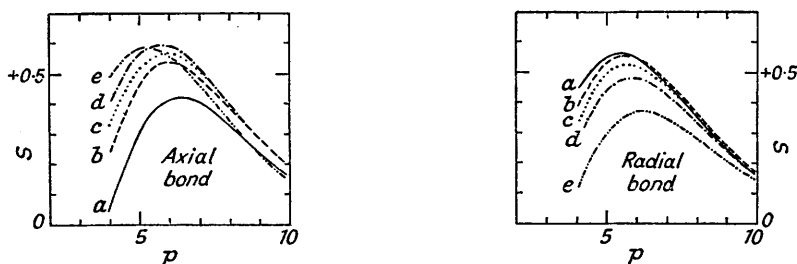
A, Overlaps for axial and for radial hybrid orbitals in phosphorus pentachloride as functions of p, with $t = 0$ and $\cos^2 \chi = (a)$ 0, (b) 0·25, (c) 0·5, (d) 0·75, (e) 1·0. The amount of s character in axial bonds increases with $\cos^2 \chi$, but in radial bonds it decreases.
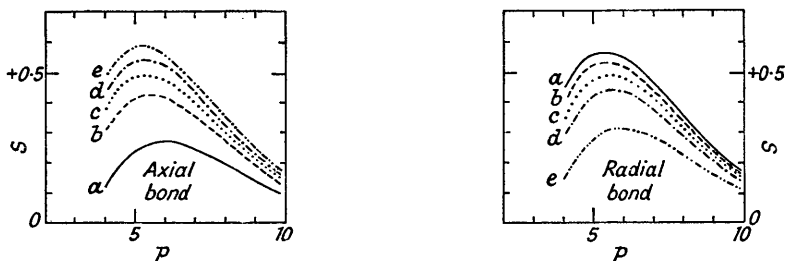
B, As A, but with $t = 0\cdot2$.

hybridisation would cause stabilisation of the whole system, *i.e.*, would lead to an exothermic increase of the number of covalencies, or would strengthen existing valencies, then we should have to admit its occurrence. In fact, we cannot do this. All we can do is to show that, *e.g.*, according to the overlap criterion, the new bonds might possibly be formed, or the old ones strengthened. We therefore apply other criteria to judge the validity of the d-hybridisation hypothesis, *e.g.*, the test of compatibility of the atomic s-, p-, and d-orbitals which we have just considered, and that of power to explain stereochemical facts. If, as now happens, we find that these criteria disagree, we have to seek a reasonable explanation of the anomaly.

One way round the difficulty is to suppose that d-orbital hybridisation does not occur at all. Pauling (*op. cit.*, p. 93) has suggested that in phosphorus pentafluoride at least one electron is ionised off the phosphorus atom, and is shared among the fluorine atoms, the other electrons providing at most four bonds resonating among the five positions. A similar explanation is possible for sulphur hexafluoride but, as Pauling realised, this suggestion is less convincing for phosphorus pentachloride and pentabromide where the ligands are much less electronegative. Furthermore, it does not, in its simple form, account for the stereochemical characteristics which were noted in the Introduction.

The next possibility is that Slater's rules are inadequate for dealing with the valence states of atoms. Where comparisons are possible with S.C.F. functions for atoms containing occupied *d*-orbitals in the ground state, the Slater functions prove to be too diffuse; but this is usually true also for the *s* and *p* functions. Also, the ionisation potentials of *d*-orbitals in the excited spectroscopic states of the sulphur atom are very low ("Atomic Energy Levels," Nat. Bur. Standards, Washington, 1949) and agree with a small exponent. Therefore, it seems probable that the disparity in exponents, while somewhat exaggerated, is essentially correct, at least for the free atoms.

Two other explanations, neither of which is entirely satisfactory, may be offered. First, we might carry to an extreme the emphasis on hybridisation by not using ionic character for interpreting polar character. We might suppose that in compounds such as those under discussion, the effect of the perturbation by the peripheral atoms is to equalise the exponents of *s*-, *p*-, and *d*-type orbitals by preferential polarisation of 3*s*- and 3*p*-orbitals. This could be by partial promotion from 3*s*- and 3*p*- to 4*s*- and 4*p*-orbitals, though such promotion, by reducing the screening of the 3*d*-orbitals, would at the same time cause these to contract. This is in direct contrast to the view put forward by Pauling, wherein the perturbation is considered to cause major polarisation of the electrons in what are normally the most polarisable orbitals, just as would a simple field acting on an isolated atom. Unfortunately, there is at present no theoretical basis for the former suggestion. It would, of course, become unsatisfactory if the ligands were sufficiently electronegative.

The last explanation is in some respects a compromise, for it admits the possibility of partial ionisation of electrons from the 3*d*-orbitals of the central atom to the ligand orbitals. This would create a positive charge on the former which, if it caused preferential contraction of the more polarisable 3*d*-orbitals, could make these compatible with the 3*s*- and the 3*p*-orbitals with which they could then hybridise effectively. The hybrid orbitals are then used by the electrons in the former 3*s*- and 3*p*-orbitals, and by the " part electron " (or electrons) in the former 3*d*-orbitals, for forming covalent bonds with the ligands. This is another way of describing the bonds as all part-ionic; but it retains more emphasis on hybridisation than does Pauling's statement.

We may emphasise that, although the *d*-electrons of the central atoms may be only partly ionised, in the sense that the total wave functions would not include large contributions from functions corresponding to one or two electrons less moving in the field of the central atom and one or two more moving in the fields of the peripheral atoms, they may contribute to the *polar* character of the bonds as if they were largely ionised, because the region of overlap of the central *d*-orbitals and the peripheral *p*-orbitals will be nearer the peripheral atom than the central atom; so the electron centroid will be nearer the latter even for a purely " covalent " type of bonding function. The relation between *ionic* character in the above sense and *polar* character is simple only if the electrons are assumed to be in compact orbitals on either atom so that overlaps are small or symmetrical. This is an arbitrary assumption, so the description in such terms is also arbitrary. Often it may be a good approximation : but in cases such as are considered above it may be a bad one and a view such as the one now expressed may be more useful. How far ionisation could proceed before the steric properties of the original electron configuration were altered is not at present known : nor is it always clear what the configuration for purely ionic bonding would be. It is a fact that all the phosphorus pentahalides so far examined in the gas phase, *viz.*, PF_5, PCl_5, PF_3Cl_2, have the same trigonal bipyramidal configuration, despite the difference of electronegativity of the ligands. Either of the last two explanations would show why only peripheral atoms of high electronegativity can excite *spd* hybridisation of the type considered. We could say that the electronegative ligands are able to confer " conditional stability " upon the *spd* hybrid orbitals. Gillespie (*loc. cit.*) has advanced a similar view.

It will be realised that, lacking a convincing proof that either of the last two explanations is correct, we cannot show beyond doubt that the overlap method is relevant to the problem of stereochemistry.

These considerations are relevant to a suggestion made by Mulliken (*J. Amer. Chem. Soc.*, 1950, **72**, 4493) that the markedly greater strength of bonds between atoms of the

elements in the second short period (*e.g.*, P–P, S–S, Cl–Cl) compared with the corresponding ones in the first is due to *d*-hybridisation. From Fig. 2 it appears that this effect could not be very large; and in such cases there is no obvious polarisation process to bring about the matching of the *d*- to the *s*- and the *p*-orbitals; so it remains doubtful whether the auto-generation of *d*-hybridisation would be very marked in such cases. A small degree of *d*-hybridisation causes a proportionately greater improvement in overlap than does further *d*-hybridisation (Mulliken, *J. Phys. Chem.*, 1952, **56**, 295) though from Fig. 2 it appears that the maximum degree available is not very large.

The great strength of Si–F bonds might also arise, in part, through tetrahedral *d*-hybridisation in the σ-bonds which could be generated by the polarisation due to the fluorine atoms. Fig. 2 suggests, however, that this would not greatly increase bond strengths. Another suggested cause is the superimposition of d_π–p_π-bonding which is discussed later.

d^2sp^3 *Hybridisation.* In the transition-metal complexes to be considered, the bonding orbitals on the central atom are 3*d*, 4*s*, and 4*p*. Overlap integrals for 4*s*–4*p* and 4*p*–3*p* bonds have been calculated only for $t = 0$; but these permit discussion of at least the simplest cases of d^2sp^3 hybridisation.

As stated on p. 335, Slater's rules, applied to the transition metals, give larger exponents for the penultimate *d*- than for the ultimate *s*- and *p*-orbitals, *e.g.*, αNi(3d) = 2·4, αNi(4s = 4p) = 1·0; αFe(3d) = 2·2, αFe(4s = 4p) = 0·68; but it is clear from comparison with self-consistent field functions (Manning and Goldberg, *Phys. Review*, 1938, **53**, 662) that in these cases the rules greatly exaggerate the ratio, which should be more like 7 : 6; so if the *t* value for the overlap of the 4*s*- or the 4*p*-functions with those of the peripheral atoms were zero, that for the corresponding 3*d* overlap would be $\gg 0·1$. The discrepancy between the results from Slater's rules and from S.C.F. treatments arises because the former assign the 3*d*-orbitals to an earlier group than the 4*s*- or 4*p*-orbitals and so attribute much greater screening power to the electrons in the former than in the latter. This is justified for the later (B sub-group) elements in this long period, for in these the *d*-electrons are genuine inner-shell electrons; but for the elements up to copper the spatial distribution of the *d*-electrons is not very different from that of the 4*s*- or 4*p*-electrons, and their screening power is therefore almost as small, so the Slater rule classification is not appropriate.

It is a sufficiently good approximation to consider that the exponents for the 3*d*-, 4*s*-, and 4*p*-orbitals of the central atom are equal, and that, relative to the ligand atom orbitals, *t* is 0 for each of them. The results presented in Fig. 2 then apply, and, as we have seen, the overlap indicates that the octahedral $3d^24s4p^3$-bond will be somewhat stronger than, or at least as strong as, the tetrahedral $4s4p^3$-bond.

The overlaps at *p* values (8·5 ± 1·0) corresponding to observed bond lengths have values between 0·25 and 0·50 and so are similar to those found by Mulliken (*loc. cit.*) in other cases. These *p* values are somewhat greater than that at which the overlap is a maximum ($p = 6·5$). This may be due to internuclear and interelectronic repulsion which are neglected in the overlap criterion.

It follows that $3d^24s4p^3$ hybridisation requires no great promotion energy, so that highly electronegative ligands are not required to bring it about. Such ligands might indeed favour $4s4p^34d^2$ hybridisation, for this process, involving promotion to higher orbitals, would cause the electron cloud charge to move nearer to them. $d\sigma$–$d\sigma$-Bonding between penultimate d_{z^2}-orbitals might occur between the iron atoms in iron enneacarbonyl (cf. Pauling, *op. cit.*, p. 254). The overlap therein has not been evaluated; but the iron–iron distance, which corresponds (if α = 2·2 for the iron *d*-orbitals) to $p = 10·25$, is probably too large for the bond to be very strong.

(2) π-*Bonding.*—π-Bonding involving *d*-orbitals can arise in several distinct ways. Two such—one involving a penultimate and the other an ultimate d_π-orbital of a central atom, bonding with an ultimate p_π- orbital of the ligand—correspond to the two cases distinguished in σ-bonding. The first type may occur, *e.g.*, in the ferricyanide ion and in metal carbonyls or nitrosyls, where the $3d_\pi$- orbitals of the iron atom may bond with the $2p_\pi$-orbitals of the carbon or nitrogen. The second may occur, *e.g.*, in thiophen, between the sulphur atom and the neighbouring carbon atoms, or in sulphoxides, sulphones, phosphine oxides, and similar compounds. d_π–d_π-Bonding is also possible in principle, with both *d*-orbitals from

ultimate or penultimate orbitals, or with one from each. The last has been suggested in the phosphine and arsine complexes of the transition metals (see Chatt, *J.*, 1952, 4300, and Nyholm, *J.*, 1951, 3245, for references). These cases will be considered *seriatim*. It may, however, first be remarked that the validity of Hund's rule in the transition-metal complexes of the iron group, in the decisive cases of low symmetry, indicates that the degeneracy of the *d*-orbitals is not seriously disturbed by molecule formation; and this means that roughly the same exponent holds for all of them independently of their use in bonding, *e.g.*, whether they hold different kinds of ligand or whether they are used for σ- or for π-bonding. On the other hand, outer *d*-orbitals are less well screened from ligands, so their degeneracy is more likely to be removed; and the exponents for d_σ- and d_π-bonds may then be different.

It is often convenient to consider double-bonding in complexes as arising from a dative σ-bond in one direction plus a dative π-bond in the opposite direction. This is an arbitrary description; but it sometimes helps in the " electron accounting."

$d_\pi–p_\pi$*-Bonding by penultimate d_π-orbitals.* For practical reasons it proved necessary to restrict the calculations to third-quantum-shell orbitals. Values for the $3d_\pi–2p_\pi$ overlaps are therefore not available; but from our calculations of 3*s* and 4*s* overlap integrals, and from Mulliken's tables (Mulliken, Riecke, Orloff, and Orloff, *J. Chem. Phys.*, 1949, **17**,

FIG. 5.
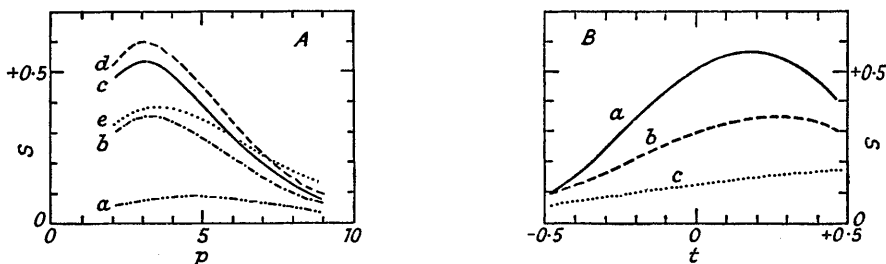
A, *Overlaps for $3p_\pi–3d_\pi$ as functions of p with t* = (*a*) −0·5, (*b*) −0·2, (*c*) 0, (*d*) +0·2, (*e*) +0·5.

B, *Overlaps for $3p_\pi–3d_\pi$ as functions of t, with p* = (*a*) 4, (*b*) 6, (*c*) 8.

1248) it follows that conclusions drawn from the $3d_\pi–3p_\pi$ integrals will be qualitatively correct, so these will suffice for our purposes.

From Slater's rules, the exponents for the transition-metal *d*-orbitals are about 2·0 (see p. 335) while that for the carbon 2*p*-orbitals is 1·6. Although these may be affected by the negative charges on both central atom and carbon in the cyanide complexes, it is probable that the exponent will be larger for the former than for the latter but that *t* for $3p_\pi–3d_\pi$ overlap * will not be much less than −0·2, whence the overlap value will be 0·1—0·2 for typical bond lengths (Fig. 5*A*). Thus it is smaller than the π-overlap values in homonuclear bonds (*e.g.*, C=C, 0·2—0·3) but is comparable with those in such bonds as C=O (0·14) or S=O (0·17).

It has been shown (Kimball, *ibid.*, 1940, **8**, 188) that in planar complexes two, and in octahedral ones three, d_π-orbitals are available for π-bonding. These are orthogonal. Hence, if, in a planar complex MX_2Y_2, Y is able to accept a π-bond from M but X is not, both Y groups could be doubly bound to M in the *cis*-isomer, whereas in the *trans*-isomer only one Y group could be so double-bonded, although the available orbital could resonate between the two positions; hence the *cis*-compound should be the more stable. The relation of this conclusion to experimental facts is discussed later.

A d_π-orbital and a p_π-orbital can hybridise just as can a p_σ-orbital and an *s*-orbital, giving strong orbitals directed oppositely (cf. Fig. 6).

Overlap values for an orbital $\cos\chi . \psi(3p_\pi) + \sin\chi . \psi(3d_\pi)$ with a $3p_\pi$-orbital, are shown below (Figs. 7*A* and *B*). In Fig. 7*A t* it assumed to be zero for both overlaps. In Fig. 7*B* it is zero for the $3p_\pi–3p_\pi$ and is taken as 0·3 for the $3d_\pi–3p_\pi$ overlaps.

From this it appears that overlap is appreciably increased by addition of *p* character to

* Note change of order of orbitals, in accordance with Mulliken's convention, p. 337.

d, or *vice-versa*; but that for p values of 5—9 the latter effect is the larger. It is comparable with that from sp–σ-hybridisation.

Such hybridisation would become effective if, in a molecule with ligands capable of double-bonding, the central atom has a d_π-orbital and a p_π-orbital of similar exponent, and has four, two, or no electrons therein according as it is necessary to form dative bonds, normal covalent bonds, or acceptor bonds to the ligands.
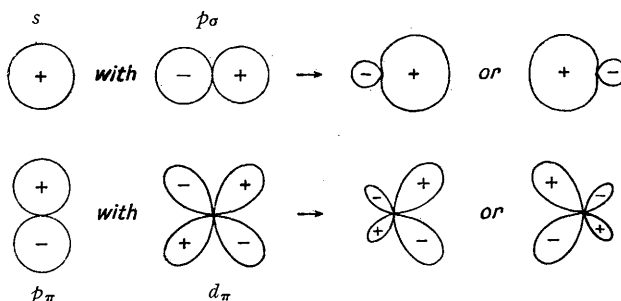

FIG. 6. *Hybridisation of s with* p_σ-, *and of* p_π- *with* d_π-*orbitals.*

If in a planar complex there are four electrons paired in two d_π-orbitals, donor π-bonds can be formed to suitable ligands, as already explained; and it is possible that these may both be strengthened by d_π–p_π hybridisation, involving the unoccupied metal p_π-orbital, in which only a small amount of p_π character is added to the d_π-orbitals. This will leave their directions of greatest overlap still nearly at right angles while appreciably increasing the overlap power of each, just as does partial s hybridisation with two p-orbitals.

FIG. 7.
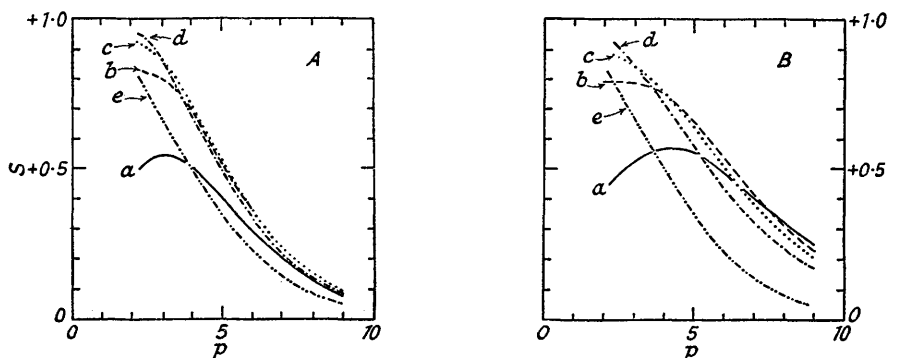
A, *Overlaps of* $3p_\pi 3d_\pi$ *hybrid orbitals with a* $3p_\pi$-*orbital, as functions of* p, *for* $t = 0$ *and* $\cos^2 \chi =$ (a) 0, (b) 0·25, (c) 0·5, (d) 0·75, (e) 1·0. *d-Character increases as* $\cos \chi$ *decreases.*

B, *As A, but with* $t = 0·3$ *for the* $3d_\pi$–$3p_\pi$ *overlap and with* $t = 0$ *for the* $3p_\pi$–$3p_\pi$ *overlap.*

π-Bonding in square complexes, as so far considered, arises from the utilisation of the d_{xz} and d_{yz} orbitals, the axis perpendicular to the plane of the square being taken as the z axis. The $d_{x^2-y^2}$-orbital, with its lobes in this plane and directed to the four ligands, hybridises with the s- and the p-orbitals to give *schedo*-σ-orbitals by which the σ-bond framework is formed. The d_{z^2}-orbital does not come into play; but there is still the d_{xy}-orbital to consider. This has its lobes in the plane but rotated at 45° to those of the $d_{x^2-y^2}$ function; so it can form a π-bond with a ligand having a suitable π-orbital, e.g., CN$^-$ or CO; but with other ligands, e.g., pyridine, only one π-orbital, say, the d_{xz} or d_{xy}, according to the orientation of the ring plane to the square plane, can be used at any one time. Ligands such as dipyridyl, *o*-phenanthroline, and dioximes which have their ring plane locked to that of the square, could not use this d_{xy}-π-bonding. Only one such bond can be drawn : so if there were several suitable ligands it could be considered to " resonate " between them.

p_π–d_π-*Bonding by ultimate d_π-orbitals.* The overlap integrals p_π–d_π when the d-orbital is in the outermost quantum shell are especially interesting. The d_π exponent is then likely to be considerably less than the p_π exponent, so t will be >0. Now from the tabulated overlap values or from Fig. 5B it can be seen that for a given p value they reach a maximum, not near $t = 0$, but at $t = 0.2$ for $p = 4$, at $t = 0.27$ for $p = 6$, and at $t = 0.4$ for $p = 8$, corresponding respectively to the ratio of exponents for p_π- and d_π-orbitals being $3 : 2$, $7 : 4$, and $7 : 3$; and decrease of overlap with further increase of t is quite slow. In fact, when the d-orbital is considerably more diffuse then the p-orbital the overlap is better than when they are commensurate : but conditions are not critical.

The reason for this may be stated very simply. In σ-bonds, and in π-bonds involving two p_π-orbitals, the overlap occurs in the region between the nuclei, and hence is largest if the exponents are approximately equal ($t = 0$). The overlap between a d_π- and a p_π-orbital tends, however, to be a maximum when the lobes of the former are nearly above and below the second atom, *i.e.*, if the d_π is more diffuse than the p_π-orbital. This may be appreciated from the diagram of the angular functions. The asymmetric overlap would make a purely covalent bond of this type highly polar (see Fig. 8).

The actual magnitudes of such overlaps may be considerable, *e.g.*, in the C–S bond (length 1.74 Å) if the ratio of exponents for S(d_π) and C(p_π) is $1 : 2$, p is 4—5; and the overlap is *ca.* 0.4. This is much larger than normal overlap values and, although it does not necessarily signify very great bond strength, since the low electronegativity of carbon and of sulphur means that the electron cloud develops in a region where the nuclear fields are
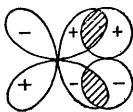

Fig. 8.
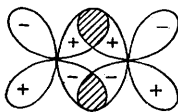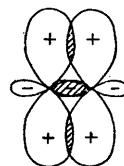
$3p_\pi$–$3d_\pi$ *Overlap.*

Fig. 9.

$3d_\pi$–$3d_\pi$ *Overlap.*

Fig. 10.

$3d_{z^2}$–$3d_{z^2}$ *Overlap.*

not very large, it emphasises that in such bonding the d_π exponent need not be increased to match the p_π one at all closely.

This means that such d_π–p_π-bonding is likely to be both common and important. In compounds such as thiophen, it may occur between sulphur and carbon despite the low electronegativity of carbon and the absence of a positive charge on the sulphur.

When, however, sulphur is attached to a highly electronegative element with very compact p_π-orbitals, such as oxygen in $>$S–O, the overlap would be diminished; but the polar character of the σ-bond gives some positive charge to the sulphur, estimated by Koch and Moffitt (*Trans. Faraday Soc.*, 1951, **47**, 7) tc be half an electron charge in the sulphones, and may, by increasing the d_π exponent, make the d_π- and the p_π-orbitals more commensurate and so may improve the overlap. Conditional stability is thus again conferred, this time on a π-bond, by a polar ligand.

Conditional stability may also be important in relation to the formation of π-bonds between highly electronegative peripheral atoms and central atoms with available ultimate d_π-orbitals, as has been suggested to occur, in, *e.g.*, silica and silicon tetrafluoride (Pauling, *op. cit.*, Chap. VII). To say that the π-orbitals on the two atoms are incompatible is another way of saying, in this context, that a highly electronegative atom is unlikely to form a dative link. If the σ-link is highly polar this incompatibility may be removed.

It may be noted that there is a formal difference between the silicon tetrafluoride case and the sulphoxide case, in that we regard the Si–F link as a dative π-bond from F to Si superimposed upon a covalent, though highly polar, σ-bond; and we can regard the S–O link as a dative π-bond from O to S superimposed on a dative σ-bond from S to O. Hence for complete neutralisation of charges we arrive at a double bond in the case of S–O, but at something which approximates to a single π-bond in the case of Si–F.

d_π–d_π-*Bonding.*—d_π–d_π-Bonding wherein both the d-orbitals are from either penulti-

mate or ultimate quantum shells of the two atoms is of somewhat uncertain occurrence. It might occur in a bond between elements of the second short period for, if an electron in each atom were promoted from a $3p$- to a $3d$-orbital, two π-bonds could be formed, a $3p_\pi$–$3p_\pi$- and a $3d_\pi$–$3d_\pi$-bond. Unless the $3d$ exponent were somehow increased, the overlap would probably be small; it might, if p were very small, be numerically large but it would then be so diffuse as to be of negligible importance for bonding (cf. Fig. 9). The only source of energy for the promotion of the two electrons and the matching of the exponents could be the formation of the new π-bonds; and this, we think, would not be adequate.

d_π–d_π-*Bonding* wherein one orbital is from a penultimate shell and the other from an ultimate one has been recently suggested by Chatt (see *J.*, 1952, 1430, for references) and by Nyholm (see *J.*, 1951, 3245) as existing in certain transition-metal complexes. Typical of these are the alkylphosphine, alkylarsine, and phosphorus trifluoride complexes. The σ-bond may be considered to be the commonly ascribed dative link from ligand to metal. The π-bond is then a dative link from metal to ligand, involving a penultimate d_π-orbital of the former and an ultimate one of the latter.

If we suppose that the dative σ-bond is first formed, then this confers a positive charge on the ligand and a negative one on the metal. These respectively increase and decrease the exponents for the ultimate d_π- and penultimate d_π-orbitals on the two atoms. Consequently these two orbitals become more nearly matched, and overlap between them is improved. If a dative π-bond from metal to ligand is now formed, the charges will be partly neutralised. The completeness of the second charge transfer, and hence of formation of the second bond, is therefore limited : but the intial formation of the σ-dative bond was itself inhibited by the development of the charges. Therefore the formation of either bond favours the development of the other. The alternative picture of the whole process, *viz.*, that there is initial electron promotion to give two unpaired electrons on each atom, and then normal double-bond formation, is equally valid; and this shows that the final charge asymmetry will depend upon the electronegativities of the two centres.

Such double bonding is likely to arise only in transition-metal complexes, for only such elements have d_π-orbitals with sufficiently small exponents : it is impossible unless the ligand is from the second short period or a later one.

If we can assume that the two exponents are roughly equal, the overlap values should be 0·2—0·3 and so are considerable. Even if $t = 0·4$, *i.e.*, if the exponent ratio is 2·3 : 1, the overlap is still about 0·15; so good bonding could arise without exact matching of exponents.

The conclusion that *two* π-bonds using d_π-orbitals can be formed only at right angles— or, very nearly at right angles, if these are hybridised with a p_π-orbital—might mean that, of isomeric *cis*- and *trans*-complexes wherein only two of the four ligands can form d_π–d_π-bonds, the *cis*-compound is the more stable.

(3) d_{z^2}–d_{z^2}-*Bonding* and δ-*Bonding*.—The overlap values for d_{z^2}–d_{z^2}-bonding are 0·13 at $p = 6$, and 0·07 at $p = 8$ (Table 6, Part II). They suggest, therefore, that such bonding cannot be entirely neglected, although it seems less important than either ordinary σ-bonding or π-bonding by d-orbitals or hybrids thereof. The overlap integrals are small because the negative lobe of one function tends to overlap with the positive lobe of the other (see Fig. 10).

The overlaps for $d\delta$-bonding are still smaller, being $< 0·1$ for $p > 6$. Overlap is poor because the dependence of ψ_{xy} on $\sin^2\theta$ (θ being the angle between the radius vector and the plane of the orbital), instead of on $\sin\theta$ as in a p_π-orbital, concentrates the orbital function in the plane and so reduces overlap with another parallel function save at very small p values.

This type of bond therefore seems unlikely to be important between atoms. It appears to occur, however, between an atom and a radical in the metal *cyclo*pentadienyls. A description of their structure in terms of molecular orbitals has already been given (Dunitz and Orgel, *Nature*, 1953, **171**, 121; Jaffé, *J. Chem. Phys.*, 1953, **21**, 156). In order to make clear the connection, this description is partly translated in an Appendix (p. 352) into the valency-bond language used in the present paper.

The main conclusions from this discussion are the following :

(1) If all the orbital exponents are equal, then (*a*) a σ-bond formed by a $3s3p^33d^2$

octahedral hybrid orbital with a $3p_\sigma$-orbital is about 10—20% stronger than one between a $3s3p^3$ tetrahedral hybrid orbital and a $3p_\sigma$ one; (b) a σ-bond formed by a $3d^24s4p^3$ octahedral hybrid orbital with a $3p_\sigma$ one is about 10% stronger than a bond between a $4s4p^3$ tetrahedral hybrid orbital and a $3p_\sigma$ one, and has almost exactly the same strength as a bond between a $3d4s4p^2$ square hybrid orbital and a $3p_\sigma$ one.

(2) d-Hybridisation with s- and p-orbitals to form σ-hybrid orbitals will be ineffective if the ratio of the exponent of the d-orbital to that of the s- and the p-orbitals is less than 0·5.

(3) This condition is not satisfied by d-orbitals in the same main group as the s- and the p-orbitals in a free atom; so, if d-hybridisation is to be effective, the perturbation by the other atoms in the molecule must make the exponents match. Polar perturbation, by highly electro-negative ligands, could probably confer such conditional stability. Increasing the number of bonds may also do it, although the more d-orbitals that have to be matched the more is the promotion energy required.

(4) In phosphorus pentachloride, the bonds are all of nearly the same strength; and the axial may be somewhat (ca. 10%) longer than the radial bonds (the reported difference is in this sense but is only 3%).

(5) Hybridisation between penultimate d-orbitals and ultimate s- and p-orbitals is permitted by the probable exponent values. Highly electronegative ligands are not necessary.

(6) Penultimate d-orbitals on a central atom may form moderately strong π-bonds with free π-orbitals on ligands.

(7) In square bond arrangements, two d_π bonds can be formed at right angles and, with little increase of this angle, they could be notably strengthened if the central atom has a vacant p_π-orbital with which they can hybridise.

(8) π-Bonding, by one d-orbital, can also arise in the plane of the square bonds if suitable ligands are present.

(9) An ultimate d-orbital can form a strong π-bond with a p_π-orbital on another centre even when it is considerably more diffuse than the latter. Polar character in the σ-bond could improve the overlap between very disparate orbitals if it tended to equalise the exponents. Such conditionally stable bonds are likely to be common and important.

(10) π-Bonding between two d_π-orbitals is possible, but is unlikely to be important unless at least one of them is a penultimate orbital.

(11) d_{z^2}–d_{z^2}-Bonding is possible but not probable.

(12) δ-Bonding, between two atomic d_{xy}-orbitals, is unlikely to be of importance.

CORRELATION OF FACT AND THEORY

So far, in this paper, the correlation of fact and theory has hardly been taken beyond the point of referring briefly to facts to indicate that there is, or may be, a phenomenon requiring theoretical investigation. There is little need to do more about those topics which have already been discussed extensively in the literature, but for the others a fuller critical appraisal is necessary. It will be convenient to follow the same order of headings as in the previous main section.

d-*Orbitals in* σ-*Bonding.*—The overlap treatment has shown that the conditions necessary for effectiveness of d-hybridisation in σ-bonds are quite different according to whether the d-orbitals are in the same main group as the s- and the p-orbitals or in the previous one. If they are in the same group, the ligands should be electronegative enough to perturb the central atom considerably; but, if not, this is neither necessary nor desirable. Another conclusion is that for strongest overlap the central atom and the ligand orbitals should be of about the same " size " : because for s–p_z-overlap S is a maximum for small positive values of t, which means that the s-orbital has the larger α value; for p_z–d_{z^2} overlap S is again a maximum (see Fig. 3B) for small positive t values, but this means that the p_z-orbital has the larger α value; while, for p_z–p_z overlap, S is a maximum when $t = 0$. For maximum overlap of a hybrid of s, p_z, and d_{z^2} on one centre with p_z on another it is therefore necessary that the α values should all be more or less equal : near $t = 0$ the variation with t is probably slow. Finally, because large overlap denotes effective bonding

only if it is fairly compact and is in a region where the combined field of the two nuclei is strong, it is necessary for good binding that the internuclear distance (ρ) is not too large and the sum of the α values for the two atoms is not too small [hence that $\rho/(\alpha_A + \alpha_B)$ is not large].

With these conclusions and with previously accepted principles in mind, it is possible to explain the occurrence of actual molecules in the 6-co-ordinated series $(ML_6)^x$ (where x is an integral positive or negative charge of from 0 to 6 electron units), when M either has no penultimate d-orbitals or has only full ones. It appears, however, that there are several factors to consider; so the argument is complicated and somewhat speculative.

In the isoelectronic series, with M an element of the second short period, there is a tendency, as the atomic number increases, for the common complexes to change successively from being cationic or rarely neutral (M = Na or Mg); to cationic, neutral, or anionic (Al); to cationic but of lower charge only, or to anionic (Si); to anionic only (P); to neutral only (S); and then to being non-existent (Cl). Such complexes are formed only with the most electronegative member in each of the common ligand series, *e.g.*, with ammonia or amines, water or ethers, or fluoride ion, or with other ligands containing nitrogen or oxygen as the co-ordinating atoms. $[PCl_6]^-$ is known but only in an unusual case (solid PCl_5). The heavier elements of the B-sub-groups tend, however, to form similar 6-co-ordinated anions with Cl^-, Br^-, and even I^-, rather than with F^-.

The characteristics of the complexes of sodium, magnesium, and aluminium may be understood by considering these, as is now usual, to be essentially electrostatic, *i.e.*, to be ion–ion or ion–dipole aggregates the stability of which, once the necessary ions have been generated, is determined by the attractions between central ion and ligands, and by the ligand–ligand repulsions (including, on occasion, the effects of ionic radius, *i.e.*, of the approach limit set by exchange forces). Polarisation of ligand by central ion increases in the order given but probably is still a minor feature in the aluminium complexes. Thus, if polarisation were sufficient to cause a transference of half an electronic charge from each ligand the charge on the central ion would be neutralised; and we might then consider that if covalent bonds were formed the central atom would use six orbitals with α values which would be calculated from Slater's rules on the supposition that there are four half-electrons in the 3s- and the 3p-orbitals and two such in the 3d. This gives $\alpha = 1.3$ for these 3s- and 3p-orbitals, and 0.33 for the 3d; while for, *e.g.*, $F^{\frac{1}{2}-}$ the α value for the 2s- and the 2p-orbitals is 2.5. Both because of the difference between the values for the aluminium s-, p-, and d-orbitals, and because of the disparity between these and the values for the ligand orbitals (t for s and p is -0.33, for d it is $+0.8$), it is clear that overlap would be very poor. The classical concept of polarisation would have to be describable in terms of a transition towards covalency, and it appears therefore that so great a degree of polarisation is unlikely.

For the complexes of phosphorus, sulphur, and chlorine, wherein the charge on the initial central ion is greater, such polarisation becomes a major feature; and it is intermediate in silicon complexes. It would produce a large positive-charge transference to the ligands; so initially neutral ligands would repel each other strongly, and initially negative ones are therefore favoured. The aggregation is now better considered as due to overlap bonding between radical ligands and a sexavalent central atom with a negative charge of $(6 - n)$ (n is the group valency), the polarisation of this central atom by the ligands decreasing as its atomic number increases (cf. Fyfe's views, *J. Chem. Phys.*, 1952, **20**, 1039).

Returning to the electrostatic picture, we see that the ionic or dipolar ligands which are co-ordinated must not be very polarisable, *i.e.*, they must be electronegative, for otherwise the charge on the central atom would be largely neutralised if they approached closely, which as we have seen would cause instability; or, if they did not approach closely, the electrostatic bonding would be weak, and the overlap would be ineffective. Even if the central atom has a positive charge large enough to absorb a fair degree of negative-charge transfer without its becoming neutral, then such polarisable ligands, if initially neutral, acquire considerable positive charges and repel each other; while if they are anionic their ionic radius may prevent them from packing round the central ion, since size and

polarisability tend to increase together. Such ligands do not, in fact, give co-ordination greater than four. A complete electron transfer from an anionic ligand to the central atom, leading to stable products $ML_5^{(6-n)-}$ or $ML_4^{(6-n)-}$ and $L\cdot$ is not possible in these cases, because the central ions do not have vacant penultimate d-orbitals and have not enough charge to hold the electron in an outer d-orbital.

From the covalent-bonding treatment we have already seen how the need for promotion energy to match the s-, the p-, and the d-orbitals requires that the ligands be electronegative. For P^-, fluorine (or exceptionally chlorine) is suitable; for S^0 only fluorine will do; for Cl^+ even fluorine is not sufficiently electronegative. Alternatively we could say that the ions PX_3^{2+} and SX_2^{4+} oxidise any but the most electronegative of the halogen ions by removing electrons from them completely, so that PI_5 and SCl_6 are unstable.

In the 5-co-ordinated phosphorus halides, fluorine, chlorine, or even bromine appear to be suitable; but because only one electron in a d-orbital has to be matched, instead of two as in sulphur, less polarisation of the central atom is required. The steric factor may also enter, because the average Cl–Cl distance in phosphorus pentachloride is somewhat greater (3·1 Å) than that expected in sulphur hexachloride (2·9 Å).

For the heavier elements of the B-sub-groups, the α values, even for s- and p-orbitals, become much smaller than those for fluorine; *e.g.*, for tin α $(s) = \alpha$ $(p) = 0.89$, whereas for fluorine the value is 2·60, so $t = -0.49$ and overlap is poor. The larger halogens give better overlap (for Sn–Cl and Sn–Br the corresponding t values are -0.39 and -0.28), so they are favoured.

The elements in the earlier A-sub-groups are highly electropositive, *i.e.*, they have very small α values even for their s- and p-orbitals; so when they form complexes these are essentially electrostatic. Those in the later A-sub-groups and in group VIII, being less electropositive, might be expected to form more covalent octahedral complexes, provided that the ligands are not too electronegative, because d-hybridisation permits of good overlap even when the ligands are somewhat more electronegative than the central atom. In fact, in such complexes the central atom always has enough d-electrons spin-paired, according to the magnetic criterion, to permit of two penultimate d-orbitals' being available for d^2sp^3 hybridisation, more especially if the metal is in its bivalent state. Thus this occurs when the ligand is CN^-, NO_2^-, CO, or a tertiary phosphine or arsine. Other, more highly electronegative ligands, such as H_2O, NH_3, ethylenediamine, acetylacetone, the oxalate ion, Cl^-, and F^- do not usually cause such hybridisation (cf. Pauling, *op. cit.*). Admittedly, however, for all ligands in the former group, but for none in the latter, the formation of double bonds with the metal atom is possible, and these may obviously stabilise the complex. Burstall and Nyholm (*J.*, 1952, 3570) indeed suggest that this possibility is the major factor in producing strong octahedral bonding in such cases. The proper degree of emphasis is not certain. Tervalent cobalt and the heavier elements of group VIII hardly give this distinction, for they appear to show d^2sp^3-bonding with any type of ligand. The only paramagnetic octahedral cobaltic complex now known is K_3CoF_6.

When such d^2sp^3 hybridisation does not occur, there is what may be variously described as ionic bonding, restricted resonance using sp^3 hybrid orbitals (Pauling, *J.*, 1948, 1461), or sp^3d^2 hybridisation, *i.e.*, the use of ultimate d-orbitals for bonding (cf. Huggins, *J. Chem. Phys.*, 1937, **5**, 527). There is fairly direct evidence in some instances that the bonds formed by the central atom are quite highly polar. Atom polarisation provides some indication of the polarity of the opposed bonds in a symmetrical molecule (see Coop and Sutton, *J.*, 1938, 1269). For the aluminium–trisacetylacetone complex which, from earlier arguments, would be expected to be quite polar, the value is large (39·7 c.c.); for the chromium compound it is 40·2 c.c.; and for the iron compound it is even larger (55·1 c.c.), which may indicate even more polar bonding or a smaller force constant for bond bending. The magnetic moment of the last compound (5·9 B.M.; Sugden, *J.*, 1943, 328) shows five unpaired electron spins. To some extent, the difference between these three descriptions is a matter only of language; but there are definite reasons for preferring the last of them.

The complex ion $[Ni(dipyridyl)_3]^{2+}$ can be resolved into optical antimers (Morgan and Burstall, *J.*, 1931, 2213); and it has been suggested that this relative stability indicates the

use of $3d^24s4p^3$ hybrid orbitals for covalent bonding (Pauling, *op. cit.*, p. 117; Johnson, *Trans. Faraday Soc.*, 1932, **28**, 845). This suggestion would, however, require the promotion of two electrons from a $3d$- to some outer orbital, presumably to a $5s$-orbital in which they would be spin-paired, giving diamagnetic character. The magnetic moment actually shows that there are two unpaired electron spins. Furthermore, by analogy with the cobalt complexes, we should expect that these two electrons could be readily removed by oxidation, giving tervalent or quadrivalent nickel, but this is not observed. A more probable explanation is, therefore, that $4s4p^34d^2$-orbitals are used to form rather weak covalent bonds, while two unpaired electrons remain in two $3d$-orbitals. This is supported by the observation that the complex $[\mathrm{Zn(en)_3}]^{2+}$ can be resolved (en = ethylenediamine) (Neogi and Mukherjee, *J. Indian Chem. Soc.*, 1934, **11**, 681; *cf. idem, ibid.*, p. 225) although $3d$ hybridisation is almost certainly impossible and only $4s4p^34d^2$ would be likely. The resolution of $[\mathrm{Fe(C_2O_4)_3}]^{3-}$ claimed by Thomas (*J.*, 1921, 1140) has been disputed by Johnson (*Trans. Faraday Soc.*, 1932, **28**, 845); but Dwyer and Gyarfas (*Nature*, 1951, **168**, 29) have observed activity in the ferric–trisacetylacetone complex the magnetic moment of which shows five unpaired electron spins. However, both the nickel and the iron complexes racemise rapidly.

Finally, when a specially powerful chelating agent, such as a ditertiary arsine, is used to form nickel complexes, it does in fact, as predicted above, give a diamagnetic ion, $[\mathrm{Ni(diarsine)_3}]^{2+}$, which apparently can be oxidised (Nyholm, *J.*, 1950, 2061). Similar compounds, $[\mathrm{NiCl_2(diarsine)_2}]^+X^-$ and $[\mathrm{NiCl_2(diarsine)_2}]^{2+}X^-{}_2$, containing $\mathrm{Ni^{III}}$ and $\mathrm{Ni^{IV}}$ respectively, have actually been isolated (Nyholm, *J.*, 1951, 2602).

The question of whether or not penultimate d-orbitals can hybridise with ultimate s- and p-orbitals has hitherto been considered only in relation to octahedral bonding, but its relevance to the question of whether certain 4-co-ordinate complexes will be planar or tetrahedral needs discussion. From the foregoing general conclusions it would be expected that the less electronegative ligands would favour planar bonds involving dsp^2-hybrid orbitals, whereas the more electronegative ones would favour tetrahedral, sp^3-bonding. Mellor and Craig (*J. Proc. Roy. Soc., N.S.W.*, 1940, **74**, 475) have shown that this is in general true. Interesting examples are that $[\mathrm{Ni\{(CH_3 \cdot S \cdot CH_2 \cdot)_2\}_2}]Cl_2$ is paramagnetic (Foss, personal communication) whereas $\mathrm{K_2[Ni(thio\text{-}oxalate)_2]}$ is diamagnetic. Now in a cationic complex, the excess of positive charge will increase the effective electronegativities of the ligands, and the reverse will be true in anions; so, as predicted, the ligand with higher electronegativity appears to cause sp^3 hybridisation and that with the lower causes dsp^2 hybridisation.

Cupric complexes with highly electronegative ligands are, however, anomalous : for whether they are anionic, e.g., $[\mathrm{CuCl_4}]^{2-}$ or cationic ($[\mathrm{Cu(H_2O)_4}]^{2+}$, they always have, in the crystalline state, four nearest neighbours in a plane and usually two more completing a distorted octahedron. Furthermore, they cannot be oxidised at all easily to tervalent copper, although for gold this happens so readily that the bivalent complexes are unknown. The usual explanation of the planar bonding, as being due to promotion of an electron from a $3d$- to a $4p$-orbital, followed by hybridisation of this $3d$- with $4s$- and $4p$-orbitals, therefore does not appear satisfactory. *Pace* Ahrens's views (*Nature*, 1952, **169**, 463) we do not consider that the planar arrangement of the valencies can be explained in terms of pure ionic bonding; hence if $3d$-orbitals are not used, presumably $4d$ are : and there is $4s4p^24d$ hybridisation. The same is true of the complexes of bivalent silver. Rây and Sen (*J. Indian Chem. Soc.*, 1948, **25**, 473), from a careful examination of the magnetic moments, have already suggested that this may be true of some copper complexes, though others involve $3d4s4p^2$ hybridisation. This hypothesis is further supported by the fact that the tervalent copper complex $\mathrm{K_3CuF_6}$ (Klemm, personal communication : Hoppe, *Angew. Chem.*, 1950, **62**, 339) has a magnetic moment of about 2·9 B.M. which indicates (see Nyholm and Sharpe, *J.*, 1952, 3579) that two $3d$-orbitals are occupied by unpaired electrons; so $3d^24s4p^3$ hybridisation is not occurring but $4s4p^34d^2$ may be.

There is, therefore, considerable positive evidence that $4d$-orbitals can hybridise with $4s$ and $4p$ in octahedral or planar complexes when the ligands are electronegative. Transition from d^2sp^3 to sp^3d^2 hybridisation requires promotion of electrons and could happen

in the combined fields of strongly electronegative ligands. In discussing such cases, Pauling has tended lately to discard the hypothesis of d hybridisation (*J.*, 1948, 1461) and to use instead the concept of sp^3 hybrids resonating among the several positions. This view is a consequence of his describing the polar character of a bond in terms of its ionic character. As we have seen, this is an arbitrary simplification and, it would appear, not always satisfactory.

A description in terms of diffuse hybrid functions on one centre overlapping with relatively compact ones on the other reduces the conceptual difficulty. Admittedly, for very large charge transfers in σ-bonds, it is adequate only if the hybridisation includes quite high orbitals of the central atom, and for some purposes the " ionic " description then has advantages; but if there is reason, either theoretical or empirical, to consider that the configuration of the molecule is determined by the central wave-functions, then it is better to use a group of wave-functions which definitely implies that configuration. If charge transfer goes far enough, molecular configuration is no longer controlled by the central wave functions, and this consideration no longer applies.

d-Orbitals in π-Bonding.—(1) d_π–p_π-*Bonding.* The case for the existence of π-bonding which involves ultimate d_π- and p_π-orbitals, respectively, of the two atoms involved as in, *e.g.*, >S=O or $\geqslant$P=O, is largely based on the analysis of bond characteristics, *viz.*, the lengths, mean energies, electric dipole moments, and vibration frequencies, empirical comparisons and arguments of analogy being used (cf. Phillips, Hunter, and Sutton, *J.*, 1945, 146; Barnard, Fabian, and Koch, *J.*, 1949, 2442). It has been criticised by Wells (*J.*, 1949, 55); but the consistency of the arguments and conclusions is nevertheless striking. Further evidence comes from the properties of systems such as thiophen, diphenyl sulphide, thianthren, and diphenyl sulphoxide and sulphone, wherein new types of conjugation can arise if *d*-orbitals can participate (cf. Moffitt, *loc. cit.*). The existence of the compound pentaphenylphosphorus, PPh_5 (Wittig and Rieber, *Annalen*, 1949, **562**, 187), may possibly be due to such bonding. Striking support for it comes from the non-basicity and planarity of trisilanylamine, $N(SiH_3)_3$ (Hedberg, personal communication) which indicates extensive use of the nitrogen lone pair for π-bonding. Furthermore, Pauling has shown that this hypothesis makes possible an explanation of the strengths of the oxy-acids (personal communication). Our theoretical results indicate that such bonding is very probable, and that the conditions as to relative electronegativities of the atoms bound by it are not critical.

Such bonding is possible between the oxygen and the silicon atoms of the backbone in a " silicone " molecule, and its occurrence is indicated by the short observed Si–O distance [*ca.* 1·64 Å (Aggarwall and Bauer, *J. Chem. Phys.*, 1950, **18**, 42; Kotera, Ueda, Yamasaki, and Yokoi, *ibid.*, p. 1414) to be compared with 1·83 Å calculated from Pauling's older covalent radii, or 1·76 Å from the newer radii and with the Schomaker–Stevenson correction (*J. Amer. Chem. Soc.*, 1941, **63**, 37)]. Nevertheless this would not, as might at first appear, affect the freedom of rotation about these bonds, because there are five orthogonal *d*-orbitals available on each silicon atom, and these make it possible for a π-bond to be formed to oxygen whatever the orientation of any one Si–O bond to any other in the chain; hence there is complete freedom of rotation in this chain so far as this effect is concerned.

General evidence for the existence of d_π–p_π bonding, with a penultimate d_π-orbital, is that : (i) complexes in which this could occur, *e.g.*, cyanide, carbonyl, and nitrosyl, are formed with elements which have suitable penultimate *d*-orbitals, such as the transition metals, copper, or silver, and even the group IIB elements (cf. Syrkin and Dyatkina, " Structure of Molecules," Butterworths Sci. Publ., London, 1950, p. 369), but not by elements such as aluminium which lack them, although one reason for this may be the suitability of such ligand sfor d^2sp^3 hybrid σ-bonding to the former (cf. p. 348); (ii) such complexes are more stable than the corresponding ones formed with Cl^- and Br^- which have no p_π-orbitals free to accept a bond from the metal atom; and (iii) the bond lengths, where known, are less than would be expected for σ-bonding alone (cf. Sidgwick, *op. cit.*; Pauling, *op. cit.*).

More particular evidence is that, towards those metals for which no double-bonding is possible, the co-ordinating power for a series of amines runs parallel to the basic constants;

so, if only σ-bonds were formed, ethylenediamine would always be stronger than dipyridyl. Since the reverse is true with the transition metals (*e.g.*, the 6-co-ordinate Ni^{2+} complex with the latter can be resolved, but that with the former cannot), we conclude that double-bonding occurs with them.

There is therefore a strong factual case for believing that such double-bonding happens : and this is supported both by the argument originally adduced by Pauling, *viz.*, that it disperses negative charge from the central negative atom of a complex, and also by our calculations.

The possibility of the reinforcement, by double-bonding, of the bonds in square complexes has been discussed on p. 342. The notable stability of the planar tetracyanide anion $[Ni(CN)_4]^{2-}$ and of the dioxime neutral and cationic complexes appears to support this sugges-tion. The oxalato-ion $[NiOx_2]^{2-}$, in which such reinforcement would be less important if it occurred at all, is as stable as the complex cyanide ion, but the oxalato-group is a chelate one.

The tetrahedral complex cyanide anions of the Group IB and IIB elements could be stabilised, since two d_π–p_π-bonds may resonate among the four sp^3 hybrid σ-bonds (cf. Syrkin and Dyatkina, *op. cit.*, p. 369). There is no reason why one electron, from a singly occupied d-orbital of the metal, should not form a part-bond of this type : or why such a d-orbital should not accept a one-electron dative bond from a ligand.

(2) d_π–d_π-*Bonding*. There appears at present to be no evidence for d_π–d_π-bonding if both d-orbitals are in ultimate groups; and instances where both d-orbitals are in penulti-mate groups are at present rare. The case of the ion $[Ni(CN)_3]_n{}^-$, where it is suggested that n is 2 (Mellor and Craig, *Proc. Roy. Soc., N.S. W.*, 1943, **76**, 281), may be relevant since the Ni–Ni bond could be a σ-bond formed by dsp^2–dsp^2-orbitals and reinforced by a π-bond.

The concept of a d_π–d_π-bond when one d-orbital is in the ultimate group of one atom and the other is in the penultimate group of the other atom was first postulated by Syrkin (*Bull. Acad. Sci. U.R.S.S.*, Cl. Sci. Chim., 1948, 75), and it has been discussed and extended independently by Chatt (*Nature*, 1950, **165**, 637 ; see also Chatt and Wilkins, *J.*, 1952, 4300, for later references), by Nyholm (Thesis, London, 1950 ; Kabesh and Nyholm, *J.*, 1951, 3245), by Orgel (see *Nature*, 1951, **167**, 434) and by Coates (*J.*, 1951, 2003) The evidence is largely of a classical chemical nature.

The order of stability of complexes formed by alkyl derivatives of the elements of the fifth and the sixth group acting as donors to atoms which can accept only with p-orbitals (such as boron, aluminium, or gallium) is in the order $R_2O > R_2S > R_2Se$ and $R_3N > R_3P > R_3As > R_3Sb$ (H. C. Brown, personal communication ; Coates, *J.*, 1951, 2003). The stability of complexes formed by such ligands with the transition metals is, however, in the order $P > As \gg N$. The complexing power of *o*-phenylenebisdimethylarsine is greater than that of dipyridyl, since it appears to be able to force electrons from a $3d$- to a $5s$-orbital (cf. p. 349 ; Burstall and Nyholm, *loc. cit.*). A strong indication that new types of bond may rise came from the isolation of complexes of phosphorus trifluoride, *e.g.*, $(PF_3)_2,PtCl_2$ (Chatt, *loc. cit.*) and $Ni(PF_3)_4$ (Irvine and Wilkinson, *Science*, 1951, **113**, 742), although this ligand shows no sign of combining with boron trifluoride. Recently, Nyholm (*J.*, 1952, 2906) has isolated the compound (I) for which the C–O vibration frequency is the same as in nickel carbonyl. This suggests that the arsine groups can play the same part in forming double bonds to nickel as can the carbonyl groups.
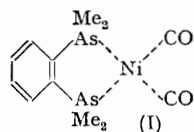
All these observations could be reconciled by postulating the formation of a d_π–d_π-bond in addition to the σ-bond. Moreover, as was previously emphasised (p. 345), because the π-bond would tend to neutralise the formal charges set up by the formation of the σ-bond, the latter might be strengthened.

Since two of these π-bonds could be formed at right angles, the *cis*-forms of compounds L_2MX_2 would be favoured if only L could form such bonds with M. Chatt and Wilkins (*J.*, 1952, 273, 4300) have shown that this effect is probably complicated by electrostatic interactions ; but they estimate it to be about 10—12 kcal./mole for platinous complexes in which L is a Group VB ligand and X is chlorine.

There is at present a relative lack of direct physical evidence for such d_π–d_π-bonding.

Jensen's measurements (*Z. anorg. Chem.*, 1935, **225**, 97; 1936, **229**, 225; 1937, **231**, 365) of the electric dipole moments of a number of *cis*-L_2PtX_2 compounds, where L is a dialkyl derivative of S, Se, or Te, or a trialkyl derivative of P, As, or Sb, and where X is a halide, indicate that the L–Pt bonds are highly polar, [about 4·5—6·1 D for the Group V ligands (2 D being allowed for each Pt–Cl bond), and about 4·7 D for the Group VI ligands]. The exact significance of this cannot be judged without more data for comparison; but it appears that if there is a reverse dative bond from metal to ligand it is not developed as much as the σ-dative bond from ligand to metal (cf. Chatt and Wilkins, *loc. cit.*).

Measurements for the bonds formed by phosphorus trifluoride (Chatt and Williams, *J.*, 1951, 3061) indicate that the F_3P–Pt grouping is almost non-polar, *i.e.*, that its moment is probably not greater than 1 D; so the P–Pt bond appears to be of low polarity, as would be expected if the d_π–d_π dative bond were of about the same moment as the σ-dative bond, the two being opposed.

The observed length of the As–Pd bond in $[Me_3AsPdBr_2]_2$ is 2·50 Å (Mann and Wells, *J.*, 1938, 702). That for the Pd–Br bonds is 2·45 Å. The Pd radius from the latter, plus the normal-valent arsenic radius, is 2·52 Å. There is, therefore, no notable contraction attributable to double-bonding between Pd and As.

The chemical evidence for such bonding is strong; and the theoretical results show that it is likely. Further studies of the physical characteristics of compounds wherein it may occur are therefore needed.

APPENDIX

Ferrocene (bis*cyclo*pentadienyliron) is known to have a " sandwich " structure (Wilkinson, Rosenblum, Whiting, and Woodward, *J. Amer. Chem. Soc.*, 1952, **74**, 2125; Fischer and Pfab,

FIG. 11.
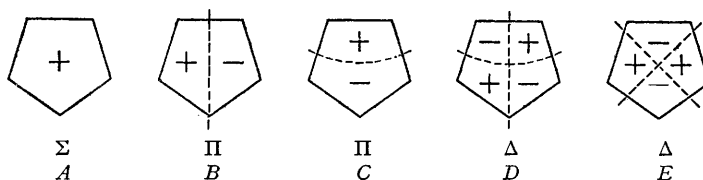
A—E, Symmetries of the molecular orbitals derived from atomic π-orbitals.

d_π–Π
F

d_δ–Δ
G

d_δ–Δ
H
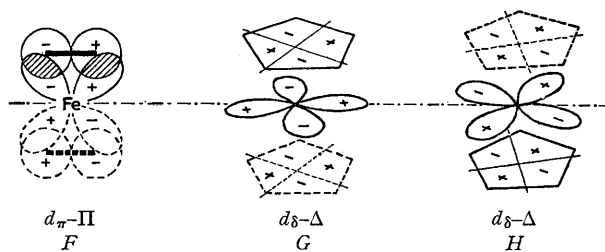
F, A d_π–Π-bond in ferrocene. G, H, The d_δ–Δ-bonds in ferrocene.

Z. Naturforsch., 1952, **7**, **b**, 377; Eiland and Pepinsky, *J. Amer. Chem. Soc.*, 1952, **74**, 4971; Dunitz and Orgel *Nature*, 1953, **171**, 121). Dunitz and Orgel, and Jaffé (*J. Chem. Phys.*, 1953, **21**, 156), have described the electronic structure in terms of molecular orbitals. A part translation into valency-bond language gives the following description. The state of each *cyclo*pentadienyl radical may be expressed in terms of molecular orbitals: these, which are formed from the π-type orbitals of the five carbon atoms, are one of Σ-type (Fig. 11*A*) containing two electrons; two of Π-type (Figs. 11*B*, *C*) which are degenerate and of which one contains two electrons while the other contains only one; and two of Δ-type (Figs. 11*D*, *E*) which are empty—the last would be similar in symmetry to the d_{xy} and $d_{x^2-y^2}$ atomic functions, being oriented with their sets of nodal planes at 45° to each other. The symmetries are shown in Fig. 11.

The iron atom has three of its $3d$-orbitals doubly occupied and two singly occupied. They are all degenerate; so we can consider the latter pair of orbitals to be the d_{xz} and the d_{yz}. One of these can then form what is essentially a d_π–p_π-bond with the Π_x-orbital of one radical (Fig. 11F) and the other with the Π_y-orbital of the other radical (exactly like 11F but turned through a right angle about the vertical axis). But these π-bonds formally resemble those in carbon dioxide; so we must consider that there is a "resonance" of both of them between alternative pairs of centres (in Fig. 11F, the lobes used for the alternative bonds are shown by solid and by broken lines respectively). It would also be possible for a dative link to be formed by the two electrons in the d_{xy}-orbital of the iron atom to an empty Δ_{xy}-orbital of one radical, and for those in the $d_{x^2-y^2}$-orbital of the iron atom to form one to the $\Delta_{x^2-y^2}$-orbital of the other. These two dative bonds would be of δ-type and they also "resonate" between alternative pairs of centres (Figs. 11G and H show the alternatives by solid and by broken lines). Although, for simplicity, the two *cyclo*pentadienyl radicals are shown with the same orientations in Figs. 11G and H, no such relative fixation would necessarily occur, because the nodal planes are not uniquely related to the atoms of the radicals. In the crystal (see above), the molecule has a centre of symmetry, *i.e.*, has a staggered configuration.

[*Added, November 23rd*, 1953.] In the light of recent work on the *cyclo*pentadienyl derivatives of other metals (see Wilkinson *et al.*, *J. Amer. Chem. Soc.*, 1952, **75**, 1011; Fischer and Huffner, *Z. Naturforsch.*, 1953, **8**, *b*, 444) it is clear that the covalent π-type bond is in general the most important one. The dative δ-type bond discussed above may increase in relative importance as the π-type bond is weakened by decrease in the number of unpaired electrons available (or by the energy required for promoting electrons from $3d$ to $4p$ orbitals if this occurs; Wilkinson *et al.*, *loc. cit.*), as, *e.g.*, in $Co(C_5H_5)_2$ and $Ni(C_5H_5)_2$. It is possible in all other such complexes, save in $[Ti(C_5H_5)_2]^{++}$, and in isoelectronic ions; but it will be less important the larger the positive charge on the ion and the fewer the $3d$ electrons. In the titanium and similar derivatives there may be a dative σ-type bond from the Σ orbital of either *cyclo*pentadienyl radical to the d_z^2 orbital of the metal atom.

The magnetic properties of the various compounds follow from the discussion by Dunitz and Orgel (*loc. cit.*) or from the theory developed above.

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