

## LIGAND-FIELD THEORY

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THE chemical and physical properties which we think of as characteristic of transition metals, for example their variable valencies and the colours of their compounds, are almost all associated with the presence of an incomplete shell of  $d$  electrons. In this Review we shall consider, qualitatively, two closely related theories which deal with the effect of the neighbours of a transition-metal ion on the behaviour of the  $d$  electrons of the metal, and hence on the properties of the ion. The first theory, usually called the crystal field or electrostatic theory, was developed by Bethe,<sup>1</sup> Van Vleck,<sup>2</sup> and many others<sup>3, 4, 5</sup> in connection with studies on magnetism. The second theory, the molecular-orbital theory, was also discussed at an early date by Van Vleck.<sup>6</sup> More recently each theory has been used to discuss the optical and chemical properties of a variety of compounds. We regard them both as expressing certain aspects of a more complete theory which we call ligand-field theory.

**Electrostatic Theory.**—In the electrostatic theory, a transition-metal ion in a compound or complex is supposed to be subjected to an electrostatic field produced by the molecules and ions in its environment. For most purposes only the nearest neighbours of the metal ion need to be considered. We may, for example, treat  $[\text{Cr}(\text{NH}_3)_6] \text{Cl}_3$  as a  $\text{Cr}^{3+}$  ion in the field of a set of six ammonia molecules, and neglect the chloride ions.

In those compounds to which the theory is applicable, the ligands are either negative ions or molecules with unshared electron pairs. In the latter case the negative end of the lone-pair dipole is invariably directed towards the metal. The ligands therefore produce a field roughly equivalent to that of a corresponding set of negative charges placed about the metal ion. The electrostatic theory is concerned with the effect of this electric field on the orbital energies of the  $d$  electrons of the central ion. In the absence of the field the five  $d$  orbitals are degenerate (*i.e.*, they all have the same energy), but their individual energies are affected to different degrees by the presence of the ligands. In order to show how this effect arises let us consider the special case of a regular octahedral complex  $\text{MX}_6$ , where M is a metal ion of the first transition series and X is a group such as  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , or  $\text{Cl}^-$ .

The five  $3d$  orbitals of M have the forms indicated in Fig. 1, in which the co-ordinate axes lie along the MX bond directions. It is clear from the

<sup>1</sup> H. Bethe, *Ann. Physik*, 1929, **3**, 133.

<sup>2</sup> J. H. Van Vleck, *Phys. Review*, 1932, **41**, 208.

<sup>3</sup> R. Schlapp and W. G. Penney, *ibid.*, 1932, **42**, 666.

<sup>4</sup> O. M. Jordahl, *ibid.*, 1934, **45**, 87.

<sup>5</sup> J. B. Howard, *J. Chem. Phys.*, 1935, **3**, 813.

<sup>6</sup> J. H. Van Vleck, *ibid.*, p. 807.

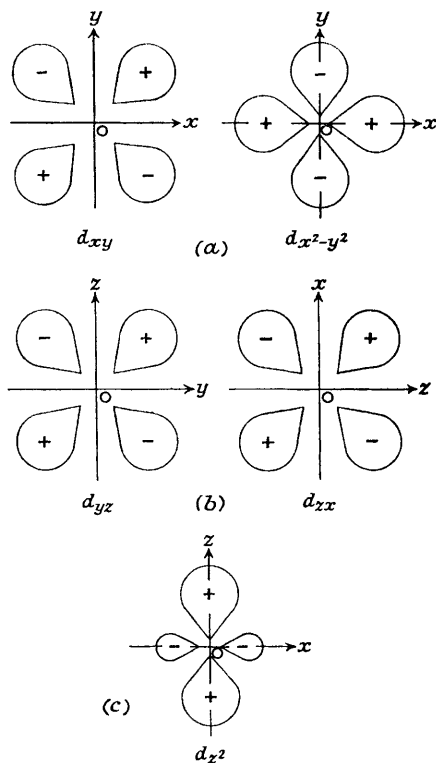


FIG. 1

*Cross-sections of the five d orbitals, chosen in real form.*

diagram that the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals have substantial amplitudes in the directions of the ligands but that the orbitals  $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$  tend to avoid them. Hence the energy of an electron in the  $d_{z^2}$  or  $d_{x^2-y^2}$  orbitals will be substantially raised by the repulsive field of the ligands whereas the energy of an electron in the  $d_{xy}$ ,  $d_{yz}$ , or  $d_{zx}$  orbitals will be comparatively little affected. Furthermore, it is obvious from symmetry that the degeneracy of the last three orbitals is maintained in the octahedral complex and it can be shown by group theory that the  $d_{z^2}$  and the  $d_{x^2-y^2}$  orbitals also remain degenerate.<sup>7</sup> Consequently the five  $d$  orbitals split into a lower group of three and an upper group of two, the two groups being usually designated as  $t_{2g}$  and  $e_g$  respectively<sup>7</sup> (or sometimes as  $\gamma_5$  and  $\gamma_3$ , or as  $d\epsilon$  and  $d\gamma$  respectively).

These facts are illustrated in Fig. 2a. In tetrahedral complexes it can be shown similarly that the  $d$  orbitals are again split into groups of three and two, respectively, but now the doubly degenerate orbital is lower

<sup>7</sup> H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry", Wiley, New York, 1950.

$\underline{d_{x^2-y^2}, d_{z^2}}$	$\underline{d_{xy}, d_{xz}, d_{yz}}$	$\frac{d_{x^2-y^2}}{d_{xy}}$	$\frac{d_{xz}, d_{yz}}{d_{z^2}}$
$\underline{d_{xy}, d_{yz}, d_{xz}}$	$\underline{d_{x^2-y^2}, d_{z^2}}$	$\frac{d_{xz}, d_{yz}}{d_{z^2}}$	$\frac{d_{x^2-y^2}}{d_{xy}}$
(a)	(b)	(c)	(d)

FIG. 2

Orbital energies according to the electrostatic theory. (a) Octahedral complex; (b) tetrahedral complex (the  $O_x, O_y, O_z$  axes bisect the edges of the tetrahedron); (c) square planar complex with ligands along the  $O_x$  and  $O_y$  axes; (d) Irregular dodecahedral complex as in  $K_4Mo(CN)_8$ . The ligands are all in the  $xz$  and  $yz$  planes, i.e., the  $xy$  plane is approximately the plane of the paper in Fig. 177 of A. F. Wells's "Structural Inorganic Chemistry", Oxford Univ. Press, 1950.

(Fig. 2b). In all other important cases the degeneracy of the  $d$  orbitals is reduced even further (Figs. 2c and 2d).<sup>8</sup>

*Application of the electrostatic theory to octahedral complexes.* In order to understand the electronic structure of an octahedral complex and the optical transitions which it can undergo, it is necessary to appreciate the principles determining the distribution of the  $d$  electrons among the  $t_{2g}$  and  $e_g$  orbitals. Let us begin by considering the ground state. Two separate tendencies are at work. The first is the tendency for the electrons to occupy, as far as possible, the orbitals of lowest energy in the ligand field. The second is for the electrons to go into different orbitals with their spins parallel, since this gives a lower electrostatic repulsive energy and a more favourable exchange energy.\* Let us now see how these ideas apply to an octahedral complex containing  $n$   $3d$  electrons.

The ion  $Ti(H_2O)_6^{3+}$  has one  $d$  electron. In the ground state this will obviously occupy one of the  $t_{2g}$  orbitals. A transition is possible in which this electron is transferred to one of the  $e_g$  orbitals, and this occurs at  $20,400 \text{ cm.}^{-1}$ .<sup>†</sup> (The intensities of such transitions are low— $\epsilon_{\max} \simeq 10$ —as they are symmetry-forbidden.) The converse situation arises in the hydrated cupric ion which has nine  $d$  electrons. In this ion the vacancy in the  $d$  shell is in one of the  $e_g$  orbitals. This vacancy can be filled by exciting an electron from one of the  $t_{2g}$  orbitals, giving rise to a transition at about  $12,500 \text{ cm.}^{-1}$ . [For reasons which will be discussed later, however, the ion  $Cu(H_2O)_6^{2+}$  is strongly distorted in its ground state so that most of the degeneracy of the  $t_{2g}$  and  $e_g$  orbitals is removed and there is more than one transition in this region.] From these two examples we see that the splitting between the  $t_{2g}$  and the  $e_g$  orbitals may be quite large, being usually in the range  $20$ — $50 \text{ kcal. mole}^{-1}$ .

It is only when we come to consider complexes with several  $d$  electrons

<sup>8</sup> Unpublished calculations; cf. also J. H. E. Griffiths, J. Owen, and I. M. Ward, *Proc. Roy. Soc.*, 1953, A, **219**, 526.

\* Exchange energy is a quantum-mechanical energy which tends to align electron spins parallel. It is part of the reason for Hund's rule in atomic spectra.

<sup>†</sup> Data on optical spectra are reviewed in refs. 9 and 10.

that complications arise. If there are only two or three  $d$  electrons, both the above-mentioned tendencies can be satisfied simultaneously by placing the electrons in different  $t_{2g}$  orbitals with their spins parallel. However, when there are more than three  $d$  electrons this is no longer possible. If there are 4—7  $d$  electrons we then have the choice either of putting as many as possible into the low-energy  $t_{2g}$  orbital or distributing them so as to maintain a maximum number of parallel spins. This is illustrated in Table 1.

TABLE 1.  $d$ -Electron arrangements in octahedral complexes.

$N$  = Number of distinct pairs of electrons with parallel spins.

Number of $d$ electrons	Arrangement in weak ligand field	$N$	Arrangement in strong ligand field	$N$	Gain in orbital energy in strong field
1	$t_{2g}$ $e_g$ ↑      —	0	$t_{2g}$ $e_g$ ↑      —	0	0
2	↑↑      —	1	↑↑      —	1	0
3	↑↑↑      —	3	↑↑↑      —	3	0
4	↑↑↑      ↑	6	↑↓↑↑      —	3	$\Delta$
5	↑↑↑      ↑↑	10	↑↓↑↓↑      —	4	$2\Delta$
6	↑↓↑↑      ↑↑	10	↑↓↑↓↑↓      —	6	$2\Delta$
7	↑↓↑↓↑      ↑↑	11	↑↓↑↓↑↓      ↑	9	$\Delta$
8	↑↓↑↓↑↓      ↑↑	13	↑↓↑↓↑↓      ↑↑	13	0
9	↑↓↑↓↑↓      ↑↓↑	16	↑↓↑↓↑↓      ↑↓↑	16	0

The former choice will be favoured if the orbital separation  $\Delta$  is large, and the latter will be realised if  $\Delta$  is small. The value of  $\Delta$  depends primarily on the nature of the ligand and the charge on the ion, and the following generalisations can be made for the first transition series:<sup>9, 10</sup> (1) For hydrated bivalent ions  $\Delta$  falls in the range 7500—12,500  $\text{cm}^{-1}$ ; (2) For hydrated trivalent ions  $\Delta$  falls in the range 13,500—21,000  $\text{cm}^{-1}$ ; (3) The common ligands can be arranged in a sequence so that  $\Delta$  for their complexes with any given metal increases along the sequence.<sup>11</sup> A shortened series is  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{H}_2\text{O}$ , oxalate, pyridine,  $\text{NH}_3$ , ethylenediamine,  $\text{NO}_2^-$ ,  $\text{CN}^-$ . Lastly,  $\Delta$  for the compounds of the second and third series is 40—80% larger than for corresponding compounds of the first series.

With these considerations in mind let us consider in turn the two extreme

<sup>9</sup> C. K. Jørgensen, Proceedings 10th Solvay Congress, Brussels, 1956.

<sup>10</sup> L. E. Orgel, *J. Chem. Phys.*, 1955, **23**, 1004.

<sup>11</sup> R. Tsuchida, *Bull. Chem. Soc. Japan*, 1938, **13**, 388, 436, 471.

possibilities, known respectively as the "strong-field" and the "weak-field" case. If  $\Delta$  is very large the tendency for electrons to go into separate orbitals will be outweighed by their tendency to occupy the  $t_{2g}$  orbitals (as against the  $e_g$  orbitals) in circumstances where these two tendencies conflict. In the strong-field case, therefore, a complex with up to six  $d$  electrons will have all these in  $t_{2g}$  orbitals with the maximum number of unpaired spins consistent with the restriction to the  $t_{2g}$  orbitals. As examples we may take the ferrocyanides and ferricyanides which possess six and five  $d$  electrons respectively, all in  $t_{2g}$  orbitals. The former has no unpaired electrons and the latter one. The next four electrons will then enter the  $e_g$  orbitals; the first two will go into different  $e_g$  orbitals with their spins parallel as in the octahedral complexes of  $Ni^{2+}$ . In  $Co^{2+}$  there is just one  $e_g$  electron.

The complex  $[Co(NH_3)_6]^{3+}$  provides a good example of the strong-field case. The ground state is  $(t_{2g})^6$  and the transitions observed at the longest wavelengths involve taking one of these electrons and putting it in an  $e_g$  orbital. According to the choice of the orbitals involved the final state may be one of two triply degenerate states, and the bands associated with the two transitions have been observed for a number of  $d^6$  complexes in each of the three transition series. (The separation between the bands is not in very good agreement with theory, however, so that it is difficult to obtain a reliable value of  $\Delta$  for such cobaltic complexes. The reasons for this are not fully understood at present.)

The weak-field case is that in which the separation  $\Delta$  is not large enough to overcome the tendency of the  $d$  electrons to go into different orbitals with their spins parallel. For example in the hydrated manganous ion the five  $d$  electrons each occupy one of the five  $d$  orbitals; this is because the separation  $\Delta$  is insufficient to break up the highly stable half-filled shell in which all the electron spins are parallel. The same is true of  $[Fe(H_2O)_6]^{3+}$  and of the hydrated ferrous ion, which has six  $d$  electrons, the extra one being in one of the  $t_{2g}$  orbitals.\* It may be noted again that only in those complexes containing four, five, six, or seven  $d$  electrons is there an important distinction between the strong- and the weak-field cases; if there are one, two, or three  $d$  electrons they will necessarily occupy  $t_{2g}$  orbitals, while if there are eight or nine the vacancies in the  $d$  shell will occur in the  $e_g$  orbitals in both the strong- and the weak-field case.

**Molecular-orbital Theory of the Bonding in Complexes.**—Before proceeding further in interpreting the physical properties of transition-metal complexes, we must take the theory a stage further and consider explicitly the nature of the bonding between the metal and the ligands. There are both theoretical and empirical<sup>12</sup> grounds for believing that a considerable

<sup>12</sup> K. D. Bowers and J. Owen, *Reports Progr. Phys.*, 1955, **18**, 304.

\* It should be mentioned, however, that in the weak-field case it is not always possible to assign integral numbers of electrons to the groups  $t_{2g}$  and  $e_g$ . This is because the states of the central ion should really be related to those of the free ion in the gaseous phase, in which there is no splitting between the two types of orbital and electron repulsion mixes together states arising from different occupations of these groups of orbitals.

amount of co-ordinate bonding occurs in transition-metal complexes. This means that we must allow for charge transfer from one directed hybrid orbital on each ligand to the metal ion. In a molecular-orbital description of this process the electrons are placed in molecular orbitals formed from the metal  $3d$ ,  $4s$ , and  $4p$  and the ligand orbitals.

In the regular octahedral complex  $MX_6$  these last orbitals may be combined together to form symmetry orbitals of which one is totally symmetric and interacts with the  $4s$  orbital of the metal, three have a single nodal plane and interact with the three  $4p$  metal orbitals, and two interact with  $3d_{z^2}$  and  $3d_{x^2-y^2}$  respectively. Each interaction between a symmetry orbital of the ligands and an atomic orbital of the metal gives rise to a bonding orbital more stable than either, concentrated primarily on the ligands, and an antibonding orbital less stable than either<sup>13</sup> and concentrated mainly on the metal. The  $3d_{xy}$ ,  $3d_{yz}$ , and  $3d_{zx}$  orbitals usually have no counterparts on the ligands and contribute nothing to the bonding. In the free di- and tri-positive ions, spectroscopic data show the  $3d$  orbitals to lie below the  $4s$  which in turn lies below  $4p$ .  $3d$  is more compact than  $4s$  or  $4p$  so one expects less bonding from the ligand orbitals with  $3d$  orbitals than with  $4s$  and  $4p$ . This means that the antibonding  $3d$  orbitals probably lie below the antibonding  $4s$  and  $4p$  orbitals as shown schematically in Fig. 3. The exact order of the bonding orbitals is uncertain.

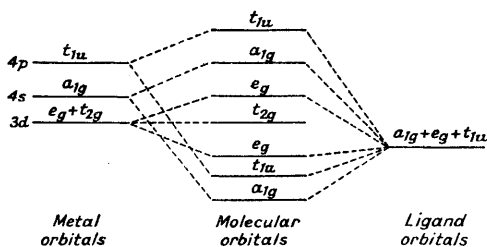


FIG. 3

*The relations between atomic and molecular orbitals in octahedral complexes.*

Starting with an ion with  $n$   $d$  electrons, we have also 12 from the ligand orbitals, making  $(n + 12)$  altogether to fit into the molecular orbitals of Fig. 3. Twelve of these go into the six bonding orbitals leaving just  $n$  to go into the three unchanged  $3d$  orbitals or into the most stable antibonding orbitals. The notation used to distinguish the  $d$  orbitals is the same as that for the electrostatic case, *i.e.*, the triplet of unchanged orbitals is represented as  $t_{2g}$  whilst the lowest antibonding orbitals are  $e_g$ . The conventional notation for all the orbitals is shown in Fig. 3.

Thus the molecular-orbital theory leads to exactly the same kind of splitting of the five levels available to  $d$  electrons as the electrostatic theory. In both cases we have a lower triplet of levels,  $t_{2g}$ , and an upper doublet,  $e_g$ . In both theories  $t_{2g}$  consists of pure  $3d$  orbitals, but we now see that the  $e_g$  electrons have a certain probability of being on the ligand atoms. The

<sup>13</sup> C. A. Coulson, *Quart. Rev.*, 1947, **1**, 144.

two theories are not in conflict, although they describe different physical effects, but should be regarded as reinforcing one another so that the energy separation between  $t_{2g}$  and  $e_g$  is larger than it would be if either effect were present alone. A more complete molecular-orbital theory, including electrostatic repulsions, would allow for both effects. It may be noted that if the ligands in an octahedral complex are capable of forming  $\pi$  bonds by using empty  $p_\pi$  or  $d_\pi$  orbitals, then according to molecular-orbital theory the  $t_{2g}$  orbital is depressed further with respect to the  $e_g$  orbital.\* On the other hand, if the ligands have filled  $\pi$  orbitals the  $t_{2g}-e_g$  separation is expected to decrease. The former effect is particularly important in cyanide complexes, where it lowers the energy of the  $t_{2g}$  orbitals of the metal and produces a very large effective value of  $\Delta$ .

A point of particular interest arises in connection with the number of electrons which occupy the  $e_g$  orbitals in  $MX_6$ . According to the preceding discussion these orbitals become antibonding between the metal and the ligands when delocalisation is allowed for, and even in the electrostatic model the presence of an electron in an  $e_g$  orbital will cause some of the ligands to be repelled. In consequence we expect the formation constant of an octahedral complex to be decreased if  $e_g$  electrons are present, and that if only one such electron is present it will repel those ligands to which it is nearest. This explains for example the unusual stereochemistry of  $Cu^{2+}$  and  $Mn^{3+}$  which form many complexes having four ligands coplanar with and close to the metal and two more distant ones above and below it.<sup>15, 16</sup> It is argued that in  $Cu^{2+}$ , for example, the  $d_{x^2-y^2}$  orbital contains only one electron while the  $d_{z^2}$  contains two, thus allowing a closer approach of the ligands in the  $xy$  plane. A similar argument applies to ions with four  $d$  electrons having the configuration  $(t_{2g})^3(e_g)^1$ .

The radii of the bivalent and trivalent ions of the metals of the first transition series were discussed from the electrostatic viewpoint by van Santen and van Wieringen,<sup>17</sup> who showed that the introduction of electrons into the unstable  $e_g$  orbitals always leads to an increase in the ionic radius. This effect also follows naturally from the molecular-orbital theory according to which the increase in ionic radius is attributed to the antibonding character of the electrons in the  $e_g$  orbitals.

**The Magnetic Criterion for Bond Type.**<sup>18</sup>—We have already indicated a distinction between two situations, the strong-field case in which the electrons occupy as far as possible the orbitals of lowest energy, and the weak-field case, in which they orient their spins parallel as far as possible. We have also seen that the expected number of unpaired spins will differ in the two cases only when there are four, five, six, or seven  $d$  electrons. The easiest experimental distinction between the two cases is therefore the

\* But see ref. 14.

<sup>14</sup> J. S. Griffith, *Nature*, 1957, **180**, 30.

<sup>15</sup> L. E. Orgel, *J.*, 1952, 4756.

<sup>16</sup> L. E. Orgel and J. D. Dunitz, *Nature*, 1957, **179**, 462.

<sup>17</sup> J. H. van Santen and J. S. van Wieringen, *Rec. Trav. chim.*, 1952, **71**, 420.

<sup>18</sup> L. Pauling, "The Nature of the Chemical Bond", Cornell Univ. Press, 1950.

magnetic susceptibility which is supposed to reflect simply the total spin  $S$  of the complex. For this reason we suggest that the phrases "high-spin" and "low-spin" complexes should be used to distinguish the two types since these are concise and since the other names which have been suggested—ionic and covalent, outer- and inner-orbital, spin-free or spin-paired—imply particular reasons for the observed distinction or are ambiguous.

As we have already remarked, in the low-spin octahedral complexes the ligand field forces the electrons together, as far as possible, into the lower triplet of orbitals. The resultant gain of orbital energy is to some extent cancelled by the increased energy of repulsion between the  $d$  electrons. This arises partly because the electrons are closer together so that the classical Coulombic repulsion between them is larger and, equally important, through a decrease in the purely quantum-mechanical exchange energy. The latter energy is zero for any pair of electrons having opposed spins but gives rise to an extra stabilisation for each pair with parallel spins. As one would expect, there are more pairs of electrons with parallel spins in a high-spin than in a low-spin complex so the exchange energy stabilises the latter less.

The gain of orbital energy is  $\Delta$  for  $d^4$  and  $d^7$ , and  $2\Delta$  for  $d^5$  and  $d^6$  complexes. If we write  $\Pi$  and  $2\Pi$  respectively for the increase of repulsive energy in the two cases, then  $\Pi$  represents a mean energy of pairing of  $d$  electrons per unit of ligand-field stabilisation  $\Delta$ . It may be regarded<sup>19</sup> as made up of the two parts,

$$\Pi = \Pi_c + \Pi_e$$

that we have just been considering.  $\Pi_c$ , the Coulombic part, varies little among the relevant  $d^n$  complexes. We illustrate the effect of the exchange energy  $\Pi_e$  by discussing the  $d^5$  and  $d^6$  complexes. With  $\alpha$  and  $\beta$  representing "spin up" and "spin down", typical electronic states of the high-spin complexes are  $(t_{2g}\alpha)^3(e_g\alpha)^2$  and  $(t_{2g}\alpha)^3(t_{2g}\beta)(e_g\alpha)^2$  for  $d^5$  and  $d^6$  complexes respectively. For each there are 10 ( $= 5 \times 4/1 \times 2$ ) distinct pairs of electrons with parallel spin. Typical low-spin states are  $(t_{2g}\alpha)^3(t_{2g}\beta)^2$  and  $(t_{2g}\alpha)^3(t_{2g}\beta)^3$  with  $4$  [ $= (3 \times 2/1 \times 2) + (2 \times 1/1 \times 2)$ ] and  $6$  [ $= (3 \times 2/1 \times 2) + (3 \times 2/1 \times 2)$ ] pairs respectively. Hence the loss of exchange energy is greater for a  $d^5$  than a  $d^6$  complex, and so a smaller ligand field  $\Delta$  is necessary to quench the spin of a  $d^6$  (*e.g.*,  $\text{Fe}^{2+}$  or  $\text{Co}^{3+}$ ) than of a  $d^5$  complex (*e.g.*,  $\text{Mn}^{2+}$  or  $\text{Fe}^{3+}$ ) (see Table 1).

We have used an elementary presentation in order to clarify the physical mechanism of the change of magnetic type. A more detailed theory has been published by each of us.<sup>19, 20</sup> Although our theories were identical in the essential mathematics, our numerical values of  $\Pi$  differ slightly because  $\Pi$  is expressed in terms of parameters which must be estimated empirically from atomic spectral data and we used slightly different methods of estimating them. Numerical values of  $\Pi$  for the bivalent and trivalent ions of the first transition series are shown in Table 2.

So far we have ignored the possibility considered by Pauling<sup>18</sup> of  $d^5$  and  $d^6$  complexes in an intermediate spin state with, respectively, spins

<sup>19</sup> J. S. Griffith, *J. Inorg. Nuclear Chem.*, 1956, **2**, 229.

<sup>20</sup> L. E. Orgel, *J. Chem. Phys.*, 1955, **23**, 1819.



TABLE 2. *Orbital splitting  $\Delta$  for aqueous ions and mean pairing energy  $\Pi$  (cm.<sup>-1</sup>)*

	Ion	$\Delta$	$\Pi$	Ion	$\Delta$	$\Pi$
$d^4$ . . .	Cr <sup>2+</sup>	13,900	23,500	Mn <sup>3+</sup>	21,000	28,000
$d^5$ . . .	Mn <sup>2+</sup>	7800	23,500	Fe <sup>3+</sup>	13,700	30,000
$d^6$ . . .	Fe <sup>2+</sup>	10,400	17,600	Co <sup>3+</sup>	(17,000— 19,000)	21,000
$d^7$ . . .	Co <sup>2+</sup>	9700	22,500	Ni <sup>3+</sup>	—	27,000

of  $1\frac{1}{2}$  (3 unpaired electrons) and 1 (2 unpaired electrons). The theory shows that one should never find such intermediate states for regular octahedral or tetrahedral complexes,<sup>21</sup> and again relates this primarily to exchange energies.<sup>19</sup>

We have now prepared the way for discussing Pauling's magnetic criterion. For each of the  $d^4$ ,  $d^5$ ,  $d^6$ , and  $d^7$  configurations, octahedral complexes can occur in one of two spin states—a high and a low. From magnetic-susceptibility measurements we can usually decide with a fair degree of certainty which spin a given complex has. However, from our theory we can predict that the low-spin should occur when and only when

$$\Delta > \Pi$$

and from analyses of molecular<sup>9, 10, 22, 23</sup> and atomic spectra<sup>20, 23</sup> we can calculate  $\Delta$  and  $\Pi$  respectively.  $\Delta$ , unlike  $\Pi$ , is very sensitive to the nature of the ligands. It is shown in Table 2 for the aquo-complexes. We can see that  $\Pi$  is much greater than  $\Delta$  for all the bivalent ions and for Mn<sup>3+</sup> and Fe<sup>3+</sup>. All of them have high susceptibility, in agreement with the theory. For Co<sup>3+</sup>  $\Pi$  is probably at least 2000 cm.<sup>-1</sup> greater than  $\Delta$ . In fact the aqueous cobaltic ion is diamagnetic, but probably has a low-lying paramagnetic state which may even be thermally accessible.<sup>24, 25</sup> In view of the approximations which are necessarily present in any theory of this kind of many-electron system, the agreement is very satisfactory. For amines there is not even this minor disagreement, [Fe(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> having a high susceptibility and [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> being diamagnetic with no evidence for a thermally accessible paramagnetic state. Further evidence that [Co(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> is very near to the cross-over point ( $\Delta = \Pi$ ) is furnished by the fact that [CoF<sub>6</sub>]<sup>3-</sup>, with only a slightly smaller characteristic  $\Delta$  for the ligand, has a susceptibility corresponding roughly to four unpaired electrons.<sup>18</sup>

$\Pi$  furnishes a threshold beyond which  $\Delta$  must lie in order to quench the spin. So, for a given metal ion, a change of magnetic type with change of ligand indicates an increase of  $\Delta$ . This need not necessarily, but usually does, reflect an increased strength of covalent bonding. However we can

<sup>21</sup> J. S. Griffith, *J. Inorg. Nuclear Chem.*, 1956, **2**, 1.

<sup>22</sup> J. Owen, *Proc. Roy. Soc.*, 1955, *A*, **227**, 183.

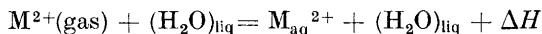
<sup>23</sup> Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, 1954, **9**, 753, 766.

<sup>24</sup> H. L. Friedman, J. P. Hunt, R. A. Plane, and H. Taube, *J. Amer. Chem. Soc.*, 1951, **73**, 4028.

<sup>25</sup> H. Taube, *Chem. Reviews*, 1952, **50**, 85.

draw no such conclusion when we change the metal ion, keeping the ligands constant. The different magnetic type for  $[\text{Fe}(\text{NH}_3)_6]^{3+}$  and  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is due to a difference of mean pairing energy  $\Pi$  as well as of  $\Delta$ . For further discussion the reader is referred to the original papers.<sup>19, 20, 26</sup>

**Thermodynamic Properties.**—The heat of formation,  $\Delta H$ , of a bivalent aqueous ion from the ion in the gas phase is defined by



If the  $d^n$  ions were spherically symmetrical in the complexes, we might expect  $\Delta H$  to increase uniformly from  $n = 0$  to  $n = 10$  (*i.e.*, from  $\text{Ca}^{2+}$  to  $\text{Zn}^{2+}$ ) owing to the gradual contraction of the  $3d$  shell with increasing nuclear charge. However, as we have already seen, the  $t_{2g}$  levels in octahedral complexes lie below the  $e_g$  levels, with the result that greater stabilisation is achieved the greater the number of  $t_{2g}$  electrons and the smaller the number of  $e_g$  ones. Restricting consideration for the moment to high-spin complexes, we see that the first three  $d$  electrons of a complex confer extra stability upon it, but that the next two electrons, by going into  $e_g$  orbitals, cancel out this stabilisation, and that the same pattern is followed as the next five electrons are added. For example, in the high-spin ferrous ion the five electrons with  $\alpha$  spin occupy one orbital each and their distribution is independent of the ligand field, but the sixth electron occupies a  $t_{2g}$  orbital rather than an  $e_g$  one and confers extra stability on the complex. The resulting stabilisations are shown in Table 3 in terms of  $\Delta$ .

TABLE 3. *Extra stabilisations for high-spin octahedral complexes in units of the orbital splitting  $\Delta$*

Number of $d$ electrons	Stabilisation
0, 5, 10	0
1, 6	0.4
2, 7	0.8
3, 8	1.2
4, 9	0.6

If one subtracts these stabilisations from the experimental plot of  $\Delta H$  against atomic number the "corrected" values of  $\Delta H$  lie on a uniformly rising curve which is actually quite close to a straight line.<sup>15, 27</sup> Values of  $\Delta H$ , corrected and uncorrected, are shown in Fig. 4.

Obviously this treatment is not restricted to the special case of bivalent aqueous ions of the first transition series. The only restriction which is implicit is the restriction to high-spin complexes. If the central members of the series are low-spin, the  $d^5$  compounds are again especially unstable\* but for different reasons.<sup>19</sup>

<sup>26</sup> L. E. Orgel, Proceedings 10th Solvay Congress, Brussels, 1956.

<sup>27</sup> P. George, D. S. McClure, J. S. Griffith, and L. E. Orgel, to be published.

\* That is, unstable relative to the free gaseous ion, but not necessarily relative to oxidation or reduction. Thus the instability we mention here does not conflict with the well-known stability of a half-filled shell relative to addition or removal of electrons.

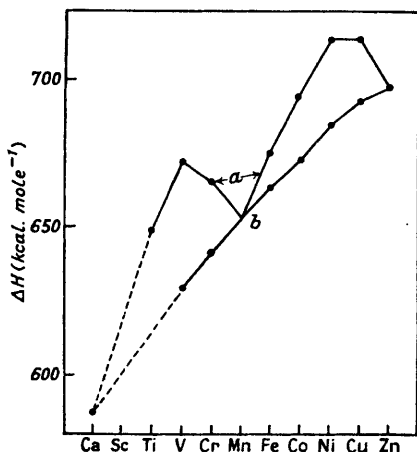


FIG. 4

Heats of formation of bivalent aqueous ions of the first transition series from the gaseous ions. (a) Uncorrected; (b) corrected.

The characteristic "two-humped" form of the uncorrected curve of Fig. 4 occurs experimentally for a wide range of compounds, not only complexes in solution but also solid compounds with and without water of crystallisation.<sup>26, 28-31</sup> The theory is just the same for solid compounds and for them also the most common arrangement of ligands or anions around the cation is octahedral. For complexes of other symmetries, the same type of argument leads one to expect a variation of  $\Delta H$  with atomic number which is different in detail, but has a minimum at  $d^5$ .

Attempts to understand formation constants in terms of electron affinities of the ions have been made by Calvin and Melchior<sup>32</sup> and by Irving and Williams.<sup>33</sup> The electron affinities can affect  $\Delta H$  and hence  $\Delta F$ , but the smooth variation with atomic number of the corrected  $\Delta H$  in Fig. 4 suggests that the irregularities do not have this origin, at least for the bivalent ions.

**Relation of Ligand-field Theory to Pauling's Theory.**—We shall now compare the ligand-field theory with Pauling's extremely important valence-bond description of metal complexes.<sup>18</sup> In the latter, octahedral complexes are classified either as ionic or as covalent with  $d^2sp^3$  bonding. The  $d$  orbitals involved in covalent bonding are the  $d_{x^2-y^2}$  and  $d_{z^2}$  ( $e_g$ ) orbitals which, when hybridised with the  $s$  and  $p$  orbitals, form a set of six equivalent directed orbitals pointing at the ligands. Pauling's theory has been modified more recently,<sup>34</sup> but the changes do not affect the following discussion.

<sup>28</sup> J. Bjerrum and C. K. Jørgensen, *Rec. Trav. chim.*, 1956, **75**, 658.

<sup>29</sup> P. George, *ibid.*, p. 671.

<sup>30</sup> J. S. Griffith, *ibid.*, p. 676.

<sup>31</sup> P. George, D. S. McClure, J. S. Griffith, and L. E. Orgel, *J. Chem. Phys.*, 1956, **24**, 1269.

<sup>32</sup> M. Calvin and N. Melchior, *J. Amer. Chem. Soc.*, 1948, **70**, 3270.

<sup>33</sup> H. Irving and R. J. P. Williams, *Nature*, 1948, **162**, 746; *J.*, 1953, 3192.

<sup>34</sup> L. Pauling, *J.*, 1948, 1461.

In discussing octahedral complexes with 4 to 7  $d$  electrons Pauling classifies those with spin less than that of the free ion as "covalent" and the others as "ionic". (We have called these complexes low-spin and high-spin respectively.) He argues that the filling of the  $t_{2g}$  orbitals, at the expense of reducing the spin, can only be enforced by the use of the  $e_g$  orbitals in bonding. Thus the pairing of electrons in the  $t_{2g}$  orbitals is taken as an indication of covalent bonding by use of the  $e_g$  orbitals. In octahedral ions with less than four  $d$  electrons the number of unpaired spins is the same as that of the gaseous ion even if covalent bonding is assumed. Octahedral ions with more than seven  $d$  electrons are assumed to be ionic.

Apart from points of nomenclature, the ligand-field and valence-bond theories are not very seriously at variance here. Both agree that the  $e_g$  orbitals are more or less utilised in bonding and so become less easily available for accommodating  $d$  electrons. At this point, however, the theories diverge for, while the ligand-field theory admits that some electrons may go into the antibonding  $e_g$  orbitals without essentially changing the nature of the bonding, the valence-bond theory in the familiar form forgets these critical orbitals. This omission is not implicit in the theory though, for by admitting three-electron bonds, in which two electrons are in a bonding and one in an antibonding orbital, it would be possible to reproduce qualitatively the results of ligand-field theory. (This modification would, however, be rather clumsy since a certain amount of unmixing of the hybrids would be necessary as  $d$ ,  $s$ , and  $p$  orbitals could no longer be treated on an equal footing.)

The antibonding  $e_g$  orbitals having been omitted, the valence-bond theory finds itself in difficulties whenever the  $d$  electrons are too numerous to occupy the  $t_{2g}$  orbitals. In high-spin complexes with more than three  $d$  electrons the only way out is to postulate a completely different type of bonding—ionic bonding—in which the  $d$  orbitals are not utilised at all. In the "covalent" complexes of  $\text{Co}^{2+}$ , for example, promotion of an electron to a  $5s$  orbital is therefore postulated, for there seems no other place to put it. A similar situation arises for planar  $\text{Cu}^{2+}$ , and promotion to a  $4p$  orbital is assumed. We cannot, of course, be sure that promotion never takes place, but at least for  $\text{Cu}^{2+}$  in planar complexes the alternative offered by ligand-field theory, namely placing the extra electron in an antibonding  $d$  orbital, in fact the  $d_{x^2-y^2}$  orbital, has been shown to be correct.<sup>35</sup>

The designation of low-spin complexes as "covalent" is not altogether without foundation, however. According to molecular-orbital theory the lower spin does make possible stronger bonding between metal and ligand. From the electrostatic viewpoint, also, the absence of  $e_g$  electrons exposes the ligands more completely to the metal ion and hence increases the extent to which their  $\sigma$  electrons are polarised.<sup>36</sup> This is as near as one can come in an electrostatic theory to the idea of a more covalent bond.

In describing bond properties the two theories differ in their estimates

<sup>35</sup> B. Bleaney and K. W. H. Stevens, *Reports Progr. Phys.*, 1953, **16**, 108.

<sup>36</sup> L. E. Orgel and L. E. Sutton, "Symposium on Co-ordination Chemistry", Copenhagen, 1953, published by the Danish Chemical Society, 1954.

of the abruptness of the change in bond character. In valence-bond theory the change is sharp, from covalent to ionic; in ligand-field theory the change is gradual, the importance of the  $d$  orbitals in bonding decreasing as the number of  $d$  electrons in the  $e_g$  orbital increases.

This discussion has shown that "covalent" and "ionic" do not have the same connotation in transition-metal chemistry as they do elsewhere, which is why we think it better to use instead the words "low-spin" and "high-spin" in this context.

**General Applications.**—Though most of the examples given in this Review have been taken from octahedral complexes it is possible to discuss the stabilities of tetrahedral complexes in a similar manner. In a tetrahedral complex the  $e_g$  orbitals lie below the  $t_{2g}$  group and the configuration  $(e_g)^4(t_{2g})^3$ , with  $e_g$  filled and  $t_{2g}$  half-filled, is therefore highly stable. This is probably why bivalent cobalt, with seven  $d$  electrons, forms many tetrahedral complexes whereas bivalent nickel, with eight  $d$  electrons, appears to prefer the stable octahedral configuration  $(t_{2g})^6(e_g)^2$ .

Another important field of application of ligand-field theory is to transition states.<sup>37</sup> This topic has received only preliminary treatment, but is potentially one of the most important applications of the theory to inorganic chemistry. Electron-transfer reactions have been discussed in two papers.<sup>26, 38</sup> Much of the available information on reaction rates has been rationalised by the realisation that the transfer of  $e_g$  electrons causes a much greater reorganisation of bond lengths than does transfer of  $t_{2g}$  electrons, since the former are antibonding and the latter non-bonding. There are, however, a few cases which are not in agreement with the theory.

Finally it may be remarked that the ligand-field theory may be successfully applied not only to compounds of the transition metals, whose valency electrons are in  $d$  orbitals, but also to those of elements possessing  $f$  electrons, that is, to compounds of the rare earths and actinides.<sup>39-41</sup> It appears that in the quinquevalent and sexivalent complexes formed by the actinides the ligand-field effects are comparable in magnitude with those found in the transition metals. Progress has already been made in interpreting the magnetic and optical properties of the ions  $\text{UO}_2^{2+}$ ,  $\text{NpO}_2^{2+}$ , and  $\text{PuO}_2^{2+}$ , and it has been shown that  $\text{PuF}_6$ , with two atomic  $f$  electrons, may be a low-spin complex. In the trivalent rare-earth and actinide compounds, however, the  $f$  electrons are apparently so well tucked away inside the metal ions that, although the electrostatic theory applies to them with special accuracy, the chemical effects associated with these electrons are much less striking.

Our thanks are offered to Professor H. C. Longuet-Higgins who is responsible for a substantial revision of this manuscript.

<sup>37</sup> L. E. Orgel, *J. Inorg. Nuclear Chem.*, 1956, **2**, 137.

<sup>38</sup> A. W. Adamson, *Rec. Trav. chim.*, 1956, **75**, 809.

<sup>39</sup> J. C. Eisenstein and M. H. L. Pryce, *Proc. Roy. Soc.*, 1955, **A**, **229**, 20.

<sup>40</sup> B. Bleaney, *Discuss. Faraday Soc.*, 1955, **19**, 112.

<sup>41</sup> J. S. Griffith and L. E. Orgel, *J. Chem. Phys.*, 1957, **26**, 988.