

CHARGE-TRANSFER SPECTRA AND SOME RELATED PHENOMENA

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When an isolated molecule absorbs visible or ultra-violet radiation an electronic transition occurs which may result in a considerable intramolecular redistribution of charge. In this review, however, we shall, for the most part, be concerned with transitions involving intermolecular or inter-ionic charge-transfer. The dividing line between these two types of transition cannot be sharp, since some degree of interaction between the components is an essential requirement for charge-transfer to be possible. However, it is convenient to restrict discussion to those systems in which more or less discrete charge-donating and charge-accepting units can be identified.

The general feature of the spectra to be discussed is that, in the transition responsible for the optical absorption, an electron, or possibly part of an electron, associated with one molecule or ion is transferred to a different molecule or ion. Thus in the visible absorption of the $\text{Fe}^{3+}(\text{CNS})^-$ ion-pair an electron is transferred from the CNS^- ion to the Fe^{3+} ion with the formation of a CNS radical and a Fe^{2+} ion. Similarly, the ultra-violet absorption of the alkali halide crystals is associated with the transfer of an electron from a halide ion to a metal ion or, more correctly, from the set of halide ions to the set of metal ions. These transitions are, in fact, photochemical oxidation-reduction reactions, and it is from this that their importance in chemistry arises.

Charge-transfer Spectra in Inorganic Systems

In this section the main topics are charge-transfer spectra in the crystalline and the gaseous state, the spectra of simple and complex ions in solution, and photochemical reactions involving charge transfer. A much fuller discussion of much of the earlier work will be found in a previous review by Rabinowitch.¹

Crystalline Alkali Halides.—Electron transfer in alkali halide crystals, brought about by optical absorption, was recognised by Przi Bram as early as 1923.² He supposed that the colour centres formed in these crystals by ultra-violet irradiation were due to neutral metal atoms formed by the photochemical transfer of electrons from the halide ions to the metal ions.

Pohl and Hilsch measured the absorption spectra of a large number of crystalline halides.³⁻⁶ They found that the spectra consisted of one or

¹ Rabinowitch, *Rev. Mod. Phys.*, 1942, **14**, 112.

² Przi Bram, *Z. Physik*, 1923, **20**, 196.

³ Hilsch and Pohl, *ibid.*, 1929, **57**, 145; 1930, **59**, 812; 1930, **64**, 606.

⁴ *Idem*, *Trans. Faraday Soc.*, 1938, **34**, 883.

⁵ Pohl, *Kolloid Z.*, 1939, **71**, 257.

⁶ *Idem*, *Proc. Phys. Soc.*, 1937, **49**, E3.

more peaks at wave-lengths shorter than 2500 Å (Fig. 1). The chlorides generally have a single peak, the bromides a pair of peaks separated by 0.48—0.60 ev, and the iodides a pair of peaks separated by 0.95—1.19 ev. The two lowest states of the halogen atoms, arising from the same electronic configuration, are ${}^2P_{\frac{3}{2}}$ and ${}^2P_{\frac{1}{2}}$. The separation between them is

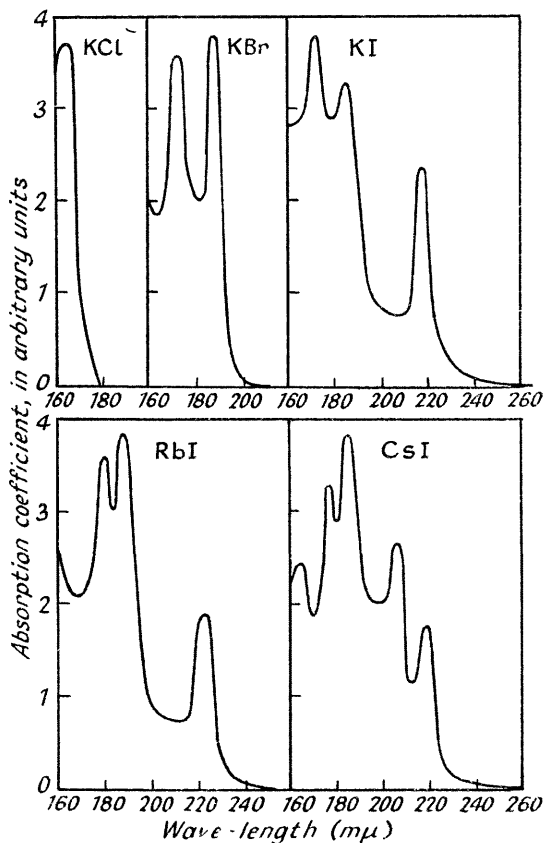


FIG. 1

Ultra-violet absorption spectra of some crystalline alkali halides. (Reproduced, by permission, from Hilsch and Pohl, *Z. Physik*, 1929, **59**, 816.)

0.94 ev in iodine, 0.46 ev in bromine, and much smaller in chlorine. The close correspondence between the separation of the peaks in the halide spectra and the separation of the energy levels in the halogen atoms suggests very strongly that free halogen atoms are formed during the absorption, the pairs of bands corresponding to the production of halogen atoms either in the ${}^2P_{\frac{3}{2}}$ or the ${}^2P_{\frac{1}{2}}$ states. This interpretation is supported by the occurrence of bands in the spectra of rubidium salts³

separated by 1.51—1.53 ev, which corresponds closely to the separation between the ground state and the first excited state of the rubidium atom.

The wave-length of maximum absorption of the halides of a given metal increase in the order chloride < bromide < iodide; that is, more energy is required to bring about the transfer of an electron from chloride than from bromide or iodide, etc. This can most easily be understood if we consider, instead of the actual charge-transfer process, a series of hypothetical reaction steps having the same final result. We suppose that an anion and a cation are removed from adjacent positions in the crystal lattice, an electron is removed from the anion and placed on the cation, and finally the pair of atoms are returned to their original positions. The energy required for this series of changes is of the form $W = E - I + \Delta$, where E is the electron affinity of the halogen, I the ionisation potential of the alkali metal, and Δ represents the difference between energy of formation of the normal crystal and the crystal with a pair of adjacent atoms substituted for a pair of ions. Other things being equal, a large electron affinity of the metal ion or a small ionisation potential of the halide ion will lower the energy required to bring about the transition. Clearly the lower energy of the transition in the iodides is associated with the lower ionisation potential of the iodide ion, that is, the smaller electron affinity of the iodine atom. Unfortunately the term Δ varies somewhat from one halide to another so that it is not possible to predict the position of the absorption maximum accurately for a given halide from a knowledge of E and I alone.

The first attempts^{7, 8} to calculate Δ , and hence the absorption frequency, took into account only the simple electrostatic forces between ions. It was found that the calculated frequencies of absorption were much larger than those found experimentally. More complete calculations in which repulsive forces between ions, the attraction of the lattice for neutral atoms, the polarisation of neighbouring ions in the unsymmetrical field created by neutralising one pair of ions, and the expansion of the lattice are taken into account can be made to give good agreement with experiment without making any unreasonable assumptions.^{9, 10}

A point of rather general interest is the quantum efficiency of the reaction to produce colour centres. It has been found for instance^{11, 12} that in potassium bromide at -100° scarcely any metal atoms are produced while at 400° almost every quantum absorbed produces a metal atom. At 0° the quantum efficiency is about a quarter. Over the whole of this temperature range the absorption spectrum is found to be very little changed.

⁷ Born, *Z. Physik*, 1932, **79**, 62.

⁸ Wolf and Herzfeld, *Handbuch d. Physik*, 1928, **20**, 623.

⁹ Klemm, *Z. Physik*, 1933, **82**, 529.

¹⁰ von Hippel, *ibid.*, 1936, **101**, 680.

¹¹ Hilsch and Pohl, *Nachricht. Ges. Wiss. Göttingen, Math.-Phys. Kl.*, 1934, No. 9; 1935, No. 19.

¹² Smakula, *Z. Physik*, 1930, **63**, 762.

This indicates that the primary absorption process is the same at all temperatures but that the production of metal atoms depends on the vibrations of the crystal lattice. The details of the lattice interaction do not concern us, but it is important to note that we are dealing with a primary process that is completely reversible; only if some specific interaction takes place within the short lifetime of the excited state is a metal atom produced.

In addition to the alkali halides the silver halides have been carefully studied. Pohl and Hilsch³ first emphasised the similarity between the photographic process and the production of colour centres in the alkali halides. Since then many studies have been made of the photochemical decomposition of the silver halides, and, while the situation is much more complicated, the general features of charge-transfer absorption already discussed are observed.

Gaseous Halides.—The spectra of the alkali halide molecules in the gas phase, which were first recognised as charge-transfer spectra by Franck and his co-workers,¹³ exhibit features very similar to those found in the crystalline state. In the region between 2000 Å and 3500 Å the chlorides usually have single peaks, the bromides and iodides have pairs of peaks (Fig. 2). The separation between the peaks in the different compounds is again almost equal to the separation between the ${}^2P_{\frac{3}{2}}$ and the ${}^2P_{\frac{1}{2}}$ state of the free halogen atom. In some cases further peaks occur at shorter wave-lengths, the separation between the peaks indicating that metal atoms are being produced in excited states. The fluorescence emission of these excited states of atoms has been observed in some cases,¹⁴ thus confirming the nature of the transition.

The positions of the absorption maxima again show that less energy is required to bring about charge transfer in the iodides than in the chlorides or bromides. The expected change with the ionisation potential of the alkali metal atom is not observed.

The absorption maxima for the gaseous molecules are at longer wave-lengths than those for the corresponding crystalline compounds. Thus sodium bromide has an absorption maximum at 1900 Å in the crystal and at 2750 Å in the gas phase. Since the ionisation potentials and electron affinities are the same in the two cases the difference must arise in the Δ term, which represents the interactions between the parts of the molecule and its environment. Qualitatively, one source of this difference is the much greater stabilisation of the ions in the symmetrical fields of the six nearest neighbours in the crystal than in the field of a single nearest neighbour in the free molecule.

It will be convenient to summarise now the points which have emerged in this brief discussion of the most fully understood class of charge-transfer spectra as they will be encountered repeatedly in more complicated situations.

(1) The frequency of a charge-transfer absorption will tend to be small

¹³ Franck, Kuhn, and Rollefson, *Z. Physik*, 1927, **43**, 155; Schmidt-Ott, *ibid.*, 1931, **69**, 724.

¹⁴ Kondratjew, *ibid.*, 1938, **39**, 191.

if the difference between the ionisation potential of the donor and the electron affinity of the acceptor is small.

(2) The energy required to bring about charge transfer cannot be equated directly to the difference discussed in (1) since the change in the interaction between the donor, the acceptor, and the environment must be taken into

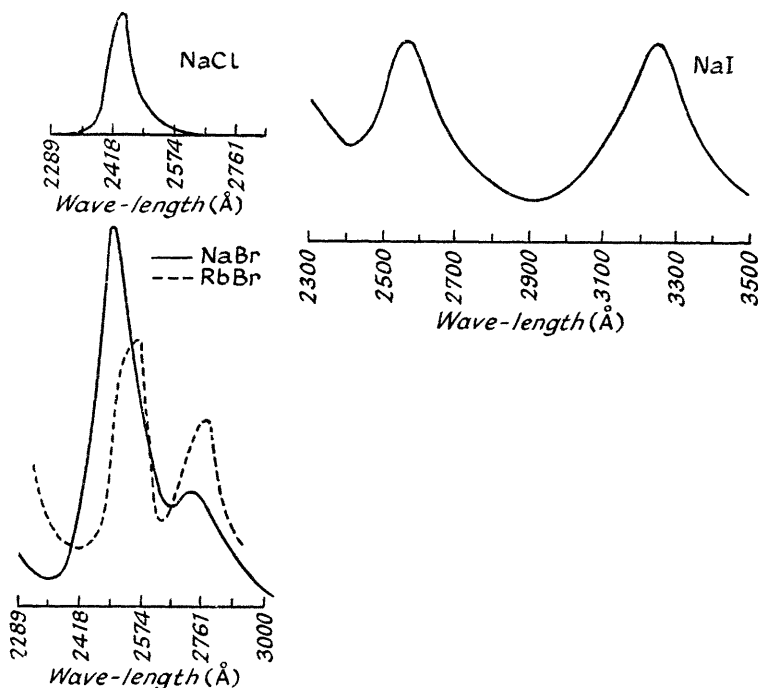


FIG. 2

Ultra-violet absorption spectra of some gaseous alkali halides. (Reproduced, by permission, from Franck, Kuhn, and Rollefson, *Z. Physik*, 1927, **43**, 155.)

account. This change may be large as shown by our comparison of the spectra of gaseous and crystalline halides.

(3) Chemical effects associated with charge-transfer absorption may be due to secondary transformations of the system which compete with other methods of deactivation.

The Spectra of Ions in Solution.—*Anions.* A characteristic feature of the spectra of anions in aqueous solution is the frequent occurrence of a very strong absorption band in the ultra-violet, usually in or near to the range 2000—2500 Å (Fig. 3). The value of the maximum extinction coefficient for these bands is commonly about 10,000. In addition the polyatomic anions often show other, much weaker, bands usually at longer wave-lengths.

The intense absorption bands were first interpreted as charge-transfer

bands by Franck and Scheibe,¹⁵ who supposed that the absorption of light by a hydrated negative ion was accompanied by the formation of a free radical and a hydrated electron. The weaker absorption bands were supposed to be due to intramolecular transitions of the ion.

The electron set free by the charge-transfer absorption was at first assumed to escape into the bulk of the solvent. Later Franck and Haber¹⁶ modified this theory by suggesting that the ejected electron remained in association with the hydration sphere of the original ion. The electron could then return to its original orbit or alternatively some permanent chemical change could take place.

The most carefully studied bands are probably those of the halogen ions.¹⁷⁻²³ The chloride band has a single maximum and the bromide and the iodide band two maxima. The wave-lengths of the absorption maxima increase in the order $\text{Cl} < \text{Br} < \text{I}$. The separation between the iodide maxima coincides quite well with the separation between the $^2P_{1/2}$ and the $^2P_{3/2}$ state of the iodine atom. In the case of the bromide the agreement is not very good, the observed separation being only half that expected. This discrepancy is not understood.

Many other ions have been studied in the far ultra-violet including OH^- , SH^- , OCl^- , CN^- , ClO_2^- , NO_2^- , ClO_3^- , NO_3^- ,²⁴ SO_3^{--} , SO_4^{--} .²⁵ Organic ions investigated include formate, acetate, oxalate and hydrogen oxalate, succinate, etc.²⁶

The absorptions of the various carboxylate ions differ somewhat from those of most of the others in that they begin at quite long wave-lengths, but have not reached a maximum at about 1800 Å, the limit of the range studied. Also there are often slight shoulders on the bands, possibly due to rather weak intramolecular absorption.

Cations. As with anions many cations absorb very strongly in the ultra-violet (Fig. 4). The transition metal ions also absorb in the visible and near infra-red, but with an intensity which is rarely more than one hundredth as great as that of the ultra-violet bands. The weak absorption bands are due to transitions which are largely localised on the metal atom. The strong absorption bands are attributed to charge-transfer processes.

The stable alkali metal ions and the alkaline earth metal ions do not show any charge-transfer bands below the limit of observation. The hydrated ions of other metals have been studied by a number of authors, particularly Fromherz and his school. The ions studied include Ag^+ ,²⁰

¹⁵ Franck and Scheibe, *Z. physikal. Chem.*, 1938, *A*, **139**, 22.

¹⁶ Franck and Haber, *Sitzungsber. Preuss. Akad. Wiss.*, 1931, 250.

¹⁷ Hantzsch, *Ber.*, 1926, **59**, 1096. ¹⁸ Scheibe, *Z. Elektrochem.*, 1928, **34**, 497.

¹⁹ *Idem*, *Z. physikal. Chem.*, 1929, *B*, **5**, 355.

²⁰ Fromherz and Menschik, *ibid.*, 1929, *B*, **3**, 1.

²¹ *Idem*, *ibid.*, 1930, *B*, **7**, 439.

²² Diamond and Fromherz, *ibid.*, 1930, *B*, **9**, 289.

²³ Lederle, *ibid.*, 1930, *B*, **10**, 121.

²⁴ Friedman, *J. Chem. Phys.*, 1953, **21**, 319, gives full references.

²⁵ Ley and Arends, *Z. physikal. Chem.*, 1932, *B*, **15**, 311.

²⁶ *Idem*, *ibid.*, 1932, *B*, **17**, 177.

Tl⁺,²⁷ Zn⁺⁺,²⁸ Cd⁺⁺,²⁸ Hg⁺⁺,²⁹ Sn⁺⁺,³⁰ Pb⁺⁺,²⁷ V⁺⁺, Cr⁺⁺, Mn⁺⁺, Fe⁺⁺, Co⁺⁺, Ni⁺⁺, Cu⁺⁺.³¹

The nature of the charge-transfer process responsible for the cation

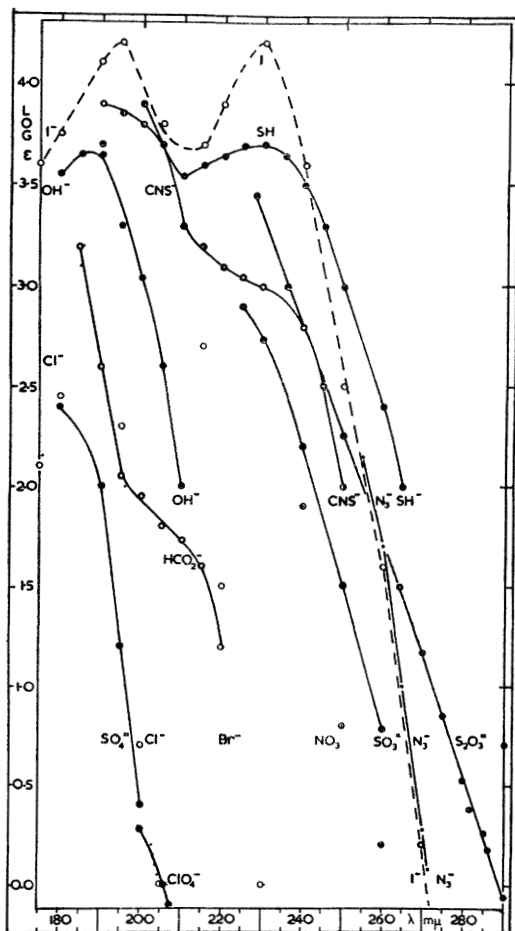


FIG 3

Absorption spectra of some anions in aqueous solution

(Reproduced by permission from Professor F S Danton³¹)

bands is not as obvious as in the case of anions. In suitable circumstances we might expect charge transfer either from the cation to the solvent or

²⁷ Fromherz and Lih, *Z physikal Chem*, 1931, *A*, **153**, 321

²⁸ Doehlmann and Fromherz, *ibid*, 1934, *A*, **171**, 353

²⁹ Fromherz and Lih, *ibid*, 1933, *A*, **167**, 103

³⁰ Fromherz and Walls, *ibid*, 1936, *A*, **178**, 29

³¹ Danton and his co workers, unpublished data

in the opposite direction. Rabinowitch¹ suggests that in the case of easily oxidised cations the charge-transfer absorption of longest wave-length is from the ion to the solvent while in easily reduced cations it is in the opposite direction. There is a certain amount of recent work supporting this idea.

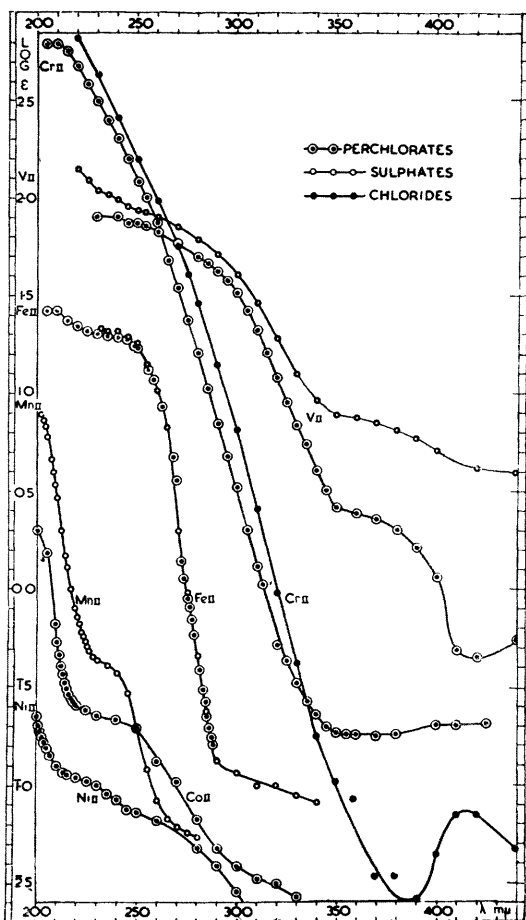


FIG. 4

Absorption spectra of some cations in aqueous solution.

(Reproduced by permission from Professor F. S. Dainton³¹)

Dainton³² has shown that if the energy corresponding to the long wave-length edge of the charge-transfer bands of the bivalent transition metal ions is plotted against the redox potential of a system consisting of a bivalent and a trivalent ion then a straight line is obtained. The

³² Dainton, *J.*, 1952, 1533.

slope of the line is about 25 kcal. per volt. This corresponds rather closely to a 45° slope if both quantities are plotted in the same units, suggesting that the minimum *energy* of the charge-transfer process itself may correspond quite closely to the energy of the process $M(aq.)^{2+} \rightarrow M(aq.)^{3+}$. It seems certain that in these ions the charge-transfer process is from bivalent ion to solvent.

The absorption of ultra-violet light by certain multivalent ions such as Fe^{3+} and Ce^{4+} has long been known to result in permanent chemical change. The interpretation of these changes in terms of charge-transfer mechanisms will be discussed later.

Charge Transfer in Complexes.—There is a large class of complexes in which the water molecules of the hydrated ions are replaced by other neutral molecules, particularly amines. As might be expected these molecules show strong absorption in the ultra-violet which is presumably due to charge-transfer processes. Unfortunately they have received little attention so that detailed comparison with the hydrates is impossible.

The experimental evidence is much more satisfactory in the case of cation-anion complexes. Some of these absorb in the visible or near ultra-violet region and it has been established that the transitions are associated with charge-transfer processes. In many other cases, the absorption has been attributed, by analogy, to charge-transfer processes, although this has not been demonstrated unambiguously. Furthermore, since the absorption may occur in the visible region, the presence of a charge-transfer band is often detectable from the colour of the substance.

The simplest spectra of this type which have been studied in detail are those of simple binary complexes such as $PbCl^+$, $PbBr^+$, PbI^+ (Fig. 5). Fromherz²⁷ was able to determine the spectra of these components of solutions of the metal salts by means of the variation of the absorption spectrum with the concentration of the halide ion. The general behaviour agrees well with that predicted for charge-transfer spectra. The maxima occur at the longest wave-length for the iodides and shortest for the chlorides. The positions of these maxima are at longer wave-lengths than those of the hydrated ions, but have extinction coefficients of the same order, *i.e.*, about 10,000.

In solutions containing high concentrations of halide ion, complex ions with more than one halide ion attached to the metal predominate. In this work it was not possible to isolate the spectra of the different species. Fromherz and Lih were of the opinion that only the highly co-ordinated ions MX_4^{2-} and the simple ions MX^+ were present in solution. However, it seems more probable that all the intermediate species are also present. The absorption spectra of the solutions change continuously with the concentration of halide, as would be expected if a complex mixture of components, each absorbing in roughly the same region, was present.

One important, rather general, point is that as the concentration of halide increases the absorption moves to longer wave-length. This indicates that the larger the number of halide ions attached to a given metal atom the less the energy required to bring about electron transfer. This

clearly has an important bearing on the problem of normal and photochemical oxidation.

In very strong halide solutions the predominant ionic species is usually of the type MX_4^{2-} . Fromherz and his co-workers have studied a number of these complexes, including those from zinc, cadmium,²⁸ mercury,²⁹ tin,³⁰ lead,²⁷ and copper.²⁰

It is generally assumed that in the complexes so far discussed the halide ions replace water molecules of the inner hydration shell. In discussing

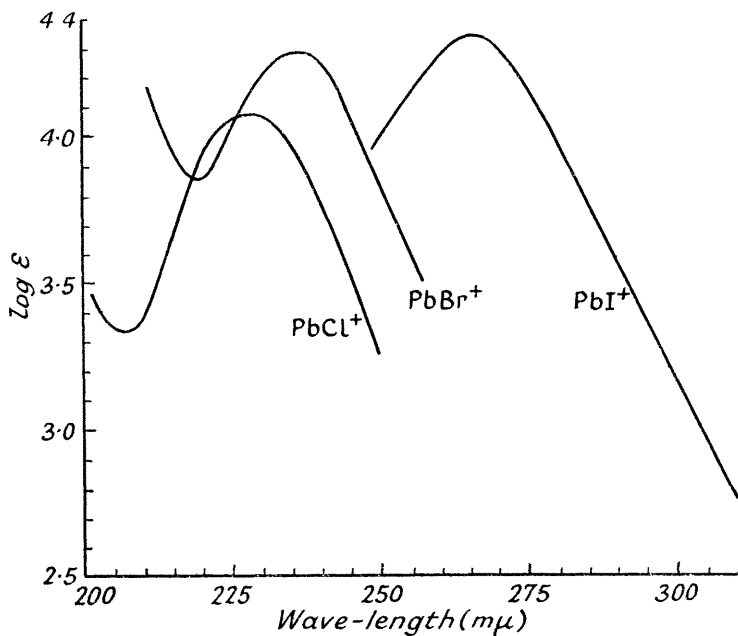


FIG. 5

*Absorption spectra of PbCl^+ , PbBr^+ , and PbI^+ . (Reproduced, by permission, from Fromherz and Lih, *Z. physikal. Chem.*, 1931, A, **153**, 321.)*

the spectra of the transition-metal compounds we must distinguish between this type of charge transfer and that which occurs in molecules such as hexa-amminocobaltic iodide. In this case it has been shown that charge transfer takes place between an iodide ion and the complete $[\text{Co}(\text{NH}_3)_6]^{3+}$ group,³³ presumably with the instantaneous formation of hexa-amminocobaltous ion and an iodine atom.

The most widely studied of the inner complexes of transition metals are those of the ferric ion. Rabinowitch and Stockmayer³⁴ in a study of the visible spectra of ferric chloride, bromide, and hydroxide succeeded in isolating the spectra of each of the FeX^{2+} ions and also those of more

³³ Linhard, *Z. Elektrochem.*, 1944, **50**, 224.

³⁴ Rabinowitch and Stockmayer, *J. Amer. Chem. Soc.*, 1942, **64**, 335.

complicated ions such as FeCl_2^+ and FeCl_3 (Fig. 6). They found that chloride spectra were to the short wave-length side of those of the bromides, in agreement with the work of Fromherz, and that the thiocyanate spectrum, measured by Kiss, Abraham, and Hegedus,³⁵ was to the longer wave-length side of the bromide. The iodide undergoes a spontaneous oxidation-reduction reaction. In general the thiocyanate ion lies between the bromide and the iodide ion in its charge-transfer properties.

Only a few of the very many transition-metal complexes which absorb intensely in the visible or near ultra-violet region can be discussed here. In the hexa-amminocobaltic complexes there are two rather weak absorption bands at about 5000 and 3300 Å, and a much stronger absorption

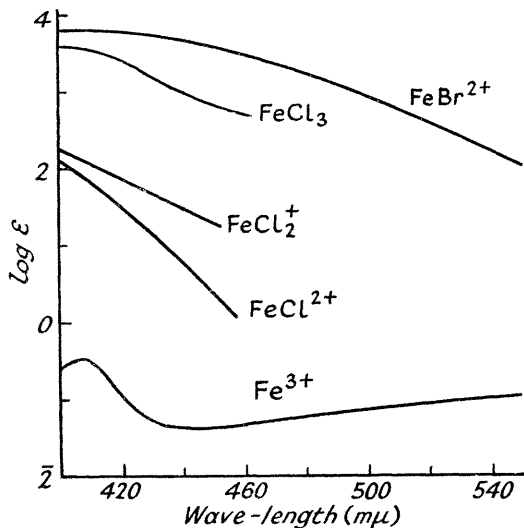


FIG. 6

Absorption spectra of Fe^{3+} and its halogen complexes in the visible region. (Reproduced, by permission, from Rabinowitch and Stockmayer, *J. Amer. Chem. Soc.*, 1942, **64**, 335.)

beginning at about 2500 Å. Replacement of an ammonia molecule by a halogen atom³⁶ other than fluorine displaces the strong absorption to longer wave-lengths so that it partly obscures the 3300-Å band. Poly-substitution leads to further displacement to longer wave-lengths. All the experimental evidence is consistent with the intense transition's being associated with transfer of an electron from the anion to the cobaltic ion.

The spectra of the complexes of trivalent chromium³⁶ are in all respects very similar to those of cobalt. The spectra of the halides of cupric copper have been studied by a number of workers.²⁰ The same general relations between the different halides, and between the different complexes of the same halide, are found in this case as in the examples discussed previously. It is interesting that while the blue colour of the simple cupric ion is due

³⁵ Kiss, Abraham, and Hegedus, *Z. anorg. Chem.*, 1940, **244**, 98.

³⁶ Linhard and Weigel, *ibid.*, 1951, **266**, 49.

to an absorption band of $\text{Cu}(\text{aq.})^{2+}$ largely in the infra-red region, the dark colour of the complex halides is due to the tail of a charge-transfer band which is mainly in the ultra-violet region. Just as with Fe^{3+} we find that the iodide is unstable, suggesting that the charge-transfer band for some attainable complex is at such low energy that the reaction can take place thermally, or possibly that the ground state of such a complex consists of the cuprous ion and an iodine atom, which of course would dissociate at once. Similar bands are observed for the polyhalide complexes of cobaltous cobalt and of most other transition metals.

Recently Evans and Uri³⁷ have provided conclusive evidence for the charge-transfer character of the transitions in FeX^{2+} complexes by detecting the X radicals produced. This they were able to do owing to the chain-initiating properties of such radicals, which enable very small numbers to be detected. This work is discussed in the section on photochemical reactions.

No detailed theory of the intensity of these transitions has so far been offered. The general theory of optical absorption³⁸ shows that transitions between largely covalent and largely ionic states will, under suitable conditions, have very high intensities. Until a more precise knowledge of the nature of the transitions involved is available it is not possible to make any detailed calculations. It seems probable that the theory of charge-transfer spectra developed by Mulliken³⁹ in connection with organic molecules is applicable, perhaps with some modifications, to these ions.

The only cases of charge-transfer interaction between a co-ordinatively saturated complex and an ion which has been studied in detail are the ammino-cobalt and -chromium halides. Linhard³³ has established that the intense new band which appears in aqueous solutions of $[\text{Co}(\text{NH}_3)_6]^{2+}$ salts as the concentration of iodide ion is increased is due to the species $[\text{Co}(\text{NH}_3)_6]^{3+}\text{I}^-$. The transition is probably $[\text{Co}(\text{NH}_3)_6]^{3+}\text{I}^- \rightarrow [\text{Co}(\text{NH}_3)_6]^{2+} + \text{I}$.

These complexes can only be found among the most stable complex amines, for in less stable systems the iodide or other halide ion would be introduced into the inner co-ordination sphere. The differences in colour observed in the different salts of the same stable complex ammine base can be interpreted as due to charge-transfer spectra of this type. A typical example, in which it is difficult to suggest an alternative explanation, is that of the amminoiridium salts.⁴⁰ $[\text{Ir}(\text{NH}_3)_6]^{3+}3\text{X}^-$ is colourless for $\text{X} = \text{Cl}$ or Br but yellow for $\text{X} = \text{I}$, as would be expected for a charge-transfer phenomenon.

The colours of many solid compounds, including iodides, bromides, and possibly some oxides and sulphides, are due to charge-transfer absorption of one of the types which we have discussed.

³⁷ Evans and Uri, *Nature*, 1949, **164**, 404.

³⁸ Mulliken and Rieke, *Rep. Prog. Physics*, 1941, **8**, 231.

³⁹ Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811.

⁴⁰ Sidgwick, "The Chemical Elements and their Compounds", Oxford, 1950, p. 1536.

The Spectra of Complexes used in the Detection of Metal Ions.—A successful colorimetric reagent must interact with a metal ion to produce a complex having a characteristic intense absorption band which does not occur in either the free reagent or the free ion. Clearly reagents which form complexes with charge-transfer bands satisfy this requirement, and in fact many inorganic complexes of this kind have been utilised, *e.g.* Fe^{3+} , CNS^- ,⁴¹ and $[\text{PbCl}_4]^{2-}$.⁴² In addition, many organic colour reagents, particularly those used with transition-metal ions, are probably effective through the charge-transfer bands of their complexes. Familiar examples are the phenols, used for the estimation of Fe^{3+} , Cu^{2+} , and V^{4+} , and thioacetic acid used for Fe^{3+} . The instability of many of these intensely coloured complexes is associated with the ready occurrence of oxidation-reduction reactions.⁴³

Charge Transfer between Atoms or Ions of an Element in Different Valency States.—The intense colour often observed in systems containing the same element in different valency states has been attributed by Sidgwick⁴⁴ to a resonance between structures differing by the exchange of an electron between atoms of that element. The precise way in which this leads to intense and selective absorption was not discussed.

Weyl⁴⁵ has suggested that these intense absorption bands are in fact charge-transfer bands. The case of charge transfer between ferrous and ferric ions dissolved in glasses seems to be particularly well-substantiated. Weyl has pointed out that glasses and minerals containing ferrous and ferric ions show a selective absorption which is not shown by either ion separately. This absorption is most prominent in borates, less so in silicates, occurs rarely in phosphates, and is not observed in sulphates. Weyl claims that a high polarisability facilitates charge transfer over considerable distances and quotes a number of other cases to support this claim. A particularly convincing argument is provided by the absorption of biotite containing ferrous and ferric ions. It is known that biotite has a layer structure. It is found that light polarised in the plane of the layers is strongly absorbed so that the material is black in this direction. In a perpendicular direction charge transfer would involve carrying an electron across a layer of slightly polarisable hydroxide ions and hence is not favoured. The crystal is transparent in this direction.

Many of the examples quoted by Weyl and other cases of interaction absorption probably involve charge transfer. In addition the extremely intense absorptions of Prussian blue and of ruthenium-purple probably arise in the same way.

Somewhat related to these views are those of Zener^{45a} who believes that the ferromagnetic susceptibility and electrical conductivity of certain

⁴¹ Sandell, "Colorimetric Metal Analysis", New York, 1950, p. 363.

⁴² Merrit, Hershenson, and Rogers, *Analyt. Chem.*, 1953, **25**, 572.

⁴³ Orgel and Williams, unpublished work.

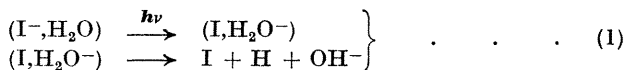
⁴⁴ Sidgwick, *op. cit.*, p. 1611.

⁴⁵ Weyl, *J. Phys. Chem.*, 1951, **55**, 507.

^{45a} Zener, *Phys. Review*, 1951, **82**, 403.

compounds containing Mn^{3+} and Mn^{4+} ions are due to charge transfer from one metal atom to another through intervening oxygen atoms. This kind of charge transfer has also been invoked to account for the detailed mechanism of the oxidation of chromous compounds by cobaltic complexes, etc.^{45b}

Photochemical Reactions and Charge-transfer Spectra.—The photochemical reaction of iodide with water, $\text{I}^- + \text{H}_2\text{O} \rightarrow \text{I} + \text{OH}^- + \text{H}$, has been studied by a number of authors. The mechanism of the reaction is uncertain. Farkas and Farkas,⁴⁶ suggested that an excited ion is formed, and that this donates an electron to a proton present in the solution. Rigg and Weiss⁴⁷ have shown that while this mechanism does predict a dependence of the quantum yield on the pH it does not reproduce the correct dependence of the quantum yield on the iodide concentration. They suggest an alternative mechanism, in many ways similar to that previously proposed by Franck and Haber.¹⁶ It is supposed that the absorption of radiation is accompanied by the transfer of an electron to a water molecule which then decomposes :



This is followed by the back reaction :



In order to account for the dependence of the quantum yield on the pH and the iodide concentration the following additional reactions are postulated :



Reactions (5) and (7) are well known and (6) is only important at high iodide concentrations. The novel feature of this scheme is the participation of H_2^+ in the reactions, as suggested by Weiss⁴⁸ in a previous paper.

The kinetic equations deduced from the above reaction scheme are rather complicated, but do reproduce the observed quantum yield quite well. An interesting conclusion drawn from this analysis is that the low quantum yields obtained are due to the efficient back reaction (2) and not to any inefficiency in process (1).

Tyson, Rigg, and Weiss⁴⁹ have interpreted the photochemical decomposition of water by the ferrous ion in a similar fashion. Weiss has also

^{45b} Taube and Myers, *J. Amer. Chem. Soc.*, 1954, **76**, 2103.

⁴⁶ Farkas and Farkas, *Trans. Faraday Soc.*, 1938, **34**, 1113.

⁴⁷ Rigg and Weiss, *J.*, 1952, 4198.

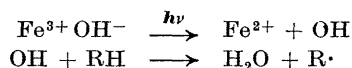
⁴⁸ Weiss, *Nature*, 1950, **165**, 728.

⁴⁹ Tyson, Rigg, and Weiss, *J. Chem. Phys.*, 1952, **20**, 1194.

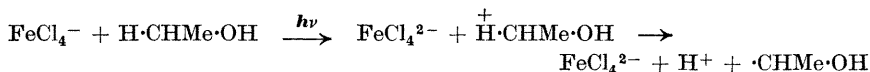
interpreted a number of other photochemical reactions, in terms of electron-transfer mechanisms.⁵⁰⁻⁵² Farkas and Klein⁵³ have interpreted the photochemistry of the chlorate, bromate, iodate, and hypobromite ions, similarly.

Evans and Uri^{37, 54} have studied the photochemistry of anion-cation complexes, and have demonstrated the presence of radicals in irradiated solutions containing such complexes. In the case of the Fe^{3+}F^- and $\text{Fe}^{3+}\text{Cl}^-$ complexes they have been able to demonstrate the presence of halogen end groups in the products of photochemical polymerisation.

A number of photochemical oxidations catalysed by ferric ions⁵⁵ have been interpreted as free-radical reactions initiated by reaction of the type :



Uri *et al.* have discussed similar reactions initiated by the action of a polyhalide as an acceptor, *e.g.* :



Similar reactions take place in systems containing PbCl_4^{2-} or CuCl_4^{2-} ions in alcoholic solution.⁵⁶ This work has been reviewed recently by Uri.⁵⁷

The importance of charge transfer in the photo-oxidation of organic dyes and other molecules has been emphasised by a number of authors,⁵⁸ and considerable support is given by Evans's discovery of oxygen charge-transfer complexes. It seems very probable that many photochemical oxidations take place by way of charge transfer, at least as an initiating step in a chain reaction.

The Relation between Normal and Photochemical Charge Transfer.—We have seen that charge-transfer spectra of metal complexes are due to transitions which result in a, possibly reversible, oxidation-reduction reaction. It has also been suggested often that normal oxidation-reduction reactions take place by means of definite intermediate complexes. If this is so the spectra of stable complexes should provide useful information about the probable mechanisms of reactions involving intermediate complexes which cannot themselves be studied.

The maximum of a charge-transfer band corresponds to the energy required to transfer an electron, all the nuclear positions being maintained as they are in the ground state. The long wave-length edge of the band

⁵⁰ Weiss, *Trans. Faraday Soc.*, 1941, **37**, 463.

⁵¹ Weiss and Fishgold, *Nature*, 1936, **137**, 71.

⁵² Porrett and Weiss, *ibid.*, 1937, **139**, 1019.

⁵³ Farkas and Klein, *J. Chem. Phys.*, 1948, **16**, 886.

⁵⁴ Evans and Uri, *J. Soc. Dyers Col.*, 1950, **65**, 709; Evans, Santappa, and Uri, *J. Polymer Sci.*, 1951, **7**, 243.

⁵⁵ Bates, Evans, and Uri, *Nature*, 1950, **166**, 869.

⁵⁶ Brealy and Uri, *J. Chem. Phys.*, 1950, **20**, 257; Copestake and Uri, unpublished work.

⁵⁷ Uri, *Chem. Reviews*, 1952, **50**, 375.

⁵⁸ See ref. 57, p. 420.

represents the minimum energy required to move an electron in any configuration of the ground state that can be attained thermally, *i.e.*, it is in a sense the difference between the activation energy required for electron transfer and the maximum thermal energy available to the complex. From this it is clear that if the charge-transfer band moves into the infra-red then spontaneous oxidation becomes possible, kinetically, as soon as the tail of the band approaches a zero frequency.

The position of the long wave-length edge of the charge-transfer band of a polyhalide complex is at longer wave-lengths the larger the number of halogen ions attached to the metal ion. This suggests that in other cases the spontaneous reaction may not take place until a complex with more than one halogen ion has been formed. Strong support for this is obtained from the kinetics of the reactions of cupric ion with thiocyanate ion.⁵⁹ The reaction of ferric ion with iodide has been interpreted in a different way, but this mechanism explains the kinetics in a very simple fashion.⁶⁰ It will be remembered that both in the stable cupric and ferric halide complexes the charge-transfer bands extend to long wave-lengths.

Possibly considerations of this type are applicable to other oxidation-reduction reactions. It must, however, be remembered that in spontaneous reactions other mechanisms involving, for example, preliminary chemical changes are also possible, and that the nature of the solvent may be critical in determining the stability to oxidation of a complex.

Charge-transfer Spectra in Organic Systems

The formation of highly coloured molecular complexes from colourless or slightly coloured components has attracted the interest of chemists for a long time. In particular the profound change in the visible absorption spectrum which often accompanies the formation of very loosely-bound complexes has proved puzzling. Only recently has a theory which accounts reasonably well for all the experimental evidence been proposed.

A large class of aromatic nitro-compounds, quinones, carboxylic acids, sulphonic acids, etc., will combine with aromatic hydrocarbons, amines, phenols, and related substances to give stable solid complexes which are frequently intensely coloured.⁶¹ In solution these complexes are usually dissociated to a considerable extent. Familiar examples of solid complexes are those of aromatic hydrocarbons with aromatic nitro-compounds which are used to characterise the former. In some cases the solid complexes cannot be isolated but the changes in the colour on mixing of the solutions leave no doubt that complex formation has taken place.

A number of non-aromatic compounds may replace the nitro-compounds, etc.; sulphur dioxide, oxalyl chloride, maleic anhydride, nitromethane, and particularly tetranitromethane will all form coloured complexes. Recently, it has been realised that the complexes formed by iodine, bromine, chlorine, iodine monochloride, and oxygen are closely related.³⁹

⁵⁹ Duke and Courtney, *J. Phys. Chem.*, 1952, **56**, 19.

⁶⁰ Fudge and Sykes, *J.*, 1952, 119.

⁶¹ Pfeiffer, "Organische Molekulverbindungen", Stuttgart, 1927.

The heats of formation of these compounds are usually rather small, being of the order of $\frac{1}{2}$ —4 kcal./mole.⁶² This strongly suggests that the interaction of the components in the ground state is of a secondary nature. It should, however, be noted that similar behaviour might be observed with stronger bond formation if sufficiently large intermolecular repulsions were present. In complete contrast to the small heats of formation are the changes in absorption spectrum. In many cases the position of the absorption maximum of the complex is some thousands of Ångström units to the long wave-length side of the nearest absorption of the components. Such differences in wave-length may correspond to an energy of 20 or more kcal./mole.

Brackman⁶³ showed that it is possible to arrange the components of the complexes in such a way that if the colours of the various nitro-complexes, etc., of a given hydrocarbon or amine, etc., are plotted against the nitro-compound, as in Table 1, a series of roughly parallel straight lines is obtained. Accurate measurements of the position of absorption maxima would undoubtedly change this Table to some extent but it is very unlikely that its main features would be altered. It will be noted that an increase in the number or power of the electron-attracting groups in the nitrobenzene nucleus increases the wave-length of absorption while an increase in the number of electron-releasing groups has the opposite effect. On the other hand the situation in the amine component is the reverse.

All available spectroscopic data show the absorption bands to be very broad and without fine structure. This is probably due to the looseness of the bonding in the ground state which allows considerable relative motions of the components. Each different configuration of the ground state leads to slightly different positions of the absorption peaks, so that the resultant absorption shows no structure. This feature of the spectra may make it almost impossible to obtain very accurate values for absorption maxima and, in some cases, leads to bands in which no maximum at all can be detected in the visible or near ultra-violet region. For detailed comparisons of these spectra low-temperature work would be particularly helpful, since one might then find much sharper bands.

Earlier theories about these complexes attributed their stability to one of two causes. Either they assumed that normal dipole-dipole and dipole-induced dipole forces were involved⁶² or they postulated the existence of covalent bonding between the atoms of the two components.⁶⁴ Neither type of theory was able to account for the characteristic intense absorption bands.

More recently several workers have commented on the fact that the complexes are almost invariably formed between molecules one of which has a high electron affinity and the other a low ionisation potential, *i.e.* between electron acceptors and electron donors. The classification as Lewis acids and Lewis bases also corresponds closely to that above.

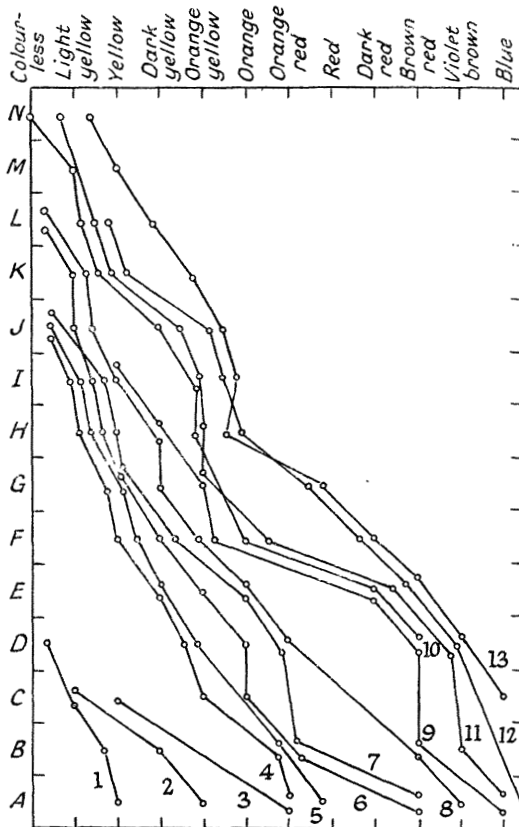
⁶² Briegleb, *Z. physikal. Chem.*, 1936, B, **31**, 58; 1936, B, **32**, 305.

⁶³ Brackman, *Rec. Trav. chim.*, 1949, **68**, 147.

⁶⁴ Baker and Bennett, *Ann. Reports*, 1931, **28**, 128.

Weiss⁶⁵ has attributed this stability to the formation of ion pairs D^+A^- , where D is the donor and A the acceptor. This theory provides a natural explanation of the occurrence of such compounds only when a

TABLE I



A, chloranil ; B, tetranitromethane ; C, benzoquinone ; D, "Tetryl" (N-methyl-2 : 4 : 6 : N-tetranitroaniline) ; E, s-trinitrobenzene ; F, m-dinitrobenzene ; G, maleic anhydride ; H, 2 : 6-dinitrotoluene ; I, nitrobenzene ; J, phthalic anhydride ; K, 1-tert.-butyl-3 : 5 dimethyl-2 : 4 : 6-trinitrobenzene ; L, 4-acetyl-1-tert.-butyl-3-methyl-2 : 6-dinitrobenzene ; M, dinitrodurene ; N, nitromethane

1, benzene ; 2, xylene ; 3, durene ; 4, naphthalene ; 5, acetanilide ; 6, phenanthrene ; 7, tribromoaniline ; 8, safrole ; 9, anthracene ; 10, aniline ; 11, diphenylamine ; 12, benzidine ; 13, dimethylaniline.

Lewis acid and a Lewis base are present. Weiss's suggestion is in fact incorporated, in a very much modified form, in Mulliken's theory. Woodward's related theory⁶⁶ supposes that a semi-polar bond is formed between the components.

⁶⁵ Weiss, J., 1942, 245.

⁶⁶ Woodward, J. Amer. Chem. Soc., 1942, **64**, 3058.

Brackman⁶³ has discussed "Complex-resonance" as the source of the stabilisation of the complexes. The two components of the complex are supposed to interact so strongly that the physical properties are to be attributed to the complex as a whole and cannot be interpreted in terms of those of the separate components. The absorption band characteristic of these complexes is not to be regarded as a modification of a band present in one of the components but as a completely new band characteristic of the whole. Brackman suggests that the interaction takes the form of a resonance between a non-bonded structure and a bonded structure but does not specify these further, nor does he offer any explanation of the intense absorption band.

Mulliken⁶⁷ in an added note to the first paper of a series on molecular complexes suggested that the new absorption band in the spectrum of the complex formed from benzene and iodine was due to the photochemical transfer of an electron from a π -orbital of the benzene molecule to a vacant orbital of the iodine. In subsequent papers^{39, 68} he has developed this theory very considerably. Its basis is that in these complexes the bonding is due to resonance between two structures that may be written formally as DA and D^+A^- . The first structure is called a no-bond structure and corresponds to the two components held together by van der Waals forces and possibly also by dipole-dipole or dipole-induced dipole forces. The structure D^+A^- corresponds to a D^+ ion derived from the donor and an A^- ion derived from the acceptor, held together by electrostatic, polarisation, and, possibly, covalent forces. However, unlike Weiss, Mulliken does not assume that the ionic structure represents the ground state but rather that there is a small admixture of it with the predominant no-bond structure in the ground state of the complex. The ions D^+ and A^- are in general derived from the neutral molecules by removing an electron from or adding an electron to an orbital which is not necessarily isolated on a particular atom. The novelty of Mulliken's theory is the suggestion that resonance may take place between structures differing in the occupation of molecular rather than of atomic orbitals, and even between non-bonded structures and those produced from them by charge transfer.

Mulliken is of the opinion that charge-transfer forces of this kind are of importance in a large number of different systems. While this may well be true it does not follow that these forces are the only source of stabilisation in molecular complexes formed by nitro-compounds, etc.; whether or not they are the predominant cause of complex formation remains an open question.

From Mulliken's theory of the ground state of these complexes, his explanation of the spectra follows by analogy with the usual ionic-covalent resonance theory of the chemical bond. Formally we may write the wave function for the ground state of the system as $a\psi(DA) + b\psi(D^+A^-)$ where $\psi(DA)$ is the wave function for the no-bond structure and $\psi(D^+A^-)$ is the wave function for the ionic structure. The ratio $b : a$ determines

⁶⁷ Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 600.

⁶⁸ *Idem*, *J. Phys. Chem.*, 1952, **56**, 801.

the contribution of the ionic state to the structure, in fact this is approximately equal to $b^2/(a^2 + b^2)$. Now, by analogy with the usual resonance theory there should be an excited state with the wave function, $a\psi(D^+A^-) - b\psi(DA)$, to which optical transitions are possible. According to our theory the ionic contribution to the ground state is small so that b is small. This implies that the covalent contribution to the excited state is correspondingly small. Thus the excited state is almost completely ionic and corresponds closely to Weiss's picture of the ground state.

The qualitative dependence of $h\nu$, the energy required to bring about charge transfer, on the electron-accepting and electron-donating powers of the components is readily understood on Mulliken's theory. Formally we may write the energy required to bring about the transition in the form, $h\nu = I_D - E_A - \Delta$ where I is the ionisation potential of the donor, E_A the electron affinity of the acceptor, and Δ the stabilisation of the ion pair. We see that, other things being equal, a reduction of the ionisation potential of D or an increase in the electron affinity of A results in a decrease in the amount of energy required and hence to a larger value of b . It should be remembered that, in very different complexes, changes in the interaction term Δ may be much more important than changes in I_D and E_A .

In a similar way we can see that a low ionisation potential of D and a high electron affinity of A should lead to a larger ionic contribution to the ground state and hence to a greater stability of the complex. Furthermore we would expect that the intensity of the absorption band would increase with the ionic contribution to the ground state. The experimental evidence seems to be consistent with the first prediction but there is one important exception to the second. We shall discuss this later.

It is a feature of the spectra corresponding to a transition from a covalent to an ionic state that they are very intense. A method of estimating the absolute intensity for such spectra in simple molecules has been given by Mulliken,³⁸ and is applicable, almost without change, to the present case. By making very plausible assumptions about the geometry of the complexes and the magnitude of b it is possible to predict intensities which agree as well as can be expected with those observed.

The further details of Mulliken's theory lead to important conclusions about the stereochemistry and other properties of complexes, but cannot be discussed here as they are not very relevant to the study of the spectra.

Very recently two pieces of evidence have appeared which weigh heavily in favour of Mulliken's theory. Nakomoto⁶⁹ has studied the optical dichroism of single crystals of a number of molecular complexes with typical intense new absorption bands. The substances studied include quinuclidine, *s*-trinitrobenzene-hexamethylbenzene, and *s*-trinitrobenzene-*p*-bromoaniline. In all cases the crystal structures are known so that it was possible to measure the absorptions parallel and perpendicular to the molecular planes. (The crystal structures will be discussed in more detail later. It is sufficient to note here that the two components of these complexes are packed with

⁶⁹ Nakomoto, *J. Amer. Chem. Soc.*, 1952, **74**, 1739.

their benzene rings parallel.) In every case the absorption perpendicular to the plane of the rings was more intense than that in that plane. The position of maximum absorption also tended to be at longer wave-length perpendicular to the ring direction than in that direction. These results are in marked contrast to those obtained by Nakomoto for ordinary aromatic compounds where both features are reversed. This difference is to be expected on Mulliken's theory since electron transport between the rings can only be brought about by that component of the incident light which is oscillating perpendicular to the ring plane, while in the transitions of aromatic systems only the component in the plane of the ring system is effective.

A second piece of evidence, which weighs heavily against all the theories ascribing the colour of the complexes to modifications of the bands of one component by some interaction in the complex, is provided by Reid's ⁷⁰ work on the phosphorescence spectra of molecular complexes of nitro-compounds with hydrocarbons. Working both with crystals and with solutions in glasses at low temperature he has shown that the phosphorescence emission is almost the same as that of the free hydrocarbon constituent, apart from some loss of detail. There is no obvious reason why molecular interactions which displace the singlet excited state of the hydrocarbon should be without effect on the triplet state. This suggests very strongly that the absorption is due to a completely new band.

Complexes formed by the Halogens.—It is well known that the colour of iodine solutions is very much dependent on the nature of the solvent.⁷¹ In most cases solutions in oxygen- or nitrogen-containing solvents are brown while those in aliphatic hydrocarbons or carbon disulphide are violet. In aromatic hydrocarbons iodine forms solutions of intermediate colour. The colour of the solutions may also depend on the temperature. Violet solutions in carbon disulphide become brown on cooling, and brown solutions in oxygen-containing solvents become violet when heated.

It has long been suspected that these brown solutions contain iodine in a combined form while the violet solutions, whose spectra are very similar to that of iodine vapour, contain essentially free iodine molecules. A number of investigations have confirmed this. Benesi and Hildebrand ⁷² have recently provided convincing spectroscopic evidence that benzene and mesitylene form simple 1:1 complexes with iodine. These authors drew attention to the existence of a completely new intense band in the region of 2900 Å in these complexes. More recently attention has been concentrated on this new band rather than on the modifications in the visible band. Mulliken ^{39, 67} in a general discussion of the spectra of iodine complexes first attributed this band to a displacement of the forbidden 2600-Å transition of benzene but in an added note ^{72a} suggested the charge-transfer interpretation, which he developed in subsequent publications.

⁷⁰ Reid, *J. Chem. Phys.*, 1952, **20**, 1212.

⁷¹ Kleinberg and Davidson, *Chem. Reviews*, 1948, **42**, 601.

⁷² Benesi and Hildebrand, *J. Amer. Chem. Soc.*, 1948, **70**, 2832; 1949, **71**, 2703.

^{72a} Mulliken, *ibid.*, 1950, **72**, 605.

Keefer and Andrews have investigated a large number of these complexes between aromatic hydrocarbons and iodine ⁷³ and also some analo-

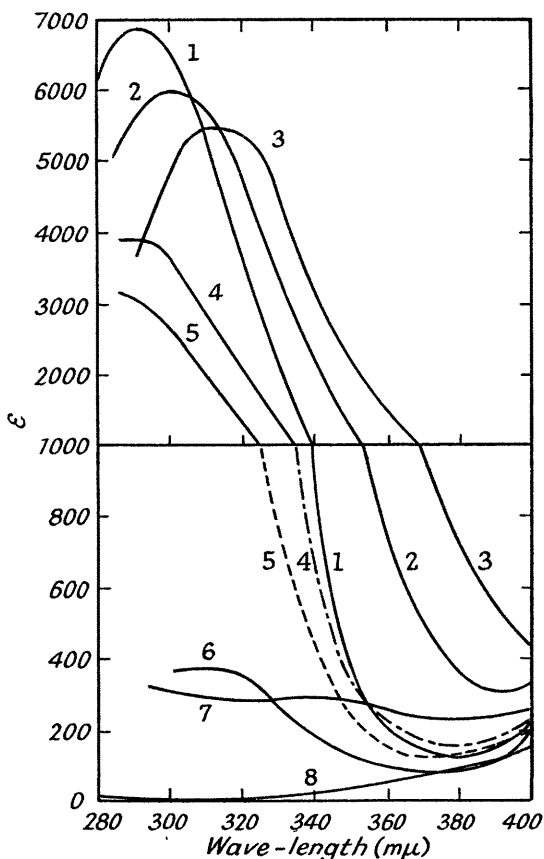


FIG. 7

Absorption spectrum of bromine in various solvents: 1 pure benzene, 2 toluene and carbon tetrachloride ($N = 0.901$), 3 *o*-xylene and carbon tetrachloride ($N = 0.890$), 4 bromobenzene and carbon tetrachloride ($N = 0.902$), 5 chlorobenzene and carbon tetrachloride ($N = 0.9047$), 6 iodobenzene and carbon tetrachloride ($N = 0.01391$), 7 anisole and carbon tetrachloride ($N = 0.366$), and 8 pure carbon tetrachloride. N is the molar fraction of the aromatic compound. The molecular extinction coefficients are based on total bromine present. (Reproduced, by permission, from Keefer and Andrews, *J. Amer. Chem. Soc.*, 1950, **72**, 4677.)

gous complexes with iodine monochloride ⁷⁴ and with bromine ⁷⁵ (Fig. 7). Typical values of λ_{\max} , ϵ_{\max} , and K (measured in carbon tetrachloride at 25°) for such complexes are given in Table 2.

⁷³ Keefer and Andrews, *J. Amer. Chem. Soc.*, 1952, **74**, 4500.

⁷⁴ *Idem, ibid.*, 1950, **72**, 5170.

⁷⁵ *Idem, ibid.*, p. 4677.

TABLE 2

	I ₂			ICl		
	$\lambda_{\max.}$	$10^{-2}\epsilon_{\max.}$	K	$\lambda_{\max.}$	$10^{-2}\epsilon_{\max.}$	K
C ₆ H ₆	2920	16.4	0.15	2820	8.13	0.54
C ₆ H ₅ Me	3020	16.7	0.16	2886	8.00	0.87
<i>o</i> -C ₆ H ₄ Me ₂	3166	12.5	0.27	2980	7.87	1.24
<i>m</i> -C ₆ H ₄ Me ₂	3180	12.5	0.31	2980	9.18	1.39
<i>p</i> -C ₆ H ₄ Me ₂	3040	10.1	0.31	2920	6.54	1.51
<i>s</i> -C ₆ H ₃ Me ₃	3320	8.85	0.82	3070	7.87	4.59
<i>s</i> -C ₆ H ₂ Me ₄	3320	9.00	0.63	3060	7.25	4.25
C ₆ HMe ₅	3570	9.26	0.88	3220	7.81	6.43
C ₆ Me ₆	3750	8.2	1.35	3340	4.00	22.70
C ₆ Et ₆	3780	16.7	0.13	3400	6.60	1.24
C ₆ H ₅ Br	2900	10.4	0.13	2860	5.91	0.32

It will be noticed that the introduction of methyl groups into the benzene ring, which leads to a lowering of the ionisation potential, results in the predicted increases in $\lambda_{\max.}$ and K . However, in this case the extinction coefficients vary in the opposite sense to that predicted by the theory, *i.e.*, they decrease; at the moment there is no satisfactory explanation of this anomaly.

One of the most important points which emerge from study of these data is the importance of the steric hindrance due to the ethyl groups in hexaethylbenzene. While K for hexamethylbenzene is at least ten times that for benzene itself, K for hexaethylbenzene is less than one tenth of K for hexamethylbenzene. This is in good agreement with Mulliken's deduction, based on the symmetry of the available orbitals in benzene and iodine, that the iodine molecule lies in a plane parallel to the plane of the benzene ring with its centre vertically above the centre of the benzene ring.

A number of complexes of iodine with naphthalene, phenanthrene, styrene, etc., have been studied by Keefer and Andrews. The spectra are described and do not raise any new points.

Freed and Sancier⁷⁶ have studied the spectra of iodine in solutions of olefins at low temperatures. They find that complexes with heats of formation of about $\frac{1}{2}$ kcal./mole are formed. This should be compared with the values of about one kcal./mole observed with aromatic hydrocarbons. The complexes have absorption peaks like those of the aromatic hydrocarbon complexes with maxima at about 2800 Å. Some values are: propene, 2800 Å; cyclopropane, 2400 Å; *cis*-but-2-ene, 3000 Å; *trans*-but-2-ene, 2980 Å; buta-1:3-diene, 2780 Å; and isoprene 3150 Å.

Among the interesting points that were established is the ability of cyclopropane to act as an electron donor. This is consistent with its low ionisation potential and generally unsaturated character. It would be

⁷⁶ Freed and Sancier, *J. Amer. Chem. Soc.*, 1952, **74**, 1273.

interesting to see whether trinitrobenzene and other aromatic acceptors would form complexes with cyclopropane and its derivatives.

If butene-iodine is treated with butadiene in propane no reaction occurs below 150° K, but at this temperature the characteristic spectrum of butadiene-iodine appears. If the solution is warmed to 154° K this spectrum disappears and chemical reaction takes place. This strongly suggests that, under these conditions, the complex is an intermediate in the reaction of iodine with butadiene. Such intermediate complexes may be formed in many reactions and, if so, could possibly be detected at sufficiently low temperatures.

Recent work on the brown solutions of iodine in alcohols, ethers,⁷⁷ and alkyl halides⁷⁸ has established the existence of 1 : 1 complexes. It seems probable that these too are charge-transfer complexes, the donated electron coming from the unshared pair on the oxygen or chlorine atoms.

McConnell, Ham, and Platt⁷⁹ have shown that there is a linear relation between the wave-length of maximum absorption of an iodine complex and the ionisation potential of the electron donor. The fit to a straight-line graph is so good that the authors have predicted the positions of the maxima for a number of complexes in which the ionisation potential of the donor is already known.

The accuracy with which this relation is obeyed is rather surprising theoretically, since it suggests that the quantity Δ representing the interaction of the ion pair is almost independent of the geometry of the donor molecule.

Hastings, Franklin, Schiller, and Matsen^{79a} have observed charge-transfer bands in solutions of iodine in inert solvents such as saturated hydrocarbons. They claim that their slight extension of Mulliken's theory leads to a better equation connecting the wave-length of the maximum of the charge-transfer band to the ionisation potential of the donor.

Ham^{79b} has compared the absorption spectra of iodine complexes in solution in solid glasses at liquid-nitrogen temperatures with those observed at room temperature. The charge-transfer bands are in general displaced to longer wave-lengths, *e.g.*, from 2880 Å to 3240 Å for benzene. However, there are a number of exceptions which are not easily interpreted.

Complexes of Molecular Oxygen.—Evans⁸⁰ has observed that solutions of oxygen in various aromatic hydrocarbons, amines, and phenols exhibit a new absorption band slightly to the long wave-length side of the aromatic band. This he ascribes to the formation of a charge-transfer complex analogous to those formed by the halogens. The new absorption band is supposed to be a charge-transfer band. It should be noted that the values of the wave-length of maximum absorption quoted by Evans are not reliable since the positions of the peaks are affected by instrumental error.⁸¹

⁷⁷ Ham, *J. Chem. Phys.*, 1952, **20**, 1170.

⁷⁸ Keefer and Andrews, *J. Amer. Chem. Soc.*, 1952, **74**, 1891.

⁷⁹ McConnell, Ham, and Platt, *J. Chem. Phys.*, 1953, **21**, 66.

^{79a} Hasting, Franklin, Schiller, and Matsen, *J. Amer. Chem. Soc.*, 1953, **75**, 2900.

^{79b} Ham, *ibid.*, 1954, **76**, 3875.

⁸⁰ Evans, *J.*, 1953, 345.

⁸¹ Evans, personal communication.

An indication that such complexing occurs in some clathrate compounds is provided by the decomposition of the quinol-oxygen clathrate compound in light of wave-length longer than that of any quinol absorption band.⁸¹ This example suggests that complex formation may well be important in other photochemical oxidations.

Complexes of Sulphur Dioxide.—Andrews and Keefer⁸² have established the existence of molecular complexes in solutions of sulphur dioxide in a

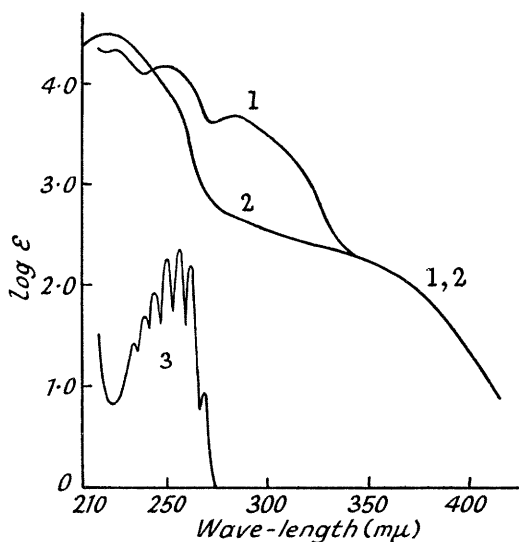


FIG. 8

Absorption spectra of 1 the *s*-trinitrobenzene-benzene molecular complex, 2 *s*-trinitrobenzene in *n*-heptane, and 3 benzene in *n*-heptane. Curves 1 and 2 are identical above 350 mμ. (Reproduced, by permission, from Lawrey and McConnell, *J. Amer. Chem. Soc.*, 1952, **74**, 6175.)

number of aromatic hydrocarbons. The spectra of the complexes differ from those of the components in the existence of a peak at about 3000 Å. However, the intensity of this peak is rather low for a charge-transfer complex. This, taken together with the existence of a weak band in sulphur dioxide at 2900 Å, makes the identification of the band as due to charge transfer uncertain, but nevertheless probable.

Complexes formed by the Silver Ion.—The expected charge-transfer band of complexes such as toluene-Ag⁺⁸³ have not been observed in the near ultra-violet region. A theoretical explanation of this is lacking. However, this band may occur at about 2300 Å.

Complexes formed by Polynitro-compounds.—Complexes formed between nitro-compounds and aromatic hydrocarbons, amines, phenols, etc., are often intensely coloured, and spectroscopic investigations have been des-

⁸² Andrews and Keefer, *J. Amer. Chem. Soc.*, 1951, **73**, 4169.

⁸³ Keefer and Andrews, *ibid.*, 1952, **74**, 640.

cribed by a number of authors (Fig. 8).⁸⁴ The colours of some of these complexes are given in Table 1; a much more complete account is given in Pfeiffer's book.⁶¹

Some crystal structures have also been determined. The complex between *s*-trinitrobenzene and *p*-iodoaniline contains discrete molecules in which the benzene rings are parallel and about 3.2 Å apart;⁸⁵ the molecules are then piled together (Fig. 9). The interplanar distance is a good

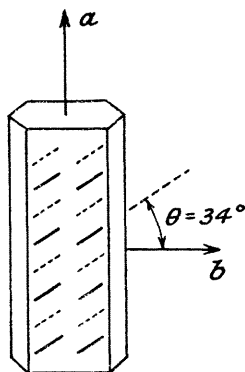


FIG. 9

The orientations of quinol and benzoquinone in the quinhydrone crystal: — quinol, --- benzoquinone. Fine lines show the molecules of the next inner layer. (The c-axis is normal to the plane of the paper.) (Reproduced, by permission, from Nakomoto, J. Amer. Chem. Soc., 1952, 74, 1739.)

deal shorter than is usual in aromatic systems (about 3.5 Å). This suggests that the charge-transfer interaction may be rather larger than the $\frac{1}{2}$ —4 kcal./mole value of the heat of formation since it must also overcome the repulsions which would occur in such a compressed system.

The complex between picryl chloride and hexamethylbenzene⁸⁶ is very similar to that described above except that the angle between the ring planes and the crystal axis is much smaller.

We have already noted that the absorption in these complexes is greatest for light oscillating in a plane perpendicular to the benzene rings.⁶⁹ Reid's work⁷⁰ on the phosphorescent emission has also been mentioned.

In solution the complexes formed by the aliphatic nitro-compounds seem to be of exactly the same type.⁸⁷ The failure to obtain stable crystalline compounds in many cases must be attributed to the geometry of the aliphatic compounds which prevents the close packing possible in the aromatic complexes.

⁸⁴ Landauer and McConnell, *J. Amer. Chem. Soc.*, 1952, **74**, 1221; Lowrey and McConnell, *ibid.*, p. 6175.

⁸⁵ Powell, Huse, and Cookes, *J.*, 1943, 153.

⁸⁶ Powell and Huse, *J.*, 1943, 435.

⁸⁷ Harper and Macbeth, *J.*, 1915, **107**, 87, 1824.

Molecular Complexes between Quinones and Phenols.—The interpretation of the properties of systems containing quinones and phenols is often complicated either by the possibility of hydrogen bonding or by the stability of an intermediate oxidation state. Only those aspects of the subject which can be more or less certainly attributed to charge transfer will now be mentioned.

Michaelis and Grannick⁸⁸ have studied the spectra of many quinone-phenol complexes in solution (Fig. 10). In all cases they discovered absorption peaks at rather long wave-lengths now attributed to charge-transfer.

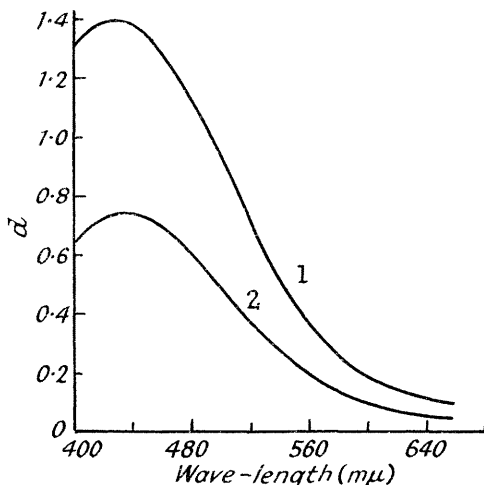


FIG. 10

*Absorption spectrum of the quinhydrone complex in alcohol. (Benzoquinone, constant at 0.02034M; quinol 0.800M for curve 1, 0.400M for curve 2.) (Reproduced, by permission, from Michaelis and Grannick, *J. Amer. Chem. Soc.*, 1944, **66**, 1023.)*

The intensity of the peaks was proportional to the product of the quinone and phenol concentrations; this establishes that 1 : 1 complexes are present.

The positions of maximum absorption in these complexes are: quinol, 4250 Å; quinol monomethyl ether, 4200 Å; quinol dimethyl ether, 4100 Å; quinol diethyl ether, 4100 Å; phenol, 3200 Å; anisole, 3200 Å; phenetole, 3500 Å; resorcinol, 3700 Å; and phloroglucinol, 4200 Å.

Michaelis and Grannick draw attention to the similarity between the spectra of phenol complexes and those of their methyl ethers. This they hold to show that hydrogen bonding cannot be important for complex formation in solution. They suggest that the complex contains the benzene rings of the components parallel, one perpendicularly above the other.

Crystal-structure determination⁸⁹ has shown that in the solid state the structure of quinhydrone is as suggested by Michaelis and Grannick. The

⁸⁸ Michaelis and Grannick, *J. Amer. Chem. Soc.*, 1944, **66**, 1023.

⁸⁹ Osaki and Matsuda, unpublished work, see ref. 69.

distance between the planes of the benzene rings is 3.16 Å, even less than that in the nitro-compounds.

Molecular Complexes of Quinones with Other Aromatic Electron-donors.—There has been little systematic work on these complexes, although a large number of highly coloured derivatives have been prepared and described.

Chloranil-hexamethylbenzene was studied in solution by Michaelis and Grannick,⁸⁸ who found an intense absorption maximum at 5120 Å. The crystal structure was shown by Anderson⁹⁰ to be very similar to that of quinhydrone described above.

It is interesting that chloranil displaces λ_{\max} further to the red than any other common complexing agent. In this sense it is the strongest common, stable electron acceptor of this class. The complex between chloranil and tetramethylphenylenediamine has an absorption maximum in the infra-red region.

Miscellaneous Organic Molecular Complexes.—Considerable numbers of complexes between carboxylic acids, sulphonic acids, acid chlorides, acid anhydrides, etc., and various electron donors have been described. In a few cases absorption spectra have been measured and the charge-transfer band identified.⁹¹

A General Relation between the Position and Intensity of the Charge-transfer Band in a Series of Benzene Complexes.—McConnell, Ham, and Platt⁷⁹ have noticed that the plot of the maximum extinction coefficient of the charge-transfer band against the wave-length of maximum absorption for a number of benzene complexes is remarkably close to linear. The slope of the graph shows that the extinction coefficient is much more sensitive to the electron affinity of the acceptor than is the position of absorption. Unfortunately no other electron donor has been studied so completely; if a similar relation holds for other donors it may well be important, both practically and theoretically.

Charge Transfer and the Quenching of Fluorescence

Weiss has shown that, in a number of photochemical reactions in solution, the initial process is the transfer of an electron from a negative to a positive ion. Typical reactions of this kind are the photochemical decompositions of oxalate and lactate in the presence of uranyl ions. Since these reactions are accompanied by a decrease in the fluorescence of the uranyl ion Weiss⁹² suggested that the quenching of fluorescence by the addition of a small amount of foreign material was in general due to a charge-transfer process. The absence of net chemical change in many cases was attributed to a rapid back reaction.

While the generality of this mechanism is not certain there is a great deal of evidence supporting it in special cases. In the quenching of the fluorescence of a number of dyes, including uranin, quinine sulphate, and uranyl sulphate, it is found that the common anions may be placed in a

⁹⁰ Anderson, *Nature*, 1937, **140**, 584.

⁹¹ Andrews and Keefer, *J. Amer. Chem. Soc.*, 1953, **75**, 3776.

⁹² Weiss, *Trans. Faraday Soc.*, 1949, **35**, 48.

series of decreasing quenching power :⁹³

$I^- > CNS^- > Br^- > Cl^- > C_2O_4^{--} > C_2H_3O_2^- > SO_4^{--} > NO_3^- > F^-$
 This series follows closely that which we have already encountered in connection with other charge-transfer phenomena, suggesting very strongly that the quenching is connected with the donor power of the anions.

There is a second class of fluorescent substances including negative ions such as sodium sulphanilate and sodium naphthionate which are quenched strongly by nitrate, less strongly by bromate, and not at all by iodide.⁹³ Presumably these fluorescent negative ions are good electron donors and hence are quenched by potential electron acceptors but not by donors.

Very similar relations have been discovered by Livingston and Ke,⁹⁴ for the quenching of the fluorescence of chlorophyll a by a variety of uncharged organic and inorganic molecules. The efficiency of quenching varies in the order :

chloranil > quinone > trinitrotoluene > *m*-dinitrobenzene > nitric oxide > oxygen > nitrobenzene ;

p-hydroxyaniline > dimethylaniline > 1 : 5-diaminopyridine. Molecules which did not quench in the concentrations employed include phenol and hydrazine.

It will be noted that quenching is now brought about by both strong electron acceptors and strong electron donors, but not by molecules of intermediate type. The interesting conclusion that chlorophyll in the excited state can act either as a donor or as an acceptor seems to follow from this work. The order of quenching efficiency of acceptors is seen to parallel closely their effectiveness as charge-transfer acceptors, deduced from Table 1.

It is necessary to emphasise that charge transfer is not necessarily the only, or even the most usual, mechanism of fluorescence quenching in solution.

Complexes with Charge-transfer Bands as Intermediates in Chemical Reactions

This aspect of charge-transfer theory has been emphasised by Mulliken and by Brackman.⁶³ The former's general theory of complex formation between electron donors and electron acceptors suggests that such complexes may be formed as intermediates in many reactions. If sufficient activation energy is present they may be transformed irreversibly into the product of a chemical reaction. This subject properly belongs to complex theory and cannot be treated here ; the reader is referred to the original papers for details.^{67, 68} We may remark that the spectroscopic identification of intermediates is certain in the case of the reaction of iodine with butadiene⁷⁶ and probable in the oxidation of iodide and thiocyanate by gaseous oxygen.⁹⁵ It is probable that many other reaction intermediates of this sort could be identified at temperatures sufficiently low to prevent their immediate transformation.

⁹³ Pringsheim, " Fluorescence and Phosphorescence ", New York, 1949, pp. 328 -335.

⁹⁴ Livingstone and Ke, *J. Amer. Chem. Soc.*, 1950, **72**, 909.

⁹⁵ Evans, unpublished work.