

132. Structure and Reactivity of the Oxyanions of Transition Metals. Part IV.* Some Relations between Electronic Spectra and Structure.

By A. CARRINGTON, D. SCHONLAND, and M. C. R. SYMONS.

The molecular-orbital level scheme derived by Wolfsberg and Helmholz¹ for MnO_4^- and CrO_4^{2-} has been extrapolated to explain the electronic spectra of the ions MnO_4^{2-} , MnO_4^{3-} , CrO_4^{3-} , and FeO_4^{3-} . A linear relation between the long wavelength absorption maxima of $3d$ and $4d$ transition-metal oxyanions isoelectronic with MnO_4^- and the ionic radii of the central metal atoms is discussed.

Details are given of the visible and ultraviolet absorption spectra in solution of the ions ReO_4^- and FeO_4^{2-} .

IN a molecular-orbital treatment of a molecule, the wave function describing its electronic structure is assumed to be a product, or a linear combination of products, of single-particle molecular orbitals which extend over the molecule as a whole. The molecular orbitals for a given molecule reflect its geometrical structure and can be classified according to their behaviour under the group of rotations and reflections which leave the molecular framework unchanged. For an XY_4 tetrahedral molecule (group T_d) it can be shown by group-theoretical methods that the molecular orbitals must belong to one or other of five distinct types. The symbols (in Mulliken's notation²) used for these types are listed in the first row of Table 1.

When the Schrödinger equation for the XY_4 molecule is solved, one obtains a system of energy levels for the individual electrons, some of which are degenerate. The orbitals associated with a given level will belong to one of the five types; their corresponding degeneracy is shown in the second row of Table 1. The total electronic state of the molecule is then specified in the first place by the number of electrons occupying each level (the electron configuration). A given configuration will in general give rise to several distinct electronic states (terms) each of which again must belong to one of the five types of Table 1 and will have the corresponding degeneracy. In addition it will have the usual degeneracy associated with the possible arrangements of the electron spins. These electronic states for the whole molecule are designated, in the usual spectroscopic notation, by the appropriate capital letters with a superior suffix giving the spin degeneracy, while the orbital type associated with an individual electron is indicated by a lower-case (small) letter.

Selection rules operate for optical transitions between different electronic states of the molecule, and the allowed transitions for XY_4 molecules are given in the third row of Table 1.

TABLE 1. Classification of XY_4 molecular orbitals.

Orbital type	A_1	A_2	E	T_1	T_2
Degeneracy	1	1	2	3	3
Allowed transitions	$A_1 \rightarrow T_2$	$A_2 \rightarrow T_1$	$E \rightarrow T_1, T_2$	$T_1 \rightarrow T_1, T_2, E, A_2$	$T_2 \rightarrow T_1, T_2, E, A_1$

Wolfsberg and Helmholz¹ have given a treatment of the tetrahedral ions MnO_4^- and CrO_4^{2-} in which the molecular orbitals of different types are approximated by suitable combinations of $3d$, $4s$, and $4p$ atomic orbitals on the central metal atom and $2p$ orbitals on the oxygen ligands and in which they make various semi-empirical assumptions about the values of the parameters that enter the equations. The level schemes they obtain for chromate and permanganate are qualitatively very similar. Their scheme for chromate is shown in Fig. 1 in which the type of orbital associated with each level is shown, with an additional number where necessary to distinguish different levels of the same type.

* Part III, *J.*, in the press.

¹ Wolfsberg and Helmholz, *J. Chem. Phys.*, 1952, **20**, 837.

² Mulliken, *Phys. Rev.*, 1933, **43**, 279.

The levels below t_1 are bonding, those above t_1 are antibonding, while t_1 itself is non-bonding, its associated orbitals being centred on the oxygen atoms. Of the bonding levels, $1a_1$ and $1t_2$ use atomic orbitals from which σ -bonds could be formed in a directed-valency treatment (d^3s or sp^3 tetrahedral hybridisation) while $1e$ represents a form of π -oxygen bonding with the central atom. Thus, as Wolfsberg and Helmholz point out, their results associate a very much greater stability with π -bond formation than is normally considered to be the case in a double bond. This is not the form of π -bonding normally postulated for complex compounds and cannot be pictured as a conventional double bond.

Expected Nature of the Transitions.—For the chromate and permanganate ions there are altogether 24 electrons to be accommodated in this scheme and, regard being had to degeneracies of the various levels given in Table 1 and the spin degeneracy, it will be seen that in the ground state these will completely fill all the levels up to and including t_1 , giving a ground state configuration $(1e)^4(1t_2)^6(1a_1)^2(2t_2)^6(t_1)^6$ which gives rise to a 1A_1 electronic

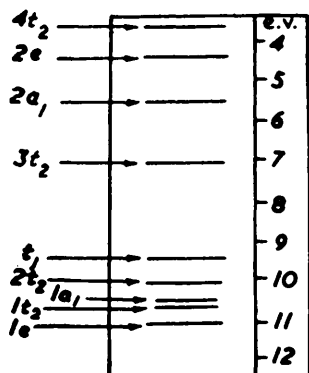


FIG. 1. Energy level scheme for CrO_4^{2-} .

state. Wolfsberg and Helmholz then interpret the two bands in the visible and ultraviolet regions shown by chromate and permanganate as due to the electron jumps $t_1 \rightarrow 3t_2$ and $2t_2 \rightarrow 3t_2$, which give rise respectively to the configurations and electronic states $\dots(t_1)^5(3t_2): {}^1T_2$ and $\dots(2t_2)^5(t_1)^6(3t_2): {}^1T_2$. Other singlet states can also be formed from these configurations, e.g., $\dots(t_1)^5(3t_2)$ can give 1T_1 , 1E , and 1A_2 , but no transitions from the 1A_1 ground state to these are allowed (Table 1).

If further electrons are fed into these ions, it is evident that they should be accommodated in the triply degenerate $3t_2$ level. The results obtained from paramagnetic-resonance experiments³ are in accord with this picture, indicating that, as one would expect, two electrons placed in the $3t_2$ level have their spins parallel, forming a triplet spin state. One is thus led to postulate the configurations and ground electronic states listed in Table 2. (Although Wolfsberg and Helmholz only discussed chromium and manganese oxyanions, it is reasonable to include iron as well.)

TABLE 2. Ground states of the ions.

Ion	Configuration	Electronic state
CrO_4^{2-} , MnO_4^-	$\dots(2t_2)^6(t_1)^6$	1A_1
CrO_4^{3-} , MnO_4^{3-}	$\dots(t_1)^6(3t_2)$	3T_2
MnO_4^{3-} , FeO_4^{3-}	$\dots(t_1)^6(3t_2)^2$	3T_1

When the $3t_2$ level is occupied, Fig. 1 shows that as well as the electron jumps $t_1 \rightarrow 3t_2$ and $2t_2 \rightarrow 3t_2$, the jumps $3t_2 \rightarrow 2a_1$ and $3t_2 \rightarrow 2e$ become possible and should give absorptions in the same general region of the spectrum.

Thus for $3t_2 \rightarrow 2a_1$ the excited configuration for CrO_4^{3-} and MnO_4^{2-} will be $\dots(t_1)^6(2a_1)$ giving rise to a 2A_1 electronic state to which a transition from the 3T_2 ground state is

³ Carrington, Ingram, Schonland, and Symons, *J.*, 1956, 4710.

allowed. For MnO_4^{3-} the excited configuration is $\dots(t_1)^6(3t_2)(2a_1)$ which can form a triplet state of type T_2 which again gives an allowed transition from the 3T_1 ground state. In the same way the $3t_2 \rightarrow 2e$ jump gives rise to states to which transitions are allowed from the ground state.

In the configurations with $3t_2$ electrons, however, the $t_1 \rightarrow 3t_2$ and $2t_2 \rightarrow 3t_2$ transitions become much more complex than for configurations in which $3t_2$ is unoccupied. Our calculations show that the $t_1 \rightarrow 3t_2$ jump in MnO_4^{2-} which produces an excited configuration $\dots(t_1)^5(3t_2)^2$ gives rise to one 2A_1 , two 2E , three 2T_2 , and four 2T_1 states to all of which transitions from the 2T_2 ground state are allowed. The probability of a transition from the ground state to any one of these excited states is fairly small compared with the transition probability for the same electron jump in MnO_4^- but the total transition probability to all the excited states is 5/6 of that for the same transition in MnO_4^- . In MnO_4^{2-} therefore, the band spectrum associated with the $3t_2 \rightarrow 2a_1$ electron jump should have a simpler structure than that due to the $t_1 \rightarrow 3t_2$ jump, and this fact is used below for the identification of these two transitions.

Discussion of the Observed Spectra.—The identification of the electronic transitions responsible for the absorption spectra of the different ions is shown in Table 3, where the figures in each column give (in cm^{-1}) the positions of the absorption maxima for the ions indicated.

TABLE 3. Identification of electronic transitions in the spectra.

Transition	CrO_4^{2-}	CrO_4^{3-}	MnO_4^-	MnO_4^{2-}	MnO_4^{3-}	FeO_4^{2-}
$3t_2 \rightarrow 2a_1$	—	16,000	—	16,530	14,810	12,720
$t_1 \rightarrow 3t_2$	26,810	28,200	18,320	22,940	30,500	17,800
$3t_2 \rightarrow 2e$	—	(a)	—	28,490	30,800	19,600
$2t_2 \rightarrow 3t_2$	36,630	(a)	32,210	33,440	(b)	(a)

(a) Not observable. (b) See discussion.

(i) CrO_4^{2-} , MnO_4^- . These are discussed by Wolfsberg and Helmholtz. Their numerical results do not predict the positions of the absorption peaks correctly but do show the trend towards longer wavelengths in passing from CrO_4^{2-} to MnO_4^- . Moreover they are able to explain the weak bands found by Teltow⁴ in his measurements on the mixed crystals $\text{K}(\text{Cl},\text{Mn})\text{O}_4$. These occur at the long-wavelength end of the region covered by the bands belonging to the main absorption at $18,320 \text{ cm}^{-1}$ and are explained as the normally forbidden transitions mentioned above, associated with the $t_1 \rightarrow 3t_2$ jump in MnO_4^- , which become allowed by the crystal symmetry. They are also able to account for the changes in the bands due to the main $t_1 \rightarrow 3t_2$ transitions as the direction of polarisation varies with respect to the crystal axes.

(ii) MnO_4^{2-} . This ion shows the four peaks,⁵ in the appropriate region of the spectrum, expected on the basis of the consideration of the preceding paragraph. Wolfsberg and Helmholtz's numerical results suggest that the $3t_2 \rightarrow 2a_1$ transition should occur at lower energy than the $t_1 \rightarrow 3t_2$ transition. Evidence that this is indeed the case is furnished by Teltow's measurements⁶ on diluted crystals $\text{K}_2(\text{S},\text{Mn})\text{O}_4$. He divided his spectrum into four regions which correspond to the peaks found in the solution spectrum. The longest-wavelength region was characterised by a very well defined system of bands with definite fine-structure; the remaining regions consisted of weak and diffuse bands with a continuous background absorption at least partly due to the overlapping of unresolved bands.

These results show that the long-wavelength absorption must be due to a transition from the ground state to a definite electronic excited state, while the transitions responsible for the other absorptions are much more complicated. Now we have seen that for MnO_4^{2-} the transition $3t_2 \rightarrow 2a_1$ gives rise to only one excited state, whereas transitions, each with

⁴ Teltow, *Z. phys. Chem.*, 1938, B, 40, 397.

⁵ Carrington and Symons, *J.*, 1956, 3373.

⁶ Teltow, *Z. phys. Chem.*, 1939, B, 43, 198.

a relatively small transition probability, to a large number of excited states (which, owing to Coulomb effects, will have slightly different energies) will occur with the $t_1 \rightarrow 3t_2$ transition. Hence one may conclude that the long-wavelength absorption in MnO_4^{2-} is due to the $3t_2 \rightarrow 2a_1$ transition.

(iii) CrO_4^{3-} . Wolfsberg and Helmholtz's numerical results indicate that the $3t_2 \rightarrow 2a_1$ transition in CrO_4^{3-} should occur at considerably lower energy than the $t_1 \rightarrow 3t_2$ transition, and on this basis one can explain the peak that appears at $16,000 \text{ cm}^{-1}$ as the $3t_2 \rightarrow 2a_1$ transition while the peak at $28,200 \text{ cm}^{-1}$ will be the $t_1 \rightarrow 3t_2$ transition. The fact that the energy difference between these transitions in CrO_4^{3-} is large compared with the energy difference between the same transitions in MnO_4^{2-} is in accord with the level schemes for these two ions. It was not found possible⁷ to make measurements at wavelengths shorter than 300μ .

(iv) MnO_4^{3-} . The absorption spectrum⁵ can be interpreted by correlating the lowest energy absorption with the $3t_2 \rightarrow 2a_1$ transition as for MnO_4^{2-} . The very large, broad peak with its maximum at $30,800 \text{ cm}^{-1}$ is interpreted as a superposition of the $t_1 \rightarrow 3t_2$ and $3t_2 \rightarrow 2e$ transitions, and there is some further experimental evidence for this in that the

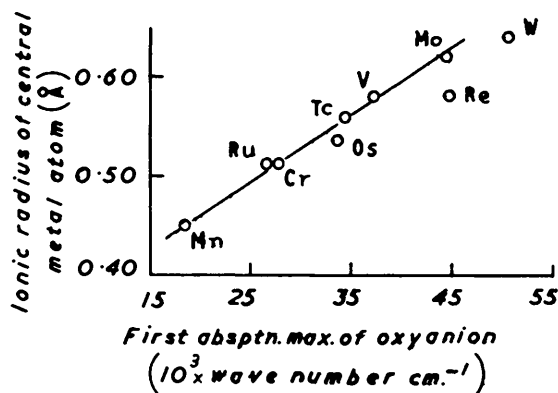


FIG. 2. Plot of the first absorption maxima of transition-metal oxyanions isoelectronic with MnO_4^- against the ionic radii of the corresponding central metal atoms. All values for the ionic radii are taken from Kordes⁹ except that of Tc^{7+} which has been estimated by Ahrens.¹⁰

peak is just resolvable into two maxima of equal intensity at $30,800 \text{ cm}^{-1}$ and $30,500 \text{ cm}^{-1}$. The peak now found at $47,000 \text{ cm}^{-1}$ may be caused by the $2t_2 \rightarrow 3t_2$ transition but the molar extinction coefficient (approximately 17,000) is of the order of magnitude expected for an absorption arising from charge-transfer to solvent⁸ which might be expected in this energy region. Since MnO_4^{3-} readily loses an electron⁵ this hypothesis seems reasonable.

(v) FeO_4^{2-} . The spectrum is very similar in appearance to that of MnO_4^{3-} , the large peak being asymmetric with a shoulder at about $17,800 \text{ cm}^{-1}$ before it reaches its maximum at $19,600 \text{ cm}^{-1}$.

It may be worth noting that the increase in the energy required for the $t_1 \rightarrow 3t_2$ transition in passing from CrO_4^{2-} to CrO_4^{3-} and from MnO_4^- to MnO_4^{2-} and also the decrease in the energy required for the $3t_2 \rightarrow 2a_1$ transition in going from MnO_4^{2-} to MnO_4^{3-} are both consistent with the expectation that, because of Coulomb repulsion, the presence of electrons in a given level will discourage transitions of more electrons into that level and encourage transition of an electron away from it into an empty level.

Regularities in the Spectra of Transition-metal Oxyanions.—It is natural to consider whether the level scheme found by Wolfsberg and Helmholtz for CrO_4^{2-} and MnO_4^- , which we have shown can be extended to explain the spectra of other valency states of these ions, can be applied to other oxyanions of metals with incomplete d -shells, for which molecular orbitals similar to those used for chromate and permanganate can be constructed. It has

⁷ Bailey and Symons, *J.*, 1957, 203.

⁸ Orgel, *Quart. Rev.*, 1954, 8, 422.

⁹ Kordes, *Z. phys. Chem.*, 1939, B, 48, 213.

¹⁰ Ahrens, *Geochim. Cosmochim. Acta*, 1952, 2, 155.

already been noted that the qualitative results obtained from paramagnetic resonance studies,³ which give information about the nature of the orbitals in which the unpaired electrons are placed, are consistent with such a level scheme.

On this scheme the long-wavelength absorption in ions with the same number of valence electrons as MnO_4^- would be due to the $t_1 \rightarrow 3t_2$ transition, *i.e.*, from the non-bonding t_1 orbital to an empty π -type antibonding orbital. To a first approximation the energy of the non-bonding t_1 orbital (centred on the oxygen ligands) might be expected to be more or less independent of the nature of the central atom so that the energy required for the $t_1 \rightarrow 3t_2$ transition would depend directly on that of the $3t_2$ level and so might be fairly simply related to properties of the central atom.

Teltow⁶ suggested that a correlation existed between the long-wavelength absorption edges of such complexes and the ionic radii of the central atoms, the edge shifting to shorter wavelengths as the ionic radius increased. Fig. 2 shows the positions of the long-wavelength absorption maxima of MnO_4^- , CrO_4^{2-} , VO_4^{3-} ($3d$ transition elements), RuO_4 , TcO_4^- , MoO_4^{2-} ($4d$), and OsO_4 , ReO_4 , and WO_4^{2-} ($5d$), plotted as a function of the ionic radii of Mn^{7+} , Cr^{6+} , V^{5+} , Ru^{8+} , Mo^{6+} , Os^{8+} , Re^{7+} , Tc^{7+} , and W^{6+} respectively.

The points for the $3d$ and $4d$ complexes lie on a good straight line, suggesting strongly that these complexes do indeed have very similar electronic structures. The $5d$ complexes do not fit on this line but a rough correlation does appear to exist for them among themselves. The reason for these deviations from the straight line might well be due to the part that f orbitals must play in complexes of the heavier metals.

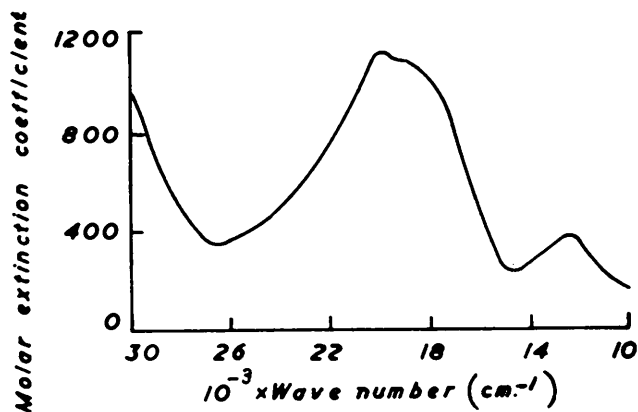


FIG. 3. Absorption spectrum of the aqueous ferrate ion, FeO_4^{2-} .

EXPERIMENTAL

The absorption spectrum of the ferrate ion in solution has recently been described by Kaufman and Schreyer¹¹ but they did not define the peak at $12,720 \text{ cm}^{-1}$, showing only a rising absorption. That this peak is due to the ferrate ion is shown if the gradual decomposition of potassium ferrate in aqueous potassium hydroxide (9M) is followed spectrophotometrically. Whilst the optical density slowly decreases, the ratio of the heights of the peaks at $19,700 \text{ cm}^{-1}$ and $12,720 \text{ cm}^{-1}$ remains constant. Furthermore the pronounced shoulder to the $19,700 \text{ cm}^{-1}$ peak, centred at about $17,800 \text{ cm}^{-1}$ was not recorded by Kaufman and Schreyer but is quite reproducible. Measurements were made down to 215μ where the optical density was still rising but the strong absorption of the excess of hydroxide ion in this region prevented definition of the peak. Potassium ferrate (97%) was prepared as described by Hrostowski and Scott¹² and analysed by Schreyer's method.¹³ The spectrum is shown in Fig. 3.

The measurements of the absorption spectrum of the hypomanganate ion reported earlier⁵

¹¹ Kaufman and Schreyer, *Chemist-Analyst*, 1956, 45, 22.

¹² Hrostowski and Scott, *J. Chem. Phys.*, 1950, 18, 106.

¹³ Schreyer, *Analyt. Chem.*, 1950, 22, 691.

have been extended further into the ultraviolet region. Again the excess of hydroxide ion present, which is necessary to prevent protonation of the MnO_4^{3-} ion, begins to absorb strongly at $215 \text{ m}\mu$. A maximum absorption was found at $216 \text{ m}\mu$ ($47,000 \text{ cm}^{-1}$), at which wavelength the total optical density of the test solution against air as blank was 1.78. Quartz cells of 0.1 mm . thickness were used and, in order to compensate for cell errors, two sets of measurements were made, the solvent and the test solution being interchanged in the cells. The two optical densities obtained for any one wavelength were then averaged. It was found impossible to make reliable measurements below $214 \text{ m}\mu$ because of light-scattering effects caused by the large slit widths necessary. Thus, whilst the observed maximum may be spurious, the magnitude of the molar extinction coefficient in this region, which will have been reduced if stray light effects are important, is greatly in excess of any values previously observed for transition-metal oxyanions.

The peak at $30,800 \text{ cm}^{-1}$ has also been examined in detail. As was discussed earlier, this peak is just resolvable into two maxima of equal intensity at $30,800 \text{ cm}^{-1}$ and $30,500 \text{ cm}^{-1}$. Detailed measurements have been made with different concentrations of hypomanganate in differing concentrations of potassium hydroxide so that readings were taken throughout the reliable range of optical densities for the instrument used. In the large majority of cases,

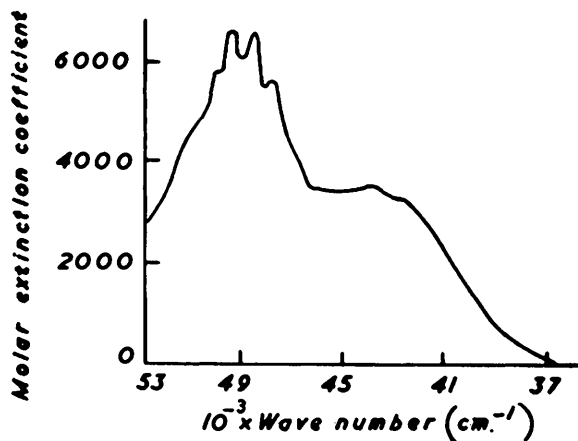


FIG. 4. *Absorption spectrum of the aqueous perrhenate ion, ReO_4^- .*

the two maxima were found although in one or two instances the absorption curve showed only a slight asymmetry. Spectrographic analysis of a single diluted crystal would settle this point. If two transitions are occurring the real separation would be somewhat greater than the apparent splitting of 300 cm^{-1} . The solutions examined were made by dissolving crystalline sodium hypomanganate in aqueous potassium hydroxide solutions of concentrations between 6M and 10M , the solvent being used in the blank cell.

The absorption spectrum of the perrhenate ion, ReO_4^- , in aqueous solution has been described by Custers¹⁴ who, however, was unable to make any measurements below $220 \text{ m}\mu$ ($45,500 \text{ cm}^{-1}$). Measurements have now been made down to $190 \text{ m}\mu$ ($52,700 \text{ cm}^{-1}$) and the complete spectrum is shown in Fig. 4. Potassium perrhenate was prepared by oxidation of powdered rhenium metal to perrhenic acid with 70% hydrogen peroxide, the solution being almost neutralised with aqueous potassium hydroxide and concentrated by evaporation. The solid obtained on cooling was recrystallised from distilled water.

The first absorption maximum of the molybdate ion, MoO_4^{2-} , was obtained by using a solution of ammonium molybdate in aqueous potassium hydroxide (0.5M), the presence of alkali being necessary to prevent the formation of condensed species. These solutions were found to obey Beer's law, whereas aqueous solutions, although showing the same first maximum at $44,000 \text{ cm}^{-1}$, exhibited slight deviations from Beer's law.

Similarly the spectrum of sodium tungstate in aqueous solution was examined. Solutions of concentrations $1 \times 10^{-3}\text{M}$ to $2 \times 10^{-4}\text{M}$ showed large deviations from Beer's law but more dilute solutions (*e.g.*, $0.5 \times 10^{-4}\text{M}$) showed only small deviations. All the solutions showed the

¹⁴ Custers, *Physica*, 1937, 4, 426.

first absorption maximum at $50,300\text{ cm.}^{-1}$. In very dilute aqueous solution, WO_4^{2-} should be the only species present.¹⁵ As a check on the position of the first maximum, a solution of sodium tungstate in aqueous potassium hydroxide (0.5M) was examined in cells 0.1 mm. thick. Because of the absorption of the excess of hydroxide ion, it was not possible to define the peak but the optical density was still rising at $48,000\text{ cm.}^{-1}$.

Other spectral data were taken from Connick and Hurley¹⁶ (RuO_4), Langseth and Qviller¹⁷ (OsO_4), and Rulfs and Wayne¹⁸ (TcO_4^-).

Spectrophotometric measurements were made with a Unicam SP 600 glass spectrophotometer, and a Unicam SP 500 quartz spectrophotometer, the latter having been calibrated down to $190\text{ m}\mu$. Calibrated quartz or glass cells of 0.1 mm., 1 mm., 2 mm., 5 mm., 1 cm., and 2 cm. thickness were used. All reagents used were of "AnalaR" grade except for hydrogen peroxide which was the unstabilised product supplied by Laporte Chemicals Ltd. and the powdered rhenium metal which was supplied on loan by Johnson, Matthey and Co. Ltd.

One of us (A. C.) thanks the Esso Petroleum Company for a Postgraduate Research Studentship.

THE UNIVERSITY, SOUTHAMPTON.

[Received, September 25th, 1956.]

¹⁵ Jander, *Chem.-Ztg.*, 1934, **58**, 247.

¹⁶ Connick and Hurley, *J. Amer. Chem. Soc.*, 1952, **74**, 5012.

¹⁷ Langseth and Qviller, *Z. phys. Chem.*, 1934, *B*, **27**, 79.

¹⁸ Rulfs and Wayne, *J. Amer. Chem. Soc.*, 1952, **74**, 235.
