409. *Oxidation–Reduction Potentials of Complex Ions.*

By J. C. Tomkinson and R. J. P. Williams.

A new procedure for the study of the oxidation–reduction potentials of complex ions is described, in which the mid-point potential is followed as the pH is varied continuously. The relation between the potentials and the degrees of formation of the complexes is discussed. A series of ferric–ferrous oxine (8-hydroxyquinoline) complex couples was examined. The relative stabilities of the two valency states depend on the electronic states of the respective cations, which are influenced by the ligand field.

The factors controlling the oxidation–reduction potentials of complex ions have never been systematically studied for a sufficiently wide range of complexes to yield any general theory. In this, and later, papers the effect upon the redox potentials of complexes of a single metal by substitution of various groups into the organic ligand will be examined. This paper is concerned with iron complexes of 8-hydroxyquinolines. Most of these complexes being insoluble in water, mixed aqueous–organic solvents have to be used. The choice of solvent is limited by the solubilities of the cations, organic ligand, and salt used as background to keep the ionic strength constant. The enforced use of mixed solvents unfortunately prohibits the study of standard potentials without very detailed examination of activity coefficients, so we merely measured a series of formal potentials at equal concentrations of ferric and ferrous iron, E_f. Such potentials refer only to the specified conditions of solvent and ionic strength. All the formal potentials quoted here refer to three solvent systems, *i.e.*, 50% and 75% (v/v) dioxan–water and water. When these solvent systems are specified below, it must be remembered that the ionic strength was always kept constant by using 0·3M-sodium chloride as background. All redox potentials were measured against a saturated calomel electrode with a potassium chloride salt bridge. The potentials given are corrected to the aqueous hydrogen electrode, but this does not place E_f on the usual hydrogen scale because its value in the dioxan-containing systems includes the differences in electrode potential between the ferric and ferrous ions *in the solvent concerned* and a liquid junction potential of unknown, constant magnitude. For example, the potential of the simple ferric–ferrous couple in 50% aqueous dioxan is +680 mv, in 75% aqueous dioxan +595 mv, and in water +690 mv. No comparison between formal potentials in different solvents is justified. However the relative potentials measured in one solvent for a series of complexes are unlikely to be much affected by changes in activity coefficient caused by minor modifications of the parent ligand molecule.

A glass electrode was used to follow changes of hydrogen-ion activity. Such measurements in mixed solvents include several unknown potentials which are functions of solvent composition. No attempt has been made to convert values to a true pH scale, and in measurements in either dioxan-containing solvent the pH-meter reading will be written p*B*.[1, 2]

In the method used to examine iron–oxine couples (*i.e.*, the system ferric–ferrous–oxine) the ratio (total ferric) : (total ferrous) remained unity throughout the experiment. The p*B* of the solution was varied by adding acid or base. After each such addition p*B* was measured by a glass electrode. Three indicator electrodes were used to follow the changes of the formal oxidation–reduction potential, E_f. The results are plotted as graphs of E_f against p*B* (Fig. 2).

As the range of potential to be covered extends to about —0·3 v measurements had to to be made in the complete absence of oxygen.

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[1] Van Uitert and Haas, *J. Amer. Chem. Soc.*, 1953, **75**, 451.
[2] Irving and Rossotti, *J.*, 1954, 2904.

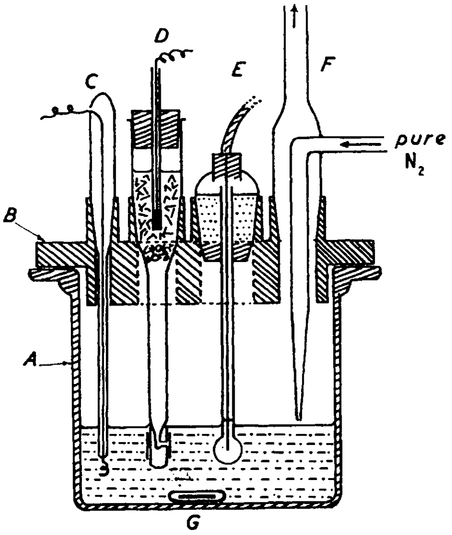
EXPERIMENTAL

Apparatus.—The gas-tight cell *A* (Fig. 1) (volume, *ca.* 200 ml.) is a flat-bottomed cylindrical glass beaker with a wide flanged top on which rests the flanged Polythene cell-cap *B* through which " Quickfit " ground glass sockets of standard 1 : 10 taper carry three redox indicator electrodes [one gold wire, one platinum wire (*C*), one platinum foil], a glass electrode, *E*, a calomel electrode, *D*, a micrometer syringe burette, a gas lead, *F*, providing both inlet and outlet for the nitrogen (arranged so that the gas impinges on the surface of the solution, and does not bubble through it), and a spare socket. *G* is a magnetic stirrer.

When *A* and *B* are fitted together after being greased, and there is a slight positive pressure of nitrogen in *A*, no measurable amount of oxygen leaks in during 50 hr.

" Oxygen-free " nitrogen (British Oxygen Co.) being not sufficiently pure, it was passed through chromous chloride solution, then through an acid trap, and through pre-saturators of the same solvent composition and temperature as used in the cell. The entire assembly was of glass. On leaving the titration cell, the nitrogen escaped through a mercury seal into the atmosphere. The presence of oxygen in the purified nitrogen could be detected in the cell by the effect on a dilute acidified solution (M/2000) of ferrous oxine complex. At pH *ca.* 3·0 this solution is very pale yellow and oxidation to the ferric complex turns it green: the effect can be observed more accurately by use of redox electrodes.

FIG. 1. *The cell.*



The titration cell is kept at 25°. The apparent pH of the solution was measured between the calomel electrode and the glass electrode on a " Cambridge " pH-meter to ±0·02 pH unit. The redox potentials were measured between the calomel electrode and each of the three redox electrodes by using a " Pye " precision potentiometer and a " Scalamp " galvanometer, which allowed an accuracy of ±1 mv.

Procedure.—In strongly reducing solution the solvent, acidified with mineral acid to provide a low initial p*B*, and the required equal amounts of ferric and ferrous ions were added to the cell. Solid ligand (about 20 mg.) was placed in a tiny glass " basket " supported above the level of the liquid by a glass rod passing through an airtight gland in the cell-cap. Nitrogen was passed through for 1—2 hr. with rapid stirring, and the ligand was added to the solution by immersing the basket. Although it dissolved quickly, at least ½ hr. was allowed for equilibrium to be established before making measurements. Passage of nitrogen continued during the subsequent titration, with rapid stirring. During the initial stages there is little danger of oxidation of the ferrous ion as the potential in the solution is high (*ca.* +0·5 v). p*B* was next increased by adding small quantities of concentrated (*ca.* 3N) carbonate-free alkali from the micrometer syringe. p*B* and the redox potential were read after each addition, time being allowed for equilibria to be established. It was necessary to isolate each circuit in turn when making measurements. The usual concentration of ligand was M/700, and that of the cations M/5600.

A typical plot of E_f against p*L* (= −log [ligand]) is shown in Fig. 2. In 50% dioxan and in water potentials at low p*B* values were usually slightly different for each of the three electrodes, and the spread of these early readings is shown. No reading was accepted as reversible (see below) unless all three electrodes gave the same potential to within ±10 mv. The potentials now quoted are not given to any higher accuracy except when a special experiment so demands. Although this may seem a very large error, equilibrium at low p*B* was often attained only slowly and such an error represents a compromise between experiments of very long duration and very high accuracy. At high p*B* the potentials are accurate to within 1 mv.

Theory.—The curves of redox potential against pH can be used to find formation functions for both ferric and ferrous complexes as follows. The concentration of a free cation [M] in the presence of ligand of concentration [L] is given by

$$[\mathrm{M}] = \frac{T_{\mathrm{M}}}{1 + K_1[\mathrm{L}] + K_1K_2[\mathrm{L}]^2 + K_1K_2K_3[\mathrm{L}]^3} \quad . \; . \; . \quad (1)$$

where K_1,K_2, and K_3 refer to the successive stability constants of ML, ML_2, and ML_3 and T_{M} is the total amount of cation.

The degree of formation is

$$\bar{n}_{\mathrm{M}} = [\mathrm{M}]\{K_1[\mathrm{L}] + 2K_1K_2[\mathrm{L}]^2 + 3K_1K_1K_3[\mathrm{L}]^3\}/T_{\mathrm{M}} \quad . \; . \; . \quad (2)$$

Differentiation of (1) with respect to [L], and conversion by appropriate operations, gives

$$\frac{\mathrm{d}\ln[\mathrm{M}]}{\mathrm{d}\ln[\mathrm{L}]} = -\bar{n}_{\mathrm{M}} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

Now $[\mathrm{L}] = T_{\mathrm{L}} - [\mathrm{HL}] - [\mathrm{H_2L}] - \bar{n}_{\mathrm{M}}T_{\mathrm{M}}$, where T_{L} is the total concentration of ligand. Substitution of the acid dissociation constants κ_1 and κ_2 gives

$$[\mathrm{L}] = \frac{T_{\mathrm{L}} - T_{\mathrm{M}}\bar{n}_{\mathrm{M}}}{1 + [\mathrm{H}]/\kappa_1 + [\mathrm{H}]^2/\kappa_1\kappa_2} \quad . \; . \; . \; . \; . \quad (4)$$

The degree of formation of proton complexes is $\bar{n}_{\mathrm{H}} = ([\mathrm{HL}] + 2[\mathrm{H_2L}])/T_{\mathrm{L}}$. Differentiating (4) with respect to [H], assuming $T_{\mathrm{L}} > T_{\mathrm{M}}\bar{n}_{\mathrm{M}}$, substituting for $\bar{n}_{\mathrm{H}}$, and carrying out suitable operations, we obtain

$$\frac{\mathrm{d}\ln[\mathrm{L}]}{\mathrm{d}\ln[\mathrm{H}]} = -\bar{n}_{\mathrm{H}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

The assumption employed in deriving eqn. (5) is good providing there is excess of ligand as $\bar{n}_{\mathrm{H}}$ changes much more slowly than [H]. Combining (3) and (5) we obtain

$$\frac{\mathrm{d}\ln[\mathrm{M}]}{\mathrm{d}\ln[\mathrm{H}]} = \bar{n}_{\mathrm{M}} \, . \, \bar{n}_{\mathrm{H}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

An equation of this form was deduced earlier in a description of the change of extraction of metal complexes with hydrogen-ion concentration.[3] Now the formation of the complexes of one cation proceeds independently of that of another cation in the same solution. Consider a metal in two valency states which are present in equal concentration

then $$E_f = E^\circ_f - (\boldsymbol{RT}/\boldsymbol{F}) \ln([\mathrm{M^{II}}]/[\mathrm{M^{III}}]) \quad . \; . \; . \; . \; . \quad (7)$$

where E° is the standard redox potential of the couple. Then

$$\frac{\mathrm{d}E_f}{\mathrm{d}\ln([\mathrm{M^{II}}]/[\mathrm{M^{III}}])} = -\frac{\boldsymbol{RT}}{\boldsymbol{F}}$$

and from eqn. (6) $$\frac{\mathrm{d}E_f}{\mathrm{d}\ln[\mathrm{H}]} = \frac{\boldsymbol{RT}}{\boldsymbol{F}} \, . \, (\bar{n}_{\mathrm{III}} - \bar{n}_{\mathrm{II}})\bar{n}_{\mathrm{H}}$$

whence at 25°c $$\frac{\mathrm{d}E_f}{\mathrm{dpH}} = -0{\cdot}059(\bar{n}_{\mathrm{III}} - \bar{n}_{\mathrm{II}})\bar{n}_{\mathrm{H}} \quad . \; . \; . \; . \; . \quad (8)$$

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[3] Irving, Rossotti, and Williams, *J.*, 1955, 1906.

Equation (8) has been thoroughly tested by independent measurements of $\bar{n}_{\mathrm{III}}$ and $\bar{n}_{\mathrm{II}}$ and of dE_f/dpH or dE_f/dp$B$. Providing the two valency states form complexes over well separated regions of pH—there is little overlap in the formation of ferrous and ferric oxine complexes—then the formation functions for the two cation complexes can be completely determined and all six step constants obtained. dE_f/dpH is zero for either $\bar{n}_{\mathrm{H}} = 0$ or $\bar{n}_{\mathrm{III}} = \bar{n}_{\mathrm{II}}$. Equation (8) has been used to obtain many constants of the ferrous and ferric oxine complexes. Thus although this paper is largely concerned with redox potentials themselves these potentials can be broken down into sets of stability constants which reveal the cause of changes of potentials. We will turn to the experimental confirmation of our method first.

FIG. 2. *Oxine complexes.*

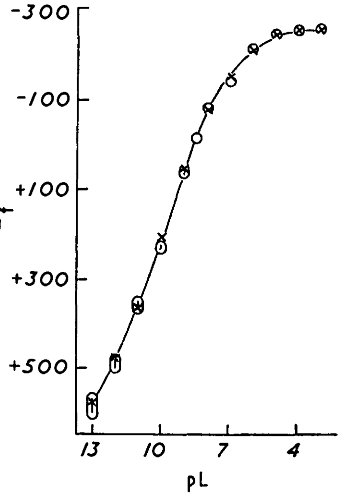
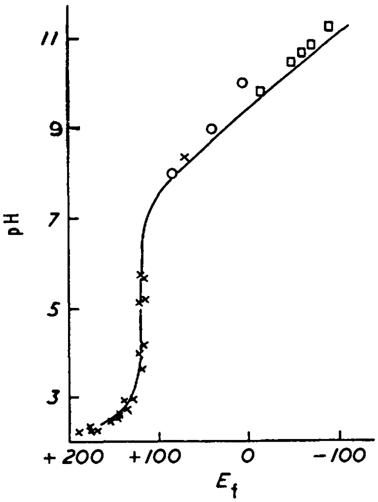


FIG. 3. *Iron–enta couples in water.*



In all Figures, E_f is in mv.

The circles and ellipses are experimental points drawn so as to show the error due to different readings of the three electrodes and the crosses are those calculated from formation functions of the individual ferrous and ferric complexes (see text).

Solid line, present work (Pt electrode) with extra points, □, showing the values for the gold electrode where these differ. × Experimental potentials and ○ points calculated from Schwarzenbach and Heller.

Results.—We first re-examined the ferrous–ferric ethylenediaminetetra-acetic acid complexes in aqueous solution, first studied by Schwarzenbach and Heller[4] (Fig. 3). The agreement is excellent over the pH range 2·5—7·5 (in this solvent the meter readings are true pH values). When both ferric and ferrous complexes are fully formed, dE_f/dpH is zero [eqn. (8)]. Above pH 8·0 there is a marked difference between the two sets of results. Our work, which is more detailed than the earlier work, shows a slope of E_f/pH = —0·059, indicating that there is one hydrogen ion difference between the ferric and ferrous complexes in this region [eqn. (8)]. The ferric complex can be written $[\mathrm{Fe^{III}(enta)(OH)}]^{2-}$. Further hydrolysis was not detected below pH 10 of either the ferric or the ferrous complex, in marked disagreement with earlier work.[4] The time involved in measurements such as ours is about one day, but the discontinuous mid-point method used originally must have taken much longer.

Iron Oxine Complexes.—The method was further tested with the redox potentials of the ferric–ferrous complexes of 8-hydroxyquinoline in 50% and 75% dioxan–water (Fig. 2). In the early stages of the titration (low pB) the ligand is present as the cation

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[4] Schwarzenbach and Heller, *Helv. Chim. Acta*, 1951, **34**, 576.

H_2 oxine$^+$. As sodium hydroxide is added, pB rises and the ligand dissociates to H oxine. This implies that $\bar{n}_{\mathrm{H}}$ falls from 2·0 towards 1·0. Also in this region $\bar{n}_{\mathrm{III}}$ is increasing while $\bar{n}_{\mathrm{II}}$ is zero, so $\bar{n}_{\mathrm{H}}(\bar{n}_{\mathrm{III}} - \bar{n}_{\mathrm{II}})$ is less sensitive to change in pB than $\bar{n}_{\mathrm{III}}$ alone. Hence the slope $\mathrm{d}E_f/\mathrm{dp}B$ (eqn. 8) changes slowly. Subsequently $\bar{n}_{\mathrm{H}}$ remains unity over a wide range of pB and $\bar{n}_{\mathrm{III}}$ tends to a maximum value of 3·0. The ferrous complex begins to be formed when $2·0 < \bar{n}_{\mathrm{III}} < 3·0$ and thereafter $\mathrm{d}E_f/\mathrm{dp}B$ decreases. At the highest pB the value of E_f is independent of pB, *i.e.*, of the hydrogen-ion concentration, and this could mean either that both ferric and ferrous complexes are at the same co-ordination stage, or that the ligand molecule is completely dissociated [eqn. (8)]. The former has been shown to be true by calculation of the degree of dissociation of the ligand acid from the known value of the acid dissociation constants, and by the study of the ferric and ferrous complexes separately by Calvin–Bjerrum titrations; these permitted a complete calculation of the form of the plot of E_f against pL, and the calculated and experimental values agreed (Fig. 2). This amply demonstrates the reversibility of the potentials measured. The reversibility was also confirmed, first by changing the titration procedure to one of adding acid to an alkaline solution of the complexes. Exactly the same values of E_f (±2 mv) were found over the whole pH range. Secondly, in experiments in which different total amounts of ligand were varied over a range of 1000 : 1 the expected change of redox potential was observed. Thirdly, similar tests with another ligand, 5-formyl-8-hydroxyquinoline (50% dioxan–water), also showed good reversibility of the electrodes. Finally, a correctly poised oxidation curve of ferrous 5-formyl-8-hydroxyquinoline, obtained by titration with potassium chloroiridate at a fixed pB, had exactly the same mid-point potential as that obtained by the continuous mid-point method.

FIG. 4. *The relation between the basicity of the ligands and the oxidation–reduction potentials of the fully formed oxine complexes (for key, see Table* 1).

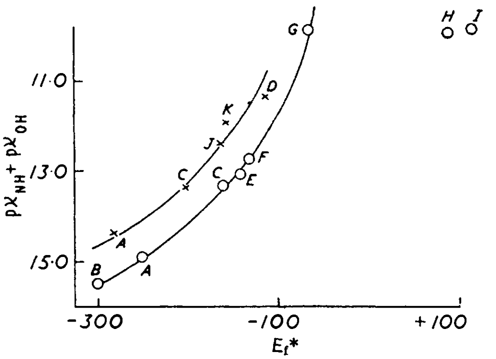
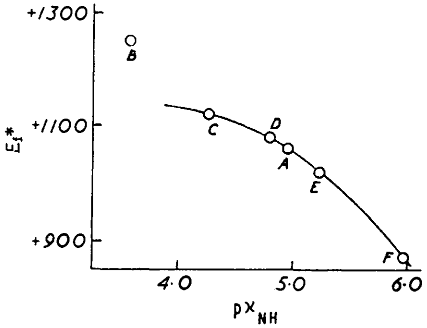


FIG. 5. *The relation between the basicity of the ligands and the oxidation–reduction potentials of the fully formed phenanthroline complexes.*



A, Phenanthroline; *B*, 5-nitro-; *C*, 5-chloro-; *D*, 5-phenyl-; *E*, 5-methyl-; *F*, 4 : 7-dimethyl-phenanthroline.

Hydrolysis.—With the ferrous ion, hydrolysis does not compete with complex formation by 8-hydroxyquinolines as it starts at a much higher pB (pH). In titrations of acid solutions of ferric salt by alkali in the three different solvents the hydrogen ion displaced by hydrolysis below the pH (or pB) at which complex formation with any oxine complex reaches $\bar{n}_{\mathrm{III}} = 1·0$ was found to be insignificant, and it may be that chloride protects the ferric ion. Hydrolysis was ignored in the consideration of the results.

Potentials of 3 : 1 *Complexes.*—At high pB the complexes of the two valency states have the same composition M(oxine)$_3$. The redox potentials of the fully-formed couples $\mathrm{Fe^{III}(oxine)_3/Fe^{II}(oxine)_3}$ of a series of substituted oxines are in Table 1. Fig. 4 shows the result of plotting these potentials (E_f*) against a preferred measure of ligand basicity [5] ($\mathrm{p}\kappa_{\mathrm{NH}} + \mathrm{p}\kappa_{\mathrm{OH}}$): these are "practical" [2] acid dissociation constants. There is no simple relation between the sum of the pκ values and E_f*. Such a relation would result if, as has often been suggested, there is a general relation between the acid dissociation constants of a series of ligands and log K (stability constant) of the metal chelates of these ligands. This was suggested for ferric phenoxides [6] and for ferrous 1 : 10-phenanthroline complexes,[7] although very few substituents were studied and the results do not obey exactly the linear relation.

TABLE 1. *Dissociation constants, stability constants, and redox potentials of iron oxine complexes.*

Substituent in 8-hydroxyquinoline	Key for Fig. 4	Solvent; dioxan (%)	$\mathrm{p}\kappa_{\mathrm{NH}}$	$\mathrm{p}\kappa_{\mathrm{OH}}$	E_f *	log β_3^{III}	log β_3^{II}
None	*A*	50	4·08	10·82	−251	38·00	22·13
		75	3·14	11·22	−283	37·20	22·23
5-methyl	*B*	50	4·24	11·25	−300	(39·5)	(23·0)
5-fluoro	*C*	50	2·76	10·55	−162	(35·6)	(21·3)
		75	2·20	11·15	−202	?	(21·1)
5-ethoxycarbonyl	*D*	50	2·88	8·72	−102	?	?
		75	2·00	9·35	−114	(33·7)	(21·7)
5-sulphonic acid	*E*	50	3·40	9·68	−141	(35·65)	(21·75)
5-aldoxime	*F*	50	3·52	9·22	−133	(34·0)	(20·2)
7-iodo-5-sulphonic acid	*G*	50	1·75	8·13	−65	(31·5)	(18·85)
5-formyl	*H*	50	2·51	7·43	87	29·5	19·45
5-cyano	*I*	50	2·02	7·85	114	(29·8)	(20·2)
5-bromo	*J*	75	1·93	10·45	−163	35·6	21·41
5-iodo	*K*	75	1·64	10·27	−158	34·2	20·96

log β_3^{III} and log β_3^{II} are ferric and ferrous formation constants for 3 : 1 complexes. The values in parentheses were obtained from the slope of the redox potential with pB (see text). Other values were obtained from the Bjerrum–Calvin method by using pH titration data alone. The acid dissociation constants are practical constants.[3]

A linear relation between E_f* for the ferric–ferrous 1 : 10-phenanthroline couples and $\mathrm{p}\kappa_{\mathrm{NH}}$ is refuted by Fig. 5, which has the same form as Fig. 4.

Marked exceptions from what can be considered to be general behaviour represented by Fig. 4 are observed with 5-formyl- and 5-cyano-oxine. The formation of the separate ferric and ferrous complexes of these ligands shows that the high potentials are attributable not only to a special stability of the *ferrous* complex, but also to destabilisation of the *ferric* complex (Table 1). When the results for 5-formyloxine complexes are compared with those for chelates of "ferron" (8-hydroxy-7-iodoquinoline-5-sulphonic acid) (both ligands have almost the same basicity) the E_f* values differ by 152 mv. The stronger ferric complexes are formed by "ferron," but with the ferrous complexes the formyloxine chelates the more strongly. Now the electronic configurations of ferric and ferrous ions in an octahedral field differ by one d_ϵ electron, and it is this that causes the properties of two valency states to differ and the $\mathrm{Fe}^{\mathrm{II}}$ cation to act as an electron donor and the $\mathrm{Fe}^{\mathrm{III}}$ as an acceptor.[8] Now the 5-formyl group is a π-electron acceptor whereas the groups in "ferron," the iodine atom and possibly the sulphonate ion also, are π-electron donors, so it is hardly surprising that the electron-donor cation should be stabilised by the electron-acceptor substituent and *vice-versa.* The two "abnormal" ligands in Fig. 4 contain strong electron-acceptor groups, formyl and cyano. The ligands which fall on the curve all contain electron-donor substituents. The quantity ($\mathrm{p}\kappa_{\mathrm{NH}} + \mathrm{p}\kappa_{\mathrm{OH}}$) being used as a measure of σ-donor strength, the change from 5-methyloxine to oxine changes E_f* much more than the same decrease in basicity caused by change from oxine to halogen-substituted oxines owing to the difference in character between the methyl group (donor

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[5] Jones, Poole, Tomkinson, and Williams, preceding paper.

[6] Milburn, *J. Amer. Chem. Soc.*, 1954, **77**, 2064.

[7] Brandt and Gullstrom, *J. Amer. Chem. Soc.*, 1952, **74**, 3532.

[8] Williams, *J.*, 1955, 137.

of both σ and π electrons) and the halogens (σ acceptors, π donors). Ferric ion is made more stable than ferrous by both effects in the first case but only by the π effect in the second. The same considerations apply to the potentials plotted in Fig. 5.

It can now be appreciated why there is no simple relation between $(\mathrm{p}\kappa_{\mathrm{NH}} + \mathrm{p}\kappa_{\mathrm{OH}})$ and E_f^* or even between $(\mathrm{p}\kappa_{\mathrm{NH}} + \mathrm{p}\kappa_{\mathrm{OH}})$ and the stability constants.[5] The stability of the complex of a transition-metal cation depends not only on the σ-electron density, but also on the π-electron density of the ligand. The latter is unlikely to affect $\mathrm{p}\kappa$. If changes of substituent affect the σ-electron density of a ligand more than they affect the π-electron density, comparison of $\log K$ and $\mathrm{p}\kappa$ is less likely to show the influence of the π-electron changes than comparison of E_f^* and $\mathrm{p}\kappa$. The greater sensitivity of E_f^* to π-electron effects arises because it represents the difference of the logarithms of two stability constants ($\log K^{\mathrm{III}} - \log K^{\mathrm{II}}$), both of which change in the same sense with changes of σ-electron density (*i.e.*, $\mathrm{p}\kappa$) but which may well change in opposite senses because of π-electron changes. Thus measurement of oxidation–reduction potentials accentuates the effect of π-electrons.

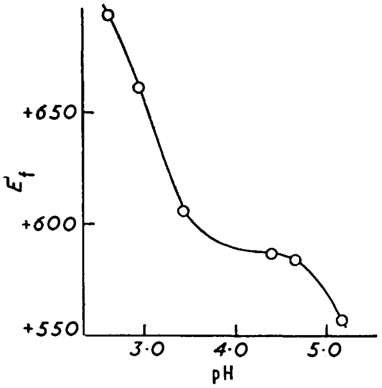

FIG. 6. *Plot of* E_f *against* pH *for the 2-methylphenanthroline complexes showing that the potential becomes independent of* pH.

E_f^* is also a preferable quantity to $\log K$, since accurate values are obtainable *directly* by experiment.

The substituents markedly affect the absorption spectra of the ferric and ferrous complexes.[9] The interpretation of the spectra fully substantiates the suggested nature of the interaction between the substituted ligands and the cations.

Other Oxidation–Reduction Potentials.—1 : 10-*Phenanthroline chelates with iron.* In the 8-hydroxyquinoline complexes both the ferric and the ferrous ion have the electron configuration of the respective gas cations, although this statement requires qualification in that the visible absorption spectra of the ferrous complexes indicate that 10—30% of the ferrous ion is present in the diamagnetic form. This " promoted " electron configuration makes for greater stability of the complex than if the ion is in its ground state, although this stabilisation can hardly be measurable if the proportion of " promoted " form is below 50%. In the tris-1 : 10-phenanthroline chelates, the ferrous ion is 100% diamagnetic and covalent, and although the ferric ion is not completely in the ground state, neither is it completely in the promoted configuration.[10] The stability of the ferrous state relative to that of the ferric must therefore be much greater in phenanthroline than in oxine complexes. This is reflected by the very high oxidation–reduction potentials of the couples, $+\sim 1{\cdot}0$ v.

A second demonstration of the effect of change of electron configuration upon redox potential is provided by the study of the iron 2-methylphenanthroline complexes. The redox potentials at room temperature (E_f), obtained by individual oxidimetric titration

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[9] Tomkinson and Williams, *J.*, 1958, 1153.

[10] Williams, *Chem. Rev.*, 1956, **56**, 299.

in aqueous solutions buffered by excess of this ligand at different pH-values, are plotted against pH in Fig. 6. E_t falls to +0·585 v, which is independent of pH. At this stage both valency states are present as tris-chelates, and this voltage is E_f^*. The redox potential (E_f^*) of the parent ferric–ferrous phenanthroline (ferriin–ferroin) couple is +1·06 v. Now ferrous 2-methylphenanthroline is paramagnetic (Irving, personal communication) and this is the only case of an iron tris-1 : 10-phenanthroline couple with a redox potential lower than that of the simple Fe^{III}–Fe^{II} (hydrates) couple. Presumably steric hindrance prevents the stabilisation of the promoted ferrous state. These observations show that no change in ligand, other than one which brings about a change of the electron configuration of the cations, stabilises ferrous relative to ferric in aqueous solution.

The very large difference in potential between the iron–oxine and the iron–phenanthroline couples is undoubtedly due to the different entropy changes which occur on formation of complexes with anionic and neutral ligands. When neutral ligands form complexes the entropy changes are small irrespective of the cationic charge,[11] but with anionic ligands they are large and increase with cationic charge. Hence the redox potentials are lower (more negative) in the latter cases. The low potentials of the iron–oxine, –oxalate, –fluoride, and –enta couples can thus be readily understood. The iron–cyanide couple has a potential of +0·36 v which is much higher than those of the other anionic complexes. The cyanides being inner-orbital, covalent complexes, the ease of promotion of the ferrous ion also raises the redox potential somewhat.

Ahrland and Chatt [12] have discussed the ferric–ferrous pentacyano-complexes with water or ammonia in the sixth co-ordination position. They observed that the ammine had the lower redox potential and took this to confirm a generalisation that the better the electron-donor character of the ligand, the more stable the higher valency state of *covalent or inner-orbital complexes*. Although the hexacyano-complexes of ferric and ferrous iron are inner-orbital complexes, and probably the pentacyano-ammines too, there is evidence that the ferric pentacyanoaquo-ion is not.[13] There is a second objection to conclusions based on studies of complexes in which the atoms within the co-ordination sphere are changed, because the higher-valency ion state is invariably smaller than the lower, so that a change in the size of the ligand introduces steric factors. These are not important when the changes in ligand character are produced by substitution remote from the bonding centre, as with the oxine complexes (above). The second objection cannot be raised against an interpretation of the potentials of the substituted 1 : 10-phenanthroline complexes, which are covalent in the ferrous form, but as the ferric ion may well be an equilibrium mixture of ionic and covalent states, this series of complexes is not a suitable basis for a generalisation.[14] The magnetic data are indecisive. The general statement that the ferric rather than the ferrous valency state among inner-orbital complexes is stabilised by increase of electron-donor character of ligands, has been established however [15] for substituted porphyrin complexes further co-ordinated with pyridine and cyanide; magnetic evidence shows that both sets of complexes are covalent.[15] Hence there appears to be a good case for the proposition that the ferric state is stabilised relative to the ferrous state by increase in the electron-donor character of the ligands provided that *both* the ions are in either the ground or the promoted state. However the ferrous state is probably somewhat stabilised by increase in the electron-acceptor character of the ligand, no matter what the electron configuration of the cations.

There is also a class of complex in which the ferrous ion is diamagnetic (inner-orbital or covalent) whereas the ferric ion is ionic. Here the ferrous ion should be the more

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[11] Williams, *J. Phys. Chem.*, 1954, **58**, 121.
[12] Ahrland and Chatt, *J.*, 1957, 1379.
[13] Simon and Knauer, *Z. Electrochem.*, 1946, **46**, 13.
[14] Gaines, Hammett, and Walden, *J. Amer. Chem. Soc.*, 1936, **58**, 1668.
[15] Martell and Calvin, "The Chemistry of the Metal Chelates," Prentice-Hall Inc., New York, 1953, p. 373.

rapidly stabilised either by increase in the σ-donor or π-acceptor character of the ligand. Biological systems appear to contain many examples of this type of variation of redox potential with change of ligand.[10]

It seems unlikely that any generalisation might profitably be extended from iron couples to other metal systems, although Ahrland and Chatt,[12] studying covalent platinum complexes, put forward the general rule that increase in ligand donor strength, either σ or π, increases the stability of the higher valency state. This rule is considered to apply only to *covalent* complexes. For platinum complexes the rule is based on comparisons of potentials for couples of the type L_2PtCl_4–L_2PtCl_2 which can be considered as: 1, between one pair of *cis–cis* and one pair of *trans–trans* complexes; or 2, between pairs of *trans*-complexes which have different L groups. Objection can be raised to interpretation of the relative values of these potentials solely in terms of electronic effects. The difference in redox potential between the *cis–cis* and *trans–trans* couple is only 18 mv, *i.e.*, a change of *ca.* 2 in the ratio of the stability constants. The entropy changes due to statistical differences, although in the wrong direction, are of this magnitude, even if steric effects are ignored. In the comparison of the three *trans–trans* couples the ligands chosen were 4-*n*-pentylpyridine, tri-*n*-propylphosphine, and di-*n*-propyl sulphide. These differ greatly in size, so steric effects could be important, and we consider that the above generalisation needs more detailed confirmation even though it may well apply in the case of the platinum couples. A second criticism of this generalisation, deduced from the study of one set of metal complexes, applies when other cations are considered. For example, the redox potential of the cobaltic–cobaltous couple in water is +1·80 v, but the cobalt–cyanide couple has a potential less than −0·8 v. These data are to be contrasted with the potentials of the ferric–ferrous hydrate couple (+0·77 v) and cyanide couple (+0·36 v). The smaller change in the iron than the cobalt couple can be regarded as due to stabilisation of the particular electronic configuration common to both ferrous and cobaltic in inner-orbital complexes. Similarly, the difference in potential between the manganic–manganous hydrate couple (+1·50 v) and cyanide couple (+0·22 v) can be regarded as due to the lack of stability of inner-orbital complexes of manganous, as of ferric, owing to the stability of the half-filled shell. Such specific effects demand an enquiry into the individual metal couples. Moreover, the dependence of complex stability upon changes in σ or π character of the ligand, even if attention is restricted to either inner- or outer-orbital complexes, has not been sufficiently studied to allow confident predictions from the case of one metal. The cyanide couples and pyridine *meso*porphyrin couples of three cations [16] are shown for comparison in Table 2. All the complexes are of the inner-orbital type, and it is difficult to see how the differences in potential can be accounted for without reference to specific electron configurations.

TABLE 2. *Potentials in* mv.

	Mn^{III}–Mn^{II}	Fe^{III}–Fe^{II}	Co^{III}—Co^{II}
$(CN)_6$	220	360	−800
*meso*Porphyrin(pyridine)$_2$	−387	−63	−265

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[16] Martell and Calvin, "The Chemistry of the Metal Chelates," Prentice-Hall Inc., New York, 1953, p. 377.