242. *Iron–Tartrate Complexes.*
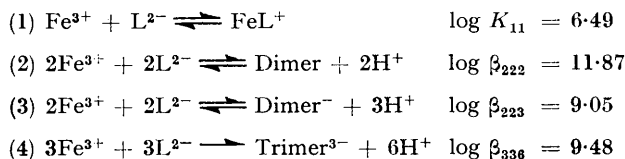
By C. F. Timberlake.

Complex-formation between ferric ions (Fe^{3+}) and excess tartaric acid (H_2L), in acid solutions at 20° and with $I = 0.1M$ ($NaClO_4$), has been studied by potentiometric, oxidation–reduction potential, colorimetric, and electrophoretic measurements. Results were consistent with the following four reactions, for which equilibrium constants were calculated, *viz.*,

$$(1)\ Fe^{3+} + L^{2-} \rightleftharpoons FeL^+ \qquad \log K_{11} = 6.49$$

$$(2)\ 2Fe^{3+} + 2L^{2-} \rightleftharpoons Dimer + 2H^+ \qquad \log \beta_{222} = 11.87$$

$$(3)\ 2Fe^{3+} + 2L^{2-} \rightleftharpoons Dimer^- + 3H^+ \qquad \log \beta_{223} = 9.05$$

$$(4)\ 3Fe^{3+} + 3L^{2-} \longrightarrow Trimer^{3-} + 6H^+ \qquad \log \beta_{336} = 9.48$$
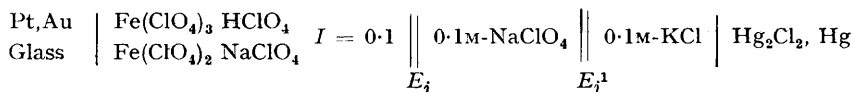
The mole ratio of iron(III) to tartrate in the complexes was unity, so that their distribution with pH depends only upon the total amount of iron(III) present. The monomer FeL^+ is believed to be quadridentate. Possible structures for the other complexes are briefly discussed. The stability constant of the ferrous tartrate complex was obtained by an ion-exchange method [$\log K(Fe^{2+}L) = 2.24$].

ALTHOUGH iron(III)–tartrate complexes have been studied for many years there has been little agreement in the findings obtained. Work before 1947 was summarised by Bobtelsky and Jordan.[1] These authors themselves suggested that complexes Fe_2L_3 and $Fe_3L_2^{5+}$, where tartaric acid is regarded as H_2L, could exist depending upon the experimental conditions. More recently, Green and Parkins[2] concluded, as a result of oxidation–reduction potential measurements, that solutions of iron(III) and tartrate below pH 4 contain two complexes in equilibrium, *viz.*, $Fe(H_3L) \rightleftharpoons (H_3L)Fe(H_2L)^{2-}$, where tartaric acid is regarded as H_4L. We have also investigated iron(III)–tartrate complexes in acid solutions by a number of methods, including oxidation–reduction potential measurements. Our results suggest that dimeric and trimeric complexes can be formed in addition to a monomer. Although the solutions investigated generally contained a large excess of tartrate over iron(III), a mole ratio of unity occurred in the complexes.

EXPERIMENTAL

Ferric perchlorate was made by Perrin's method.[3] Ferric perchlorate solutions were analysed for iron by titration with standard ethylenediaminetetra-acetate using Variamine Blue as indicator,[4] and for excess of perchloric acid by passage through a column of Amberlite IR-120 (H^+ form). Solutions of ferrous perchlorate, prepared by double decomposition between barium perchlorate and ferrous sulphate, were standardised with potassium permanganate. No appreciable oxidation occurred during several weeks if sufficient acid ($0.1N$-$HClO_4$) was present. Excess of perchloric acid was determined with Amberlite IR-120 (H^+ form). Sodium perchlorate was made by the exact neutralisation of perchloric acid with sodium carbonate. Analytical grade (+)-tartaric acid was used without further purification.

All measurements were carried out at 20° on solutions containing sodium perchlorate added in amounts calculated to give an ionic strength of $0.1M$. For the potentiometric investigations a cell similar to that described by Anderegg[5] was used.

$$\begin{array}{c|c|c|c|c} \text{Pt,Au} & Fe(ClO_4)_3\ HClO_4 & & 0.1M\text{-}NaClO_4 & 0.1M\text{-}KCl & Hg_2Cl_2,\ Hg \\ \text{Glass} & Fe(ClO_4)_2\ NaClO_4 & I = 0.1 & & \\ & & & E_j \qquad\qquad E_j^1 & \end{array}$$

[1] Bobtelsky and Jordan, *J. Amer. Chem. Soc.*, 1947, **69**, 2286.
[2] Green and Parkins, *J. Phys. Chem.*, 1961, **65**, 1658.
[3] Perrin, *J.*, 1958, 3120.
[4] Schwarzenbach, "Complexometric Titrations," Methuen, London, 1957, p. 78.
[5] Anderegg, *Helv. Chim. Acta*, 1960, **43**, 1535.

The potential E (mv) is given by

$$E = E_0 + E_j + 58.16 \log ([Fe^{3+}]/[Fe^{2+}]) \qquad (1)$$

where
$$E_0 = E^0(Fe^{3+}, Fe^{2+}) - E(0.1\text{N-Cal}) + E_j^1$$

E_j was calculated from the Henderson equation, $E_j = 58.16 \log (1 + 26.6[H])$. E_0 increased with decreasing pH and assumed the constant value of 406.4 mv at low pH (1.1—1.4). pH was defined as $-\log_{10} [H^+]$. The glass electrode was standardised daily with perchloric acid;[6] pH values below 3 were corrected for the liquid-junction potential E_j by using the relationship $\Delta pH = E_j/58.16$. pH was measured with an E.I.L. C33B pH-meter and the potentials with a Doran Universal D.C. Potentiometer calibrated to 0.1 mv. The water-jacketed titration vessel held 100 ml. of solution which was stirred magnetically and also by a stream of purified nitrogen which maintained an inert atmosphere in the solution and flask. The nitrogen was purified by passage through Fieser's solution, dilute alkali, dilute sulphuric acid, and water, The titration vessel was covered with black paper and cloth; if this precaution was not taken the potentials fell rapidly owing to photochemical reduction of the ferric complexes to ferrous ions. Sodium hydrogen carbonate (0.1 and 0.2M) was used to alter and adjust the pH values.

At the lower pH values, the potential was usually taken as the mean of the readings of a gold and of a platinum electrode immersed in the solution. Occasionally, a platinum electrode was sluggish and approached the reading of the gold electrode only slowly; in these cases the potential of the gold electrode was taken. At pH values above 3.5, the platinum electrodes became unreliable and two gold electrodes were employed. For 67 measurements, the average difference between their readings was 0.36 mv. Their mean value was therefore <0.2 mv different from the reading of either, and within experimental error. Equilibrium was assumed to be reached when the potentials altered by not more than 0.2 mv in 5 min. Generally each measurement occupied some 10—15 min. except at pH values near 5, when the solutions were less buffered and attainment of constant pH and potential values was much slower. Before use, electrodes were dipped into concentrated nitric acid and washed thoroughly with distilled water.

To check the accuracy of our measurements, some previously published work was repeated and is described here in some detail, since our findings with the iron tartrates differ from those of Green and Parkins.[2]

Tests on Solid Electrodes.—(a) *Titration of* Fe^{2+} *with* Fe^{3+}. Ferrous perchlorate solution (100 ml.; 5×10^{-4}M) was titrated at constant pH with ferric perchlorate (0.01 and 0.1M) from $[Fe^{III}]_t$ 0.025×10^{-3} to 10^{-3}M. Constant values of E_0 were obtained[5] and a plot of E against $-58.16 \log [Fe^{III}]_t$ was linear[7] with a slope of 1.0, as expected for mononuclear iron.

(b) *Ethylenediaminetetra-acetate* (EDTA). Tests were made with EDTA using both the discontinuous method of oxidising ferrous EDTA with iodine, originally used by Schwarzenbach,[8] and the continuous titration method used by later workers.[9,10] With most of the electrodes tried the mid-point potential in the pH range 4—6 was -217.9^{+3}_{-2} mv (mean of 12 determinations) against the 0.1N-calomel electrode used, or $+116.7^{+3}_{-2}$ mv on the hydrogen scale (assuming the normal potential of Fe^{3+}/Fe^{2+} to be 741.0 mv[8]), a value in good agreement with previous findings.[8-10] Some platinum electrodes occasionally gave a higher reading and were not used further.

(c) *Picolinic acid.* Solutions of ferrous perchlorate and excess of picolinic acid (HL) were titrated with ferric perchlorate at the constant pH values 2.46 and 4.82. The acid ionisation constant and stability constants of the ferrous complexes were assumed.[11] The distribution of the ferric complexes FeL_2 and FeL_2OH at pH 2.46 was calculated from their known stability constants. From our measured potentials, we confirmed that the complexes were monomers at pH 2.46 with $\log \beta_2 = 12.88 \pm 0.03$ and $\log \beta_{121} = 23.92 \pm 0.03$, in good agreement with Anderegg's[5] values of $\log \beta_2 = 12.80$ and $\log \beta_{121} = 23.84$ obtained in 0.1M-sodium nitrate. At pH 4.82, a plot of $[Fe^{III}]_t/[Fe^{3+}][L]^2[OH]$ against $2[Fe^{3+}][L]^2[OH]$ was linear, confirming

[6] Anderegg, *Helv. Chim. Acta*, 1961, **44**, 1673.
[7] Perrin, *J.*, 1959, 1710.
[8] Schwarzenbach and Heller, *Helv. Chim. Acta*, 1951, **34**, 576.
[9] Tomkinson and Williams, *J.*, 1958, 2013.
[10] Bond and Jones, *Trans. Faraday Soc.*, 1959, **55**, 1310.
[11] Andreregg, *Helv. Chim. Acta*, 1960, **43**, 414.

that only complexes FeL_2OH and $Fe_2L_4(OH)_2$ were present. From the intercept, $\log \beta_{121} = 23 \cdot 92$, and from the slope, $\log \beta_{242} = 50 \cdot 72$, in excellent agreement with Anderegg's findings of $\log \beta_{121} = 23 \cdot 84$ and $\log \beta_{242} = 50 \cdot 76$, obtained in 0·1M-sodium nitrate.

(d) *Dipicolinic acid.* A solution of ferrous perchlorate and excess of dipicolinic acid was titrated with ferric perchlorate at constant pH 3·93. Assuming the values of the acid ionisation constants and stability constants of the ferrous complexes,[11] the monomer FeL_2 was shown to be present, $\log \beta_2^{III} = 16 \cdot 74 \pm 0 \cdot 01$, in good agreement with $\log \beta_2^{III} = 16 \cdot 63$ obtained previously in 0·1M-sodium nitrate.[12]

(e) *Acetate.* For this system the solutions to be investigated were connected through an ammonium nitrate (1·60M)–sodium nitrate (0·20M) bridge to a saturated calomel electrode (Perrin[3]), and the glass electrode was standardised with 0·05M-potassium hydrogen phthalate. E_0 which equals $E^0(Fe^{3+}, Fe^{2+}) - E(sat. cal.)$ was 496·3 mv in M-sodium perchlorate. Using Perrin's methods it was confirmed that the complex present from pH 1·90 to 3·31 at very high acetate concentrations was $Fe_3L_6(OH)_2$. Log β found was $20 \cdot 0^{+0 \cdot 16}_{-0 \cdot 22}$ (mean of 26 values), in good agreement with the mean value of 19·9 found by Perrin.[7]

Ionisation Constants of Tartaric Acid.—The acid ionisation constants of (+)-tartaric acid were determined by titration of 10^{-3}M-acid (100 ml.) with 0·1N-sodium hydroxide. Analysis of the data by the methods of Speakman,[13] Schwarzenbach *et al.*,[14] and Noyes[15] gave $pK_{c1} = 2 \cdot 80 \pm 0 \cdot 03$ and $pK_{c2} = 3 \cdot 96 \pm 0 \cdot 02$.

Ferrous Tartrate.—The depression in pH which occurred on titration of ferrous perchlorate and tartaric acid with alkali was very small, and only an approximate value of $\log K(Fe^{2+}L)$ could be obtained. A more suitable method was considered to be the ion-exchange method of Schubert.[16] The ion-exchange resin Amberlite CG120 (H^+ form) (100—200 mesh) was washed with 6% nitric acid, to remove iron, converted into the Na^+ form, and equilibrated for a few hours with excess of 0·1M-sodium perchlorate adjusted to pH 3·5. After filtration, the resin was washed thoroughly with water, and air-dried. A sample was dried to constant weight *in vacuo* at 100°, and the remainder was stored in a closed bottle. The speed of equilibration was first tested under our experimental conditions by measuring the potential of a mixture of Fe^{3+} and Fe^{2+} in the presence of the resin while maintaining constant pH. The potential fell to a constant value, indicating equilibrium conditions, after $1\frac{1}{2}$—2 hr.

The results are shown in Table 1. The solutions containing resin were stirred and kept in

TABLE 1.

Determination of the stability constant of ferrous tartrate.

$102 \cdot 6 \pm 1$ ml. of 0·1M-NaClO$_4$ containing $1 \cdot 86 \times 10^{-4}$M-Fe(ClO$_4$)$_2$ with and without tartrate at constant pH 3·63.

Expt.	Resin (mg.) *	$10^3[L]_t$	E	K_d	$(K_d^0/K_d) - 1$	$-\log [L]$	$\log K(Fe^{2+}L)$	
1	—	—	0·656	—	—	—	—	
2	100	—	0·262	1528 (K_d^0)	—	—	—	
3	100	4·89	0·308	1160	0·317	2·85	2·35	
4	100	6·82	0·323	1057	0·445	2·70	2·35	
5	100	9·75	0·317	1097	0·393	2·55	2·14	
6	100	14·6	0·339	959	0·594	2·37	2·14	
7	100	19·5	0·361	838	0·824	2·24	2·16	Mean 2·24

* Moisture-free basis.

an inert atmosphere at constant pH for 2 hr. Aliquot parts were withdrawn from the titration vessel by means of pipettes, and filtered through glass wool; ferrous ion was determined colorimetrically using 4,7-diphenyl-1,10-phenanthroline.[17] The stability constant of ferrous tartrate was calculated as follows.

$$K(Fe^{2+}L) = [Fe^{2+}L]/[Fe^{2+}][L] = \{(K_d^0/K_d) - 1\}/[L] \qquad (2)$$

[12] Anderegg, *Helv. Chim. Acta*, 1962, **45**, 1643 (footnote).
[13] Speakman, *J.*, 1940, 855.
[14] Schwarzenbach, Willi, and Bach, *Helv. Chim. Acta*, 1947, **30**, 1303.
[15] Noyes, *Z. phys. Chem. (Leipzig)*, 1893, **11**, 495; cf. Britton, " Hydrogen Ions," Vol. 1, Chapman and Hall, London, 1955, p. 218.
[16] Schubert in " Methods of Biochemical Analysis," ed. Glick, Vol. 3, Interscience, London, **1956**, p. 247.
[17] Timberlake and Hunt, *Ann. Report Long Ashton Res. Stn.*, 1960, 147.

where $K_d{}^0$ and K_d are the distribution coefficients in the absence and in the presence of tartaric acid, and $[L] = [L]_t/\alpha$, where

$$\alpha = 1 + [H]/K_{c2} + [H]^2/K_{c1}K_{c2} \qquad (3)$$

The variation in log $K(Fe^{2+}L)$ corresponds to an error of about $\pm 3\%$ in measuring the extinctions of the solutions. Within these limits of error a plot of log $\{(K_d{}^0/K_d) - 1\}$ against log $[L]$ was approximately unity, indicating that higher complexes such as FeL_2 could be neglected. From a plot of $1/K_d$ against $[L]$, $K_d{}^0$ was 1561 ± 46, in good agreement with the value of 1528 found (Table 1).

Ferric–Tartrate Complexes.—Oxidation–reduction potential measurements. The possibility of the formation of polynuclear complexes was first investigated by measuring the potentials of solutions of constant pH and nearly constant tartrate and ferrous ion concentrations, but containing variable amounts of ferric ion. As shown by Anderegg,[5] the difference in potential (ΔE) produced by doubling the total ferric concentration ($[Fe^{III}]_t$) indicates the degree of polymerisation. The differences found for an increase of $[Fe^{III}]_t$ from 2×10^{-4} to 4×10^{-4}M, with total tartrate concentration ($[L]_t$) equal to 10^{-2}M and total ferrous concentration ($[Fe^{II}]_t$) equal to 2×10^{-4}M, at a number of pH values, were as follows:

pH	1·49	1·92	2·37	3·06	3·51	3·85	4·06	4·47	4·95
ΔE (mv)	16·6	14·9	11·6	10·5	8·8	7·9	7·4	6·9	5·5

A transition from monomeric ($\Delta E = 17\cdot5$ mv), through dimeric ($\Delta E = 8\cdot75$ mv), to trimeric complexes ($\Delta E = 5\cdot8$ mv) with increasing pH was indicated.

Estimates of the average number of ligand ions (n) in the complexes were then made by potential measurements at constant pH, $[Fe^{III}]_t$, and $[Fe^{II}]_t$, but with varying amounts of

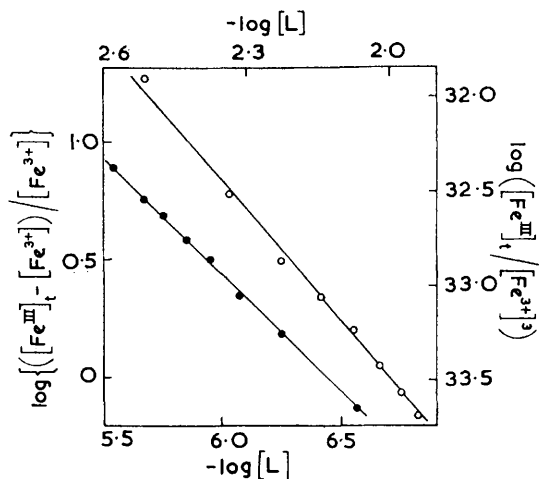Fig. 1. Determination of the number of tartrate radicals in the complexes.

● pH = 1·48; $[Fe^{III}]_t = 1\cdot98 \times 10^{-4}$M $= [Fe^{II}]_t$; $[L]_t$ varied in the range 0·97—19·5 $\times 10^{-3}$M.

○ pH = 4·91; $[Fe^{III}]_t = [Fe^{II}]_t$, varied in the range 8·85—6·78 $\times 10^{-4}$M; $[L]_t$ varied in the range 5·69—14·8 $\times 10^{-3}$M.

Scales at the top and at the right are for the open circles.

tartrate. Assuming a monomer to exist at pH 1·48 and a trimer at pH 4·91, plots of log $([Fe^{III}]_t - [Fe^{3+}])/[Fe^{3+}]$ and log $([Fe^{III}]_t/[Fe^{3+}]^3)$, respectively, against log $[L]$ were found to be linear at these pH values, with slopes giving n as 1·0 and 3·0, respectively[7] (Fig. 1). The formation of a complex FeL at pH $\sim$1·5 and Fe_3L_3 at pH $\sim$5, for our experimental conditions was indicated. Confirmation that polymerisation did not go beyond the trimer stage is shown by the constancy of $[Fe^{III}]_t/[Fe^{3+}]^3[L]^3$ for $[Fe^{III}]_t$ above 2×10^{-4}M (Table 2), when $[Fe^{III}]_t$ was varied at constant pH 4·95. At lower pH the appropriate quantity ($[Fe^{III}]_t - [Fe^{3+}])/[Fe^{3+}][L]$ or $[Fe^{III}]_t/[Fe^{3+}]^2[L]^2$ always increased with increasing $[Fe^{III}]_t$, showing that the complexes became more polymeric during a titration. These quantities were constant, however, when $[L]_t$ was varied at constant pH and $[Fe^{III}]_t$. This is to be expected for a system in which the mole ratio of ferric to tartrate remains at unity. With a mixture of FeL and Fe_2L_2 complexes, and neglecting $[Fe^{3+}]$, it can be shown that $[Fe^{3+}][L] = \{(K_{11}{}^2 + 8K_{11}[Fe^{III}]_t)^{\frac{1}{2}} - K_{11}\}/4K_{22}$, where K_{11} and K_{22} are constant at constant pH. Thus, $[Fe^{3+}][L]$ is independent of $[L]$, and is constant provided that $[Fe^{III}]_t$ is constant. Similarly, it can be shown that,

TABLE 2.

Titration of tartrate with ferric perchlorate at constant pH.

Initial volume = 100 ml.; pH = 4·95; ferric perchlorate = 0·106M.

Fe(ClO$_4$)$_3$ (ml.)	10^3M-[Fe^{III}]$_t$	10^3M-[L]$_t$	10^3M-[Fe^{II}]$_t$	E (mv)	$-\log$ [L]	$-\log$ [Fe^{3+}]	$\log$ ([Fe^{III}]$_t$/[Fe^{3+}]^3[L]^3)
0·1	0·104	9·80	0·208	−77·0	2·06	12·41	39·40
0·2	0·207	9·76	0·207	−73·2	2·06	12·33	39·48
0·4	0·401	9·66	0·205	−67·7	2·08	12·23	39·53
0·6	0·609	9·56	0·203	−64·6	2·09	12·17	39·57
0·8	0·804	9·47	0·201	−61·6	2·11	12·12	39·58
1·2	1·186	9·30	0·198	−57·0	2·13	12·03	39·57
1·6	1·552	9·13	0·194	−53·8	2·16	11·97	39·48
2·2	2·074	8·88	0·189	−49·0	2·21	11·87	39·56

with a mixture of Fe$_2$L$_2$ and Fe$_3$L$_3$ complexes, [Fe^{3+}][L] depends only on [Fe^{III}]$_t$, and constants K_{22} and K_{33}. Representative figures are as follows:

| [L]$_t$/[Fe^{III}]$_t$		5	10	15	20	30	40	45	50
	pH 2·37	10·57	10·59	—	10·56	---	10·55	—	10·57
$-\log$ [Fe^{3+}][L]	pH 3·06	11·14	11·15	—	11·18	11·19	11·22	---	11·22
	pH 4·04	—	—	12·60	12·62	12·64	12·67	12·68	—
	pH 4·54	—	—	13·53	13·54	13·56	13·57	13·60	—

At the two highest pH values, the slight decrease in log [Fe^{3+}][L] can be partly accounted for by a slight decrease in [Fe^{III}]$_t$ during the experiments.

If [Fe^{3+}][L] is constant, the distribution of complexes and the average number (y) of ferric ions in the complexes should also remain constant, when [L]$_t$ is varied at constant pH and [Fe^{III}]$_t$. The equation developed by Perrin,[7] and applied by him to a single complex, should now be applicable to this mixture of complexes, *viz.*,
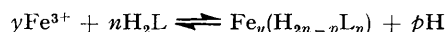
$$\log ([Fe^{III}]_t - [Fe^{3+}]) - y \log[\text{ } Fe^{3+}] = n \log [L] + y\, pH + \log K + \log y$$

where $K = [Fe_yL_n]/[Fe^{3+}]^y[L]^n$. Using the appropriate value of y, the same value of n was obtained from the slope of the linear plot of the left-hand side of the equation against log [L] for several pH values.

The results of experiments made at constant pH were analysed, therefore, using equations which assumed that FeL and Fe$_2$L$_2$ existed together at the lower pH values and Fe$_2$L$_2$ and Fe$_3$L$_3$ at the higher pH values. Formation constants designated by K were obtained; where these varied with pH, constant values of equilibrium constants β were sought by multiplying by [H] and by powers of [H]. Hydrogen ions liberated during complex-formation could result from (*a*) ionisation of co-ordinated water molecules, giving hydroxylated complexes,

$$y Fe^{3+} + nL + x H_2O \rightleftharpoons Fe_yL_n(OH)_x + xH$$
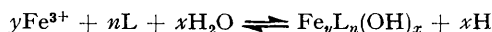
or (*b*) ionisation of the alcoholic groups of tartaric acid

$$y Fe^{3+} + n H_2L \rightleftharpoons Fe_y(H_{2n-p}L_n) + pH$$

where tartaric acid is regarded as H$_4$L, or (*c*) a combination of both schemes.

Since it is uncertain, at this stage, how the protons are liberated, the following scheme is adopted, which makes no assumptions as to the type of complex-formation and which allows tartaric acid to be represented in its more usual form, H$_2$L.

$$y Fe^{3+} + nL + (H_2O) \rightleftharpoons \sum_{q=0}^{Q} Fe_yL_n(-H)_q + \sum_{q=0}^{Q} qH$$
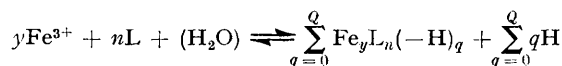
Constants obtained from measurements at constant pH are defined as

$$K_{yn} = \sum_{q=0}^{Q} [Fe_yL_n(-H)_q]/[Fe^{3+}]^y[L]^n.$$

For simplicity in presentation, however, $\sum_{q=0}^{Q} Fe_yL_n(-H)_q$ is put equal to Fe$_y$L$_n$, that is, the complexes are represented without regard to their degree of protonation, with constants

$K_{11} = [FeL]/[Fe^{3+}][L]$, $K_{22} = [Fe_2L_2]/[Fe^{3+}]^2[L]^2$, and $K_{33} = [Fe_3L_3]/[Fe^{3+}]^3[L]^3$.

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Equilibrium constants β are defined: $\beta_{ynq} = [Fe_yL_n(-H)_q][H]^q/[Fe^{3+}]^y[L]^n$.

Thus,

$$\beta_{222} = [Fe_2L_2(-H)_2][H]^2/[Fe^{3+}]^2[L]^2$$

$$\beta_{223} = [Fe_2L_2(-H)_3][H]^3/[Fe^{3+}]^2[L]^2$$

$$\beta_{336} = [Fe_3L_3(-H)_6][H]^6/[Fe^{3+}]^3[L]^3$$

The general equations used for the calculations were:

$$[Fe^{III}]_t = [Fe^{3+}] + [FeL] + 2[Fe_2L_2] + 3[Fe_3L_3] \qquad (4)$$

$$[L]_t = \alpha[L] + [FeL] + 2[Fe_2L_2] + 3[Fe_3L_3] + [Fe^{2+}L] \qquad (5)$$

$$[Fe^{II}]_t = [Fe^{2+}] + [Fe^{2+}L] = [Fe^{2+}]\{1 + K(Fe^{2+}L)[L]\} \qquad (6)$$

[L] was obtained from $[L] = ([L]_t - [Fe^{III}]_t - [Fe^{2+}L])/\alpha$. $[Fe^{2+}L]$ in eqn. (5) was negligible except at high $[Fe^{II}]_t$ and high pH.

From a knowledge of $[Fe^{2+}]$ and E, $[Fe^{3+}]$ was calculated from eqn. (1). The hydrolysis products of ferric iron were assumed to be negligible, since the ferric–tartrate complexes were sufficiently strong. The results indicated that four complexes were formed, *viz.*, FeL, $Fe_2L_2(-H)_2$, $Fe_2L_2(-H)_3$, and $Fe_3L_3(-H)_6$. The method of evaluation was as follows.

Complexes $Fe_3L_3(-H)_6$ and $Fe_2L_2(-H)_3$. A summary of the results of 8 experiments is given in Table 3.

TABLE 3.

Evaluation of β_{336} and β_{223} for the complexes $Fe_3L_3(-H)_6$ and $Fe_2L_2(-H)_3$.

Expt.	Method	Readings	pH	$\log K_{22}$	$\log K_{22}[H]^3$	$\log K_{33}$	$\log K_{33}[H]^6$
1	vary $[Fe^{III}]_t$	6	4·95	—	—	39·07	9·37
2	,,	10	4·47	22·40	8·99	36·31	9·49
3	,,	11	4·06	21·22	9·04	33·82	9·46
4	,,	11	3·85	20·60	9·05	32·59	9·49
5	vary $[L]_t$	7	4·91	—	—	39·05	9·62
6	,,	7	4·54	21·57	8·96	36·70	9·49
7	,,	7	4·04	21·25	9·14	33·73	9·54
8	vary pH	9	4·00—4·81	—	9·25	—	9·34
					Mean 9·09		Mean 9·48

Experiments 1 and 5. In these experiments it was demonstrated, as already mentioned, that a 3 : 3 complex was the only one present in solution. K_{33} was therefore calculated directly from $K_{33} = [Fe^{III}]_t/3[Fe^{3+}]^3[L]^3$.

Experiments 2—4. Assuming $[Fe^{III}]_t = 2[Fe_2L_2] + 3[Fe_3L_3]$, then

$$[Fe^{III}]_t/[Fe^{3+}]^2[L]^2 = 2K_{22} + 3[Fe^{3+}][L]K_{33}.$$

Plots of $[Fe^{III}]_t/[Fe^{3+}]^2[L]^2$ against $[Fe^{3+}][L]$ were linear (Fig. 2). K_{22} was obtained from the intercept/2 and K_{33} from the slope/3.

Experiments 6 and 7. From the preceding data y was calculated at every pH and $[Fe^{III}]_t$ value, using the equation

$$y = [Fe^{III}]_t/(K_{22}[Fe^{3+}]^2[L]^2 + K_{33}[Fe^{3+}]^3[L]^3).$$

Graphs of y against pH for the various values of $[Fe^{III}]_t$ enabled y to be obtained at pH values 4·54 and 4·04 and the appropriate values of $[Fe^{III}]_t$. Then

$$K_{22} = (3 - y)[Fe^{III}]_t/y[Fe^{3+}]^2[L]^2 \text{ and } K_{33} = (y - 2)[Fe^{III}]_t/y[Fe^{3+}]^3[L]^3.$$

Since K_{22} and K_{33} varied with pH they were multiplied by powers of [H]. Best constancy was shown by $K_{22}[H]^3$ and $K_{33}[H]^6$. That only complexes $Fe_2L_2(-H)_3$ and $Fe_3L_3(-H)_6$ were present was confirmed by the following experiment at various pH values.

Experiment 8. Assuming $[Fe^{III}]_t = 2[Fe_2L_2(-H)_3] + 3[Fe_3L_3(-H)_6]$ then

$$[Fe^{III}]_t[H]^3/[Fe^{3+}]^2[L]^2 = 2\beta_{223} + 3[Fe^{3+}][L]/[H]^3\beta_{336}.$$

A plot of $[Fe^{III}]_t[H]^3/[Fe^{3+}]^2[L]^2$ against $[Fe^{3+}][L]/[H]^3$ was linear (Fig. 3). β_{223} was obtained from the intercept/2 and β_{336} from the slope/3. From the preceding experiments, mean values

of log $\beta_{336} = 9.48$ and log $\beta_{223} = 9.09$ were calculated. The value of $K_{22}[\mathrm{H}]^3$ at pH 3·85 was excluded because of slight interference from $\mathrm{Fe_2L_2(-H)_2}$.
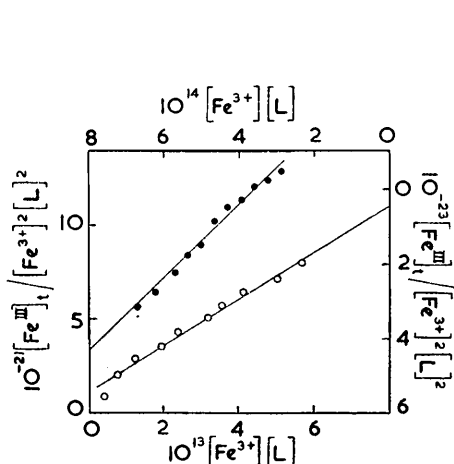

FIG. 2. Determination of K_{22} and K_{33} by varying $[\mathrm{Fe^{III}}]_t$ at constant pH.

● pH = 4·06; $[\mathrm{Fe^{III}}]_t$ 0·103—3·43 × 10^{-3}M; $[\mathrm{Fe^{II}}]_t$ 2·05—1·71 × 10^{-4}M; $[\mathrm{L}]_t$ 9·76—8·14 × 10^{-3}M.

○ pH = 4·47; $[\mathrm{Fe^{III}}]_t$ 0·016—3·23 × 10^{-3}M; $[\mathrm{Fe^{II}}]_t$ 2·12—1·80 × 10^{-4}M; $[\mathrm{L}]_t$ 19·96—16·91 × 10^{-3}M.

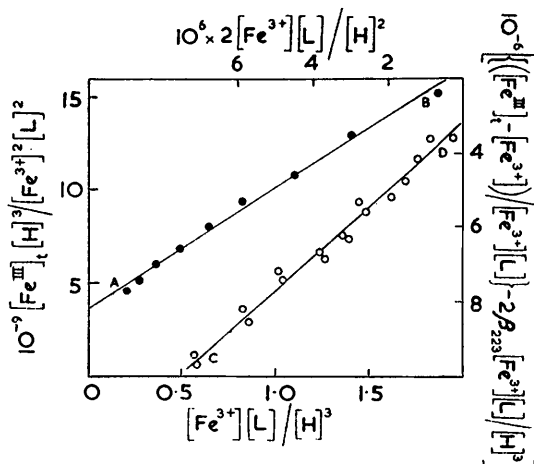Scales at the top and at the right are for the open circles.

FIG. 3. Evaluation of equilibrium constants by varying the pH.

● β_{336} and β_{223}; pH increased from 4·00 (A) to 4·81 (B); $[\mathrm{Fe^{III}}]_t = [\mathrm{Fe^{II}}]_t = 2.05$—1·96 × 10^{-4}M; $[\mathrm{L}]_t = 9.63$—9·25 × 10^{-3}M.

○ K_{11} and β_{222}; pH decreased from 2·69 (C) to 1·85 (D); $[\mathrm{Fe^{III}}]_t = [\mathrm{Fe^{II}}]_t = 2.03$—1·81 × 10^{-4}M; $[\mathrm{L}]_t = 10.0$—8·93 × 10^{-3}M.

Scales at the top and at the right are for the open circles.

Complexes FeL, $\mathrm{Fe_2L_2(-H)_2}$ and $\mathrm{Fe_2L_2(-H)_3}$. The results are summarised in Table 4. It was assumed that the amount of complex $\mathrm{Fe_3L_3(-H)_6}$ was negligible under the conditions of Experiments 9—16.

TABLE 4.

Evaluation of K_{11}, β_{222}, and β_{223}, for the complexes FeL, $\mathrm{Fe_2L_2(-H)_2}$, and $\mathrm{Fe_2L_2(-H)_3}$.

Expt.	Method	Readings	pH	log K_{11}	log K_{22}	log $K_{22}[\mathrm{H}]^2$	log $K_{22}[\mathrm{H}]^3$	log β_{222}	log β_{223}
9	vary $[\mathrm{Fe^{III}}]_t$	5	1·49	6·38	(15·19)	(12·21)	—	—	—
10	,,	7	1·92	6·47	15·81	11·97	10·05	11·92	—
11	,,	5	2·37	6·58	16·72	11·98	9·61	11·82	—
12	vary $[\mathrm{L}]_t$	9	1·48	6·42	—	—	—	—	—
13	,,	7	2·37	6·57	16·82	12·08	9·71	11·96	—
14	vary pH	17	1·85—2·69	6·50	—	12·11	—	11·94	—
15	vary $[\mathrm{Fe^{III}}]_t$	10	3·06	6·59	18·27	12·16	9·10	11·72	8·89
16	vary $[\mathrm{L}]_t$	9	3·06	6·64	18·33	12·22	9·16	11·78	8·95
17	vary $[\mathrm{Fe^{III}}]_t$	6	3·51	—	—	—	—	—	8·98
18	,,	8	3·54	—	—	—	—	—	9·02
19	,,	11	3·85	—	—	—	—	—	9·01
20	vary $[\mathrm{L}]_t$	9	3·56	—	—	—	—	—	9·10

Experiments 9—11. Assuming $[\mathrm{Fe^{III}}]_t = [\mathrm{Fe^{3+}}] + [\mathrm{FeL}] + 2[\mathrm{Fe_2L_2}]$, then

$$([\mathrm{Fe^{III}}]_t - [\mathrm{Fe^{3+}}])/[\mathrm{Fe^{3+}}][\mathrm{L}] = K_{11} + 2[\mathrm{Fe^{3+}}][\mathrm{L}]K_{22}.$$

Plots of $([\mathrm{Fe^{III}}]_t - [\mathrm{Fe^{3+}}])/[\mathrm{Fe^{3+}}][\mathrm{L}]$ against $[\mathrm{Fe^{3+}}][\mathrm{L}]$ were linear. K_{11} was obtained from the intercept, and K_{22} from the slope/2.

Experiments 12 and 13. From the preceding data, y was calculated at every pH and $[\mathrm{Fe^{III}}]_t$ from

$$y = ([\mathrm{Fe^{III}}]_t - [\mathrm{Fe^{3+}}])/(K_{11}[\mathrm{Fe^{3+}}][\mathrm{L}] + K_{22}[\mathrm{Fe^{3+}}]^2[\mathrm{L}]^2).$$

Graphs of y against pH were then made which enabled y to be estimated at the appropriate pH and $[Fe^{III}]_t$ values. Then

$$K_{11} = (2 - y)([Fe^{III}]_t - [Fe^{3+}])/y[Fe^{3+}][L]$$

and

$$K_{22} = (y - 1)([Fe^{III}]_t - [Fe^{3+}])/y[Fe^{3+}]^2[L]^2$$

Experiments 9—13 show that K_{11} was reasonably constant, but that K_{22} varied with pH. Best constancy was shown by $K_{22}[H]^2$. The dimeric complex mainly present under these conditions was therefore $Fe_2L_2(-H)_2$. In calculating β_{222} allowance was made for the presence of small amounts of $Fe_2L_2(-H)_3$, using the mean value of log $\beta_{223} = 9\cdot09$ previously obtained (Table 3), as follows

$$\beta_{222} = \{K_{22} - (\beta_{223}/[H]^3)\}[H]^2$$

Experiment 14. Assuming $[Fe^{III}]_t = [Fe^{3+}] + [FeL] + 2[Fe_2L_2(-H)_2] + 2[Fe_2L_2(-H)_3]$

$$([Fe^{III}]_t - [Fe^{3+}])/[Fe^{3+}][L] - 2[Fe^{3+}][L]\beta_{223}/[H]^3 = K_{11} + 2[Fe^{3+}][L]\beta_{222}/[H]^2$$

A plot of the left-hand side of the equation against $2[Fe^{3+}][L]/[H]^2$ was linear (Fig. 3). K_{11} was obtained from the intercept, and β_{222} from the slope.

From the preceding 6 experiments, mean values of log $K_{11} = 6\cdot49$ and log $\beta_{222} = 11\cdot91$ were calculated. The values of β_{222} at the lowest pH values were not included in the mean since $[Fe_2L_2(-H)_2]$ was very small.

Experiments 15 and 16. At pH $3\cdot06$, the data analysed by the above methods showed that the complexes present were mainly $Fe_2L_2(-H)_2$ and $Fe_2L_2(-H)_3$, with a lesser amount of FeL. Further values of β_{222} and β_{223} were obtained using the mean values of log $\beta_{222} = 11\cdot91$ and log $\beta_{223} = 9\cdot09$, and the relationship

$$[Fe_2L_2(-H)_2] : [Fe_2L_2(-H)_3] = \beta_{222} : \beta_{223}/[H]$$

The values of log K_{11}, also obtained, agreed with those found at lower pH values but were not included in the overall mean since [FeL] was small (approximately $[Fe^{III}]_t/7$).

Experiments 17—20. Using mean values of log $K_{11} = 6\cdot49$, log $\beta_{222} = 11\cdot87$ (including values at pH $3\cdot06$), and log $\beta_{336} = 9\cdot48$, additional values of log β_{223} were obtained at pH values where this complex predominates, from the equation

$$\beta_{223} = \left\{[H]^3\left(\frac{[Fe^{III}]_t}{[Fe^{3+}]^2[L]^2} - \frac{K_{11}}{[Fe^{3+}][L]}\right) - 2\beta_{222}[H] - \frac{3\beta_{336}[Fe^{3+}][L]}{[H]^3}\right\}\Big/2$$

Table 5 gives one example.

<div align="center">TABLE 5.</div>

<div align="center">Calculation of β_{223}.</div>

Titration of 100 ml. of $0\cdot01$M-tartrate and $2\cdot12 \times 10^{-4}$M-ferrous perchlorate with $0\cdot106$M-ferric perchlorate at constant pH $3\cdot54$. $I = 0\cdot1$M (NaClO$_4$). log $K_{11} = 6\cdot49$; $-$log $2\beta_{222}[H] = 7\cdot37$; log $\beta_{336} = 9\cdot48$.

Fe(ClO$_4$)$_3$ (ml.)	E (mv)	$-$log $[Fe^{3+}]$	$-$log $[L]$	log $[H]^3\dfrac{([Fe^{III}]_t - K_{11}[Fe^{3+}][L])}{[Fe^{3+}]^2[L]^2}$	log $\dfrac{3\beta_{336}[Fe^{3+}][L]}{[H]^3}$	log β_{223}
0·1	80·5	9·43	2·62	9·47	8·54	9·03
0·2	89·3	9·28	2·62	9·47	8·69	9·01
0·4	98·0	9·13	2·63	9·50	8·84	8·99
0·6	103·7	9·02	2·64	9·49	8·92	8·96
0·8	106·8	8·97	2·65	9·52	8·97	8·98
1·2	112·7	8·87	2·69	9·57	9·03	9·04
1·6	117·5	8·79	2·72	9·58	9·08	9·03
2·0	120·6	8·74	2·75	9·62	9·11	9·09

The following is a summary of the reactions and constants.

(1) $Fe^{3+} + L^{2-} \rightleftharpoons FeL^+$ \qquad log K_{11} (mean of 6 means) $6\cdot49 \pm 0\cdot079$

(2) $2Fe^{3+} + 2L^{2-} \rightleftharpoons Fe_2L_2(-H)_2 + 2H^+$ \qquad log β_{222} (,, ,, 6 ,,) $= 11\cdot87$

(3) $2Fe^{3+} + 2L^{2-} \rightleftharpoons Fe_2L_2(-H)_3^- + 3H^+$ \qquad log β_{223} (,, ,, 11 ,,) $= 9\cdot05$

(4) $3Fe^{3+} + 3L^{2-} \rightleftharpoons Fe_3L_3(-H)_6^{3-} + 6H^+$ \qquad log β_{336} (,, ,, 8 ,,) $= 9\cdot48 \pm 0\cdot074$

The tolerances given for K_{11} and β_{336} are 95% confidence limits to the mean of the number of mean observations.

$$(5) \quad Fe_2L_2(-H)_2 \rightleftharpoons Fe_2L_2(-H)_3^-; \quad pK_c = 2\cdot83.$$

Distribution of complexes. Since the mole ratio of iron to tartrate is unity in the complexes, it can be shown that, provided that $(L)_t$ is greater than or equal to $[Fe^{III}]_t$ and $[Fe^{3+}]$ is negligible, the distribution of complexes with pH depends only on $[Fe^{III}]_t$ and is independent of $[L]_t$. A knowledge of the constants enables such distributions to be made. Those made at $[Fe^{III}]_t = 10^{-4}M$ and $[Fe^{III}]_t = 10^{-3}M$ (Fig. 4) confirm that the assumptions made in calculating the constants were correct. The distribution at $[Fe^{III}]_t = 2 \times 10^{-2}M$, that used for the paper electrophoresis investigation, is also illustrated.

Potentiometric titration. Mixtures of disodium tartrate and ferric perchlorate in mole ratios $1:1$, $1:\frac{1}{2}$, and $1:\frac{1}{3}$ were titrated with $0\cdot1M$-sodium hydroxide. For each titration an inflection was obtained when the ratio $[NaOH]/[Fe^{III}]_t$ was 2. The liberation of $2H^+$ per iron atom is consistent with the overall equation represented by reaction (4).

Colorimetric methods. A Unicam S.P. 500 spectrophotometer was used, and solutions were kept in the dark at all times. Measurements were made at low pH using Job's method of continuous variations. Ferric iron and tartrate were mixed in the proportions $x:(1-x)$ while the sum of their concentrations was kept constant. Maximum extinction was found at $x = 0\cdot5$ at 346 and 370 mμ, confirming that iron and tartrate were combined together in a mole ratio of unity (Fig. 5). The extinction due to ferric iron alone at these wavelengths was negligible. The formation constant of FeL was determined using Agren's [18] method. Since FeL is the only complex present, it can be shown from eqns. (4) and (5) and $E = \varepsilon[FeL]$, where E is the measured extinction and ε is the molecular extinction coefficient of FeL, that

$$K_{11} = (E\alpha/\varepsilon)/\{[L]_t - (E/\varepsilon)\}\{[Fe^{III}]_t - (E/\varepsilon)\} \qquad (7)$$

When $[L]_t \gg [Fe^{III}]_t$,

$$[Fe^{III}]_t/E = (1/\varepsilon) + (\alpha/[L]_t)(1/K_{11}\varepsilon)$$

Plots of $[Fe^{III}]_t/E$ against $\alpha/[L]_t$ were linear at the two wavelengths measured (346 and 370 mμ), the intercepts and slopes giving values of $1/\varepsilon$ and $1/K_{11}\varepsilon$, respectively (Fig. 6). When $[L]_t = [Fe^{III}]_t = c$, then $c/E = (1/\varepsilon) + (\alpha/E)^{\frac{1}{2}}(1/K_{11}\varepsilon)^{\frac{1}{2}}$. Plots of c/E against $(\alpha/E)^{\frac{1}{2}}$ were linear at 346 and 370 mμ, the intercepts and slopes giving values of $1/\varepsilon$ and $(1/K_{11}\varepsilon)^{\frac{1}{2}}$, respectively (Fig. 6). The mean value of $\log K_{11}$ was $6\cdot47 \pm 0\cdot079$ (95% confidence limits to the mean of 4 observations), and the mean value of ε was 1890 at 346 mμ and 1450 at 370 mμ.

The absorption spectrum of FeL (at pH $1\cdot5$) was a smooth curve with a maximum at 346 mμ and a minimum at 304 mμ. The spectra of the ferric–tartrate complexes at some pH values higher than $1\cdot5$ are shown in Fig. 7. Excess of tartrate showed negligible absorption over the wavelength range shown. As the pH is increased, with formation of the dimers, so the peak wavelength is decreased and the peak becomes less pronounced. At pH $3\cdot44$, the peak maximum is at 335 mμ. Calculation showed that at this pH and $[Fe^{III}]_t$, the iron was mainly present as complex $Fe_2L_2(-H)_3$ with a lesser amount of $Fe_2L_2(-H)_2$ and very small amounts (6—8%) of FeL and $Fe_3L_3(-H)_6$. At pH $5\cdot03$, when the iron is present almost entirely as $Fe_3L_3(-H)_6$, there is no peak, but a flat shoulder between 295 and 307 mμ. The results indicate that the dimers show a peak near 335 mμ. With decreasing pH from $3\cdot44$ the peak wavelength moves towards that of FeL (346 mμ), and with increasing pH the peak is obscured by the greater extinction of the increasing amount of $Fe_3L_3(-H)_6$. Absorption peaks in this region have been attributed to olated hydroxyl bridges of the type $>Fe\begin{smallmatrix}H\\O\\ \\O\\H\end{smallmatrix}Fe<$, such as $Fe_2(OH)_2^{4+}$

(peak at 335 mμ) [19] and the ferric dimer of picolinic acid (peak at $342\cdot5$ mμ).[5] The iron–phenanthroline complex, which shows a peak at 340 mμ, was examined by infrared and magnetic measurements, and a structure involving the Fe–O–Fe linkage was suggested.[12] At pH values

[18] Agren, *Acta Chem. Scand.*, 1954, **8**, 266.
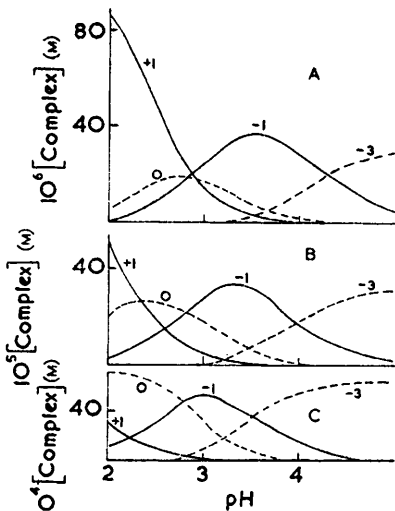[19] Mulay and Selwood, *J. Amer. Chem. Soc.*, 1955, **77**, 2693.

FIG. 4. Distribution of complexes with pH.

$+1 = [FeL^+]$; $0 = [Fe_2L_2(-H)_2]$; $-1 = [Fe_2L_2(-H)_3{}^-]$; $-3 = [Fe_3L_3(-H)_6{}^{3-}]$; $[Fe^{III}]_t = A\ 10^{-4}$, B 10^{-3}, C 2×10^{-2}M.
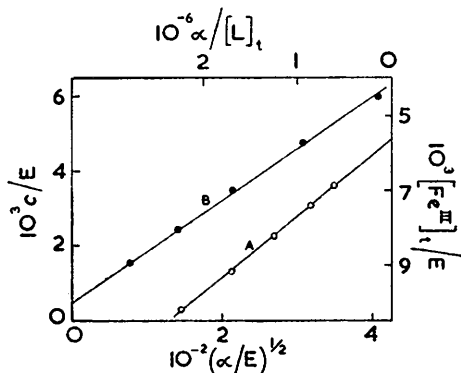
FIG. 6. Determination of K_{11} and ε at 346 mμ.

A $[L]_t = 0\cdot0100$M; $[Fe^{III}]_t = 4\cdot24 \times 10^{-4}$M; 1-cm. silica cells. $[H]_t$ from $0\cdot0312$ to $0\cdot0610$.

B $c = [L]_t = [Fe^{III}]_t = 8\cdot48 \times 10^{-4}$M; 1-cm. silica cells. $[H]_t$ from $0\cdot0214$ to $0\cdot0614$.

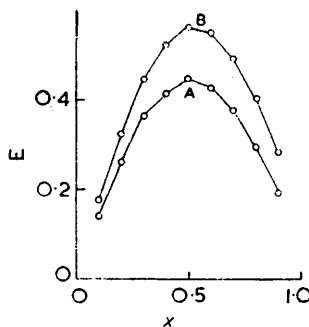Scales at the top and at the right are for the open circles.

FIG. 5. Method of continuous variations. $[H]_t = 0\cdot0316$; $[Fe^{III}]_t + [L]_t = 3\cdot39 \times 10^{-3}$M; $0\cdot5$-cm. cell. A 370 mμ, B 346 mμ.
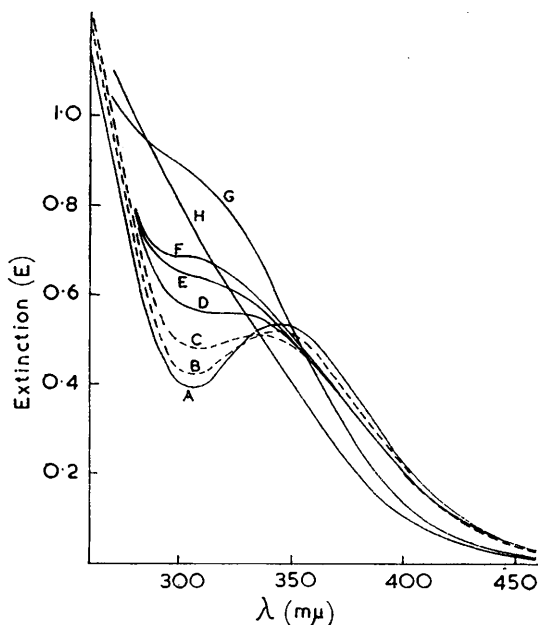
FIG. 7. Absorption spectra of ferric–tartrate complexes.

$[L]_t = 0\cdot01$M; $[Fe^{III}]_t = 3\cdot18 \times 10^{-4}$M; 1-cm. silica cells.

pH A $2\cdot39$, B $2\cdot85$, C $3\cdot44$, D $3\cdot86$, E $44\cdot1$, F $5\cdot03$, G $9\cdot43$, H $11\cdot0$.

$9\cdot43$ and $11\cdot0$, the spectra (Fig. 7) are greatly different from those in acid solutions, suggesting that $Fe_3L_3(-H)_6$ undergoes further transformation in alkaline conditions.

Paper electrophoresis. Shandon horizontal and vertical electrophoresis tanks containing Whatman No. 54 paper were covered with black cloths. A higher concentration of iron than those used previously was necessary in order to give visible spots on development with spray reagents. The spots (5 μl.) of ferric–tartrate solution ($[Fe^{III}]_t = [L]_t = 0\cdot020$M) applied to the paper were of the same pH as the tartrate solvent. The distribution of complexes at the

pH values studied was calculated from the known constants, on the assumption that the same complexes were formed at this higher ($Fe^{III}]_t$ and that dilution of the spot by the solvent was small. Spots of ferrous perchlorate and glucose were also applied to the paper. Colour development was made with solutions of potassium ferrocyanide, potassium ferricyanide,[20] and *p*-anisidine hydrochloride.[21]

The findings, summarised in Table 6, show that the mean charge on the complexes changes from positive (pH 1·92 and below) to negative as the pH is raised. At pH 3·61, there was a

<div align="center">

TABLE 6.

Paper electrophoresis of ferric–tartrates.

Applied potential = 10 v/cm.(approx.); running time = $2 \pm \frac{1}{4}$ hr.; solvent $[L]_t = 0.02$M, 0·1M (NaClO$_4$).
</div>

pH	10^4M-[Complex] of charge				Movement of Fe^{III} relative to glucose
	+1	0	−1	−3	
1·92	38	72	8	—	towards cathode (0·8 cm.)
2·95	—	39	51	8	,, anode (1·7 cm.)
3·61	—	5	35	40	,, ,, (2·4 ⟶ 4·8 cm.)
4·50	—	—	4	64	,, ,, (4·1 cm.)

partial separation into two spots, the faster-moving spot being more coloured than the slower one, indicating that it contained the larger amount of iron. Although at this pH the concentrations of the two anionic complexes are practically equal, the amount of ferric iron in the form of $Fe_3L_3(-H)_6$ is $1\frac{1}{2}$ times that in $Fe_2L_2(-H)_3$. The findings therefore appear to be in agreement with those expected from the potentiometric work.

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DISCUSSION
</div>

The above results suggest that ferric ion is combined with the two ionised carboxyl groups of tartaric acid in each of the four complexes identified. In the monomer FeL, additional participation of one or both alcoholic hydroxyl groups is indicated. The absorption band at 346 mμ appears to be characteristic of this latter type of chelation, since the corresponding monomeric ferric–malate and ferric–citrate complexes also exhibit peaks in the same region (341 and 350 mμ, respectively), while little absorption is shown by the ferric complexes of succinic and tricarballylic acid.[22] Tridentate chelation of the above type has been suggested previously on similar grounds for the uranyl tartrate, citrate and malate complexes.[23,24] Since the hydroxyl groups of tartaric acid are in equivalent positions, there appears to be no reason why both could not be involved in chelation; indeed, this is suggested by the more pronounced peak obtained with tartrate than with citrate or malate.[22] Quadridentate chelation is therefore proposed.

There is no evidence that an alcoholic hydroxyl group is ionised as suggested by Green and Parkins.[2] The small increase in log K_{11} with pH (0·2 log unit over 1·5 pH units; Table 4) is probably within experimental error, but even if real would suggest only a very slight tendency of FeL to ionise or become hydroxylated. Where dimerisation involving structures containing internuclear hydroxyl bridges has been described,[5,19] the mononuclear hydroxy complexes have had stable existence. The lack of a similar hydroxylated species FeL(OH) in the ferric–tartrate system, however, is not evidence against dimeric structures containing oxygen bridges, since Anderegg[12] has shown that phenanthroline and 2,2'-bipyridyl can form binuclear ferric complexes without the preliminary formation of mononuclear hydroxy-complexes. It is possible, therefore, and suggested by the absorption spectra, that the dimer $Fe_2L_2(-H)_2$ contains Fe–(OH)$_2$–Fe or Fe–O–Fe groupings and that complex $Fe_2L_2(-H)_3$ is formed by ionisation of one of the co-ordinated alcoholic hydroxyl groups.

[20] Frahn, *Austral. J. Chem.*, 1958, **11**, 399.
[21] Dobbie, Kermack, and Lees, *Biochem. J.*, 1955, **59**, 240.
[22] Timberlake, unpublished results.
[23] Feldman, Havill, and Neuman, *J. Amer. Chem. Soc.*, 1954, **76**, 4726.
[24] Feldman, North, and Hunter, *J. Phys. Chem.*, 1960, **64**, 1224.

Alternatively, it is possible to formulate non-olated structures for $Fe_2L_2(-H)_2$ which involve ether linkages (see reference 24 for possible uranyl–tartrate structures) and there is abundant evidence in the literature to show that induced ionisation of the hydroxyl proton can occur readily in ferric complexes in quite acid solutions.[25]   However, it is difficult to imagine why a third hydroxyl group should ionise to give $Fe_2L_2(-H)_3$ unless this group was also co-ordinated to ferric ion.

Comparison of the infrared spectrum of the solid obtained by evaporation of a solution of the sodium salt of the trimer with that of tartaric acid confirmed that both carboxyl groups were involved in complex-formation but indicated that secondary alcoholic groups were still present.   If the alcoholic groups remain un-ionised, a cyclic structure with iron bridged by oxygen atoms seems possible; although a band at 850 cm.$^{-1}$, attributed to the $-O-Fe-O$ grouping in the iron(III)–phenanthroline complex,[12] did not occur, there was strong absorption in the region of 1100 cm.$^{-1}$.   Further complex-formation which may occur in alkaline solution would then involve ionisation of the alcoholic groups.

The formation of dimeric and trimeric ferric malates and a dimeric ferric citrate has also been observed,[22] and suggests that polynuclear iron complexes of hydroxy-acids may occur more frequently than suggested by a survey of the literature.[26]

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[25] Chaberek and Martell, " Organic Sequestering Agents," Chapman and Hall, London, 1959, pp. 72, 149, 311.
[26] Bjerrum, Schwarzenbach, and Sillén, " Stability Constants, Part I, Organic Ligands," *Chem. Soc. Special Publ.*, No. 6, 1957.