[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Gluconate Complexes. II. The Ferric–Gluconate System

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Ferric ion and gluconic acid form a series of complexes with increasing *p*H. The complexes have been studied by means of polarography, spectra, *p*H titration and potentiometry. The series consists of the following species (HGH_4 = gluconic acid; *pK* values for the acid ionizations are inserted between formula): $HFeGH_3^{++}$, 4.6 (two step), HFeGH, 4.0, $FeGH^-$, 13.3, $FeGH(OH)^-$. The equilibrium constant for the formation of $FeGH^-$ from ferric ion and gluconate ion is 3×10^{-6} and involves 3 protons, making the complex extremely stable at high *p*H. The true stability constant of the complex cannot be obtained until the second, third and fourth dissociation constants of gluconic acid are known. Structures are proposed which are compatible with the data. Although the treatment is approximate in some respects due to the simultaneous presence of several iron species, this represents the first detailed study of this type of complex.

The stability of the glucono-ferric complex has been suggested by Prescott, *et al.*,[1] who claimed that gluconic acid is more effective on a weight basis than ethylenediaminetetraacetic acid in any solution with *p*H greater than 6. They further state that gluconic acid is effective as an iron sequestrant in caustic soda solutions up to 35% (12 *M*) concentrations. More recently, Mehltretter, *et al.*,[2] have compared the sequestering power of a number of sugar acids, and found that gluconic acid is generally superior to all others as an iron sequestrant except for sodium saccharate at very high *p*H. The glucono-ferric complex was precipitated as a double calcium salt by Traube, *et al.*[3] They proposed the formula $[C_6H_7O_7Fe]Ca$, and on the basis of an elemental analysis for carbon, iron and calcium, they suggested that three hydrogen ions are displaced from the secondary hydroxyl groups when the complex is formed. In an analogous situation, Warner and Weber[4] have recently demonstrated that the hydroxyl hydrogen is more easily displaced than the third carboxylic hydrogen in the formation of citrato-ferric complex.

The present study is an attempt to ascertain the nature and stability of the glucono-ferric complex in greater detail. The procedures used are similar to those described in the first paper of this series[5] concerning the copper-gluconate system. Due to the complex nature of the solutions which frequently contained four or more iron species (many of which yielded overlapping physical data), much of our treatment and the constants obtained are approximate. However, by placing together numerous pieces of evidence obtained by a number of independent methods, we have obtained a fairly complete picture of this rather complicated system.

Experimental

Apparatus and Technique.—Spectra were run either on a Cary Model 11 PMS recording spectrophotometer or on a Beckman Model DU spectrophotometer. A 1 *M* sodium perchlorate solution was used as a blank, and an equivalent amount of potassium nitrate was added to the blank when ferric nitrate solutions were used.

Measurements of *p*H were made with a Beckman Model G or H-2 *p*H meter. All titrations were performed under nitrogen at 25°. The Model G meter served also as a potentiometer for e.m.f. measurements.

Polarograms were recorded according to usual technique with a calibrated Sargent Model XXI polarograph, utilizing a three-compartment cell previously described.[6]

Conductometric titrations were made with an Industrial Instruments Model RC-16 bridge at 1000 cycles per second.

Migration experiments were performed in an 8 mm. o.d. U-tube containing a large stopcock in each arm. The center compartment was filled with a solution containing iron in the presence of a ten-fold excess of gluconate. The stopcocks were then closed and the upper arms filled with a gluconate solution of the same concentration and *p*H. The solutions in each arm were adjusted to the same height, platinum electrodes inserted, and the stopcocks carefully opened. An e.m.f. of 20 v. was applied overnight. Migration was readily detected by the movement of the yellow color. The absence of migration was checked by withdrawing a portion, acidifying and adding potassium thiocyanate.

Materials.—Ferric perchlorate was prepared by repeated precipitation of reagent grade ferric nitrate with ammonium hydroxide followed by solution in perchloric acid. In some cases the ferric nitrate was used directly. Solutions were standardized volumetrically with permanganate or dichromate by standard methods. The excess perchloric acid was determined by conductometric titration with standard sodium hydroxide.

Ferrous perchlorate solutions were prepared by dissolving G. F. Smith reagent grade ferrous perchlorate in 0.01 *M* perchloric acid (air-free) and transferring to a storage buret[7] under nitrogen. Both ferrous and total iron were determined volumetrically by standard methods and the ferric iron by difference. About 93% of the iron was in the reduced state.

Sodium gluconate solutions were prepared as previously described.[5]

Results and Discussion

Polarographic Characteristics.—All polarograms taken of iron(III) in gluconate solutions were irreversible. The first reduction wave for the ferric-gluconate complex is spread out over several tenths of a volt and is not well developed, preventing accurate measurement of either half-wave potential or diffusion current. Therefore only qualitative conclusions can be drawn from the polarographic data. The second reduction wave, for iron(II) to the metal, becomes nearly reversible at *p*H greater than 11, and is discussed in detail below.

Below *p*H 3, the diffusion current is reached at an applied potential of *ca.* + 0.4 v. *vs.* the saturated calomel electrode (S.C.E.), and the polarograms cannot be distinguished from those of ferric ion in perchlorate media at the same *p*H. An amperometric titration of a 2 m*M* gluconate solution in an acetate buffer of *p*H 3.7 with ferric nitrate gave points which fell on a single straight line up to a threefold excess of iron. A second amperometric titration un-

(1) F. J. Prescott, J. K. Shaw, J. P. Bilello and G. O. Cragwall, *Ind. Eng. Chem.*, **45**, 338 (1953).

(2) C. L. Mehltretter, B. H. Alexander and C. E. Rist, *ibid.*, **45**, 2782 (1953).

(3) W. Traube, F. Kuhbier and W. Schroder, *Ber.*, **69B**, 2655 (1936).

(4) R. C. Warner and I. Weber, THIS JOURNAL, **75**, 5086 (1953).

(5) R. L. Pecsok and R. S. Juvet, Jr., *ibid.*, **76**, 202 (1954).

(6) R. L. Pecsok and R. S. Juvet, Jr., *Anal. Chem.*, in press.

(7) H. W. Stone, *ibid.*, **20**, 747 (1948).

der the same conditions but without gluconate gave a straight line which coincided with the former. The coincidence of the two lines indicates that the complex at low *p*H is relatively weak since it is unlikely that the diffusion coefficients of the complex and simple ion are the same. As the *p*H of the solution is increased above 3, the wave appears at more negative potentials; its long, drawn out nature must be due in part to the presence of several species. At a *p*H greater than 4, uncomplexed iron is completely precipitated as the hydroxide yielding no polarogram, while the presence of an equimolar amount of gluconate is sufficient to retain the iron in solution, yielding a poorly defined wave but with definite reduction.

If the *p*H is greater than *ca.* 11, approximate measurements may be made of the half-wave potential and fairly accurate (±2–5%) measurements of the diffusion current. The ratio of the diffusion current of the second wave to that of the first is always greater than the theoretical value of 2. With a large excess of gluconate, the ratio is *ca.* 2.2, but when the ratio of iron to gluconate becomes equal to or greater than unity, the ratio of the diffusion currents continues to increase to as much as 4. This behavior can be observed in Fig. 1, which shows the results of an amperometric titration of 2 m*M* sodium gluconate in 1 *M* sodium hydroxide with ferric nitrate, together with the results for a similar titration without gluconate. Obvious breaks occur at points corresponding to a 2:1 (iron:gluconate) and 1:1 complex.

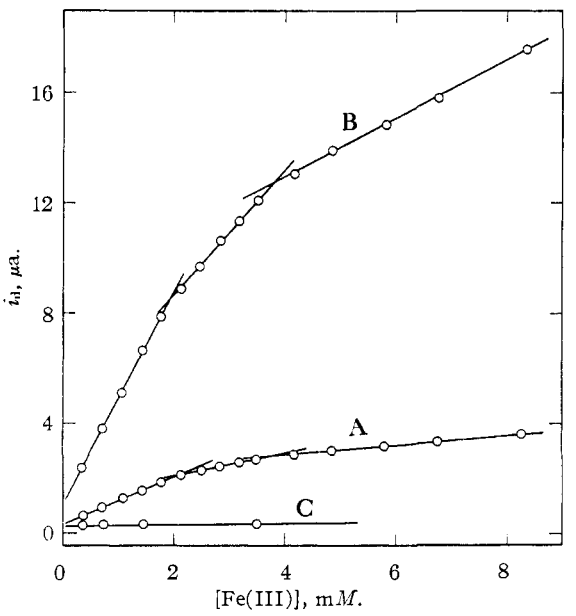


Fig. 1.—Amperometric titration of 2 m*M* sodium gluconate in 1 *M* sodium hydroxide with 0.1 *M* ferric nitrate: A, first wave; B, second wave; C, second wave for similar titration without gluconate.

The second wave is well developed in gluconate solutions containing 1 *M* (or more) sodium hydroxide. The half-wave potential becomes more negative with increasing concentrations of hydroxide or gluconate, and with increasing concentration of iron when the gluconate is not in large excess. In 2 *M* sodium hydroxide–0.2 *M* sodium gluconate, the half-wave potential is −1.68 v. *vs.* the S.C.E., independent of the iron concentration. Plots of log $(i_d - i)$ *vs.* E yielded straight lines for the upper half of the wave, as should be the case for the reduction of a metal insoluble in mercury.[8] Plots of log $(i/i_d - i)$ *vs.* E for the same polarograms yielded straight lines for the lower half of the wave only, as should be the case for the reduction of a metal soluble in mercury.[8] The solubility of iron in mercury is 10^{-17}%,[9] and is exceeded instantaneously. Therefore, either a considerable amount of iron must be deposited before the drop is completely covered, or else the iron is deposited in some state in which its activity depends on the amount present. Furthermore, the slopes of the log plots were 0.051 and 0.058 v., and the reductions cannot be considered reversible.

The large negative displacement of the ferric–ferrous wave in alkaline gluconate solutions makes this an attractive supporting electrolyte in which to determine such elements as copper in the presence of large amounts of iron. For example, in 2 *M* sodium hydroxide–0.1 *M* gluconate, the half-wave potential of copper is −0.52 v. *vs.* the S.C.E.,[5] whereas the iron wave does not begin until −1.0 v. Polarograms of 0.2 m*M* copper in this electrolyte were unchanged when iron was added up to 50 m*M* iron (a 250-fold excess). Procedures for the determination of trace amounts of copper in iron materials are being investigated in this Laboratory and will be reported elsewhere.

A few polarograms of ferrous ion in gluconate solutions were made. Anodic waves were obtained in solutions with a *p*H greater than 3. In the *p*H range 3 to 4, the half-wave potential of the anodic wave, which is nearly reversible in this region, is given by: $E_{1/2} = (+0.69 - 0.131\ pH)$ v. *vs.* the S.C.E. Thus two protons are involved, lending support to reaction (8) proposed below. The ferrous complex is oxidized rapidly in alkaline gluconate solutions and no detailed investigation was attempted.

Spectrophotometry.—Three series of solutions were prepared, each solution containing 0.396 m*M* ferric nitrate and 1 *M* sodium perchlorate to maintain constant ionic strength. In the first series no sodium gluconate was added (1:0); in the second series 0.396 m*M* gluconate was added (1:1); and in the third series 3.96 m*M* gluconate was added (1:10). The *p*H was adjusted with perchloric acid or sodium hydroxide when the solutions were nearly to volume and was checked at the time the spectra were taken. All solutions were allowed to stand in the dark at room temperature for several days in order to ensure equilibration. Solutions containing gluconate did not change on standing. Spectra run 2 hours after preparation were identical to those run 3 days later, and the *p*H of these solutions changed no more than 0.1 unit in 3 weeks.[10] Solu-

(8) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers Inc., New York, N. Y., 1952, p. 203.

(9) N. V. Sidgwick, "The Chemical Elements and their Compounds," Oxford University Press, London, 1950, p. 289.

(10) A few solutions containing gluconate exposed to daylight for several days decomposed, apparently from oxidation of the gluconate and ferric hydroxide was precipitated. No ferrous iron could be de-

tions above pH 3 without gluconate were unstable, and ferric hydroxide precipitated immediately or within a few hours.

In the 1:1 series, spectra were taken for seventeen solutions with pH's varying from 1.73 to 14.7.[11] Several typical spectra are shown in Fig. 2 for solutions containing the maximum amounts of each successive complex (*vide infra*). In the series without gluconate, spectra were taken only up to pH 4.0, beyond which the iron could not be retained in solution.

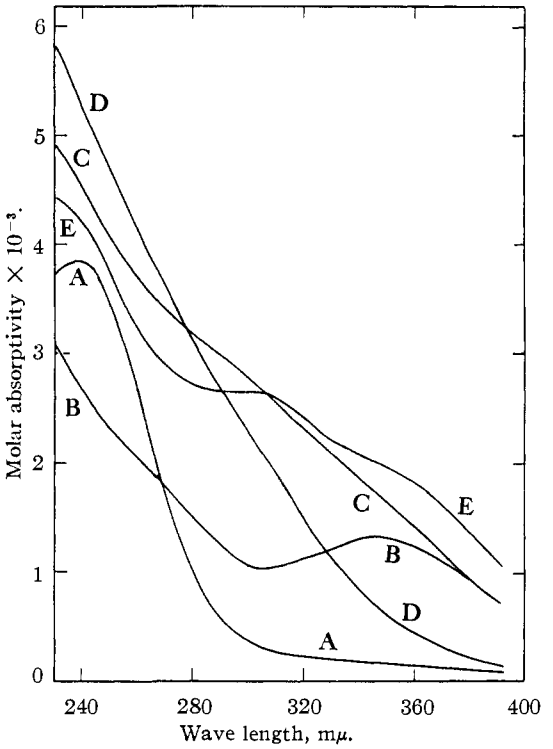


Fig. 2.—Absorption spectra of 0.396 mM ferric gluconate at various pH: A, 1.75; B, 3.15; C, 6–12; D, 14.7; E, 3.03 without gluconate.

At pH 1.75 the spectra are nearly the same in the 1:1 and the 1:0 series. The absorption peak at 240 mμ due to the $Fe(H_2O)_6^{+++}$ ion[12] is slightly depressed in the 1:1 series. As the pH is increased to 3, the 240 mμ peak disappears, and a new peak appears at 345 mμ. In the pH region 3 to 6, the absorption increases in the far ultraviolet, eliminating the peak at 345 mμ. The spectra for solutions in the pH region 6 to 12 are essentially the same. Above pH 13 there is a further increase in absorption in the far ultraviolet and a decrease in the near ultraviolet and visible with an isosbestic point at 278 mμ. The complex at pH 14 is colorless.

In order to prove the presence of complexes below pH 3, a difference plot was prepared in which the difference between the absorbance at a given pH of the 1:0 and the 1:1 solutions was plotted *vs.* wave length. Several curves are shown in Fig. 3, along with similar plots for the difference in absorbance between the 1:0 and the 1:10 solutions. In each case, deviations in the 1:0–1:1 curves are accentuated in the 1:0–1:10 curves, indicating there is complexing even at pH 1.75.

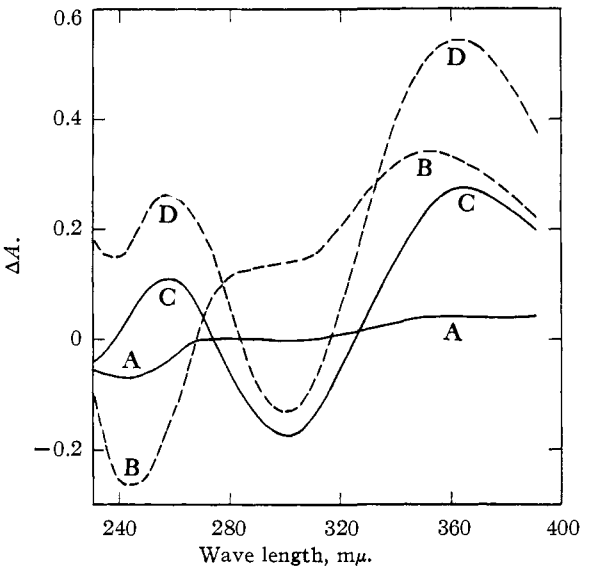


Fig. 3.—Absorbance difference: curves A and B at pH 1.75, curves C and D at pH 2.65. Curves A and C for 1:1–1:0 difference, curves B and D for 1:10–1:0 difference (see text).

Because several species, complexed and uncomplexed, were present in these solutions, all with overlapping spectra lacking sharp absorption peaks, no effort was made to determine stability constants from these data. However, acid dissociation constants of the complexes can be obtained. For this purpose, the spectra were replotted as absorbance *vs.* pH for constant wave length, giving a series of curves for 10 mμ intervals of wave length. Several of these curves are shown in Fig. 4. The region between pH 6 and 12 consists of parallel straight lines and has been omitted. In regions where these curves have a maximum slope, the spectra are changing at the greatest rate. Curves for all wave lengths will not have inflections at a given pH; if there is an isosbestic point, the curve for its wave length must have a zero slope. These inflection points therefore represent the pH values at which there is the greatest rate of change in the concentration of the absorbing species, *i.e.*, the pK value for the acid dissociation of the ferric-gluconate complex. The values obtained for the successive pK's are 2.3, 3.8 and 13.3.

A similar series of curves prepared for the 1:0 series exhibited an inflection at pH 2.8, in reasonable agreement with values reported for the first ionization constant of the hexaaquoferric ion.[12,13]

pH Measurements.—The release of hydrogen ion in complex formation at low pH was established in a titration of 3 mM ferric perchlorate, initial pH

tected. Solutions which had been stored unchanged in the dark for several weeks suffered a similar decomposition when exposed to daylight for a few hours. However, exposure to the spectrophotometer beam was not sufficient to cause noticeable decomposition.

(11) The pH in the region 10–13 was measured with a Beckman Type E glass electrode, and above pH 13, the pH was calculated from the known concentration of sodium hydroxide and its activity coefficient.

(12) E. Rabinowitch and W. H. Stockmayer, THIS JOURNAL, **64**, 335 (1942).

(13) (a) W. C. Bray and A. V. Hershey, *ibid.*, **56**, 1889 (1934); (b) A. B. Lamb and A. G. Jacques, *ibid.*, **60**, 1215 (1938); (c) T. V. Arden, *J. Chem. Soc.*, 350 (1951).

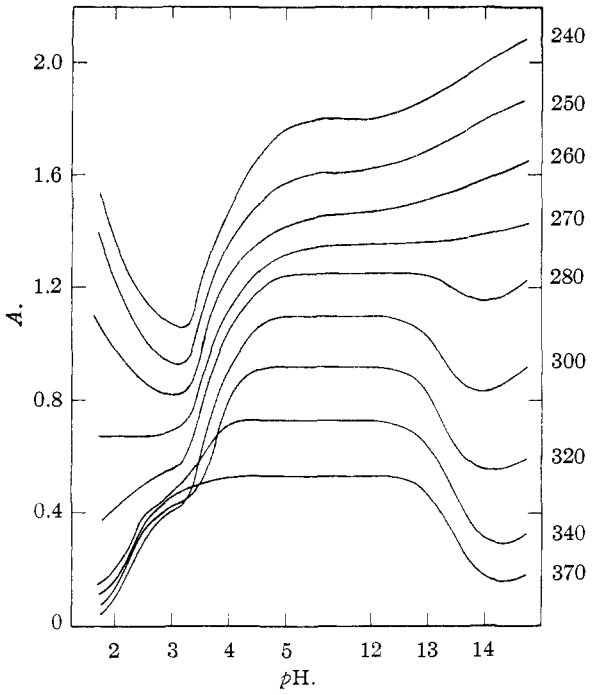


Fig. 4.—Absorbance at constant wave length (indicated in mμ to right of figure) as a function of pH.

adjusted to 2.90, with gluconic acid pH 2.40. In the course of this titration, the pH steadily decreased to 2.62 at a point where one gluconic acid per iron was present and then remained constant upon further addition of gluconic acid. A blank was run with an equal concentration of potassium nitrate adjusted to pH 2.90. When the same amount of gluconic acid had been added as above, the pH had decreased only to 2.80, thus establishing that the reaction between gluconic acid and ferric ion at pH 3 does release hydrogen ion.

The calculation of an equilibrium constant was attempted from the interpretation of a pH titration curve of a solution containing 1 mM each of sodium gluconate and ferric perchlorate. In the titration with sodium hydroxide, equilibrium was reached very slowly; in the center portion of the curve, the pH drifted for *ca.* 1 hour after each increment of base. The reverse titration with perchloric acid, first adding a known excess of base, was performed with no difficulty, and little drift in the pH. Furthermore, solutions made up identical in composition to various points on the titration curve were allowed to stand for five days. At the end of that time, the pH was measured and the points so obtained fell exactly on the reverse titration curve. Apparently equilibrium is approached much more rapidly from the basic side, indicative that the hydroxyl hydrogens are involved. All calculations have been based on the reverse titration curve shown in Fig. 5. The abscissa values are calculated in terms of a, the equivalents of base added per mole of metal (or per mole of gluconate) corrected for the known amounts of perchloric acid in the reagent and the back titration in accordance with the usual practice. As in the first paper,[5] gluconic acid is represented as HGH_4, the first H representing the carboxyl hydrogen and the latter four H's representing the secondary hydroxyl hydrogens. We have assumed that the formation of the complex can be represented by the reaction

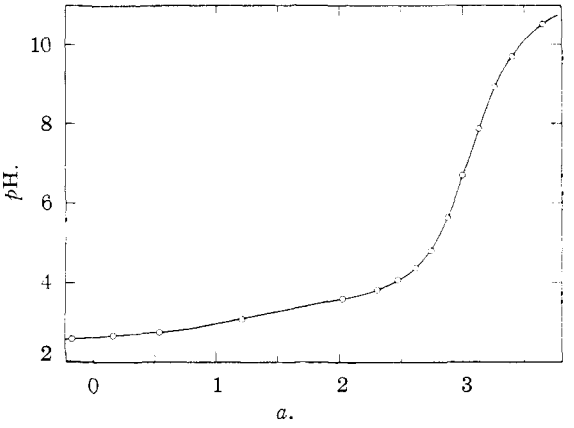


Fig. 5.—Titration curve of 3 mM ferric gluconate with 0.1 M sodium hydroxide. Abscissa is equivalents of base added per mole of iron.

$$Fe^{+++} + GH_4^- = FeGH_{(4-x)}^{(2-x)+} + xH^+ \quad (1)$$

Assume now that $x = 3$; *i.e.*, that the ferric ion displaces 3 hydroxyl hydrogens in complex formation, as proposed by Traube, *et al.*[3] The equilibrium constant for reaction (1) is thus

$$\frac{[FeGH^-][H^+]^3}{[Fe^{+++}][GH_4^-]} = K_1$$

As a basis for calculation, the following three equations were set up

$$C = [Fe^{+++}] + [Fe(OH)^{++}] + [Fe(OH)_2^+] + [FeGH^-] \quad (2)$$

$$C = [HGH_4] + [GH_4^-] + [FeGH^-] \quad (3)$$

$$[Na^+] + [H^+] + 3[Fe^{+++}] + 2[Fe(OH)^{++}] + [Fe(OH)_2^+] = [ClO_4^-] + [GH_4^-] + [FeGH^-] \quad (4)$$

where C is the known stoichiometric concentration of iron and gluconate. In addition to equations 2, 3 and 4, we have available the ionization constant of gluconic acid, $pK_G = 3.56$,[14] and the first and second acid ionization constants of the hexaaquoferric ion, $pK^1_{Fe} = 2.60$ and $pK^2_{Fe} = 4.70$.[12,13] It is thus possible to compute the concentrations of all species in terms of known constants, and the experimentally determined C, a and pH. Details of these calculations are omitted since they have been previously discussed by Martell and Calvin[15] and others. In this manner, values for the equilibrium constant for reaction (1) with $x = 3$, pK_1, were computed for a number of points on the titration curve. Values obtained were not constant but increased as a was increased.

The next assumption was that the release of the third hydrogen ion in equation 1 is not as complete as the first two, resulting in the species HFeGH. Equations 2 and 3 were then modified to include this species. Another constant, pK_5, is now required for the dissociation

$$HFeGH = FeGH^- + H^+ \quad (5)$$

which is not known and could not be directly meas-

(14) R. K. Cannan and A. Kibrick, THIS JOURNAL, **60**, 2314 (1938).
(15) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, New York, N. Y., 1952, p. 90ff.

ured. (A similar situation was observed in the vanadium ethylenediaminetetraacetate system by Schwarzenbach and Sandera,[16] and we have adopted a similar approach.) Equations 2, 3 and 4 as modified above were then solved in the following manner. Terms were collected and simplified algebraically: from (2)

$$C = \beta[Fe^{+++}] + \delta[FeGH^-] \quad (6)$$

From (3)

$$C = \alpha[GH_4^-] + \delta[FeGH^-] \quad (7)$$

From (4)

$$b = \gamma[Fe^{+++}] + \sigma[FeGH^-] + [GH_4^-] \quad (8)$$

Where

$$\alpha = 1 + [H^+]/K_G$$

$$\beta = 1 + K^1_{Fe}/[H^+] + K^1_{Fe}K^2_{Fe}/[H^+]^2$$

$$\gamma = K^1_{Fe}/[H^+] + 2K^1_{Fe}K^2_{Fe}/[H^+]^2$$

$$\delta = 1 + [H^+]/K_5, \quad \sigma = 4 + \frac{3[H^+]}{K_5}$$

$$b = C(a + 1) + [H^+]$$

Equations 6, 7 and 8 can be solved in terms of $[GH_4^-]$ to yield

$$[GH_4^-] = \frac{\sigma C - \delta b}{(\alpha\sigma - \delta) - \alpha\gamma\delta/\beta} \quad (9)$$

in which δ contains the unknown constant K_5. An arbitrary value was given to K_5, which made it possible to solve equation 9 for $[GH_4^-]$ and thus for the other quantities required to compute K_1 at a given a value. The calculated value for pK_1 was plotted *vs.* several arbitrary values given to pK_5 at $a = 0.5$. This procedure was repeated at $a = 1.0$, 2.5, 2.0 and 2.5. Thus a series of lines was obtained which intersected within a small region around a point at which $pK_5 = 4.0$ and $pK_1 = 5.5 \pm 0.2$. The constancy of pK_1 throughout the titration curve substantiates the interpretation given above, including the nature of reaction (1) with $x = 3$. The constant obtained for reaction (1) is not an obvious measure of the stability of the ferric-gluconate complex. It contains the concentration of hydrogen ion to the third power indicating that the effective stability is increased tremendously with increasing pH. The determination of the true stability constant requires a knowledge of the ionization constants of the second, third, and fourth protons of gluconic acid, and is equal to $pK_1 - (pK_2 + pK_3 + pK_4)$, where the last three terms refer to gluconic acid.

The computations required above yielded values for the concentrations of the various iron species in the pH region 2.6 to 5.0. These have been plotted in Fig. 6 as per cent. of the total iron present. It should be noted that in determining the various points, the value of pK_1 was not used, yet for any given pH, the sum of the species adds up to 98–104% (98–100% in the pH range 3.0 to 5), a further check on the accuracy of the interpretation. It should be noted that no account has been taken of another species, $HFeGH_3^{++}$, which is present in solutions of pH less than 3 as shown in the section on spectrophotometry. The equilibrium constant, pK_{10}, for the reaction

$$HFeGH_3^{++} = HFeGH + 2H^+ \quad (10)$$

(16) G. Schwarzenbach and J. Sandera, *Helv. Chim. Acta*, **36**, 1089 (1953).

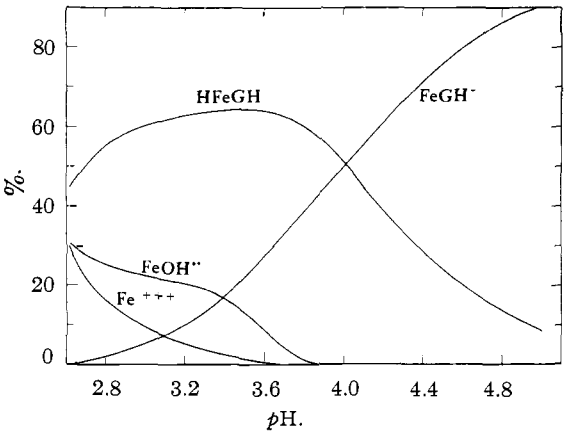


Fig. 6.—Relative concentrations of various iron species present in a 3 mM ferric gluconate solution as a function of pH.

was found to be 4.6. (This is the sum of two pK's for the individual dissociations which are approximately equal.) It can be shown that at pH 2.63, where $a = 0$ in the titration curve of Fig. 5, the $HFeGH_3^{++}$ species is present to the extent of *ca.* 5% and rapidly decreases as a is increased since the square of the hydrogen ion concentration is involved.

Conductometric Measurements.—The number of species present with increasing alkalinity was also indicated by a conductometric titration of a solution of 9.5 mM ferric nitrate and 9.5 mM sodium gluconate. A slight excess of base was added and the solution titrated with 0.2 M perchloric acid. A sharp minimum in the conductance occurred upon titration of the excess base. Further breaks (slight increases in slope) were observed upon additions of 1, 2 and 3 equivalents of acid per mole of iron. Very slight changes in slope were observed at 4 and 5 equivalents of acid, but these changes were probably within the experimental error and cannot be regarded as significant.

Migration Studies.—Since the above experiments determine the relative charge on the various species, migration experiments were conducted to determine which of the ferric-gluconate species is neutral. A large excess of gluconate was used (1:10) and the pH adjusted to a value at which the complex was expected to be predominately in one form. Three experiments were performed; at pH 1.8 the complex migrated toward the cathode and is positively charged, at pH 3.0 no migration was detected and the complex is neutral, and at pH 9.3 the complex migrated toward the anode and is negatively charged.

Potentiometric Measurements.—Increments of ferrous perchlorate were added to known amounts of ferric ion in gluconate solutions of various concentrations and pH giving solutions in which the ratio of Fe(III)/Fe(II) varied from 10 to 0.1. (Allowance was made for the ferric ion in the ferrous solution.) Both a platinum and a stationary mercury electrode were unsatisfactory, but a dropping mercury electrode used as an indicator electrode yielded nearly reversible potentials. Reversibility was assumed if a plot of the log [Fe(III)]/[Fe(II)]

vs. E yielded a straight line with the correct slope as required by the Nernst equation. In solutions above *p*H 13, ferrous iron is not complexed by gluconate and ferrous hydroxide precipitated. Although the amount of precipitate increased as more ferrous solution was added, the electrode responded as if the total ferrous iron were in solution. Since no buffers could be used, the *p*H changed during the addition of the ferrous solution. The *p*H was measured continuously and the e.m.f. corrected to a constant *p*H value, using the previously determined dependence of 118 mv./*p*H unit obtained in both strongly acidic and strongly alkaline solutions in which the *p*H change was negligible. No E^0 values could be obtained in the *p*H region 7 to 11, because the electrode failed to perform reversibly. In this region the predicted E^0 (−0.3 to −0.8 v. *vs.* S.C.E.) falls close to the electrocapillary maximum of the dropping mercury electrode and it was observed that the galvanometer movement upon the fall of a drop changed direction as this point was passed.

In this manner, E^0 values were obtained for the Fe(III)–Fe(II) couple in gluconate solutions and plotted *vs.* *p*H and concentration of gluconate. All points for constant gluconate concentration fall on the same straight line with a slope of 118 mv. per *p*H unit, indicating that in the reduction two hydroxide ions are released (or two hydrogen ions required). These observations are accommodated by the half-reactions

$$p\mathrm{H} > 13,\ \mathrm{Fe(OH)_2} + \mathrm{GH_4^-} + 2\mathrm{OH^-} = \mathrm{FeGH(OH)^-} + 3\mathrm{H_2O} + \mathrm{e^-};\ E^0 = +0.88 \text{ v. } vs. \text{ N.H.E.} \quad (11)$$

$$p\mathrm{H} < 4,\ \mathrm{FeGH_4^+} = \mathrm{HFeGH} + 2\mathrm{H^+} + \mathrm{e^-};\ E^0 = -0.80 \text{ v. } vs. \text{ N.H.E.} \quad (12)$$

With the additional half reaction

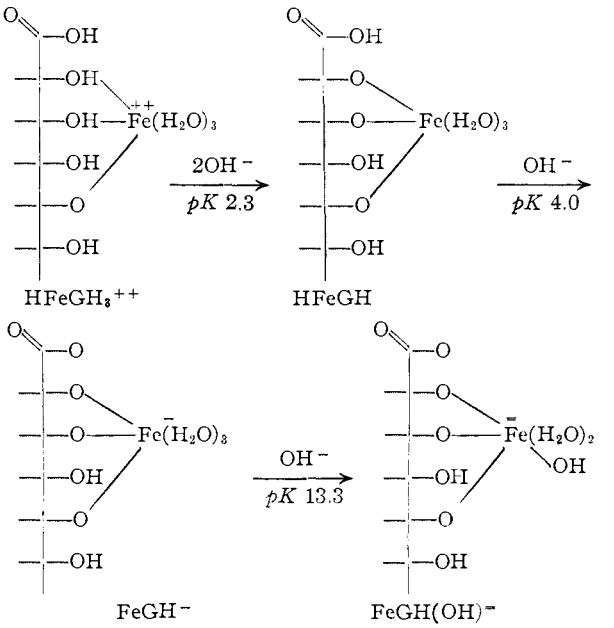
$$\mathrm{Fe^{++}} = \mathrm{Fe^{+++}} + \mathrm{e^-};\ E^0 = -0.77 \text{ v.} \quad (13)$$

equations 1, 5, 12 and 13 can be combined to yield

$$\mathrm{Fe^{++}} + \mathrm{GH_4^-} = \mathrm{FeGH_4^+} \quad (14)$$

for which the equilibrium constant, pK_{14}, is the stability constant of the ferrous gluconate complex and is equal to 1.0. In comparing the stability constants for the ferrous and ferric complexes, it should be remembered that the latter inherently contains the ionization constants for the second, third and fourth protons of gluconic acid, which are extremely small numbers and not directly measurable.

Structures.—The experimental evidence given above is sufficient to establish the molecular formulas of the ferric-gluconate complexes. The remaining uncertainty is the exact position of the protons. The possibility that hydrogen ions are removed from the water molecules coördinated to the iron has not been disproved. However, between *p*H 1 and 14, five protons are involved and it is most likely that more than one of them is derived from gluconic acid. The stability and solubility at high *p*H suggest that not more than two come from water molecules in the iron coördination sphere. The proton on the δ OH group is easily removed in lactonization and is probably easily removed when the coordination complex is formed at low *p*H. Two protons are relatively easily removed and the third with a pK of 4 is most likely that from the carboxy group. The following structures are thus compatible with our observations and are sterically possible when constructed with Hirschfelder–Taylor models



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