[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Hydrolysis of Fe^{3+}: Magnetic and Spectrophotometric Studies on Ferric Perchlorate Solutions[1]

BY L. N. MULAY AND P. W. SELWOOD

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The hydrolysis of Fe^{3+} ion has been investigated in the light of recent reports which describe a new species $Fe_2(OH)_2^{4+}$ in addition to $FeOH^{2+}$ and $Fe(OH)_2^+$. From measurements of magnetic susceptibility, over a range of temperature, of 0.04 *M* ferric perchlorate and 3 *M* sodium perchlorate aqueous solutions of varying acidity, we have found that the species, $Fe_2(OH)_2^{4+}$, which we shall call the "dimer," is diamagnetic. The reaction for the formation of the dimer has been shown to be endothermic, with $\Delta H \cong 9.8$ kcal. per mole. Thus, the dimer is more stable at higher temperatures, in the room temperature range. The absorption spectra in the ultraviolet, of the above solutions at 15 and 51°, and in some cases at 25°, have also been studied. The spectra show peaks at 240 ± 0.5 mμ and 335 ± 0.5 mμ. We have established that the peak at 335 mμ is almost entirely due to the dimer, and that the one at 240 mμ is due to contributions both from Fe^{3+} and $FeOH^{2+}$. The results have been used to evaluate the equilibrium constant for the formation of the dimer at 15 and 51°, and these are found to be in agreement with those obtained from the magnetic data within limits of experimental error. The value obtained at 25° from magnetic data is in reasonable agreement with that reported in the literature. This work adds to the small group of known substances or ions in which exchange effects destroy all the paramagnetism normally present in iron(III). It also suggests that the well known subnormal magnetic moment for the iron in hydrous ferric oxide may be due to part of the iron being present as dimers built into the gel structure. Just prior to precipitation almost half of the iron in a 0.04 *M* solution is present as dimer.

Introduction

The behavior of Fe^{3+} ion with respect to its hydrolysis or association with other ions has been investigated by several workers, who employed mainly magnetic, spectrophotometric and electrochemical techniques.

Pascal[2] observed that the magnetic moment attributable to iron in colloidal ferric oxide is lower than that found for iron in typical ferric salts such as ferric sulfate. Bose[3] observed that the magnetic moment of Fe^{3+} decreases with decreasing acidity of ferric chloride solutions, while Vosburgh and coworkers[4] found that this ion in perchlorate solutions with concentrations larger than 0.1 *M* has a moment practically equal to the theoretical moment of 5.92 Bohr magnetons, and that this value does not change in oxalate, chloride, thiocyanate, etc., complexes, but decreases when acetate, lactate, etc., complexes are formed. Myers and Metzler[5] observed a moment equal to 5.96 Bohr magnetons for iron in an ethereal complex. Aumeras and Mounic[6] calculated the degree of hydrolysis of ferric salts at the final state of equilibrium from magnetic data, while Chevalier and Mathieu[7] showed that the rate of change of susceptibility of Fe^{3+} increases, and that the time for attaining final hydrolysis decreases, with decreasing acidity of the solutions. The magnetic properties of iron in compounds of type $[Fe_3(CH_3COO)_6(OH)_2]NO_3 \cdot 6H_2O$ has been studied by Tsai and Wucher.[8] They concluded that at high temperatures, the three moments in each molecule orientate independently giving values for the Curie constant expected of Fe^{3+} compounds, while at low temperatures the moments are rigidly coupled, thus giving low values.

Absorption spectroscopy also has been used with advantage by Bent and French,[9] Rabinowitch and Stockmayer,[10] Olerup,[11] and Gamlen and Jordan[12] to calculate the association of Fe^{3+} with Cl^- ions, leading to the formation of species like $FeCl^{2+}$, $FeCl_2^+$, $FeCl_3$ and $FeCl_4^-$. The last named authors have reviewed this type of work in detail. The spectra of ferric chloride or perchlorate in solutions of hydrochloric acid of varying concentration have been recorded by Abraham,[13] by Kiss and co-workers,[14] and by Metzler and Myers.[5] Spectra of ferric nitrate solutions of varying acidity were obtained by Cathala and Cluzel.[15] Although these workers did not study the association of Fe^{3+} with other ions quantitatively, their results characterize the spectra of ferric salts under varying environment. Whitakar and Davidson[16] obtained spectra for the iron(III) sulfate complexes, while Ibers and Davidson[17] studied the interaction between the iron(III) hexacyanato complexes and iron(III) and iron(II) hexacyanato complexes.

The hydroxy complexes of Fe^{3+} in particular have been studied by Rabinowitch and Stockmayer[10] and by Siddall and Vosburgh,[18] who calculated the equilibrium constant for formation of the first hydrolysis product $FeOH^{2+}$ over a range of ionic strengths. Olson and Simonsen[19] investigated this formation in the presence of various perchlorates and found that the equilibrium depends on the concentration of the perchlorate ion. Glickman and co-workers[20] observed a maximum at 240 mμ in the spectrum of ferric perchlorate in water. When ethyl alcohol is substituted for water,

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[16] R. A. Whitakar and N. Davidson, THIS JOURNAL, **75**, 3081 (1953).

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[18] T. H. Siddall and W. C. Vosburgh, *ibid.*, **73**, 4270 (1951).

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this maximum remains unaffected, whereas another maximum of small intensity is observed at 320 mμ. They ascribed the first maximum to solvated Fe^{3+} ion and the second one to products of solvolysis or hydrolysis of Fe^{3+}.

Bjerrum[21] has also calculated the equilibrium constant for the first hydrolysis product from conductivity measurements, while Lamb and Jacques[22] employed in addition colorimetric methods for studying the formation of this product. Brossett[23] subsequently obtained widely differing values for this equilibrium constant from e.m.f. measurements. Bray and Hershey[24] in addition calculated the equilibrium constant for the formation of the second hydrolysis product $Fe(OH)_2^+$. The lack of agreement between the results, obtained by the previous workers, led Hedström[25] to investigate in detail the hydrolysis of Fe^{3+}, employing new e.m.f. methods developed by Biedermann and Sillén[26] and other workers for studying complex equilibria. Further reference to Hedström's work will be made later.

The present work deals with a magnetic and spectrophotometric study of ferric perchlorate solutions at constant ionic strength. The authors gratefully acknowledge the benefit derived from the earlier phases of the magnetic investigation, carried out by M. J. Joncich in this Laboratory. Dr. Joncich first obtained a curve at room temperature showing the dependence of magnetic moment on *p*H, as in Fig. 3.

Experimental Procedure

Materials.—Ferric perchlorate was formed by dissolving hydrated ferric nitrate (Analytical grade reagent) in perchloric acid (72% Mallinckrodt), evaporating the solution to a small bulk and repeating the evaporation with excess of perchloric acid several times. The violet crystals that separated on cooling the solution were drained off the excess perchloric acid, and crystallized twice from distilled water. The crystals contained water of crystallization and perchloric acid. Anhydrous sodium perchlorate (G. Frederick Smith Co.) was used.

A stock solution of ferric perchlorate was prepared and iron was estimated gravimetrically. A solution containing 0.04 *M* of iron and 3.0 *M* sodium perchlorate was prepared by diluting the required quantity of the stock solution. The *p*H of this solution (A) was found to be 1.0 ± 0.1. Another solution (B) containing the same amounts of iron and sodium perchlorate was similarly prepared but with enough perchloric acid to make it strongly acidic and with a *p*H less than zero. This was designated as $pH < 0$. Most of the *p*H measurements were made on a Beckman *p*H meter; some measurements requiring temperature compensation above 40° were made on a Leeds and Northrup *p*H meter. The free perchloric acid in these solutions tended to dissolve the sealed-in fiber of the small calomel electrode, thereby vitiating the measurements, and hence a fresh pair of glass-calomel electrodes was used for each set of three measurements. The measurements below and above *p*H 1 are correct within ±0.1 and ±0.05 unit, respectively.

The *p*H of solutions was adjusted by adding sodium bicarbonate to aliquots of solutions B and A, which gave values intermediate between the ranges <0 to 1 and 1 to 2.5, respectively. The solutions were stirred vigorously and freed from carbon dioxide by applying suction. These were stored in polyethylene bottles and maintained at 15°, as the solutions in the higher *p*H range inclined to become turbid when stored in glass bottles at room temperature for several days.

Magnetic Measurements.—A Gouy balance was modified in some respects for making magnetic measurements of the solutions over a temperature range of 15 to 60°. A small electrical heating pad was placed against the back wall of the plastic casing surrounding the pole pieces, so that the air inside could be preheated to the same temperature as that of the solution. The heating was controlled by a Variac.

Twenty-five cc. of the solution was placed in a Pyrex tube 13.5 cm. in length and 2.0 cm. in diameter. The ground glass stopper for the tube was constructed to hold a small thermometer (3" in length, blood gas analysis type with 2° markings) in a collar with an external transparent Teflon tubing. The position of the thermometer was adjusted so that its bulb dipped in the solution. The stopper was smeared with a drop of glycerol and inserted in the tube; this rendered the ground glass portion transparent and facilitated clear viewing of the thermometer. Care was taken to avoid any contamination of the solution with glycerol. The tube containing the solution was heated in an electrical air-bath to a desired temperature and was quickly hung inside the plastic casing between the pole pieces. As the air in the plastic box surrounding the tube was preheated to the same temperature as that of the solution, there was not any significant fall in the temperature of the solution, and this arrangement facilitated the maintenance and measurement of temperature within 1°. Further, with this arrangement, it did not become necessary to widen the pole gap to accommodate the conventional heating furnace, which weakens the magnetic field and thereby affects the accuracy of the magnetic measurements. Measurements beyond 60° were not made, as appreciable evaporation of the solution was observed. Measurements at temperatures lower than the room temperature were made by cooling the solution and wiping off the moisture on the tube with filter paper. The susceptibilities were measured at two field strengths of approximately 5400 and 6400 oersteds and the average of the two values was taken. The susceptibility of distilled water freed from carbon dioxide was taken as -0.720×10^{-6} c.g.s. unit.

The densities of solutions were measured with a 25-cc. density bottle from room temperature to 60°, at intervals of about 5°. The density corresponding to a particular temperature, at which the magnetic susceptibility was measured, was read off from experimental density *versus* temperature curves.

Spectrophotometric Measurements.[27]—All measurements were made on the Beckman model DU spectrophotometer. Matched 10-mm. silica cells with quartz inserts 9.95 mm. thick were used; this gave an effective optical path of 0.05 mm. The spectra were measured from 220 mμ to about 500 mμ. Absorbancy values were obtained at intervals of 5 mμ, except in the regions of maxima, where measurements were made at 2 mμ intervals. The slit width was maintained constant and as narrow as possible at wave lengths where a comparison of the spectra of the solutions of varying acidity was desired. Measurements were made at 15 and 51°, and in some cases at 25° also; the constant temperatures were obtained by water jackets. During measurements at 15°, care was taken to wipe off moisture from the cells, and to seal the top lid of the cell compartment with adhesive tape, which prevented the formation of a moisture film on the cells. These measurements were made when the humidity was very low, which helped to keep the cell faces dry and clean.

Results

Magnetic Data.—Magnetic susceptibility data are given in Tables I and II. In these tables

κ = susceptibility per cc. of soln.
χ = susceptibility per gram of soln.
χ_{Fe} = susceptibility/g. atom of total iron in the soln., obtained from the susceptibility per gram ion of ClO_4^- (-34×10^{-6}) and the molar susceptibility of ferric perchlorate. The susceptibility per gram of ferric perchlorate was calculated from χ and the weight fractions of the components. Wiedemann's additivity law and the following values for the susceptibility per gram of the constituents were assumed to apply: $H_2O = -0.720$; $HClO_4 = -0.423$, and $NaClO_4 = -0.355$ (all $\times 10^{-6}$).

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(27) The nomenclature given in Letter Circular LC-857 of the National Bureau of Standards has been used here.

TABLE I

MAGNETIC SUSCEPTIBILITIES OF 0.04 *M* FERRIC PERCHLORATE–3 *M* SODIUM PERCHLORATE SOLUTIONS OF VARYING ACIDITY

	$pH < 0$			pH 0.05 ± 0.05			pH 0.4 ± 0.1			pH 0.7 ± 0.1			pH 1 ± 0.1		
Temp., °C.	$-\kappa \times 10^5$	$-\chi \times 10^6$	$\chi_{Fe} \times 10^2$	$-\kappa \times 10^6$	$-\chi \times 10^6$	$\chi_{Fe} \times 10^2$	$-\kappa \times 10^6$	$-\chi \times 10^6$	$\chi_{Fe} \times 10^2$	$-\kappa \times 10^6$	$-\chi \times 10^6$	$\chi_{Fe} \times 10^2$	$-\kappa \times 10^6$	$-\chi \times 10^6$	$\chi_{Fe} \times 10^2$
16	...	...	..	0.145	0.117	1.54	0.177	0.142	1.43	...	...	..	...	...	..
22	0.169	0.136	1.45	...	...	..	.188	.152	1.39	0.220	0.177	1.35	0.207	0.164	1.36
26	.182	.147	1.42	.186	.150	1.43	.203	.164	1.36	...	...	..	.216	.172	1.34
30	.194	.155	1.39	...	...	..	.229	.185	1.30	.254	.205	1.26	.242	.198	1.26
35	.205	.166	1.36	.195	.161	1.40	...	...	..	.272	.224	1.21	.250	.204	1.24
38	.214	.174	1.33	...	...	..	.269	.218	1.20	...	...	..	.267	.218	1.19
45	.219	.178	1.32	.212	.172	1.36	.282	.230	1.15	.291	.237	1.16	.287	.234	1.13
49	...	...	..	...	...	..	.304	.248	1.10	.317	.258	1.10	.302	.247	1.10
53	.227	.185	1.30	...	...	..	...	...	..	.317	.258	1.08	...	...	..
56	.227	.185	1.29	.234	.191	1.30	.335	.273	1.02	...	...	..	.304	.249	1.10
61	.231	.189	1.29	.238	.195	1.29	.342	.280	1.00	.339	.277	1.03	...	...	..

TABLE II

MAGNETIC SUSCEPTIBILITIES OF 0.04 *M* FERRIC PERCHLORATE–3 *M* SODIUM PERCHLORATE SOLUTIONS OF VARYING ACIDITY

	pH 1.15 ± 0.05			pH 1.35 ± 0.05			pH 1.75 ± 0.05			pH 1.95 ± 0.05			pH 2.45 ± 0.05		
Temp., °C.	$-\kappa \times 10^6$	$-\chi \times 10^6$	$\chi_{Fe} \times 10^2$	$-\kappa \times 10^6$	$-\chi \times 10^6$	$\chi_{Fe} \times 10^2$	$-\kappa \times 10^6$	$-\chi \times 10^6$	$\chi_{Fe} \times 10^2$	$-\kappa \times 10^6$	$-\chi \times 10^6$	$\chi_{Fe} \times 10^2$	$-\kappa \times 10^6$	$-\chi \times 10^5$	$\chi_{Fe} \times 10^2$
16	0.195	0.157	1.38	0.308	0.244	1.11	0.340	0.270	1.03	0.501	0.398	0.63	0.507	0.402	0.62
22	...	...	..	.318	.253	1.08	.365	.290	0.97	.509	.406	.61	.512	.409	.60
26	.295	.238	1.13	.325	.260	1.06	.370	.296	.95	.506	.404	.61	.528	.422	.57
32	.314	.254	1.08	.353	.283	0.99	.390	.312	.90	.515	.413	.58	.539	.428	.54
36	...	...	..	.357	.287	.97	.393	.315	.89	...	...	..	...	...	..
40	.338	.274	1.02	...	...	..	.395	.318	.88	.519	.417	.57	.537	.432	.53
45	.340	.276	1.02	.376	.303	.93	.405	.327	.85	.519	.419	.57	.534	.431	.52
49	.349	.284	0.99	.383	.310	.91	.412	.333	.83	.527	.426	.54	...	...	...
55	.368	.300	.94	.408	.331	.84	.419	.339	.81	.530	.430	.53	.550	.446	.48
61	...	...	..	.425	.346	.79	.431	.351	.78	.535	.435	.52	...	...	..

Weighings were made on the Gouy balance to within 0.2 mg., and the change in weight of the solutions observed on applying the magnetic field was of the order of several milligrams. With water, for instance, the decrease in apparent weight on application of the field was 33.3 and 48.7 mg., while a ferric perchlorate solution (pH 1 ± 0.1) at 30°, showed a decrease of 10.7 and 15.6 mg., at field strengths of approximately 5400 and 6400 oersteds, respectively.

The volume susceptibilities of the solutions measured at the two field strengths agreed generally within about 4% of the mean value. The error in the final values of the susceptibility per gram atom of total iron, χ_{Fe}, calculated from experimental observations is estimated to be less than 2.5%.

The pH values shown at the top of each column in Tables I and II represent only the pH of the solutions as measured at room temperature, and are not those used in calculating equilibrium constants at several temperatures. The effect of temperature on pH is discussed later.

Spectrophotometric Data.—Figures 1 and 2 show a few of the several spectral curves obtained with 0.04 *M* ferric perchlorate–3 *M* sodium perchlorate solutions of varying acidity, and represent the characteristic spectral behavior of these solutions in specific regions of pH, studied at 15 and 51°. In the case of the solution with $pH < 0$, only the spectrum obtained at 25° is shown. This and a solution with pH 0.05 ± 0.05 at 15° show only one maximum at 240 mμ, while others within the pH range 0.1–1.8 show an additional maximum at 335 mμ at the same temperature. Similar curves with peaks at 240 and 335 mμ were obtained by Abraham and co-workers[13,14] with ferric perchlorate solutions containing other anions. All the curves pass through an isosbestic point at 272 mμ, which was also observed by Siddall and Vosburgh,[18] who calculated the equilibrium constant for the formation of $Fe(OH)^{2+}$ using the intensities at this point. They do not, however, give a complete description of the actual spectral curves obtained by them which prevents any further comparison.

The intensity at 240 mμ decreases when these solutions are heated to 51°, and that at 335 mμ increases. It is interesting to note in Fig. 1 that the solution with pH of approximately 0.2, which has only one maximum at 240 mμ at 15°, develops an additional maximum at 335 mμ when it is heated to 51°. In all cases, the curves at the lower and the higher temperatures pass through the same isosbestic point at 272 mμ, indicating that at the higher temperature the solution has a new equilibrium having a pH different from that at the lower temperature, and containing different concentrations of the ionic species.

The solutions with pH greater than 1.8 gave only a broad absorption band extending far into the visible region, without any definite peaks. But even these solutions, on being warmed, showed a decrease of absorbance in the region up to 280 mμ, and an increase at longer wave lengths.

Values of absorbances for a 0.005-cm. path as observed at 240 mμ and at 335 mμ over a range of temperature and of acidity are given in Table III.

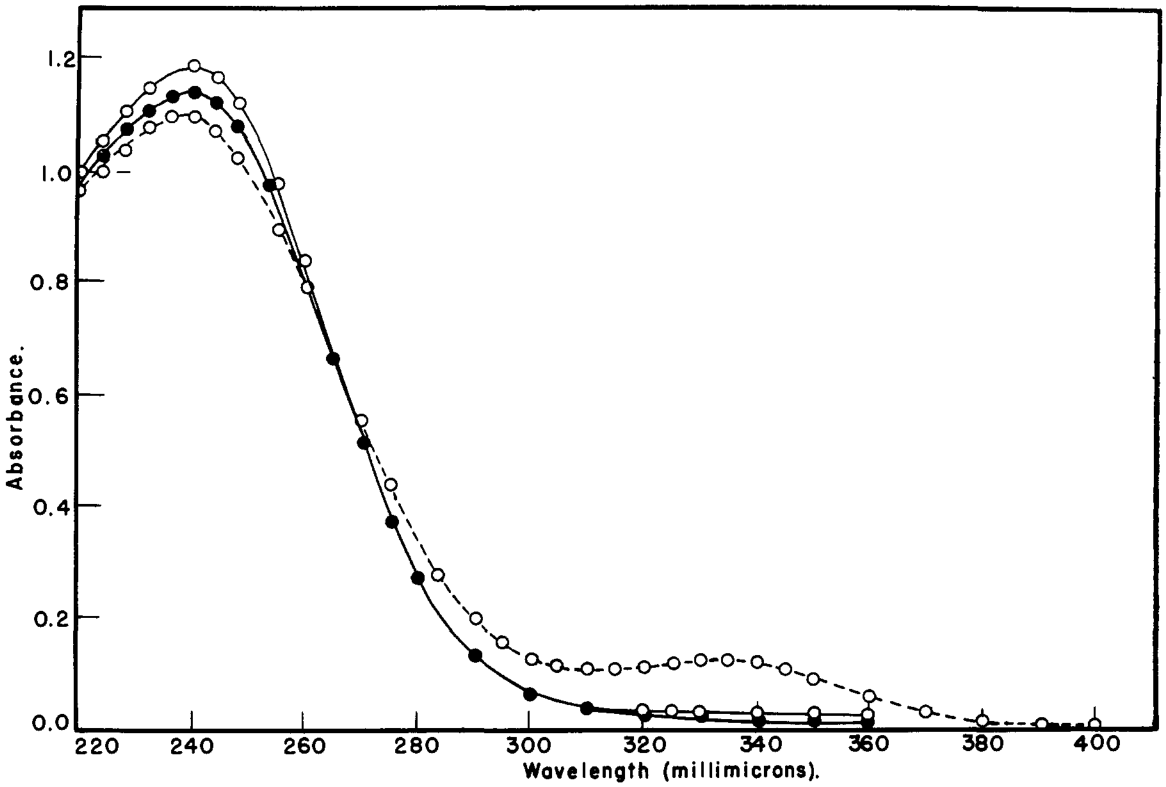

Fig. 1.—Absorption spectra of 0.04 *M* ferric perchlorate–3 *M* sodium perchlorate solutions (light path = 0.005 cm.). Curve with closed circles is for solution with $pH < 0$ at 25°. Solid and dashed curve with open circles is for solution with approximate pH of 0.2 at 15 and 51°, respectively.

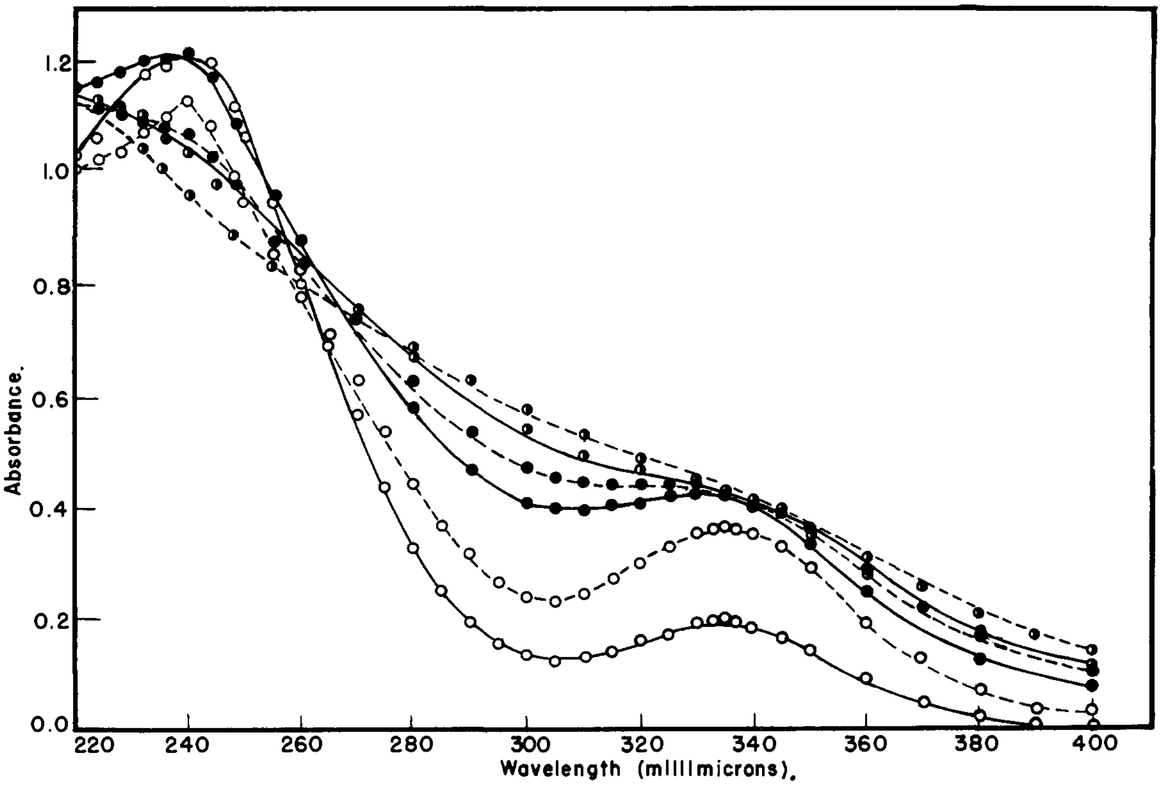

Fig. 2.—Absorption spectra of 0.04 *M* ferric perchlorate, 3 *M* sodium perchlorate solutions (light path = 0.005 cm.). Curves with open, closed and half circles correspond to solutions with approximate pH of 1.0, 1.7 and 2.0, respectively. Solid and dashed curves correspond in each case to spectra observed at 15 and 51°, respectively.

TABLE III

VALUES OF ABSORBANCE FOR 0.005 CM. PATH AT 240 mμ AND AT 335 mμ ON 0.04 *M* $Fe(ClO_4)_3$—3 *M* $NaClO_4$ SOLUTIONS AT SEVERAL TEMPERATURES AND ACIDITIES

	240 mμ			335 mμ	
*p*H	15°	25°	51°	15°	51°
<0	1.165	1.135	1.075	0.000	0.000
0.05	1.164	...	1.071	.000	.000
.5	1.184	1.150	1.097	.028	.100
.7	1.195	...	1.116	.087	.255
.8	1.200	1.200	1.140	.106	.275
.95	1.215	1.205	1.185	.240	.380
1.15	1.217	1.210	1.200	.440	.447
1.75	1.220	1.220	1.200	.450	.450

Discussion of Results

Figure 3 shows magnetic moment in Bohr magnetons for total iron in each solution as a function of acidity and of temperature. The magnetic moment was calculated from the usual formula $\mu = 2.84\sqrt{\chi_{Fe} \times T}$ where T is the absolute temperature. Neglect of any interaction term is believed to be justified because all solutions are magnetically dilute.

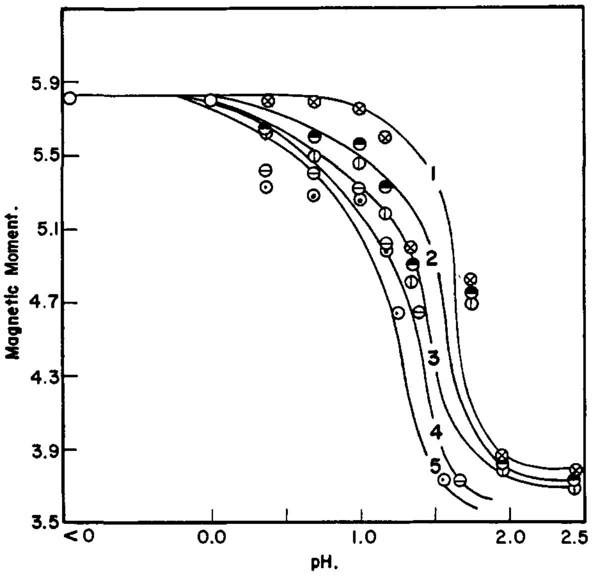

Fig. 3.—Magnetic moment as a function of *p*H and temperature. Curves 1, 2, 3, 4 and 5 correspond to observations at 15, 25, 35, 45 and 51°, respectively.

Hydrolysis is presumably negligible in a strongly acid solution. It is, therefore, concluded that the average effective magnetic moment of 5.82 Bohr magnetons in the low *p*H range is that of the free (or merely hexaaquo-coördinated) Fe^{3+} ion. This value is a little lower than the spin-only value of 5.92, and than the range of values (5.9–6.0) often reported for magnetically dilute crystalline compounds containing the ion Fe^{3+}.

Above *p*H 0.2 the effective magnetic moment is seen from Fig. 3 to be a function of temperature. This might imply some exchange interaction leading to non-zero values of the Weiss constant. There is, however, ample electrometric and spectroscopic evidence, to be discussed later, which shows that above *p*H 0.1 hydrolysis becomes appreciable and that the solutions then contain measureable concentrations of ionic species other than Fe^{3+}.

We shall now explore the view that some of the ionic species present above *p*H 0.1 have magnetic susceptibilities quite different from that of Fe^{3+}, and that these species are in equilibrium with Fe^{3+}.

The most complete study on the hydrolysis products of the ion Fe^{3+} is that of Hedström.[25] From his electrometric titrations on systems similar to those described in the present paper he derived the following equilibrium constants for the three stages of hydrolysis

$$Fe^{3+} + H_2O \rightleftarrows FeOH^{2+} + H^+ \qquad k_{11} = (9.0 \pm 1.0) \times 10^{-4}$$

$$Fe^{3+} + 2H_2O \rightleftarrows Fe(OH)_2^{+} + 2H^+ \qquad k_{12} = (4.9 \pm 1.0) \times 10^{-7}$$

$$2Fe^{3+} + 2H_2O \rightleftarrows Fe_2(OH)_2^{4+} + 2H^+ \qquad k_{22} = (1.22 \pm 0.10) \times 10^{-3}$$

In the above expressions concentrations are taken as moles per liter of solution. The temperature reported is 25°.

Dashed curves in Fig. 4 give concentrations of the four ionic species: Fe^{3+}, $FeOH^{2+}$, $Fe(OH)_2^{+}$ and $Fe_2(OH)_2^{4+}$ calculated from Hedström's data at 40 millimoles of total iron, and 3.0 *M* sodium perchlorate, over the *p*H range 0 to 2.5, all at 25°.

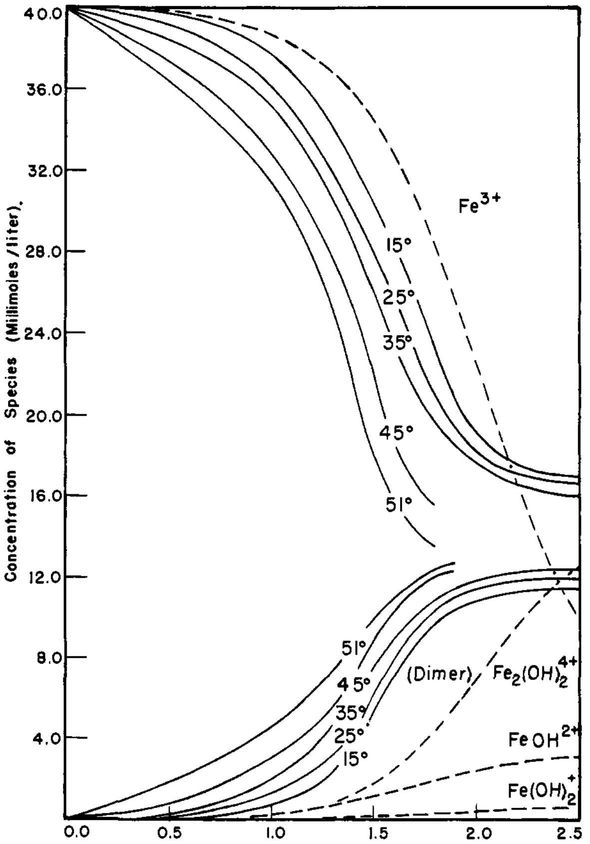

Fig. 4.—Concentration of species *versus* *p*H. Dashed curves represent Hedström's data at 25°. Solid curves represent the magnetic data.

It is clear from Fig. 4 that at all pH values above about 1.0 most of the iron is present either as Fe^{3+} or as $Fe_2(OH)_2^{4+}$. (Note that a mole of $Fe_2(OH)_2^{4+}$ contains twice as much iron as a mole of $FeOH^{2+}$.) At pH 2.0 we find the magnetic susceptibility per gram-atom of total iron to be less than half that at $p\mathrm{H} < 0$. Inspection of Fig. 4 can only lead to the conclusion that the ion $Fe_2(OH)_2^{4+}$ hereafter called the "dimer" is the only species present in anything approaching sufficient concentration to cause this large magnetic change, and that to produce such a diminution of susceptibility the dimer itself must be *diamagnetic*.

Assuming that the dimer is diamagnetic, and that $FeOH^{2+}$ has a moment equal to that of Fe^{3+} (the concentration of $Fe(OH)_2^+$ is negligible) we may use the magnetic data to calculate the concentrations of Fe^{3+} and of $Fe_2(OH)_2^{4+}$ present in solution at various pH values. This is done very simply as follows.

We shall ignore the contributions of $FeOH^{2+}$ and of $Fe(OH)_2^+$ to the susceptibility of total iron, and hence write

$$\chi_{Fe} = f\chi_1 + (1 - f)\chi_2$$

where

χ_{Fe} as before = susceptibility/g. atom of total iron
χ_1 = susceptibility/g. atom of iron present as Fe^{3+}
χ_2 = susceptibility/g. atom of iron present as $Fe_2(OH)_2^{4+}$
f = wt. fraction of total iron present as Fe^{3+}

The justification for ignoring the species $FeOH^{2+}$ is that its concentration never exceeds 7% of the total iron, so that even if it has a susceptibility moderately different from that of Fe^{3+}, the effect would be barely detectable. The concentration of $Fe(OH)_2^+$ does not exceed 1% of total iron.

If the dimer is assumed to be diamagnetic, then whatever actual value χ_2 may have is negligible in comparison with the susceptibility of the strongly paramagnetic Fe^{3+}. Hence we may write

$$f = \chi_{Fe}/\chi_1$$

The values of χ_{Fe} corresponding to 15, 25, 35, 45 and 51° were interpolated from the experimental $1/\chi_{Fe}$ *versus* temperature curves (not shown) drawn for solutions of different acidity. The values of χ_1 corresponding to these temperatures were calculated from the average magnetic moment of 5.82 Bohr magnetons, observed for iron in the strongly acidic solutions ($p\mathrm{H} < 0$ and $p\mathrm{H} = 0.05 \pm 0.05$). Millimoles of Fe^{3+} and of $Fe_2(OH)_2^{4+}$ obtained in this way at the above temperatures and over the whole pH range are shown in solid lines in Fig. 4. Moles of $Fe_2(OH)_2^{4+}$ are simply $0.04[(1 - f)/2]$. A comparison of these results obtained from magnetic data at 25° with those reported by Hedström for Fe^{3+} and $Fe_2(OH)_2^{4+}$ in Fig. 4 shows agreement within experimental error. Sacconi and Cini[28] have reached a similar conclusion concerning the dimerization of Mo(V) to form a diamagnetic species. Jezowska-Trzebiatowska and Wajda[29] have also attributed the diamagnetism of μ-oxychlororhenate-(IV) to the mutual antiparallelism of the spins of both Re atoms in a binuclear complex.

It should be noted that a decrease in pH with increasing temperature was observed in all the solutions with pH greater than 0.4. This change could not be measured with precision in the case of solutions with pH up to 1.5, and in the temperature range 15–35°, due to limitations of the method employed. However, in the case of the two solutions originally having pH values (a) 1.75 ± 0.05, and (b) 1.95 ± 0.05, a definite decrease of about (a) 0.3 and 0.5 and (b) 0.3 and 0.4 pH unit corresponding to 45 and 50°, respectively, was observed. These observations have been adequately represented in Fig. 4 and the curves corresponding to 45 and 51° have been drawn accordingly.

It was ascertained that time had no effect on the magnetic susceptibility of the solutions, which were being studied at different temperatures and that the equilibrium between the species was reached almost instantaneously at these temperatures.

The following average estimates for the equilibrium constant k_{22} for the formation of the dimer have been obtained from the magnetic data.

$k_{22} \times 10^3$ (15°) 4.9 ± 0.9; (25°) 7.3 ± 0.8; (35°) 10.2 ± 2.2; $k_{22} \times 10^3$ (45°) 16.3 ± 1.7; (51°) 25.1 ± 5.8

For this purpose, the concentrations of Fe^{3+} and the dimer were read off from the corresponding curves in Fig. 4, using the pH range 1.25 to 1.75, as the values of k_{22} are found to be fairly consistent in this range. The concentrations are more accurate in this pH range as compared with the lower and the higher pH ranges.

It is seen that the value of k_{22} at 25° obtained from the magnetic data is about six times greater than that obtained by Hedström. This may be ascribed to the fact that the presence of the first and second hydrolysis products has been ignored in the calculations from the magnetic data, and since the values of molecular concentration of the dimer are based on the difference between the total iron concentrations and that of the Fe^{3+} ions, these are somewhat higher than the actual ones. Further the concentrations of H^+, calculated from the observed pH values are not very precise. In view of these circumstances the agreement is believed to be satisfactory.

The increase of k_{22} with increasing temperature shows that the dimer is more stable at higher temperatures, within the moderate range investigated. A plot of log k_{22} against reciprocal temperature (Fig. 5) gives a reasonably straight line from the slope of which we compute $\Delta H \simeq 9.8$ kcal. per mole from the relation $\mathrm{d} \log k/\mathrm{d}T = \Delta H/2.303RT^2$. The situation has some analogies to the association of paramagnetic triarylmethyl radicals to form a diamagnetic hexaarylethane. But the heat of reaction is opposite in sign.

We turn now to a quantitative interpretation of the absorption spectra. It will be shown that at high acidities the absorption band at 240 mμ is due solely to Fe^{3+}, that at lower acidities the ionic species $FeOH^{2+}$ contributes to the absorbance at 240 mμ, and that the band at 335 mμ is due to $Fe_2(OH)_2^{4+}$.

A solution of sodium perchlorate in perchloric acid (free from iron) shows no absorption in this region of the spectrum. A strongly acid solution ($p\mathrm{H} < 0$) containing ferric perchlorate shows a single band with a maximum at 240 mμ. The magnetic

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(28) L. Sacconi and R. Cini, THIS JOURNAL, **76**, 4239 (1954).

(29) B. Jezowska-Trzebiatowska and S. Wajda, *cf. C. A.*, **48**, 13518 (1954).

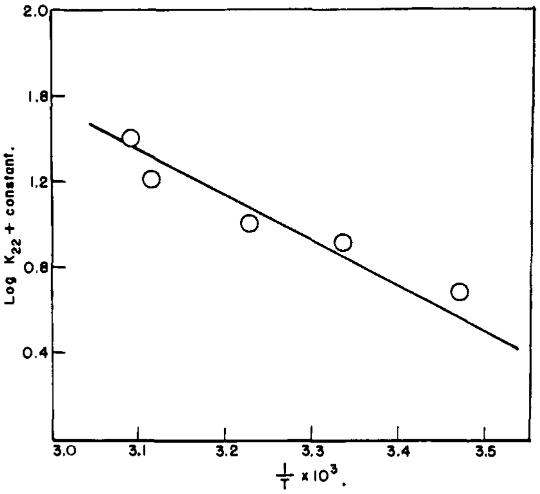


Fig. 5.—Log k_{22} (from magnetic data) *versus* reciprocal of absolute temperature.

data presented here support the view of Hedström that only one ionic form of iron, namely Fe^{3+}, is present (in appreciable concentrations) under these conditions. We, therefore, attribute the band at 240 mμ solely to Fe^{3+}. The curve presented for pH < 0 at room temperature is similar to those given by Gamlen and Jordan,[12] and by Rabinowitch and Stockmayer,[10] who attributed the band at 240 mμ to the species Fe^{3+}.

As the pH is raised the absorbance at 240 mμ actually increases, although the magnetic data confirm Hedström's view that the concentration of Fe^{3+} decreases with decreasing acidity. Hence we conclude that, at lower acidities, some species other than Fe^{3+} contributes to the absorbance at 240 mμ. In Fig. 6 absorbance at 240 mμ is plotted against concentration of Fe^{3+}; the values of absorbance being taken from Table III and the concentrations as calculated from Hedström's equilibrium constants. Each point in Fig. 6 corresponds to a given pH, and all points to the fixed temperature, 25°.

If the absorbance at 240 mμ were due solely to Fe^{3+}, the relationship expected would be the straight line shown joining the origin with the observed absorbance for 40 millimoles of Fe^{3+} per liter. Let δ be the difference between observed absorbance and the straight line. Then δ is the contribution of some species other than Fe^{3+} to the absorbance at this wave length. In Fig. 7 δ is plotted against the concentrations of each of the three hydrolysis products $FeOH^{2+}$, $Fe(OH)_2^+$ and $Fe_2(OH)_2^{4+}$ as calculated from Hedströms data, at the several acidities. It will be seen that δ is most nearly linear with the concentration of the species $FeOH^{2+}$. We conclude, therefore, that this species has an absorption band in the region of 240 mμ, but that this is obscured by the band due to Fe^{3+}.

By following a similar procedure with the values of absorbance corresponding to pH < 0 (at which the concentration of Fe^{3+} is 40 millimoles per liter) from Table III, the molar absorbancy index for the Fe^{3+} ion at 15° and at 51° are found to be 5.80 × 10^3 and 5.55 × 10^3, respectively. But as no data for the concentration of $FeOH^{2+}$ at these two temperatures are available, the molar absorbancy index for this species could not be evaluated. At 25° the molar absorbancy index for $FeOH^{2+}$ is found to be 4.6 × 10^4 from the straight line in Fig. 7.

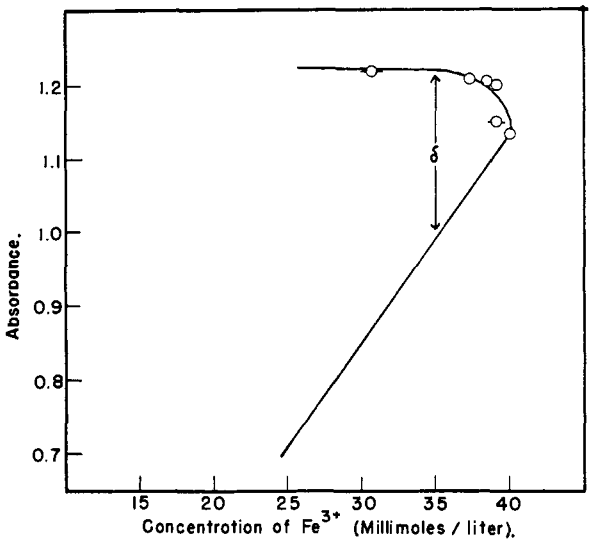


Fig. 6.—Absorbance at 240 mμ (with 0.005 cm. light path) *versus* concentration of Fe^{3+}. Curve with open circles shows the observed values. The straight line represents the theoretical absorbance assumed for Fe^{3+}.

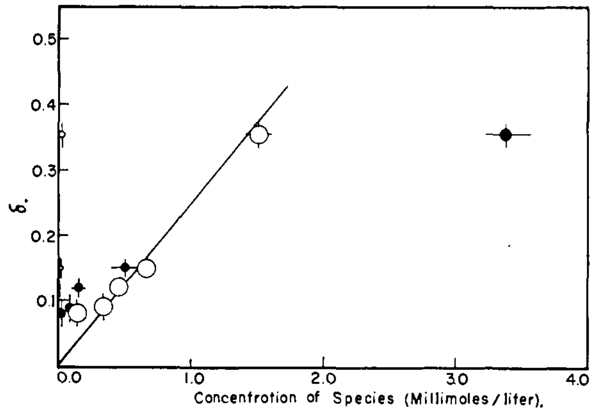


Fig. 7.—Difference (δ) between the observed and the theoretical absorbance at 240 mμ (from Fig. 6) *versus* the concentration of other species, derived from Hedström's data at 25°. Large and small open circles correspond to $FeOH^{2+}$ and $Fe(OH)_2^+$, respectively. Closed circles correspond to the dimer $Fe_2(OH)_2^{4+}$.

The band at 335 mμ presents a simpler problem As shown in Fig. 9 the absorbances at this wave length (interpolated from the absorbance–pH curve in Fig. 8) over the pH range 0 to 1.1 show a linear relation within limits of experimental error, with the concentration of the species $Fe_2(OH)_2^{4+}$ as derived from the magnetic data. We assume, therefore, that this band is due entirely to the dimer, and that the contribution of the second hydrolysis product, $Fe(OH)_2^+$, is negligible. It will be noted that the maximum concentration of $Fe(OH)_2^+$ does not exceed 1% of total iron at 25°. We are forced to use the magnetic data as a source of concentration of $Fe_2(OH)_2^{4+}$ because no other data are available over a temperature range.

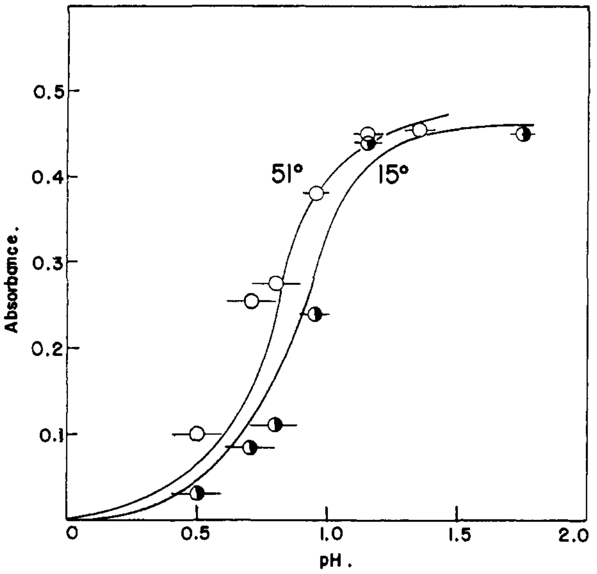


Fig. 8.—Absorbance at 335 mμ (with 0.005 cm. light path) *versus* *p*H.

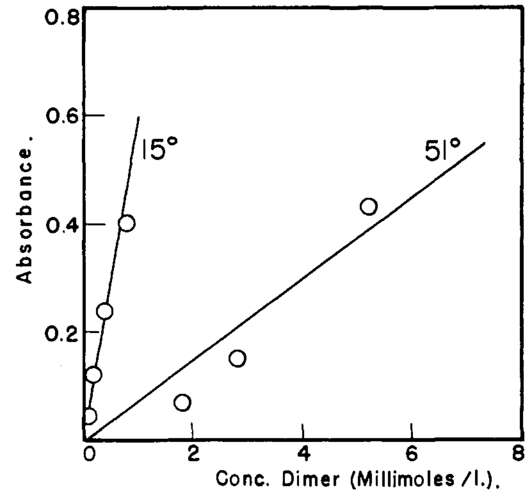


Fig. 9.—Absorbance at 335 mμ (with 0.005 cm. light path) *versus* concentration of the dimer, obtained from magnetic data.

The above approach of assigning the band at 240 mμ to Fe^{3+} and $FeOH^{2+}$, and that at 335 mμ to $Fe_2(OH)_2{}^{4+}$ is in agreement with the observations of Glickman and co-workers.[20]

It is now possible to obtain the equilibrium constant k_{22} for formation of the dimer, from the molar absorbancy indices and the absorbances for Fe^{3+} and $Fe_2(OH)_2{}^{4+}$ and to compare the value so obtained with that derived from the magnetic data, with a view to testing the assumptions made above in interpreting the absorption spectra. But this procedure was abandoned because evaluation of the molar absorbancy indices for the dimer over a temperature range itself involved use of concentrations derived from the magnetic data.

The following procedure gives k_{22} from consideration of the spectroscopic data alone.

The equilibrium constant for the reaction

$$2Fe^{3+} + 2H_2O \rightleftarrows Fe_2(OH)_2{}^{4+} + 2H^+$$

may be written

$$k_{22} = \frac{[\text{dimer}][H^+]^2}{(C - 2\,[\text{dimer}])^2}$$

where C is the total iron concentration and [dimer] is the concentration of $Fe_2(OH)_2{}^{4+}$, both expressed in moles per liter.

In this calculation the concentrations of $FeOH^{2+}$ and of $Fe(OH)_2{}^+$, being small, are ignored, and it is assumed that neither $FeOH^{2+}$ nor $Fe(OH)_2{}^+$ shows any absorption in the 335 mμ region.

If d_D is the absorbance at 335 mμ (with 1 cm. light path) and a_M is the molar absorbancy index of the dimer, then [dimer] $= d_D/a_M$. Substituting for [dimer] we have

$$k_{22} = \frac{[d_D/a_M][H^+]}{[C - 2[d_D/a_M]]^2}$$

In the expansion the term $4d^2{}_D/a^2{}_M$ may be neglected because a_M is of the order of 10^4 (as found from Fig. 9). Hence

$$k_{22} = \frac{[d_D/a_M][H^+]^2}{C^2 - 4(Cd_D/a_M)}$$

and

$$C^2 - 4(Cd_D/a_M) = \frac{d_D[H^+]^2}{a_M k_{22}}$$

Dividing by C^2d_D and rearranging

$$\frac{1}{d_D} = \frac{1}{C^2 a_M k_{22}}[H^+]^2 + \frac{4}{Ca_M}$$

If, now, $1/d_D$ is plotted against $[H^+]^2$ as in Fig. 10,

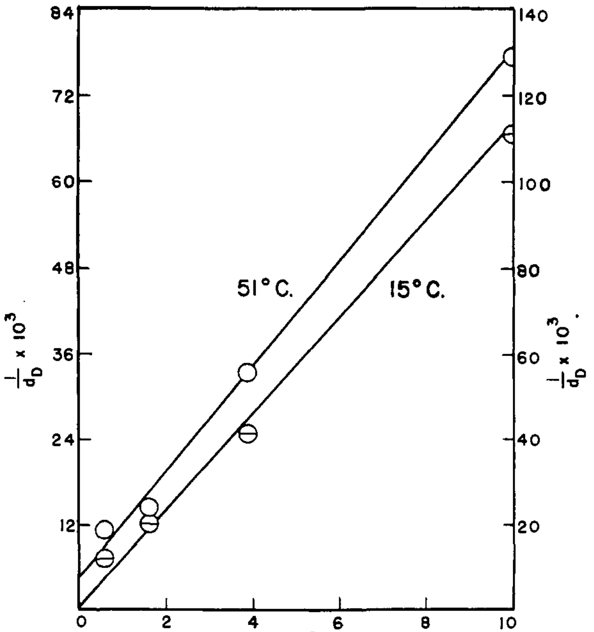


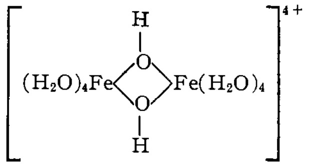
Fig. 10.—Reciprocal of absorbance at 335 mμ with 1 cm. light path *versus* square of the hydrogen ion concentration. Scale to the left is for data at 51°, that on the right is for data at 15°.

using the interpolated values of absorbance from the curve in Fig. 8, we have the intercept on the vertical axis equal to $4/(Ca_M)$, and the slope equal to $1/(C^2a_Mk_{22})$, whence

$$k_{22} = \frac{\text{intercept}}{4C\,\text{slope}}$$

In this way k_{22} is found to be 6.7×10^{-3} and 33×10^{-3} at 15 and 51°, respectively. These are in reasonable agreement with the corresponding values ($4.9 \pm 0.9 \times 10^{-3}$ and $25.1 \pm 5.8 \times 10^{-3}$) obtained from the magnetic data. It should be noted that this method is independent of the absorbances observed at 240 mμ and is, therefore, free of the assumptions made with regard to Fe^{3+} and $FeOH^{2+}$ contributing to absorption at this wave length. The method also affords evaluation of the molar absorbancy index a_M, since this is simply 4 divided by the product of C and the intercept. The values for a_M were found to be 8.3×10^4 and 2.5×10^4 at 15 and 51°, respectively. The corresponding molar absorbancy indices calculated directly from Fig. 9 in which the concentrations of dimer derived from magnetic data are employed, are 10.0×10^4 and 1.5×10^4.

From this work it is clear that a partially hydrolyzed solution of ferric ions contains a diamagnetic species in substantial amounts. This species, which possesses a characteristic absorption spectrum, is probably, as suggested by Hedström, a binuclear complex



in which exchange interaction between adjacent irons destroys all their paramagnetism. It is to be noted that just prior to precipitation of hydrous ferric oxide the solution contains a large fraction of the iron in the form of this dimer. Furthermore, precipitation occurs without any large change of magnetic moment per atom of total iron. It seems probable, therefore, that hydrous ferric oxide owes its subnormal magnetic moment to the presence of the diamagnetic $Fe_2(OH)_2^{4+}$ built into its structure.

It also seems probable that the low magnetic moment of iron in alkaline glass, observed by Abd-El-Moneim Abou-El Azm[30] may be due in part to dispersion of some type of diamagnetic dimers in the glass, rather than entirely to colloidal ferric oxide. Mattock[31] has recently pointed out that the tendency toward dimerization by metal ions increases with the probable increase of covalence in metal–hydroxyl bonds. Without disputing this correlation, it should be pointed out, however, that metal–metal covalent bonds may influence the formation of dimers, and that no amount of covalence between metal and one or more hydroxyls could be expected to reduce the magnetic moment of the dimer, $Fe_2(OH)_2^{4+}$, below that for one unpaired electron.

(30) Abd-El-Moneim Abou-El-Azm, *J. Soc. Glass Technol.*, **38**, 101T (1954).

(31) G. Mattock, *Acta Chem. Scand.*, **8**, 777 (1954).

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Studies on the Raschig Synthesis of Hydrazine: The Reaction between Aqueous Chloramine and Ammonia Solutions

BY MARK M. JONES, L. F. AUDRIETH AND ERVIN COLTON

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Although the reaction between chloramine and ammonia in aqueous solutions containing gelatin is shown to occur in the absence of permanent base, addition of sodium hydroxide to such a synthesis solution increases the yield of hydrazine. A spectrophotometric investigation of the synthesis solutions showed no trace of hypochlorous acid above a *p*H of 7.5. The effect of ammonium salts is shown to be due to a reduction in the basicity of the synthesis solutions. That there is no electrolyte effect in the Raschig synthesis appears probable from these experiments.

We have undertaken to define more specifically some of the factors which influence the yields of hydrazine in the Raschig synthesis. Based upon the experimental work presented in this paper supplemented by consideration of the pertinent literature it may be concluded: (a) that sodium hydroxide is not required in the Raschig synthesis although its presence increases the yield of hydrazine; (b) that hypochlorous acid is not present under conditions employed in the Raschig synthesis, in aqueous or in wet ether solutions of chloramine; (c) that the mechanism for the Raschig synthesis involving direct attack of ammonia by chloramine is to be preferred to any involving hypochlorous acid as an intermediate; and (d) that the influence of ammonium salt addition is due solely to the effect of the ammonium ion in reducing the basicity of the solution.

Experimental

Preparation of Chloramine Solutions.—A cold aqueous solution of chloramine, prepared by mixing aqueous sodium hypochlorite and ammonia in equimolar amounts, was shaken with diethyl ether resulting in the extraction of up to 80% of the haloamine in the non-aqueous phase. The ether extract was then shaken with an equal volume of distilled water and the two liquid layers again separated. Approximately one-half of the chloramine is found in each layer. Aqueous solutions of chloramine were thus prepared covering a large range of concentrations. The solutions were analyzed iodometrically.[1] These solutions were found to be sufficiently stable to ensure that less than 1% of the chloramine suffered decomposition between the time of analysis and the completion of the desired reaction.

Reaction of Chloramine and Ammonia in Aqueous Solution.—Previous work from this Laboratory has shown that the yields of hydrazine formed by interaction of both ammonia[2] and urea[3] with *t*-butyl hypochlorite are markedly increased by the addition of sodium hydroxide to the synthesis solution. Sisler and co-workers[4] have recently shown that good conversions of chloramine into hydrazine can be

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(1) W. Marckwald and M. Wille, *Ber.*, **56**, 1319 (1923).

(2) L. F. Audrieth, E. Colton and M. M. Jones, THIS JOURNAL, **76**, 1428 (1954).

(3) E. Colton, M. M. Jones and L. F. Audrieth, *ibid.*, **76**, 2572 (1954).

(4) H. H. Sisler, C. E. Boatman, F. T. Neth, R. Smith, R. W. Shellman and D. Kelmers, *ibid.*, **76**, 3912 (1954).