(where T_R is the reduced temperature) and the equation for the sum of the saturated liquid and vapor densities

$$\rho_L + \rho_V = \alpha + \beta t + \gamma t^2$$

The values of the constants in the equations, derived from the experimental data, are given in Table III when the density is expressed in g./cc. and temperature in °C. The extent to which the equation represents the data is shown by the curves in Fig. 3 where the difference between the calculated and experimental values of both liquid and vapor densities have been plotted against the temperature. The precision of the measurements is of the order of 0.0015 g./cc. for the liquid and 0.0002 g./cc. for the vapor at near room temperature and increases for the liquid and decreases for the vapor with an increase in temperature becoming the same somewhere between these values at the critical temperature. As will be noted the points fall within these limits except for methylcyclopentane whose liquid density data below 140° show relative large deviations. It is believed that the data in this temperature region are subject to large accidental errors of observation and that the equations, the constants of which were derived from the data above 140°, represents more nearly the true densities. Near the critical point the deviations become large for all compounds. This results from the form of the equation since the quantity $(1 - T_R^2)$ becomes so small as to be greatly influenced by errors in the measurement of the critical temperature. Hence, in this narrow region the equation cannot be expected to hold with the same accuracy as at lower temperatures.

Acknowledgment.—Grateful acknowledgment is made to the American Petroleum Institute and the National Bureau of Standards for the loan of the samples measured in this investigation.

Summary

1. The standard boiling points and the critical constants for cyclopentane, methylcyclopentane, ethylcyclopentane and methylcyclohexane were carefully determined.

2. The vapor pressures and saturated liquid and vapor densities of these compounds were determined from near their standard boiling points to their critical points. The data have been represented by empirical equations: (a) the vapor pressure data by equations of the type $\log p = A + B/T$ supplemented by deviation curves; (b) the density data by means of the equation of Fales and Shapiro, $\log \log \rho_L/\rho_V = \log k + m \log (1 - T_R^2) - n \log T_R$ together with the equation for the sum of the liquid and vapor densities, $\rho_L + \rho_V = \alpha + \beta t + \gamma t^2$. Values of the constants in the equations are given for each hydrocarbon.

WHITING, INDIANA RECEIVED DECEMBER 7, 1946

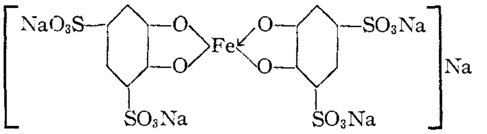
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

A Magnetic Study of the Type of Bonding Existing in Some Complexes of Ferric Iron with Sulfonated Pyrocatechol

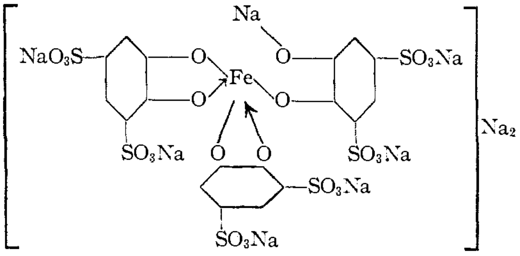
BY A. L. JONES[1] AND L. B. YEATTS

According to investigations conducted by Yoe and Jones,[1a] disodium 1,2-dihydroxybenzene-3,5-disulfonate was found to produce an intensely colored, stable complex with ferric iron which exhibited various color changes upon altering the *p*H of solutions of the complex. Below a *p*H of 5.7 the color of the complex with iron is blue; from 5.7–7 it is violet; and above a *p*H of 7, red.

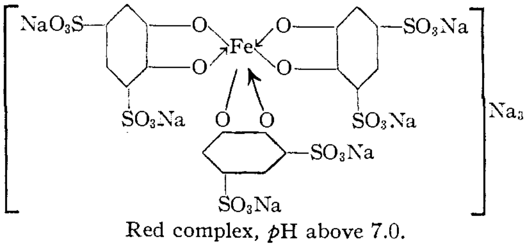
As a result of their spectrophotometric studies and by analogy with the iron–pyrocatechol complexes,[2,3] Yoe and Jones postulate the complexes



Blue complex, below *p*H of 5.7



Violet complex, *p*H 5.7–7.0.



Red complex, *p*H above 7.0.

shown for the three iron–pyrocatechol disulfonate complexes formed.

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[1] Present address: Standard Oil Company (Ohio), 2127 Cornell Road, Cleveland 6, Ohio.

[1a] Yoe and Jones, *Ind. Eng. Chem., Anal. Ed.*, **16**, 111 (1944).

[2] Karrer, "Organic Chemistry," by A. J. Meek, Nordeman Publishing Co., N. Y., 1938, p. 397.

[3] Reihlen, *Z. anorg. Chem.*, **43**, 173 (1922).

In the preceding configurations, the straight lines used to join oxygen atoms to iron are meant to show either the presence of a simple covalent bond or an electrovalent bond. An arrow from oxygen to iron, on the other hand, signifies the formation of a coördinate covalent or donor-acceptor bond with oxygen as the donor atom.

The purpose of this investigation is to determine, by measuring the magnetic susceptibility of the various complexes, the type of bonding existing and, in so far as is possible, to postulate the configuration to be expected for these complexes on the basis of the data obtained.

Experimental Procedure

The Gouy method[4] of measuring magnetic susceptibility, using a chainomatic balance, was the means used to determine the magnetic moment of solutions of the three complexes.

A direct current regulator was utilized in the circuit to maintain a constant current through the magnet during use. Circular pole pieces of wrought iron were used because they exhibit little permanent magnetism. These were maintained the same distance apart throughout the experiments. The field strength existing between the poles was approximately 7000 gauss. A 13-in. soft glass tube, of 8 mm. inside diameter, was filled to the same height for each determination and was used for all runs. The mark to which the tube was filled was located at such a height that the upper portion of the solution extended beyond the effective field of the magnet. The tube was lowered to the same depth each time in the magnetic field by means of a cotton thread which was attached to the bottom of one of the balance pans. It was shielded from air currents by the use of large bore glass tubing. Iron clamps were insulated to prevent their becoming magnetic.

Ferric Ion Solution.—The ferric ion solution was prepared by dissolving electrolytic iron wire (99.87% pure) in 10 N hydrochloric acid, heating gently to aid solution. The ferrous ion yielded by this reaction was oxidized by perhydrol-30% hydrogen peroxide. During this oxidation

$$6Fe^{++} + 3H_2O_2 \longrightarrow 2Fe(OH)_3 + 4Fe^{+++}$$

with a limited amount of acid present, hydrated ferric oxide precipitated. Concentrated hydrochloric acid was added until the precipitate dissolved and then in excess until the concentration of hydrogen ion was approx. 0.85 M. At this point, potassium ferricyanide produced a negative test for ferrous ion in the solution. In previous tests a small amount of hydrogen peroxide was present and the solution of ferric ion and ferricyanide ion slowly gave a blue precipitate, showing that the hydrogen peroxide was reducing some of the ferric iron to ferrous

$$2Fe^{+++} + H_2O_2 \longrightarrow 2Fe^{++} + 2H^+ + O_2$$

After allowing the acidified ferric iron to stand for a few days, it gave a negative reaction to the above test for hydrogen peroxide.

Nickelous Solution.—A nickelous chloride solution of approximately 10% strength was made by dehydrating the hexahydrate of this salt at 140° overnight and dissolving it in distilled water. The purity of the hexahydrate was known.

Hydrolysis, which had been found to occur, was prevented by the addition of a small volume of hydrochloric acid. The percentage composition was determined by weighing each constituent as it was added.

Solutions of Complex Ions.—Solutions of the desired complex ions were prepared in the following manner. Quantities of disodium 1,2-dihydroxybenzene-3,5-disulfonate were added to a basic solution and to a neutral solution of the stock ferric chloride such that the ratio existing between the complexing reagent and ferric iron was three to one. An acid solution was prepared from the same starting materials in which the ratio was two to one. These solutions were kept in glass-stoppered volumetric flasks under a bell-jar to prevent contamination.

The hydrochloric acid used gave only the faintest test for ferric ion with ammonium thiocyanate solution.

Analyses.—The nickel chloride and ferric chloride solutions were analyzed for chloride ion content by adding excess standard silver nitrate solution (0.1 N) and back titrating with standard potassium thiocyanate (0.1 N). The iron content of the ferric chloride solution was found by reducing the hot solution with stannous chloride, adding mercuric chloride, then phosphoric acid, and titrating with a standard solution of potassium dichromate (0.1 N), using diphenylamine as the indicator. The hydrogen ion concentration was equal to the difference in concentration of the chloride ion and the positive ion other than hydrogen ion which was present in each case.

Calculations and Results

All measurements were made at a temperature of approximately 27° between the pole pieces. Rigid control of the temperature is unnecessary since a variation of as much as 3° would introduce only a 1% error. This is lower than the experimental error to be found in making some of the weighings.

The concentration of the solutions with respect to iron varies between 0.2073 and 0.2436 M.

In Table I are listed the measurements obtained and certain data necessary for the calculation of results.

The apparatus was standardized through the use of a 10% solution of nickelous chloride whose molar susceptibility is 4448×10^{-6}.[5]

Since the upper portion of the sample extended beyond the effective magnetic field, the force acting on the glass cylinder along its axis is given by

$$F = \Delta Wg = {}^1/_2(K_1 - K_2)AH^2 \qquad (1)$$

where

ΔW = change in weight upon application of the magnetic field
g = gravitational constant
K_1 = volume susceptibility of sample
K_2 = volume susceptibility of air
A = cross-sectional area of sample
H = maximum field strength to which sample is subjected

Application of Wiedemann's mixture law and Weiss' law for temperature correction will yield the specific susceptibility (X) of the nickelous chloride solution. Knowledge of the density of the solution enables one to calculate the volume susceptibility (K). Figure 1 indicates the variance of AH^2 values with amperage.

The specific susceptibility values for the solutions, as given in Table I, were obtained by using equation (1) after reading from the curve in Fig. 1 the value of AH^2 for a given amperage and by using the relationship $K = Xd$. Use of the slight temperature coefficient of water was deemed unnecessary. Wiedemann's mixture law was then applied to determine $X_{Fe^{+++}}$.

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[4] Stoner, "Magnetism and Matter," E. P. Dutton and Co., Inc., New York, N. Y., 1934, p. 81.

[5] Weiss and Bruins, *Verhandel. Verslag. Akad. Wetenschappen Amsterdam*, **24** (1), 313 (1915–1916).

TABLE I

Solution	Composition, %	Density	Av. ΔW,[a] g.	Amp.[b]	X[c] × 10^6	$X_{\text{Fe}^{+++}}$ × 10^6	μ_B[d]
$NiCl_2$	$NiCl_2$, 9.66	1.105	+0.0336	2.30	2.88, T = 300°		
	HCl, 3.42		+ .0360	2.45			
			+ .0380	2.58			
Complexing reagent[e]	C. r., 24.21	1.034	− .0103	2.48	−0.569		
$FeCl_3$	Fe^{+++}, 1.30	1.045	+ .0402	2.50	3.01	286	6.22
	H^+, 0.08						
	Cl^-, 5.37						
Blue complex[f]	Fe^{+++}, 1.10	1.136	+ .0318	2.48	2.21	264	5.97
	H^+, 0.07						
	Cl^-, 4.53						
	C. r., 15.50						
Violet complex[f]	Fe^{+++}, 0.97	1.194	+ .0275	2.50	1.81	255	5.87
	Na^+, 2.60						
	Cl^-, 4.00						
	C. r., 20.86						
Red complex[f]	Fe^{+++}, 0.96	1.210	+ .0254	2.40	1.72	250	5.81
	Na^+, 2.80						
	Cl^-, 3.94						
	OH^-, 1.06						
	C. r., 21.66						

[a] ΔW, the difference in weight with magnet off and magnet on, previously corrected for diamagnetism of the glass tube. [b] Amp., the current passing through the circuit which produces the magnetic field. [c] X, specific susceptibility or susceptibility per gram. [d] μ_B, magnetic moment expressed in Bohr magnetons. [e] Complexing reagent, disodium 1,2-dihydroxybenzene-3,5-disulfonate (C. r.). [f] Blue, violet, and red complexes, complexes formed between ferric ion and disodium-1,2-dihydroxybenzene-3,5-disulfonate in acid, neutral, and basic solutions, respectively.

Since the paramagnetic part of the susceptibility of a transition group element is approximately represented by the "spin only" formula, the expression which yielded the results given in Table I is

$$\mu_B = 2.84\sqrt{X_{\text{molal}}T}$$

where

μ_B = magnetic moment in Bohr magnetons
X_{molal} = molal susceptibility
T = absolute temperature

Discussion

The magnetic moment expressed in terms of Bohr magnetons is related to the number of unpaired electrons in this manner

$$\mu_{\text{eff.}} = \sqrt{n\ (n + 2)}$$

where

$\mu_{\text{eff.}}$ = effective moment
n = number of unpaired electrons

For ferric iron, where there are twenty-three planetary electrons, the following electronic distribution exists

$$Fe^{+++} - 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, \overbrace{\underset{\cdot}{-}\ \underset{\cdot}{-}\ \underset{\cdot}{-}\ \underset{\cdot}{-}\ \underset{\cdot}{-}}^{3d}$$

This shows that there are five unpaired electrons in this ion, producing a calculated magnetic moment of 5.92 Bohr magnetons. Four unpaired electrons yield a magnetic moment of 4.90 Bohr magnetons when calculated in the same manner. The values obtained from the experimental data for the iron complexes studied vary between 5.81 and 5.97 Bohr magnetons. It may be concluded that the bonding is essentially of the ionic type because apparently all five of the 3d electrons are, for the most part, still unpaired.

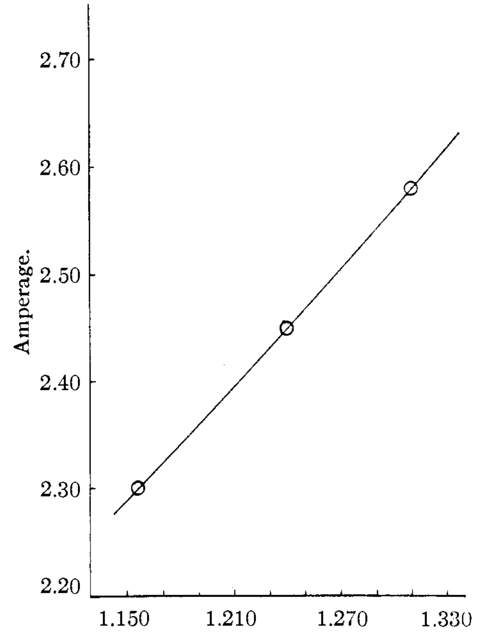

Fig. 1.—Field strength as a function of amperage, as determined with nickelous chloride solution.

According to Cambi and Cagnasso,[6] the full paramagnetism of ferric ion is to be expected in complexes where oxygen is bonded to it and only the presence of other active elements can induce

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(6) Cambi and Cagnasso, *Gazz. chim. ital.*, **63**, 767–778 (1933).

oxygen to participate in the formation of diamagnetic complexes. On the other hand, bonding with active coördinated groups containing the elements sulfur, nitrogen and carbon is expected to produce complexes of low paramagnetic susceptibility. An example of the latter is the ferricyanide ion.

The striking color changes which occur upon varying the hydrogen ion concentration are not uncommon for ionic complexes. Similar color changes occur with ferric tartrate complexes.[7] The latter are yellow at low *p*H values and green at high *p*H values. These abrupt color changes at a definite *p*H might be attributed to a replacement on the ferric ion of an active group of the organic complexing agent by a water molecule.

The tendency of the iron complexes, formally studied in this work, to form ferric ions and pyrocatechol disulfonate ions must be very slight for the extreme stability of them has been pointed out by Yoe and Jones.[1a] This is no anomaly for ionic complexes since the ferric fluoride complex, $FeF_6^{\equiv}$, is known to be quite stable. The ferric tartrate complex, $Fe_2(C_4H_4O_6)_3$, showing ionic bonding,[8] has an equilibrium constant of an extremely low value, 10^{-75}.[9] An indication of the order of stability of these iron complex ions is presented in the paper by Yoe and Jones.[1a] They found that the iron complex formed in basic solution by ferric ion and disodium 1,2-dihydroxybenzene-3,5-disulfonate is more stable than the fluoride, oxalate, and tartrate complexes of iron in basic solution; in acid solutions, the results were just the opposite.

In view of the preceding data, assuming that ionic bonds lie at the largest possible angle from one another, it seems likely that the configuration of the red iron complex, $Na_3[Fe(C_6H_2(SO_3Na)_2O_2)_3]$, is ionic octahedral in structure with all the oxygen atoms equivalent. Since the complex $Fe(H_2O)_6^{+++}$ is known to be ionic, possibly the iron in the violet complex maintains a coördination number of six by having one molecule of water replace an active group of the substituted pyrocatechol. This seems even more likely to be true when one recalls that a coördination number of five does not produce a system of high stability, generally speaking, and that such systems are usually covalent ones. Even in the case where a coördination number of four is suggested, that of the blue complex between iron and pyrocatechol disulfonate, there may actually be two ion-dipole bonds existing between ferric ion and two molecules of water, again giving iron a coördination number of six. Weinland and Seuffert[10] have analyzed 2,5-dihydroxynaphthalene ferriate salts, $[Fe(C_{10}H_6O_2)_2]^-$, and have concluded that in these cases iron has a coördination number of four. However, in all but one case their analyses show sufficient water present to satisfy a coördination number of six for iron, assuming two water molecules form ion-dipole bonds with the iron.

Summary

1. Magnetic studies show that iron apparently has five unpaired electrons when in the form of the three complexes studied.
2. This information leads to the conclusion that the bonding is essentially of the ionic type, since the ferric ion is known to have the same number of unpaired electrons.
3. The probability of iron maintaining a coördination number of six is discussed.
4. A consideration of an octahedral structure for the complexes is given.

CLEVELAND, OHIO RECEIVED FEBRUARY 14, 1947

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(7) Franke, *Ann.*, **486**, 282–284 (1931).

(8) Welo, *Phil. Mag.*, **6**, 481–509 (1928).

(9) Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice Hall, Inc., New York, N. Y., 1938, p. 213.

(10) Weinland and Seuffert, *Arch. Pharm.*, **266**, 455–464 (1928).

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF TECHNICAL AND ECONOMICAL SCIENCE, BUDAPEST, HUNGARY]

The Crystal Structure of Sodium Iodate

BY I. NÁRAY-SZABÓ AND J. NEUGEBAUER

Sodium iodate crystallizes according to Eakle[1] in the holohedral class of the orthorhombic system with the axial ratio $a:b:c = 0.9046:1:1.2815$. Its density determined by Kremers[2] and Ditte[3] is $d = 4.277$ and 4.252 g./cc., respectively.

In the course of our systematic examination of the perovskite structure family,[4,5] we examined this compound in order to complete the series of these "sister structures" as defined by one of us.

Zachariasen[6] has studied the lattice of sodium iodate by the aid of powder diagrams; his results were: cell dimensions, $a = 5.75$ Å., $b = 6.37$ Å., $c = 4.05$ Å.; therefore, $a:b:c = 0.903:1:0.636$. Accordingly the ratio $b:c$ of Eakle should be halved. In this unit cell two formula weights of sodium iodate are contained, with a calculated density $d = 4.40$ g./cc. Twenty-six reflections

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(1) Eakle, *Z. Krist.*, **26**, 565 (1896).

(2) Kremers, *Ann.*, **99**, 435 (1856).

(3) Ditte, Thesis, Paris (1870).

(4) I. Náray-Szabó, *Naturwissenschaften*, **31**, 202 (1943); *Matematik. Természcetud. Értesito*, **61**, 913 (1942).

(5) I. Náray-Szabó, *Naturwissenschaften*, **31**, 466 (1943).

(6) Zachariasen, "Untersuchungen über die Kristallstruktur von Sesquioxyden und Verbindungen ABO_3," Oslo, 1928.