during polymerization chain transfer with both monomeric styrene and with polymer must occur. By analogy with benzene, the contribution of the aromatic nucleus to chain transfer with the monomer may be small, but analogies between polystyrene and ethylbenzene suggest that chain transfer with the polymer, leading to chain branching, should be appreciable, particularly at high temperatures and high conversions. Studies of solvents with appropriate structures may therefore assist in attacking the difficult problem of estimating chain branching. Finally, the solvent studies discussed in this paper suggest a simple and accurate procedure for comparing the reactivities of several types of free radicals with a large number of solvents.

Acknowledgment.—The author is indebted to Dr. H. C. Tingey of these Laboratories for helpful suggestions.

Summary

It is postulated that certain solvents reduce the molecular weight of polymerizing styrene because they transfer hydrogen or chlorine atoms to growing polymer radicals. The activity of the polymer radical is thus transferred to the solvent residue which may then start a new chain. In order to compare solvent reactivities in these chain transfer reactions, a simple theoretical development leads to definition of the "transfer constant" which is characteristic of a solvent. Several transfer constants have been calculated from data in the literature. The results give quantitative support to the theoretical development and permit quantitative comparisons of solvent activities. Activation energies for chain transfer are calculated for some hydrocarbon solvents.

The results suggest that chain transfer between polymer radicals and both monomer and polymer molecules must occur. Chain transfer studies offer a possible attack on the problem of chain branching and a convenient way of studying reactions of free radicals in solution.

PASSAIC, NEW JERSEY RECEIVED AUGUST 13, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

Complex Ions. VI. The Magnetic Moments of Some Iron(III) Complex Ions[1]

BY BURTON WERBEL, V. H. DIBELER AND W. C. VOSBURGH

Complex ion formation by a paramagnetic ion is often accompanied by a decrease in magnetic susceptibility. Pascal[2] found this to be true in a large number of cases, and believed it to be a general phenomenon. Schaffer and Taylor[3] found it true of several complex ions of nickel and copper. More recently it has become clear that complex ions can be divided into two classes on the basis of magnetic measurements.[4] In the formation of some ions two or more electrons that are unpaired in the free paramagnetic ions become paired, and the magnetic moment decreases. When others are formed the number of unpaired electrons is unchanged, but even so a relatively small decrease in moment may take place.[3,5] It is probable that this is a decrease in the orbital contribution to the moment and is the result of the change in the electrostatic field when the atoms immediately surrounding the paramagnetic ion are changed.[6]

Van Vleck[6] (p. 301) has pointed out that manganese(II) and iron(III) ions are in S states and their moments should be pure spin moments with the theoretical value of 5.92 Bohr magnetons. Accordingly, having no orbital contributions the moments of these ions should be unchanged by complex formation, provided that no change in the number of unpaired electrons takes place.

Iron(III) ammonium alum was found by Onnes[7] to have a susceptibility corresponding to the theoretical moment. Jackson[8] found that the moments of solid iron(III) acetylacetonate and potassium trioxalatoferrate(III) are practically equal to the theoretical value, as are those of some solid iron salts. Welo[9] found that many iron(III) solid compounds have moments less than the theoretical, but he found some that approached the theoretical value. Bose[10] measured the susceptibilities of iron(III) chloride, nitrate and sulfate in solution with varying acidity and temperature. The observed moments were lower than the theoretical, but the addition of acid caused the moments to increase, and in the solutions of highest acidity the approach to the theoretical was quite close. Bose suggested that the deviations from the theoretical value might be the result of hydrolysis. He had previously found practically the theoretical moments for manganese salts[10] (p. 605).

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(1) Part of a thesis submitted by Burton Werbel in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University. May, 1943.

(2) Pascal, *Ann. chim.*, [8] **16**, 571 (1909).

(3) Schaffer and Taylor, THIS JOURNAL, **48**, 843 (1926).

(4) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 104.

(5) Russell, Cooper and Vosburgh, THIS JOURNAL, **65**, 1301 (1943).

(6) Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," The Clarendon Press, Oxford, 1932, p. 287.

(7) (a) Onnes and Oosterhuis, *Proc. Acad. Sci. Amsterdam*, **16**, 917 (1914); (b) Cambi and Szegö, *Ber.*, **66**, 657 (1933).

(8) Jackson, *Proc. Roy. Soc.* (London), **A140**, 705 (1933).

(9) Welo, *Phil. Mag.*, [7] **6**, 481 (1928).

(10) Bose, *Proc. Indian Acad. Sci.*, **A1**, 754 (1935).

In this investigation iron(III) ion in perchlorate solutions containing perchloric acid has been found to have the theoretical moment when the perchloric acid concentration is larger than 0.1 *M*. Certain iron(III) complex ions in solution have also been shown to have moments practically equal to the theoretical.

For other complex compounds the apparent moments were less than 5.92 Bohr magnetons and varied with the composition of the solution.

Apparatus and Materials.—Measurements of susceptibility were made by the Gouy method with the use of the apparatus previously described.[5] The sample tube always had water in the lower compartment and either air or the sample in the upper. All values of ΔW were corrected by subtraction of the value for ΔW with water in both compartments. Repeated measurement of ΔW_{air} (air in upper compartment and water in lower) showed that conditions were controlled satisfactorily. Calculations were made as in the previous work, the moments being calculated by the equation

$$\mu = 2.828\ (\chi T)^{1/2} \tag{1}$$

where χ is the molal paramagnetic susceptibility and T is the absolute temperature. Van Vleck[6] (p. 242) has pointed out that μ so calculated is the true moment only when Curie's law is obeyed.

All measurements were made at 28° and with a current of 15.0 amp. through the magnet coils except as otherwise noted. Spectrophotometric measurements were made by means of a Coleman spectrophotometer at room temperature. Reagent grade chemicals were used except as otherwise mentioned.

Solutions of most of the salts of organic acids were prepared from standard solutions of the acids by neutralization with the calculated quantities of a standard sodium hydroxide solution or with sodium hydrogen carbonate.

Iron(III) perchlorate was prepared from iron(III) chloride and perchloric acid and was recrystallized from water. Solutions were made from the recrystallized material and the iron(III) content determined iodometrically.[11] Gravimetric determination as oxide was shown to give the same results. The solution contained a little free perchloric acid, and this was determined by titration with sodium hydroxide, with correction for the iron(III) hydroxide precipitated.[12] The effect of this acid has been taken into account in the statement of the composition of solutions in the tables below.

Iron(III) Ion.—The moment of iron(III) ion in perchlorate solutions containing little more free acid than necessary to prevent precipitation was found to be lower than 5.92 Bohr magnetons, in agreement with Bose.[10] The moment increased rapidly with increasing acidity and became constant within the limits of error at concentrations of perchloric acid larger than 0.1 *M*, as shown in Table I.

TABLE I

MAGNETIC MOMENT OF IRON(III) ION

$Fe(ClO_4)_3$, *M*	$HClO_4$, *M*	$\Delta W_{\text{solution}}$,[a] mg.	$\Delta W_{\text{solvent}}$, mg.	μ
0.07173	0.118	41.66	−0.15[b]	5.927
.06812	.200	41.76[c]	− .04	5.900
.06499	.284	37.68	− .03	5.916
.07188	.305	42.13	− .09[b]	5.949
.06499	.473	37.87	− .02	5.930
.07188	.585	42.03	− .01	5.936
.06499	.93	37.97	.02	5.934
.06499	1.88	37.84	.09	5.916[d]
.06499	1.88	24.23[e]	.06	5.928
.07188	2.47	42.38	.13	5.951
.07173	2.46	41.91	.13	5.924[f]

[a] $\Delta W_{\text{air}} = 29.94$ mg. except as otherwise noted. [b] Sodium perchlorate present. [c] $\Delta W_{\text{air}} = 31.79$ mg. [d] Average of three. [e] Current 10 amp., $\Delta W_{\text{air}} = 19.09$ mg. [f] Average of two.

The average of the moments in Table I is 5.93 Bohr magnetons which is as close to the theoretical spin moments as could be expected. The average deviation from the mean is ±0.01 and the maximum −0.035.

The lower moments found for iron(III) ion in solutions of lower acidity can be explained qualitatively on the assumption that the hydroxo complex ions have moments lower than 5.92. As acid is added, the concentration of the hydroxo ions decreases, and the effect on the moment becomes negligible at about 0.1 *M* acidity.

Rabinowitch and Stockmayer[13] found that the ultraviolet absorption band of the ion $FeOH^{++}$ in a perchlorate solution does not disappear until the perchloric acid concentration reaches 3 *M*. However, it can be calculated from the equilibrium constant of Lamb and Jacques[14] for the reaction

$$Fe^{+++} + H_2O \rightleftarrows FeOH^{++} + H^+$$

that the amount of iron(III) ion hydrolyzed when the acidity is 0.1 *M* is of the order of magnitude of 1% of the total. The exact value would depend considerably on the assumptions as to activity coefficients. Hydrolysis of 1% of the iron(III) ion would make the moment too low by about 0.02 Bohr magneton if the ion $FeOH^{++}$ should have a moment as low as 1.7 Bohr magnetons. This is probably too low, and the observed moment of the iron ion should not be expected to change appreciably above 0.1 *M* acidity.

Pascal's observation[2] that colloidal iron(III) oxide has a lower moment than iron(III) chloride is in agreement with the assumption that low moments in the iron(III) compounds may be the result of hydrolysis. Two iron(III) oxide sols made in this investigation had an apparent moment of 4.69 Bohr magnetons when freshly prepared, but the moment changed somewhat with time.

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(11) Swift, THIS JOURNAL, **51**, 2682 (1929).

(12) Schumb and Sweetser, *ibid.*, **57**, 871 (1935).

(13) Rabinowitch and Stockmayer, *ibid.*, **64**, 335 (1942).

(14) Lamb and Jacques, *ibid.*, **60**, 1218 (1938).

Complex Ion Formation without Change in Magnetic Moment.—Iron(III) ion forms complex ions in solution with oxalate ion, 8-hydroxyquinoline-5-sulfonate ion,[15] chloride ion and thiocyanate ion without appreciable change in magnetic moment.

TABLE II

COMPLEX IONS FORMED WITHOUT CHANGE IN MAGNETIC MOMENT

$Fe(ClO_4)_3$, M	Reagent, M	$\Delta W_{solution}$,[a] mg.	$\Delta W_{solvent}$, mg.	μ
Reagent, $(NH_4)_2C_2O_4$				
0.0573	0.229	35.22	−0.23	5.924
.0573	.287	35.62	− .27	5.961
.0573	.344	35.21	− .32	5.931
.0573	.459	35.34	− .41	5.949
Reagent, $(NH_4)HC_2O_4$				
0.0573	0.229	35.11	−0.23	5.915
.0681	.272	41.96	− .27	5.931
.0573	.344	35.07	− .33	5.922
.0573	.459	35.02	− .42	5.923
Reagent, disodium salt of 8-hydroxyquinoline-5-sulfonic acid				
0.0573	0.229	35.49	−0.38	5.959
.0573	.287	35.30	− .46	5.950
.0573	.344	35.34	− .55	5.961
.0573	.459	35.37	− .72	5.978
.03262	.108[b]	18.54[d]	− .35	5.907
.0650	.230[c]	37.18[d]	− .43	5.904
Reagent, hydrochloric acid				
0.0573	1.00	35.32	−0.37	5.944
.0573	1.50	35.48	− .49	5.967
.0573	2.00	35.65	− .70	5.999
.0650	2.35	36.82[d]	− .76	5.902
.0650	4.76	36.27[d]	−1.47	5.916[e]
Reagent, $NH_4CNS + 1.9\ M\ HClO_4$				
0.0650	0.07	37.39[d]	−0.08	5.881
.0650	.10	37.48[d]	− .08	5.888
.0657	.15	37.68[d]	− .07	5.871

[a] ΔW_{air} = 31.79 mg. except as otherwise noted. [b] Solution was also 0.180 M with respect to the monosodium salt. [c] Solution was also 0.057 M with respect to the monosodium salt. [d] ΔW_{air} = 29.94 mg. [e] Average of two.

Solutions were prepared in which one of these anions was present in excess along with a known amount of iron(III) ion. The source of the iron(III) ion was a stock solution of iron(III) perchlorate. Often the solutions were allowed to stand overnight before the magnetic susceptibilities were measured. The results are given in Table II.

As a source of oxalate ion both ammonium oxalate and ammonium acid oxalate were used, without any significant difference in the results. Variation in the amount of excess oxalate ion had no effect. The average moment was 5.93$_5$ Bohr magnetons which is not significantly different from the moment of iron(III) ion. Thus, the very stable oxalatoferrate ion is formed from iron(III) ion with no change in magnetic moment.

The results for 8-hydroxyquinoline-5-sulfonate and chloride ions were similar. The first four measurements of the former and the first three of the latter were made before the technique was entirely perfected. The moments are probably a little too high in view of the last two of each set which are more reliable. Neither set can be considered significantly different from the iron(III) ion moment. The chloride complex is not very stable,[16] so a large excess of hydrochloric acid was added to furnish excess chloride ion as well as to prevent hydrolysis.

The moment of the thiocyanate complex ion is a little lower than the others. Hydrolysis could not have been responsible in view of the large concentration of perchloric acid. It was observed that the susceptibility of these solutions decreased with time. The data in the table were obtained about one hour after preparation of the solutions. Some experiments showed that in this length of time appreciable auto-reduction of the complex takes place.[17] Some *o*-phenanthroline was added to a ferric thiocyanate solution about an hour after its preparation; then the acid present was neutralized by ammonia and the precipitated ferric hydroxide removed by filtration. Some red ferrous-phenanthroline ion remained, and spectrophotometric determination showed that the iron(II) present was about 1% of the total iron originally present.

Reduction of 1% of the iron(III) would not in itself account for the lower moment of the thiocyanate complex, because iron(II) ion differs too little in moment from iron(III) ion. However, Møller[17] found that strongly colored complexes were formed from the iron ions and the product of oxidation of the thiocyanate ion. It is possible that the formation of these complexes involves electron pairing, with considerable reduction in moment. Therefore, it seems reasonable to include thiocyanate ion among the ions that cause little or no change in magnetic moment on uniting with iron(III) ion.

Iron(III) Acetate and Chloroacetates.—The existence in solution of the ion $[Fe_3(CH_3CO_2)_6(OH)_2]^+$ has been shown by means of potentiometric titrations by Treadwell and Fisch[18] and by dialysis coefficient measurements by Brintzinger and Jahn.[19] Solid compounds of this cation have been prepared by Weinland and Gussmann.[20] The preparation of iron(III) triacetate, which has been formulated[21] as $(Fe_3Ac_6)Ac_3$ or $(Fe_3Ac_8)Ac$,

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(15) Molland, THIS JOURNAL, **62**, 541 (1940).

(16) (a) Bray and Hershey, *ibid.*, **56**, 1893 (1934); (b) Moller, *J. Phys. Chem.*, **41**, 1123 (1937); (c) Bent and French, THIS JOURNAL, **63**, 571 (1941); (d) ref. 12, p. 343.

(17) Møller, *Kem. Maanedsblad*, **18**, 138 (1937); *Chem. Abs.*, **33**, 9179 (1939).

(18) Treadwell and Fisch, *Helv. chim. acta*, **13**, 1209 (1930).

(19) Brintzinger and Jahn, *Z. anorg. allgem. chem.*, **230**, 176 (1936).

(20) Weinland and Gussmann, *Ber.*, **42**, 3881 (1909); *Z. anorg. Chem.*, **66**, 157 (1910).

(21) (a) Gmelins "Handbuch der anorganischen Chemie," 8th ed., System-nummer 59, B, Berlin, 1932, p. 526; (b) Reilen, *Z. anorg. Chem.*, **114**, 72 (1920).

is more difficult. Krause[22] has shown that it can be crystallized from solution if a sufficiently large concentration of excess acetic acid is maintained. Harrar and Germann[23] have shown that iron(III) acetate in solution has colloidal properties.

Pascal[2] (p. 570) found that the molar susceptibility of iron(III) acetate in solution was much less than that of other iron salts and was unchanged by heating. He concluded that the salt had been completely hydrolyzed to colloidal oxide. Hagen[24] observed an increase in the susceptibility of an acetate solution with time. Cambi and Szegö[7b] found that the solid compound $[Fe_3Ac_6(OH)_2]$ Cl has a much smaller susceptibility than normal iron(III) compounds, for example, iron(III) ammonium alum. However, the moment μ calculated by

$$\mu = 2.828\ [\chi_m(T - \Theta)]^{1/2} \qquad (2)$$

with the very large value −705 for Θ was 5.85 Bohr magnetons.

In this investigation solutions were prepared from iron(III) perchlorate solutions and varying excess of sodium acetate and acetic acid. The solutions usually stood overnight so that any slow changes could be completed before measurement, but no such changes were observed when the measurements were made soon after preparation of the solutions. The results of susceptibility measurements are shown in Table III, the moments having been calculated as in Tables I and II, assuming Θ in Equation 2 to be zero.

TABLE III

IRON(III) ACETATE IN SOLUTION

CH_3COONa M	CH_3COOH M	$\Delta W_{solution}$, mg.	$\Delta W_{solvent}$, mg.	μ
A. $Fe(ClO_4)_3$, 0.0650 M, ΔW_{air} = 29.94 mg.				
0.134	0.163	20.54	−0.07	4.37
.183	.211	16.49	− .07	3.92
.381	.407	11.73	− .09	3.27
B. $Fe(ClO_4)_3$, 0.0681 M, ΔW_{air} = 31.79 mg.				
0.204	0.80	16.84	−0.02	3.75
.204	1.30	16.74	.05	3.73
.204	1.80	15.64	.12	3.60
.204	2.80	15.05	.27	3.50

The variation in the moment with change in the composition of the solution can best be interpreted as indicating the presence of two or more compounds of which at least one has a low susceptibility. In Table IIIA the moment decreases with increased acetate ion concentration when the acidity is roughly constant. In Part B the moment decreases with increasing acidity when the acetate ion concentration is practically constant. Both of these changes in composition would favor the replacement of hydroxo groups with acetato groups. On the basis of existing information the change in moment can be explained qualitatively by assuming that the triacetate has a lower susceptibility than the hydroxo acetate.

According to Treadwell and Fisch[18] (p. 1223) chloroacetate ion forms an iron(III) complex similar to that formed by acetic acid, but less stable. Harrar and Germann[23] (p. 1666) found qualitative evidence of complex formation by the three chloroacetic acids. In this investigation the relative strengths of the acetate and chloroacetate complexes were tested spectrophotometrically by the effect of these ions on the thiocyanate complex. In agreement with Treadwell and Fisch the chloroacetate complex was less stable than the acetate. The dichloroacetate complex was still less stable, and no complex formation was detected by this method for the trichloroacetate ion. Magnetic data for the chloroacetate and dichloroacetate complexes are given in Table IV.

TABLE IV

CHLOROACETATE AND DICHLOROACETATE COMPLEXES

Iron(III) perchlorate 0.0650 M. ΔW_{air} = 29.94 mg.

Acid		Na salt	$\Delta W_{solution}$,	$\Delta W_{solvent}$,	
	M	M	mg.	mg.	μ
Chloro-	2.11	0.18	23.92	−0.38	4.75
acetic	2.11	.39	18.20	− .50	4.16
Dichloro-	1.16	.27	37.23	− .75	5.93
acetic	1.16	.55	36.64	−1.13	5.92

It is interesting that whereas the chloroacetate has a low moment, the dichloroacetate has the theoretical moment for five unpaired electrons. Harrar and Germann[23] observed that the chloroacetate is red in color like the acetate while the dichloroacetate is green like the oxalate, which also has the theoretical moment.

Aminoacetate ion added to an iron(III) perchlorate solution gave complexes with susceptibilities that increased with time, but which were much like those of the acetate complexes in magnitude.

Phosphate and Pyrophosphate Complexes.—Lanford and Kiehl[25] have shown that the ion $FeHPO_4^+$ is formed from iron(III) nitrate and phosphoric acid. Pascal[26] showed the existence of a pyrophosphate complex ion of the composition $[Fe_2(P_2O_7)_3]^{6+}$ and found[2] (p. 545) that its magnetic susceptibility was less than that of iron(III) chloride.

In Table V are given some magnetic data for solutions prepared from iron(III) perchlorate and either phosphoric acid or sodium pyrophosphate. To some of the phosphoric acid solutions sodium dihydrogen phosphate was added, and to some of the pyrophosphate solutions perchloric acid, as shown in the first two columns of the table.

The calculated moment was found to vary with the composition of the solution for both phosphates. The lowest moments, about 5.6 Bohr magnetons, were much higher than the moments

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[22] Krause, *Z. anorg. Chem.*, **169**, 287 (1928).

[23] Harrar and Germann, *J. Phys. Chem.*, **35**, 2210 (1931).

[24] Hagen, *Kolloid-Z.*, **13**, 4 (1913).

[25] Lanford and Kiehl, THIS JOURNAL, **64**, 291 (1942).

[26] Pascal, *Compt. rend.*, **146**, 231 (1908).

TABLE V

PHOSPHATE AND PYROPHOSPHATE COMPLEX IONS

Salt, M	Acid, M	$\Delta W_{soln.}$, mg.	$\Delta W_{solvent}$, mg.	μ
A. Phosphate. $Fe(ClO_4)_3$, 0.0650 M; ΔW_{air} = 29.94 mg.; salt, NaH_2PO_4; acid, H_3PO_4.				
..	0.10	34.22	−0.09	5.64
..	.21	35.49	− .12	5.75
..	.31	35.67	− .16	5.76
0.036	.27	35.45	− .16	5.74
.10	.21	35.33	− .17	5.74
B. Pyrophosphate. $Fe(ClO_4)_3$, 0.0573 M; ΔW_{air} = 31.79 mg.; salt, $Na_4P_2O_7$; acid, $HClO_4$.				
0.172	..	31.50	−0.55	5.63
.229	..	31.85	− .71	5.68
.278	..	32.20	− .89	5.73
.344	..	32.53	−1.05	5.77
.172	0.01	32.34	−0.55	5.71
.172	.02	32.31	− .55	5.70
.172	.12	33.25	− .55	5.78
.172	.15	34.01	− .55	5.85
.172	.17	34.37	− .55	5.88

found for the acetate complexes, but definitely lower than 5.92. Increase in phosphoric acid concentration caused an increase in the moment of the phosphate complex, but addition of sodium dihydrogen phosphate had little effect. The change could be explained qualitatively as resulting from the partial elimination of hydroxo compounds of low moment.

The addition of excess pyrophosphate ion to the pyrophosphate complex caused an increase in moment, as did also the addition of acid. The acid was the more effective. These changes can be explained qualitatively as resulting from the elimination of hydroxo compounds. The moment 5.88 found for the most acid solution suggests that the pure pyrophosphate complex ion might have the theoretical moment.

Lactate, Tartrate and Citrate Complex Ions.—It is known that iron(III) ion forms complex ions with lactate, tartrate and citrate ions.[27] Tartrate and citrate ions each form more than one complex ion.[28] Less seems to be known about lactate ion.

The magnetic behavior of complexes of these anions is shown in Table VI. The iron(III) ion was supplied by an iron(III) perchlorate solution and the anions by various combinations of acids and salts or acid salts and neutral salts. The *p*H values of some of the solutions were measured by means of a glass electrode and are given.

All of the moments were lower than 5.92 Bohr magnetons, but in the more acid solutions they were not much lower. For the lactate and citrate complexes the moment increased in acid solutions on adding the salt of the acid. This increase might be the result of the replacement of hydroxo groups with lactato or citrato groups.

TABLE VI

LACTATE, TARTRATE AND CITRATE COMPLEX IONS

$Fe(ClO_4)_3$, 0.0650 M in all cases. ΔW_{air} = 29.94 mg.

Acid, M	Acid, Salt, M	Salt, M	*p*H	$\Delta W_{soln.}$, mg.	$\Delta W_{solv.}$, mg.	μ
A. Lactic acid and sodium lactate						
0.86	..	0.20	..	36.52	−0.25	5.84
.86	..	.41	..	36.98	− .32	5.88
B. Tartaric acid, sodium acid and sodium tartrate						
0.31	0.18	..	..	36.45	−0.45	5.85
.015	.19	..	..	31.76	− .25	5.45
..	.015	0.113	2.4	17.75	− .21	4.08
..	.015	.140	2.9	16.07	− .24	3.89
..	.015	.180	3.3	17.38	− .30	4.05
..	.015	.29	..	20.01	− .66	4.38
..	.015	.57	4.3	27.19	− .78	5.09
C. Citric acid and mono, di, and trisodium citrates						
1.00	0.25[a]	..	..	32.45	−0.64	5.54
1.00	.50[a]	..	..	35.16	− .87	5.78
..	.015[b]	0.120	4.2	23.96	− .37	4.75
..	.015[b]	.185	5.2	23.62	− .53	4.73
..	.015[b]	.285	5.5	24.06	− .79	4.80

[a] Monosodium citrate. [b] Disodium citrate.

For the tartrate and citrate, considerable decrease in acidity led to a decrease in the moment, followed by an increase again as the anion concentration became larger. This also might be explained qualitatively in terms of first the increase in hydroxo groups as the acidity decreased, then replacement of hydroxo groups as the anion concentration became larger. In each of the three cases more than one compound must be formed since the apparent moment changes with composition.

Nitroso-R-Salt Complexes.—Van Klooster[29] mentions that nitroso-R-salt forms a green iron(II) compound. In attempting to form iron(III) complexes with nitroso-R-salt it was observed that iron(III) and iron(II) gave solutions of the same color. The magnetic moment for the solution made from iron(III) varied erratically, but most values were in the vicinity of 1.7 Bohr magnetons, with some appreciably lower. Iron(II) solutions gave about the same results, and the presence of iron(III) compounds could be detected even when air was excluded. It is concluded that iron(III) ion is reduced somewhat by nitroso-R-salt and iron(II) oxidized, so that both give the same mixture of complex compounds.

Summary

Iron(III) ion in perchlorate solutions containing excess perchloric acid at a concentration larger than 0.1 M has been found to have a magnetic moment practically equal to the theoretical spin moment of 5.92 Bohr magnetons.

There is no change in moment when oxalate, 8-hydroxyquinoline-5-sulfonate, chloride, thiocy-

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[27] Reinders and de Minjer, *Rec. trav. chim.*, **57**, 594 (1938).

[28] (a) Franke, *Ann.*, **486**, 242 (1931); (b) Delsal, *J. chim. phys.*, **35**, 356 (1938); (c) Belloni, *Gazz. chim. ital.*, **50**, II 159 (1920); (d) Bobtelsky and Simchen, *Compt. rend.*, **208**, 1646 (1939).

[29] Van Klooster, THIS JOURNAL, **43**, 747 (1921).

anate and dichloracetate complexes are formed in solution from iron(III) ion.

A decrease in moment takes place when acetate, monochloracetate, hydrogen-phosphate, pyrophosphate, lactate, tartrate, citrate and aminoacetate complexes are formed. In these cases the apparent moment varies with the concentration of excess anion, or with the acidity, or both, indicating the presence of more than one compound.

DURHAM, N. C. RECEIVED AUGUST 28, 1943

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Systems with Boron Trifluoride. III[1]

BY HAROLD SIMMONS BOOTH AND JOHN HARPER WALKUP[2]

This paper presents the results of further[3] studies by thermal analysis on coördination of boron trifluoride and seven fluoride gases.

Sources of Gases.—Commercial boron trifluoride, supplied by the kindness of the Harshaw Chemical Co., was purified further as previously described. The dichlorodifluoromethane was kindly supplied by Kinetic Chemicals, Inc. The monochlorotrifluoromethane was from a stock made by Dr. Ralph McNabney of this Laboratory by the arc decomposition of CF_2Cl_2. The tetrafluoromethane was generously supplied by Professor Lucius A. Bigelow of Duke University. The phosphorus trifluoride,[4] the phosphoryl fluoride,[5] the thiophosphoryl fluoride,[6] and the thionyl fluoride[7] were made by fluorination of the corresponding chloride by means of antimony fluoride.

Method.—The method of thermal analysis used is the improved procedure described by Booth and Martin.[3c] Before use the gases were purified by fractional distillation in columns as previously described in papers from this Laboratory.

1. The System Dichlorodifluoromethane–Boron Trifluoride

It has been found that fluorine is a member of that small group of elements that are capable in some compounds of donating electrons to boron of boron trifluoride to form "addition" compounds. For this reason the system of dichlorodifluoromethane–boron trifluoride was investigated.

It was found upon mixing the first mole fraction that the two liquids were practically completely immiscible. Fourteen mixtures between 0 and 1.0 mole fraction of BF_3 were tried with the same results.

2. The System Monochlorotrifluoromethane–Boron Trifluoride

After it had been found that dichlorodifluoromethane and boron trifluoride were immiscible, the question arose as to what effect an increase in the fluorine content of the molecule would have upon the mutual solubility of the two liquids. For that reason the system monochlorotrifluoromethane–boron trifluoride was studied.

It was found that the increase of the fluorine content and the consequent reduction of the chlorine content of the compound increased the miscibility of the two liquids. Boron trifluoride was soluble in monochlorotrifluoromethane up to 20.0

TABLE I

DATA FOR SYSTEM MONOCHLOROTRIFLUOROMETHANE–BORON TRIFLUORIDE

Mole fraction BF_3	Freezing point, °C.	Eutectic temp., °C.	Mole fraction BF_3	Freezing point, °C.
0.0000	−181.6		0.0000	−181.6
.0381	−140.3	−183.2	.0663	−137.8
.0836	−136.0	−183.2	.1193	−134.1
.1165	−134.5		.1605	−133.1
.1568	−132.1		.1968	−131.1
.2069	−130.5		.2281	−130.5
.2526	−130.6		.2811	−130.5
.3030	−130.6		.3190	−130.5
.3483	−130.6		.3797	−130.5
.4001	−130.5		.4155	−130.5
.4559	−130.5		.4772	−130.5
.5032	−130.6		.5296	−130.5
.5538	−130.4		.6580	−130.5
.5961	−130.6		.7261	−130.5
.6499	−130.6		.7760	−130.4
.6989	−130.6		.8282	−130.4
.7467	−130.5		.8613	−130.4
.7975	−130.6		.9310	−128.6
.8331	−130.5		1.0000	−127.6
.8633	−130.5			
.9020	−129.5			
.9289	−128.8			
.9652	−128.1			
1.0000	−127.6			

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(2) From a thesis submitted by John Harper Walkup in partial fulfillment of the requirements of the degree of Doctor of Philosophy in Chemistry to the Graduate School of Western Reserve University, February, 1943.

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