The Magnetic Susceptibility of Potassium Ferrate

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$\theta = 180°$ a large share of the recoils have energies over 5 ev, and for $\theta = 135°$ (the most probable angle in one theory) all recoils have energies above 8.9 ev. For any case the maximum recoil energy is 63.5 ev. For any of the distributions it seems likely that a large fraction of recoil Cr^{+6} ions would be able to oxidize water readily.

When a comparison is made of the decay of Mn^{51}(II) ions in solution with the decay of permanganate ions in solution, an apparent anomaly is encountered. In the former case all Cr^{51} daughters were reduced, while in the later only about one-half were reduced. If no molecular disruption were to occur, an equation for the decay reaction of permanganate might be written, $MnO_4^- = CrO_4^= + \beta^+$, and in that case all the daughter atoms would initially have the oxidation number VI. As it has been assumed that highly oxidized Cr^{51} ions are produced by the ionization accompanying decay of Mn^{51}(II), the question arises as to why all of these were usually completely reduced whereas only a part of the Cr^{51}(VI) ions from permanganate decay were reduced. To answer this question is difficult but a possible explanation may be as follows. In the case of Mn(II) decay it was assumed that highly charged chromium ions were produced. These ions in almost all cases were assumed to have sufficient kinetic energy to undergo chemical reduction reactions with water. In the case of decay of permanganate, momentum may be conserved not by Cr^{51} alone, but by motion of the whole chromate ion. The suggestion that a large fraction of recoil energy may appear as translational energy for a whole molecule (or ion) with a small fraction as "internal" energy, has been made by Suess.[16] As the mass of chromate is greater than the mass of a bare chromium ion by a factor of 2.24, the recoil kinetic energy of chromate could be at most 0.44 that of the bare Cr^{51} ion. This could partially account for the observation that some of the Cr^{51} grown from permanganate is not chemically reduced. A further consideration involves the assumption that bare highly charged Cr^{51} ions result from Mn(II) decay whereas Cr(VI) resulting from permanganate decay is initially bonded to some oxygen atoms. A non-oxygenated Cr(VI) ion would probably be a much better oxidizing agent than one bound to oxygen atoms.

The preceding argument takes little account of the effect of the ionization on the stability of chromate. Cooper[17] has calculated that the acquisition of positive charge by a bromine atom in bromate can result in formation of excited vibrational states in the ion. In the bromine case the positive charge was assumed to be built up by Auger processes following internal conversion. In the present experiments if ionization of Cr^{51} in chromate were to occur, a similar effect might be expected. As a result one or more oxygen ions might be split out of the chromate ion leaving fragments such as CrO_3, CrO_2^{+2}, etc. The rupture of chromium-oxygen bonds could also occur in cases with high initial recoil energy. If such fragments were produced by either process they could undergo two competing types of reactions.[9] The first is hydration to stable acid chromate ion by over-all reactions such as:

$$CrO_3 + H_2O = HCrO_4^- + H^+$$
$$CrO_2^{++} + 2H_2O = HCrO_4^- + 3H^+$$

The second-type reaction is chemical reduction to Cr(III) as has already been mentioned.

Of course if singly charged or neutral oxygen is split out of the chromate ion this could account for reduction in such cases. From all of the considerations it is evident that the factors which can determine chemical forms are quite complex and the tentative descriptions offered are probably over simplified.

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[16] H. Suess, Zeits. f. physik. Chemie **B45**, 312 (1939).

[17] E. P. Cooper, Phys. Rev. **61**, 1 (1942).

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The Magnetic Susceptibility of Potassium Ferrate*

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A method of preparation of potassium ferrate of 97 percent purity is described. Although the product contained an inseparable ferromagnetic impurity, the susceptibility of the ferrate was determined by extrapolation to infinite field strength of data obtained by the Gouy method. The observed effective magnetic moment of the ferrate ion agrees approximately with that expected for hexavalent iron.

INTRODUCTION

The difficulty of preparing pure salts of hexavalent iron has resulted in a scarcity of reliable physical data regarding its compounds. No magnetic data are available with the exception of qualitative measurements made on solutions containing ferrate.[1] A method for preparing potassium ferrate has been developed in this laboratory, resulting in a product of sufficient purity to make possible the determination of the magnetic susceptibility of the ferrate ion. This investigation

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[1] O. Liebknecht and A. P. Wills, Ann. d. Physik. (4) **1**, 380 (1900).

was undertaken in an attempt to verify the moment expected of hexavalent iron.

PREPARATION OF K_2FeO_4

In concentrated sodium hydroxide solution Na_2FeO_4 is very soluble[2] whereas sodium chloride is quite insoluble.[3] Since chloride was expected as the main impurity in the synthesis of K_2FeO_4, the ferrate ion was prepared by treatment of $Fe(OH)_3$ with sodium hypochlorite in very concentrated sodium hydroxide solution and then precipitated as K_2FeO_4 by addition of KOH after filtration.[4] This procedure eliminates most of the chloride without resorting to repeated reprecipitations. The equation may be written

$$2Fe(OH)_3+3ClO^-+4OH^-=2FeO_4^{--}+3Cl^-+5H_2O$$

although the ferrite ion is probably an intermediate.

A paste of 32 g of $FeCl_3$ and 40 g of NaOH in 100 ml of water was added to 350 ml of an aqueous solution containing 17 percent each of NaClO and NaOH. With continual stirring 300 g of NaOH were added while the temperature was kept between 50 and 55°C. After having been maintained in this temperature range for one or two hours, the mixture was allowed to cool below 40°C and was filtered through a fritted glass funnel into a flask containing 30 g of KOH. The solid K_2FeO_4, which formed immediately as the KOH dissolved, was filtered off and redissolved in 500 ml of 20 to 40 percent KOH solution. Decomposition, which is minimized by rapid filtration, occurred quite noticeably on the surface of the filter funnel and $Fe(OH)_3$ present, but to a lesser degree on the container walls. The filtrate was saturated with potassium hydroxide and the recrystallized K_2FeO_4 separated by filtration. Three thorough washings with 300 to 400 ml of 95 percent ethanol cooled to −5°C and subsequent washing with small amounts of ether[2] left the product free of all traces of NaCl, NaOH, and C_2H_5OH. The product was a stable, homogeneous, black powder which was stored for long periods of time over P_2O_5 without noticeable decomposition.

Yields ranging from 10 to 15 percent of the theoretical were obtained, while deviation from this procedure decreased the yield substantially. The sample used for magnetic measurements consisted of three thoroughly mixed batches.

TABLE I. Variation of χ_M with H.

H (oersteds)	Determinations	$\chi_M \times 10^5$ (c.g.s. units)
1750	3	815±3
4670	6	666±4
6460	2	607±2
8150	2	569±0

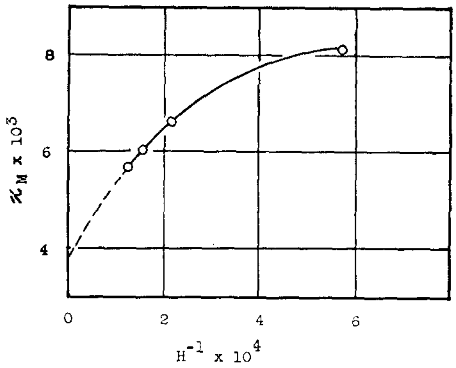

FIG. 1. Variation of χ_M with reciprocal field strength for potassium ferrate sample.

Analysis for carbonate by absorption of CO_2 on ascarite[5] showed the presence of 2.94±0.06 percent K_2CO_3 if the CO_2 is assumed present in this form. Volumetric iron determination** proved the iron content to be 27.52±0.08 percent. The theoretical percent K_2FeO_4 calculated from this was 97.6 with a probable error of ±0.1 percent while that calculated from the percent K_2CO_3 impurity was 97.1 percent. Incompatibility of these figures indicated the presence of an iron compound having a higher proportion of iron than K_2FeO_4. Assuming the foreign iron compound to be ferric oxide, the composition of the sample was calculated to be 96.9 percent K_2FeO_4, 2.9 percent K_2CO_3, and 0.2 percent Fe_2O_3. It is doubtful whether the undesired iron compound can be removed, since further reprecipitations showed the strongly alkaline ferrate solutions to be unstable to some degree.

EXPERIMENTAL

Apparatus

A Gouy magnetic balance[6] employing a Christian Becker micro-analytical balance was used for all susceptibility measurements although weights were taken only to the nearest milligram except for the calibrations with water. Small permanent magnets produced the weaker fields while the stronger ones were obtained with the electromagnet from the apparatus of Scott and Cromwell.[7] To avoid lateral motion of the samples in the field, the mass of the sample tubes was increased by adding glass rod to the lower ends.

Calibration

Water and an approximately 29 weight percent $NiCl_2$ solution were used as calibrating agents. The latter was prepared by dissolving "Baker's Analyzed" $NiCl_2\cdot 6H_2O$

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[2] J. M. Schreyer, Ph.D. thesis, Oregon State College, 1948. Part of this thesis was presented at the 114th meeting of the American Chemical Society, September 16, 1948, at Portland, Oregon by W. E. Caldwell.

[3] A. H. Hooker, Chem. and Met. Eng. **23**, 961 (1920).

[4] Suggestion of J. Schulein and J. Miller, Chem. Eng. Dept., Oregon State College.

[5] H. H. Willard and N. H. Furman, *Elementary Quantitative Analysis* (D. Van Nostrand Company, Inc., New York, 1940), third edition, pp. 402–406.

** Iron was determined by titration of the reduced sample with potassium bichromate.

[6] L. G. Gouy, Comptes Rendus **109**, 935 (1889).

[7] A. B. Scott and T. M. Cromwell, Am. Chem. Soc. **70**, 3981 (1948).

in distilled water. Nickel was determined gravimetrically by precipitation with dimethylglyoxime. The gram susceptibility of the solution at the experimental temperature of 26°C was calculated from the data given by Selwood.[8]

Since each tube was filled to the same mark, first with $NiCl_2$ solution and then with K_2FeO_4, the apparatus was calibrated in terms of the quantity $A(H_1^2-H_2^2)/2g$, H_1 and H_2 being the field strengths acting on the ends of the sample, A the cross-sectional area of the sample tube, and g the gravitational constant. Simultaneous measurements of susceptibility and density were accomplished by this procedure.

Because the experimental method permitted determination only of relative field strength, an absolute measurement of one magnetic field was made using a flip coil and a ballistic galvanometer of known sensitivity. The value found was 1750±40 oersteds.

MEASUREMENTS

The molar susceptibility of the K_2FeO_4 sample was determined at four different field strengths. Results are recorded in Table I. The errors indicated are errors of observation only. Values of χ_M were calculated from the equation

$$\chi_M = M\kappa_N \Delta W / d\Delta W_N,$$

where M and d are the formula weight and density of the K_2FeO_4 sample, and ΔW and ΔW_N the apparent weight changes respectively of the solid ferrate and the $NiCl_2$ solution in the field. The density of the sample was quite reproducible and varied only within a few percent during the measurements justifying the assumption of homogeneous packing of the powder in the sample tube. All determinations except three at 4670 oersteds were made using $NiCl_2$ solution for calibration. For these three, water was used for calibration.

DISCUSSION

Although the sample of potassium ferrate showed marked field strength dependence, there is no evidence for assuming a ferrate to be ferromagnetic. The analytical data indicate the presence of an amount of iron-containing impurity sufficient to account for this behavior. The ferromagnetic contaminant may be a ferrite or, more likely, a ferromagnetic form of ferric oxide.

When the Gouy method is employed, the volume susceptibility at any field strength, κ_H, of a sample containing a small amount of ferromagnetic impurity is given by the equation[9]

$$\kappa_H = \kappa_\infty + 2c'\sigma_s/H,$$

where κ_∞ is the true volume susceptibility in an extremely high field; c' is the concentration of the ferromagnetic impurity in g/cc of sample, and σ_s its saturation specific magnetization. In terms of χ_M the equation retains its linear form. Plotting χ_M at any field strength as a function of reciprocal field strength yields the true molar susceptibility on extrapolation to $H^{-1}=0$.

Figure 1 shows the experimental variation of χ_M with H^{-1} for the K_2FeO_4 sample.

It is difficult to extrapolate this curve to infinite field strength accurately since the slope has not yet become exactly linear. More points at higher field strengths would increase the accuracy of the extrapolation. However, at field strengths greater than 8150 oersteds the lateral forces exerted on the sample tubes became so great that little confidence could be placed in weighings made in the field.

No simple function of $1/H$ was found which yielded a linear curve throughout this region. Consideration of possible limits of the intercept introduces a possible error of about seven percent in the value 380×10^{-5} obtained by extrapolation of the actual curve. The error of extrapolation is the limiting error of the experiment and is large enough so that corrections for ionic diamagnetism would merely exaggerate the accuracy of the results. However, correction for the estimated purity of the sample seems justified. The value, $(392\pm26)\times10^{-5}$, is effectively the susceptibility of the ferrate ion.

The effective magnetic moment calculated from the relation $\mu_{\text{eff.}} = 2.83(\chi_M T)^{\frac{1}{2}}$ is 3.06±0.08 Bohr magnetons. Iron in an oxidation state of six should have two $3d$ electrons not used in bond formation; these would be expected to be unpaired, leading to a theoretical magnetic moment of 2.83 Bohr magnetons.

It is not possible to arrive at a structure for the ion by consideration of its moment. Since in any case three $3d$ orbitals are available for bond formation, the most likely structure is tetrahedral.[10] This configuration is further indicated by the suggestion of Retgers,[11] based on an examination of microscopic crystals, that K_2FeO_4, K_2SO_4, and K_2CrO_4 should be isomorphous.

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[8] P. W. Selwood, *Magnetochemistry* (Interscience Publishers, Inc., New York, 1943), pp. 29, 46.

[9] L. F. Bates, *Modern Magnetism* (Cambridge University Press, London, 1948), second edition, pp. 115–117.

[10] O. K. Rice, *Electronic Structure and Chemical Binding* (McGraw-Hill Book Company, Inc., New York, 1940), pp. 268, 275.

[11] J. W. Retgers, Zeits. f. physik. Chemie **10**, 529 (1892).