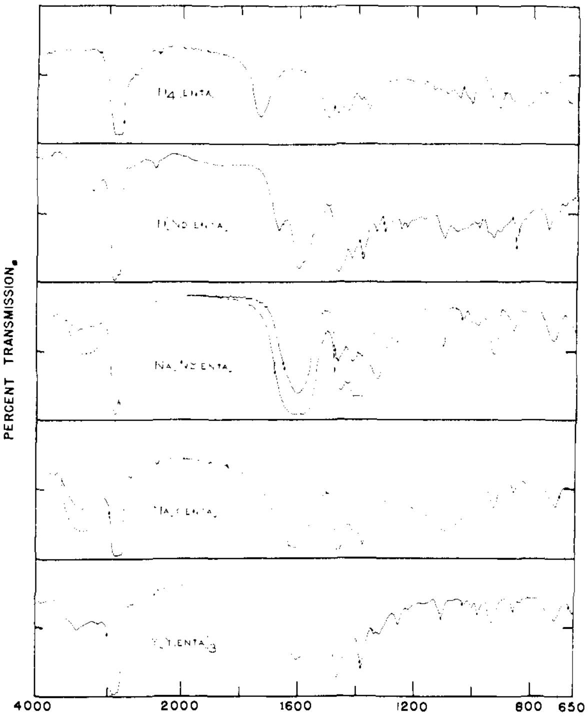

Fig. 1.—Infrared spectra of [Ln(enta)]$^-$ type compounds.

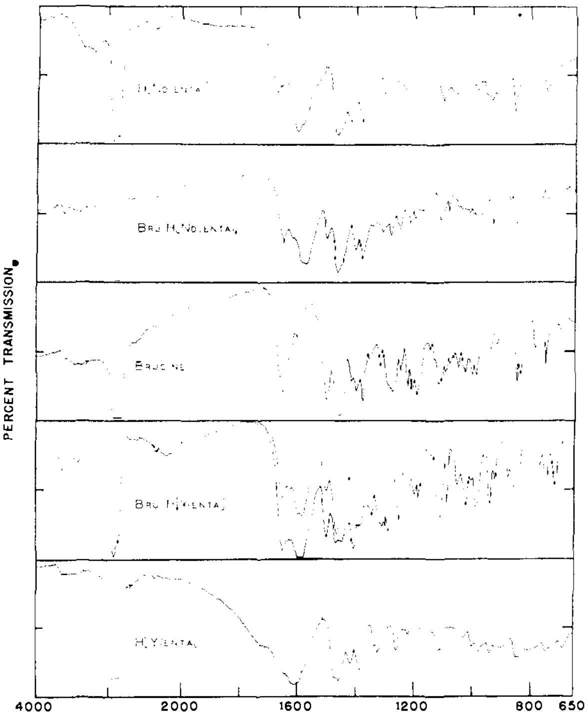

Fig. 2.—Infrared spectra of [Ln(enta)]$^-$ type compounds.

these considerations, should be asymmetric in an octahedral geometry and thus potentially capable of resolution providing the bonding present is sufficiently highly covalent in character. Inasmuch as complexes of this type give rather low equilibrium concentrations of Ln^{+3} ions,[17] a certain amount of covalency is undoubtedly present. However, the lack of any observed resolution by two methods of the species [Y(enta)(H_2O)]$^-$, where the presence of the comparatively small Y^{+3} material should enhance covalent character, suggests that even in this species sufficient covalency to maintain the rigid geometrical arrangement essential to asymmetry is probably absent. Such a conclusion is a reasonable one and is in agreement with the generally ionic characteristics of yttrium and rare earth metal salts.

Acknowledgments.—Grateful appreciation is expressed to the Office of Naval Research, to the Lindsay Chemical Company, and to E. I. du Pont de Nemours and Company for the support which rendered these studies possible. Appreciation is also expressed to Mr. James Brader for his assistance in interpreting the infrared data.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Interaction of Chromium(III) and Chromium(VI) in Acidic Solution[1]

BY EDWARD L. KING AND JOHN A. NEPTUNE

RECEIVED DECEMBER 13, 1954

It is observed that acidic solutions containing chromium(III) and chromium(VI) exhibit an enhanced absorbancy compared to that expected on the basis of no interaction. Measurements at 290 and 700 mμ demonstrate that the complexes responsible for this absorbancy enhancement contain one chromium(III) atom and one chromium(VI) atom. Studies as a function of the hydrogen ion concentration indicate that the complex species are $CrCrO_4^{+}$ and $CrCrO_4H^{++}$. These complex ions are not of sufficient stability to allow the evaluation of the equilibrium quotients for the reactions in which they are formed. Although the complexes form rapidly, it is believed that they are of the "inner-sphere" variety, the chromium(VI)-oxygen bond being broken and formed in the formation reaction. That is, the chromium(III)–chromium(VI) bonding involves an oxygen bridge Cr(III)-O–Cr(VI), the lability of the system being due to the high rate at which the chromium(VI)–oxygen bond can be formed and broken.

Although a number of investigators have reported the preparation of solid compounds containing chromium(III) and chromium(VI),[2-4] little attention has been devoted to the interaction of these two oxidation states in solution. In fact, little attention has been devoted to the complexes of any metallic cations and the chromium(VI) anionic species although a recent study of cerium(IV)–chromium(VI) complexes[5] has demonstrated that for cerium(IV), the chromate complex is more stable

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(1) This work has been supported in part by the United States Atomic Energy Commission.

(2) H. B. Dunnicliff and G. S. Katwani, *J. Phys. Chem.*, **35**, 3214 (1931).

(3) M. L. Blanc, *Bull. soc. chim.*, [4] **39**, 718 (1926).

(4) P. C. R. Chaudhury, *J. Ind. Chem. Soc.*, **16**, 652 (1939).

(5) J. Y-P. Tong and E. L. King, THIS JOURNAL, **76**, 2132 (1954).

than the corresponding sulfate complex. Interest in the possibility of complex ion formation between chromium(III) and chromium(VI) is enhanced by the fact that we are dealing with the same element in the cationic and anionic forms. For many systems involving chromium(III), it is possible to distinguish "outer-sphere" and "inner-sphere" complexes.[6,7] This possibility exists because the rate at which ligands replace water molecules in the first coördination sphere of chromium(III) is low except in the cases of replacement occurring without the breaking of the chromium(III)–oxygen bond. Such an exception is observed in the reaction of hexaaquochromium(III) ion or the polymeric oxygen-bridged chromium(III) species and molybdate ion[8] where the "inner-sphere" complex forms rapidly due to the lability of the molybdenum(VI)–oxygen bonds and such may also be possible for chromium(VI).

Knowledge of the extent to which chromium(III) and chromium(VI) associate in solution is essential in the interpretation of kinetic studies on oxidation–reduction reactions involving chromium(III) and chromium(VI). In particular, the dependence of the rate of exchange of chromium(III) and chromium(VI) upon their concentrations will reflect any interaction between these two oxidation states which results in appreciable association.

Experimental

Spectrophotometric Measurements.—All measurements were made with a Beckman model DU spectrophotometer using cylindrical type cells of 5 and 10 cm. length which were held in a metallic block cell holder through which thermostat water at 25.0° was circulated. (In one series of experiments, one cm. cells were used. These were less efficiently thermostated.)

Preliminary observations indicated that solutions containing chromium in both the +3 and +6 oxidation states exhibited an enhanced absorbancy[9] compared to that expected on the basis of no interaction. Measurements have been made at 290 and 700 mμ. At 290 mμ, the molar absorbancy indices of hexaaquochromium(III) ion and hydrogen chromate ion ($HCrO_4^-$) are 0.72 and 1280, respectively. At 700 mμ, the molar absorbancy index of hexaaquochromium(III) ion is 0.52. Hydrogen chromate ion is as transparent as water at this wave length. In carrying out the experiments, it was desirable to realize high concentrations of chromium(III) and chromium(VI) which favor the interaction, but on the other hand only a limited range of absorbancy can be conveniently measured. The realizable concentration of chromium(VI) was much larger in the solutions studied at 700 mμ.

In all of the measurements, the quantity of interest was ΔA, the enhancement of absorbancy per cm. of cell length in the mixed solution compared to that expected on the basis of no interaction. At 700 mμ where chromium(VI) is essentially transparent, the quantities measured were the absorbancy of a solution containing perchloric acid, sodium perchlorate, chromium(III) perchlorate and sodium dichromate and the absorbancy of a similar solution containing no sodium dichromate. In general, the value of ΔA was obtained by measuring each solution against a water blank. In some cases, however, the solution containing sodium dichromate, which has the greater absorbancy, was measured directly against a blank consisting of the solution containing chromium(III) perchlorate and no sodium dichromate. The desired ΔA is obtained directly[10]; it was shown that the slit width required to make this type of measurement was not large enough to introduce any errors.

The measurements at 290 mμ were made upon three types of solutions: (*a*) chromium(III) perchlorate, perchloric acid and, if necessary, sodium perchlorate, (*b*) sodium dichromate, perchloric acid and sodium perchlorate, and (*c*) chromium(III) perchlorate, sodium dichromate, perchloric acid, and, if necessary, sodium perchlorate. The measurements consisted in measuring (*a*) *versus* water, (*b*) *versus* water, (*c*) *versus* (*a*), and (*c*) *versus* (*b*). The desired ΔA is obtained in two different ways from these data: ((*c*) *versus* (*a*)) minus ((*b*) *versus* water) and ((*c*) *versus* (*b*)) minus ((*a*) *versus* water).[10] An average difference of 0.015 was observed between the values of ΔA calculated in the two ways. This corresponds to 5.7% of ΔA. It is to be noted that these measurements involved, in some cases, the use of a relatively opaque solution as the blank. Such measurements were possible at narrow slit widths (~0.07 mm.) because the spectrophotometer is equipped with a photomultiplier unit.

Reagents.—The perchloric acid and sodium dichromate were reagent grade and were used without further purification. The sodium perchlorate was recrystallized once from water. The chromium(III) perchlorate was prepared by the reduction of chromium trioxide with a slight excess of formic acid in the presence of excess perchloric acid; this was recrystallized two times from perchloric acid solution.

The solutions which were studied spectrophotometrically were prepared from stock solutions which had been analyzed by standard procedures. The one analysis which is of critical importance and which is not completely straightforward is that for perchloric acid in the chromium(III) perchlorate solution. This analysis was carried out by the titration of the acid with a dilute solution of sodium hydroxide, the chromium(III) having been converted to the oxalate complex, presumably $Cr(C_2O_4)_3^{-3}$, by heating with a large excess of potassium oxalate (60 g. per 100 ml.). This method, which was suggested by the work of Blaedel and Panos[11] on the determination of the acidity of aluminum(III) solutions, is open to question when applied to solutions of chromium(III). In the course of the titration, a localized excess of base may cause the conversion of the oxalate complex to chromium(III) hydroxide or a basic chromium(III) oxalate which does not then reconvert to the oxalate complex as mixing causes the base to be consumed. It has been found that the concentrations of acid determined in the titration of varying amounts of the chromium(III) perchlorate–perchloric acid solution in the same final volume are in agreement. The hysteresis in the back titration with perchloric acid, the end-point having first been passed, is small but appears to be measurable.[12] On the basis of rather limited measurements on the hysteresis, it appears that an error in the concentration of hydrogen ion as large as 0.5% of the concentration of the chromium(III) could arise. It is concluded, however, that the error in the acidity of the solutions used in the spectral measurements is not large enough to render uncertain the interpretation of the data.

The Rapidly Established Equilibria.—In the interpretation of the dependence of the enhancement of the absorbancy upon the concentrations of chromium(III) and chromium(VI), it is necessary to take into account the chromium(VI) monomer–dimer equilibrium. The acidity of the solutions studied was in a range (0.003 to 0.03 molar hydrogen ion) in which the important chromium(VI) species are $HCrO_4^-$ and $Cr_2O_7^=$. The concentrations of $HCrO_4^-$ in the solutions were calculated using the equilibrium quotient determined by Tong and King.[13] The chromium(III) present as $CrOH^{++}$ is of negligible importance from the point of view of determining the true concentration of hexaaquochromium(III) ion but is of considerable importance

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[6] The "outer-sphere" complexes are those in which the ligand is separated from the central metal ion by the metal ion's first coördination sphere of water molecules and the "inner-sphere" complexes are those in which direct coördination exists between the metal ion and the ligand.

[7] H. Taube and F. A. Posey, THIS JOURNAL, **75**, 1463 (1953).

[8] H. T. Hall and H. Eyring, *ibid.*, **72**, 782 (1950).

[9] In this paper, the nomenclature recommended in National Bureau of Standards Letter Circular No. 857 is adopted. The absorbancy is defined $A = \log I_0/I$. The molar absorbancy index, a_X, of a species X is related to the contribution to the absorbancy by that species $A_X = a_X(X)\,b$ where (X) is the molar concentration of X and b is the cell length.

[10] As will be shown, the complex is not of sufficient stability to tie up a significant fraction of the chromium(VI), the reagent which is present at the lower concentration. Thus, ΔA is directly identified as the absorbancy due to the complex.

[11] W. J. Blaedel and J. J. Panos, *Anal. Chem.*, **22**, 910 (1950).

[12] Experiments performed by H. S. Gates.

[13] J. Y-P. Tong and E. L. King, THIS JOURNAL, **75**, 6180 (1953).

in determining the true concentration of hydrogen ion. The calculations of the extent to which the reaction

$$Cr^{+++} + H_2O = CrOH^{++} + H^+$$

occurs were made using values of $K = (CrOH^{++})(H^+)/(Cr^{+++})$ extrapolated from the work of Postmus and King[14] which does not extend to as high an electrolyte concentration as was studied here. The extrapolated values are 1.2, 1.1 and $1.0_5 \times 10^{-4}$ at ional concentrations of 1.2, 2.0 and 2.4, respectively.

The results of experiments in which the concentrations of chromium(III) and chromium(VI) were varied at different acidities are presented in Table I. Because of the acid ionization of hexaquochromium(III) ion, the concentration of hydrogen ion was not exactly constant in the first three series. By using the hydrogen ion dependence of the absorbancy enhancement evaluated in other series of experiments (presented in Fig. 1), it was possible to convert the value of the quotient to that which would be obtained at constant acidity; this has been done to the data presented in Table I. The small average deviation of the individual experimental values of the function $\{(\Delta A)/(Cr^{+++})(HCrO_4^-)\}$ from its average value for each series indicates that the species responsible for the enhancement of the absorption contains one chromium(III) atom and one chromium(VI) atom. (This concentration dependence clearly rules out the equilibrium $Cr^{III} + Cr^{VI} \rightleftarrows Cr^{IV} + Cr^{V}$ as an explanation of the observations. If the enhancement were due to chromium(IV) and/or chromium(V), the value of ΔA would be proportional to $\sqrt{(Cr^{+++})(HCrO_4^-)}$.)

TABLE I

Γ^a	$(H^+) \times 10^2$	No. of solns. studied	Concn. ranges $(Cr^{+++}) \times 10$	$(HCrO_4^-) \times 10^4$	$\left\{\frac{\Delta A}{(Cr^{+++})(HCrO_4^-)}\right\}^b$ 290 mμ	700 mμ	Av. dev., %
2.0	0.50	10	0.3-1.0	30-87		46.6	3
2.0	0.80	24	0.3-1.7	17-98		34.0	5
2.0	2.0	9	0.3-1.6	30-87		19.5	4
2.4	1.05	4	2.1	0.47-4.4	2.1×10^3		2

[a] Γ, the ional concentration, is defined $\Gamma = \Sigma C_i Z_i^2$, where C_i is the *molar* concentration of an ion and Z_i, its charge. This quantity, thus, differs from μ, the ionic strength, by the factor 2 as well as by the concentration scale used. [b] The value of this quotient is calculated using the value of ΔA per 1 cm. of light path. The measurements at 700 mμ were all made using 10-cm. cells while those at 290 mμ involved 1, 5 and 10-cm. cells.

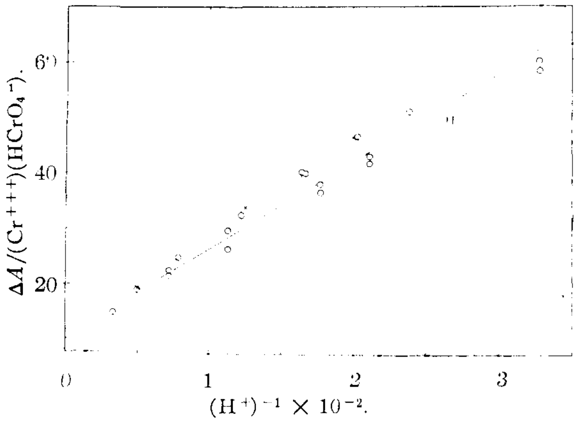

Fig. 1.—Values of $\Delta A/(Cr^{+++})(HCrO_4^-)$ *versus* $1/(H^+)$; wave length = 700 mμ; ional concentration = 2.0: x, values at $(H^+) = 5.0 \times 10^{-3}$, 8.0×10^{-3} and 2.0×10^{-2} from Table I (each point is average values for series); O and ♀ distinguish experiments using different chromium(III) perchlorate stock solutions.

The direct proportionality between the absorbancy enhancement and the concentration of chromium(III), the reagent in excess, persists to the highest concentrations of chromium(III) studied. This demonstrates that a relatively small fraction of the chromium(VI) is tied up as the complex under these conditions and that only the product of an equilibrium quotient and an absorbancy index can be evaluated. This statement cannot be made quite as emphatically in reference to this system as it might with regard to a system where no monomer–polymer equilibria existed. In solutions containing a significant fraction of the chromium(VI) as dichromate ion (25–65% in the solutions studied at 700 mμ), the dichromate acts as a "buffer" which dissociates to yield monomeric chromium(VI) as monomeric chromium(VI) is tied up as the chromium(III)–chromium(VI) complex. The system is one, then, in which the achievement of saturation of the monomeric chromium(VI) by chromium(III) is inherently difficult to achieve; it has not been achieved under the concentration conditions of these studies. It is not possible, therefore, to evaluate both the molar absorbancy index of the complex ion and the equilibrium quotient for the reaction in which it is formed. A comparison of the values of the quotient at the two wave lengths indicates that the complex has a much larger molar absorbancy index at 290 mμ than at 700 mμ. This is not surprising since the ions which unite to form the complex are more opaque at the shorter wave length.

The values of $\{\Delta A/(Cr^{+++})(HCrO_4^-)\}$ obtained in measurements upon solutions of three different concentrations of hydrogen ion are not the same and, in addition, are not inversely proportional to the concentration of hydrogen ion. Thus, the absorbancy enhancement is not due exclusively to either $CrCrO_4^+$ or $CrCrO_4H^{++}$.

The results of one series of experiments at 700 mμ in which the hydrogen ion concentration was varied over wider limits are presented in Fig. 1. In these experiments, the concentration ranges were: chromium(III) perchlorate 0.031–0.123 molar, and sodium dichromate 2.4×10^{-3} to 1.9×10^{-2} gram atoms of chromium(VI) per liter; the value of Γ was maintained at 2.0 by the addition of sodium perchlorate. It is seen that the relationship between the quotient $\{\Delta A/(Cr^{+++})(HCrO_4^-)\}$ and the concentration of hydrogen ion is

$$\frac{\Delta A}{(Cr^{+++})(HCrO_4^-)} = \frac{\alpha}{(H^+)} + \beta \qquad (1)$$

A straightforward derivation identifies α, the slope of the line, as K_1a_1 and β, the intercept, as K_2a_2. ($K_1 = (H^+)(CrCrO_4^+)/(Cr^{+++})(HCrO_4^-)$, $K_2 = (CrCrO_4H^{++})/(Cr^{+++})(HCrO_4^-)$, and a_1 and a_2 are the molar absorbancy indices of $CrCrO_4^+$ and $CrCrO_4H^{++}$, respectively.) The straight line shown in the figure was calculated by the method of averages[15]; the values of α and β so obtained are α = 0.156 and β = 11.0; using these values, one calculates values of $\{\Delta A/(Cr^{+++})(HCrO_4^-)\}$ which have an average deviation of 5.4% from the observed values. Measurements were made upon a less extensive series of solutions of varying acidity at 290 mμ. The solutions had an ional concentration of 1.3 and the concentration ranges were: chromium(VI) 5×10^{-5} to 3×10^{-4} gram atom per liter, chromium(III) 0.02–0.10 molar, and hydrogen ion 3.2×10^{-3} to 1.6×10^{-2} molar. The values of $\{\Delta A/(Cr^{+++})(HCrO_4^-)\}$ obtained in the seven experiments were treated by the method of averages to obtain values of α and β of 19.4 and 940, respectively. The average deviation between the observed values of $\{\Delta A/(Cr^{+++})(HCrO_4^-)\}$ and the values calculated using these parameters is 6.1%. The calculated value of $\{\Delta A/(Cr^{+++})(HCrO_4^-)\}$ at 290 mμ for a hydrogen ion concentration of 1.05×10^{-2} molar is 1.32-fold higher than the value reported in Table I; this difference is in the direction expected in view of the difference of electrolyte concentration.

Does an "Inert" Chromium(III)-Chromium(VI) Complex Exist?—In most of the experiments reported in the preceding section, the spectrophotometric measurements were made several hours after the solutions were prepared from the individual stock solutions. In some cases, however, the solutions were measured within ten minutes after preparation and in other cases measurements were made as a function of time. Some of the solutions were measured 12 to 15 months after preparation. Small changes in absorbancy with time were observed both for some of the solu-

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(14) C. Postmus and E. L. King, forthcoming publication.

(15) F. Daniels, J. H. Mathews and J. W. Williams, "Experimental Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 369.

tions containing chromium(III) alone and for some of those containing chromium(III) and chromium(VI). The behavior was somewhat erratic and the changes, when observed, were small. It seems reasonable to attribute these observations to errors in setting the wave length scale and possibly to the formation of small amounts of polymeric chromium(III) species.

Other evidence that there are no slowly established equilibria involving chromium(VI) and monomeric chromium(III) has been obtained. The solution containing the largest concentration of chromium(III) and chromium(VI) in the series at 8×10^{-3} molar hydrogen ion (see Table I) was allowed to stand for 15 months. A portion of this solution was treated with acidified lead nitrate solution. The absorbancy of the supernatant solution was within experimental error of that of a solution of the same composition which contained no chromium(VI). These measurements were made at 350–380 mμ, a wave length region in which chromium(VI) is strongly absorbing.[13] It can be concluded that: (1) the excess lead ion has reduced the concentration of chromium(VI) to a very low value ($<10^{-5}$ molar), and (2) there was present in the original solution no complex containing chromium(VI) which is not broken up by this treatment. The basis for the latter conclusion is the belief that a complex ion containing chromium(VI) will show an appreciable absorbancy compared to the absorbancy of uncomplexed chromium(VI) in this wave length region.

An additional piece of negative evidence regarding the existence of an *inert*[16] complex was obtained by passing a portion of the same aged solution as was used in the preceding experiment through a column containing Dowex-1 anion-exchange resin. There was no spectrophotometric evidence for chromium(VI) coming straight through the column. Since the complexes present in this solution would undoubtedly be cationic (chromium(III) in large excess), this experiment indicates that no *inert* complexes were present in the aged solution.

Discussion

The data presented in this paper demonstrate that there are rapidly formed in acidic solutions of chromium(III) and chromium(VI), the species $CrCrO_4^+$ and $CrCrO_4H^{++}$. The rapidity with which the equilibria are established might suggest, at first, that the complex is of the "outer-sphere" type.[6] The lability of the chromium(VI)–oxygen bonds as demonstrated by the relatively rapid establishment of the hydrogen chromate ion–dichromate ion equilibrium,[17] indicates, however, that an "inner-sphere" complex may be formed rapidly. The mechanism of formation would involve the breaking and making of bonds to chromium(VI) and not chromium(III). Since no clear evidence was obtained for a further slow reaction, it seems reasonable to postulate that among the complexes which are formed rapidly are the "inner-sphere" complexes, which are pictured as having an oxygen bridge between the two chromium atoms, Cr^{III}–O–Cr^{VI}. The equilibrated solutions may contain an appreciable amount of both the 'inner-sphere" and "outer-sphere" complexes.[7]

The oxygen bridge between the chromium(III) and chromium(VI) atoms in this proposed structure of the species responsible for the absorbancy enhancement is analogous to the chlorine bridge in the structures proposed for the species responsible for the absorbancy enhancement in hydrochloric acid solutions containing copper(I) and copper(II)[18] or iron(II) and iron(III).[19] The chromium(III)–chromium(VI) species is, at the same time, a metal ion–oxy anion complex similar to the cerium(IV)–chromium(VI) complex[5] or any metal ion-sulfate complex.

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[16] "Inert" used in the sense defined by H. Taube, *Chem. Revs.*, **50**, 72 (1952).

[17] V. K. LaMer and C. L. Read, THIS JOURNAL, **52**, 3098 (1930).

[18] H. McConnell and N. Davidson, *ibid.*, **72**, 3168 (1950).

[19] H. McConnell and N. Davidson, *ibid.*, **72**, 5557 (1950).

[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS BRANCH, REGION III, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heat Capacities at Low Temperatures and Entropies at 298.16°K. of Aluminates and Ferrites of Lithium and Sodium

BY E. G. KING

RECEIVED FEBRUARY 18, 1955

Heat capacity measurements of lithium aluminate, lithium ferrite, sodium aluminate and sodium ferrite were conducted throughout the temperature range 51 to 298°K. The substances showed normal thermal behavior and gave regular heat capacity curves. The entropies at 298.16°K. were obtained as 12.7 ± 0.1, 18.0 ± 0.2, 16.9 ± 0.2, and 21.1 ± 0.2 cal./deg. mole, respectively. The entropies of formation from the pure oxide constituents range from 0.2 to 2.3 cal./deg. mole at 298.16°K.

In continuation of a program of determining low temperature heat capacities and entropies at 298.16°K. of interoxidic compounds, measurements of lithium aluminate ($LiAlO_2$), lithium ferrite ($LiFeO_2$), sodium aluminate ($NaAlO_2$) and sodium ferrite ($NaFeO_2$) were undertaken. Thermodynamic data for these substances are almost entirely lacking; and, in particular, no entropy values were available previously. Earlier papers[1,2] from this laboratory have dealt with some analogous compounds of calcium and magnesium.

Materials

The substances were prepared[3] by prolonged, repeated sintering of stoichiometric mixtures of appropriate pure ingredients. In the intervals between heats, the materials were finely ground, screened, mixed, analyzed and adjusted in composition as necessary.

The starting materials for preparing lithium aluminate were reagent-grade lithium carbonate and pure hydrated alumina. Four heats, totaling 50 hours at 900–1,000°, were made. The final product analyzed 77.36% alumina, as compared with the theoretical 77.34%. The X-ray diffraction pattern agreed with that reported by Hummel.[4]

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[1] E. G. King, THIS JOURNAL, **76**, 5849 (1954).

[2] E. G. King, *J. Phys. Chem.*, **59**, 218 (1955).

[3] These preparations were conducted by K. C. Conway of this Laboratory.

[4] F. A. Hummel, *J. Am. Ceram. Soc.*, **34**, 235 (1951).