

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 $m\mu$, 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

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

chromium(III) and chromium(VI), the species CrCrO_4^+ and $\text{CrCrO}_4\text{H}^{++}$. 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, $\text{Cr}^{\text{III}}\text{--O--Cr}^{\text{VI}}$. 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) complex⁵ or any metal ion–sulfate complex.

(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).

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

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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.

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

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

Materials

The substances were prepared³ 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

(3) These preparations were conducted by K. C. Conway of this Laboratory.

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

Lithium ferrite was prepared from reagent-grade lithium carbonate and pure ferric oxide. Five heats, totaling 138 hours at 1,000–1,050° and 7 hours at 1,150–1,200°, were made. The final product contained 84.15% ferric oxide, as compared with the theoretical 84.24%. Silica, in the amount of 0.09%, was present as an impurity. The X-ray diffraction pattern agreed with that in the A. S. T. M. catalog.

Sodium aluminate was prepared from reagent-grade sodium bicarbonate and pure hydrated alumina. Six heats, totaling 89 hours at 1,000–1,050°, were made. The final product contained 62.08% alumina, as compared with the theoretical 62.19%. The X-ray diffraction pattern showed all the lines listed in the A. S. T. M. catalog, plus a few additional faint lines. The latter could not be attributed to alumina, sodium oxide, or any other reasonable impurity and it is presumed that the A. S. T. M. listing is incomplete.

Reagent-grade sodium carbonate and pure ferric oxide were the starting materials for preparing sodium ferrite. Twelve heats, totaling 60 hours at 1,000–1,050° and 10

hours at 1,100–1,150°, were made. The final product analyzed 72.05% ferric oxide, as compared with the theoretical 72.04%. A small amount of silica, 0.06%, was present as an impurity. The X-ray diffraction pattern showed no evidence of impurities and agreed with the lines listed in the compilation of Silverman and co-workers.⁵

Measurements and Results

The heat-capacity measurements were conducted with apparatus previously described.⁶ The results are expressed in defined calories (1 cal. = 4.1840 abs. joules) per deg. mole. All weighings were reduced to vacuum, and molecular weights accord with the 1953 "International Atomic Weights."⁷ The following sample masses were employed in the measurements: 159.10 g. of lithium aluminate, 218.12 g. of lithium ferrite, 114.15 g. of sodium aluminate and 165.92 g. of sodium ferrite.

The experimental heat capacity values appear in Table I. All four substances showed a normal thermal behavior throughout the measured temperature range, and the results give entirely regular heat capacity *vs.* temperature curves.

Entropies at 298.16°K.—The entropy increments between 51 and 298.16°K. were evaluated by Simpson-rule integrations of C_p against $\log T$ plots. The extrapolated portions, below 51°K., were obtained from empirical Debye- and Einstein-function sums, which were derived to fit the measured heat capacities. These function sums are listed below, the temperature range of validity and maximum deviation from the measured data being indicated in parentheses.

LiAlO_2 : $D(381/T) + 2E(594/T) + E(1,190/T)(51-298^\circ\text{K.}; 1.5\%)$

LiFeO_2 : $D(293/T) + 3E(529/T)(51-298^\circ\text{K.}; 1.5\%)$

NaAlO_2 : $D(275/T) + E(382/T) + E(595/T) + E(1,087/T)(51-298^\circ\text{K.}; 0.6\%)$

NaFeO_2 : $D(210/T) + 2E(389/T) + E(868/T)(51-200^\circ\text{K.}; 1.2\%)$

The entropy values appear in Table II. It is worthy of note that the extrapolated portions constitute only 2.8–7.2% of the totals for 298.16°K.

TABLE II
ENTROPIES AT 298.16°K.

	LiAlO_2	LiFeO_2	NaAlO_2	NaFeO_2
0–51°K. (extrap.)	0.36	0.71	0.84	1.51
51–298.16°K. (meas.)	12.39	17.30	16.03	19.63
$S_{298.16}^{\circ}$ (cal./deg. mole)	12.7 ± 0.1	18.0 ± 0.2	16.9 ± 0.2	21.1 ± 0.2

From recent determinations^{8,9} of the entropies of aluminum, and lithium oxides and values listed by Kelley¹⁰ for ferric and sodium oxides, the following entropies of formation from the oxides (cal./deg. mole) at 298.16°K. were obtained: 0.2 for lithium aluminate, 0.8 for lithium ferrite, 2.3 for sodium aluminate and 1.9 for sodium ferrite.

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(7) E. Wichers, THIS JOURNAL, **76**, 2033 (1954).

(8) E. C. Kerr, H. L. Johnston and N. C. Hallett, *ibid.*, **72**, 4740 (1950).

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(10) K. K. Kelley, U. S. Bur. Mines Bull. 177 (1950).

TABLE I
HEAT CAPACITIES

$T, ^\circ\text{K.}$	$C_p,$ cal./deg. mole	$T, ^\circ\text{K.}$	$C_p,$ cal./deg. mole	$T, ^\circ\text{K.}$	$C_p,$ cal./deg. mole
LiAlO_2 (mol. wt., 65.92)					
52.91	1.070	114.71	5.430	216.04	12.42
57.24	1.306	124.43	6.195	226.00	12.96
62.24	1.594	135.64	7.053	235.96	13.47
67.17	1.901	145.98	7.826	245.70	13.94
71.78	2.205	155.83	8.546	256.28	14.46
76.54	2.537	165.91	9.255	266.35	14.90
80.85	2.848	176.18	9.970	276.13	15.31
85.69	3.207	186.01	10.60	286.62	15.75
94.75	3.889	195.85	11.21	295.98	16.12
104.89	4.675	206.24	11.83	298.16	(16.20)
LiFeO_2 (mol. wt., 94.79)					
53.43	1.942	114.16	8.171	215.98	16.54
57.78	2.297	124.50	9.278	225.97	17.09
62.54	2.712	135.78	10.42	235.98	17.56
67.12	3.128	145.48	11.38	245.68	17.98
71.79	3.576	160.79	12.76	256.28	18.44
76.46	4.051	165.72	13.14	266.33	18.79
81.09	4.543	175.93	13.95	276.12	19.11
85.47	5.021	185.82	14.67	286.34	19.44
94.60	6.018	195.64	15.33	296.01	19.75
104.75	7.140	205.96	15.96	298.16	(19.81)
NaAlO_2 (mol. wt., 81.97)					
53.10	2.319	114.46	7.986	216.38	14.40
57.90	2.753	124.64	8.805	226.04	14.86
62.61	3.204	136.21	9.682	236.05	15.27
66.71	3.595	145.78	10.36	245.70	15.68
70.91	3.999	155.84	11.04	256.15	16.11
75.58	4.454	165.90	11.67	266.66	16.47
80.57	4.942	175.94	12.29	276.25	16.78
85.14	5.381	185.79	12.83	286.50	17.18
94.57	6.258	195.94	13.36	296.10	17.46
104.83	7.176	206.09	13.88	298.16	17.52
NaFeO_2 (mol. wt., 110.84)					
53.16	3.457	114.65	10.03	216.22	16.95
57.70	3.959	124.32	10.91	225.93	17.44
62.23	4.493	135.73	11.84	236.18	17.88
66.82	5.020	145.63	12.63	245.65	18.31
71.34	5.537	155.71	13.37	256.39	18.74
75.95	6.068	166.10	14.07	266.34	19.11
81.17	6.671	176.17	14.70	276.20	19.43
85.68	7.166	186.17	15.33	286.67	19.85
94.60	8.113	196.09	15.89	296.11	20.14
104.84	9.135	206.14	16.42	298.16	(20.20)