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Heats of Formation of Crystalline Aluminates of Sodium and Lithium

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RECEIVED JANUARY 11, 1957

Heat of solution measurements of crystalline $NaAlO_2$, $LiAlO_2$, Al, NaCl and LiCl were conducted at 303.15°K. in 4.360 *m* hydrochloric acid solution. Based upon these data the following heats of formation from the component oxides at 298.15°K. are derived: −20,890 ± 780 cal./mole for $NaAlO_2$ and −12,880 ± 1,030 cal./mole for $LiAlO_2$. Corresponding heats of formation from the elements are −270,840 ± 170 cal./mole and −284,330 ± 210 cal./mole, respectively.

A recent article dealt with the heats of formation of three calcium aluminates.[1] In continuation of this activity, the present paper reports the heats of formation of crystalline sodium aluminate ($NaAlO_2$) and lithium aluminate ($LiAlO_2$). Sodium aluminate is of interest as an important intermediary in the extraction of pure alumina from bauxite. Low temperature heat capacities and entropies at 298.15°K. of these substances were reported by King.[2]

Materials

The sodium and lithium aluminates were prepared by prolonged, repeated sintering of stoichiometric mixtures of appropriate pure ingredients. These compounds were portions of the samples used by King[2] who reported the results of chemical analyses and X-ray diffractions. The samples used in this work contained, in addition, small amounts of moisture (0.11% for $NaAlO_2$ and 0.08% for $LiAlO_2$) for which appropriate corrections have been applied to the thermal measurements.

The lithium aluminate sample was very difficultly soluble and required special treatment to obtain material that would dissolve completely within 90 minutes. The sample was repeatedly ground and elutriated in a stream of oxygen traveling vertically at a rate of 1.2 cm./sec. The maximum particle size, calculated from Stoke's law, was equivalent to a sphere 14 μ in diameter.

Analytical data and heat of solution measurements for aluminum metal already have been reported by the author.[1] Also outlined in that paper are the method of standardizing the hydrochloric acid solution and methods of applying minor corrections to the heat of solution measurements.

The sodium chloride sample was analytical reagent grade, containing less than 0.03% total impurities originally, plus 0.01% moisture picked up in handling.

The lithium chloride sample was also an analytical reagent with original impurities totaling less than 0.55%; the sample picked up 0.08% water in handling for which a correction has been applied. To check the possibility of sample hydrolysis during drying a ten-gram portion which had been dried at 550–600° was titrated with 0.1 *N* acid and the indicated alkalinity, as lithium hydroxide, was found to be only 0.014%. As the total heat of solution was quite small, and the principal impurities are other alkali chlorides, the correction for impurities is considered negligibly small and therefore omitted.

Method and Results

The calorimetric apparatus is essentially the same as described by Southard,[3] with minor improvements by the author.[4] The results are expressed in defined calories (1 cal. = 4.1840 abs. joules), and all molecular weights are based on the 1953 International Atomic Weights.[5] Sample weights were corrected to vacuum using the following densities: Al, 2.70; H_2O, 0.997; 4.360 *m* HCl, 1.062; LiCl, 2.068; NaCl, 2.49; $NaAlO_2$, 2.6 (estimated); and $LiAlO_2$, 2.554.

The heat of solution measurements were conducted in a two-quart glass Dewar containing 1,936.2 g. of 4.360 *m* hydrochloric acid ($HCl\cdot 12.731H_2O$). The amounts of samples employed were 0.02 mole each of aluminum, sodium chloride, sodium aluminate, lithium chloride and lithium aluminate, and requisite amounts of water and hydrochloric acid solution as shown in reactions 6 and 14.

The amounts of water impurities and the equivalent net corrections applied to the various measurements are as follows: sodium aluminate, 0.11% impurity and −64 cal./mole; sodium chloride, 0.01% and −0.3 cal./mole; lithium aluminate, 0.08% and −41 cal./mole; and lithium chloride, 0.08% and −14 cal./mole. A small correction was applied to adjust the electrical calibration measurements to the mean temperatures of the corresponding heat of solution measurements. This correction amounted to −12 cal./mole for sodium aluminate, −10 cal./mole for lithium aluminate, −1 cal./mole for lithium chloride, and was negligible for the other measurements.

All measurements, except one, were made within 0.04° of 30.00° and required no correction to 30.00°. The first measurement of sodium aluminate was made at approximately 29.74°[6] and required a correction of −8 cal./mole.

$NaAlO_2$(c).—Table I gives the skeleton equations for the reactions measured to obtain the heat of formation of sodium aluminate. Reactions 1, 2 and 3 were measured consecutively in the same acid solution; reactions 4 and 5 were measured consecutively in a second portion of acid. Thus the final solution from reactions 1, 2 and 3 and the final solution from reactions 4 and 5 are identical, so that $\Delta H_6 = \Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4 - \Delta H_5$.

Reaction 1 has been discussed in an earlier paper.[1] The molal heat of solution of aluminum in 4.360 *m* hydrochloric acid, including all corrections, is −127,050 ± 120 cal./mole at 303.15°K.

Six measurements were made of the heat of solution of sodium chloride in the final solutions from reaction 1, resulting in +1,924 ± 4 cal./mole as the mean of +1,920, +1,917, +1,920, +1,930, +1,928 and +1,926.

The heat of reaction 3, −1,196 ± 12 cal. for 14.731 moles of water, is the resultant of five meas-

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[1] J. P. Coughlin, THIS JOURNAL, **78**, 5479 (1956).

[2] E. G. King, *ibid.*, **77**, 3189 (1955).

[3] J. C. Southard, *Ind. Eng. Chem.*, **32**, 442 (1940).

[4] J. P. Coughlin, THIS JOURNAL, **77**, 868 (1955).

[5] E. Wichers, *ibid.*, **76**, 2033 (1954).

[6] All calorimeter temperature readings were made in terms of microvolt potentials and never converted to degrees. The resistance thermometer was calibrated at one fixed point, 30.00° being equivalent to 8890 ± 10 μv.; the sensitivity was approximately 1180 μv. per degree.

TABLE I

HEAT OF FORMATION OF $NaAlO_2$(c) (CAL./MOLE)

Mol. wt. = 81.97

	Reaction	$\Delta H_{303.15}$	Uncertainty
(1)	$\mathrm{Al(c) + 3H^+(sol) = Al^{+++}(sol) + 3/2\ H_2(g)}$	−127,050	±120
(2)	$\mathrm{NaCl(c) = Na^+(sol) + Cl^-(sol)}$	+ 1,920	± 10
(3)	$\mathrm{14.731\ H_2O(l) = 14.731\ H_2O(sol)}$	− 1,200	± 20
(4)	$\mathrm{NaAlO_2(c) + 4H^+(sol) = Na^+(sol) + Al^{+++}(sol) + 2H_2O(sol)}$	− 51,220	± 20
(5)	$\mathrm{HCl\cdot 12.731\ H_2O(sol) = H^+(sol) + Cl^-(sol) + 12.731\ H_2O(sol)}$	− 10	± 10
(6)	$\mathrm{Al(c) + NaCl(c) + 14.731\ H_2O(l) = NaAlO_2(c) + HCl\cdot 12.731\ H_2O(sol) + 3/2\ H_2(g)}$	− 75,100	±130
	At 298.15°K., $\Delta H_6 = -74{,}880 \pm 130$ cal./mole		

urements conducted in solutions containing 0.02 mole of aluminum and 0.02 mole of either sodium chloride or lithium chloride (see Table II).

TABLE II

HEAT OF SOLUTION OF H_2O(l) IN SOLUTIONS CONTAINING SODIUM CHLORIDE OR LITHIUM CHLORIDE

H_2O sample size (g.)	NaCl or LiCl	$\Delta H_{303.15}$ (cal./mole)
0.9306	NaCl	−81.0
1.0191	NaCl	−82.0
4.8205	NaCl	−81.9
5.5531	LiCl	−81.3
5.2210	LiCl	−80.0
Mean $\Delta H_{303.15} = -81.2 \pm 0.8$ cal./mole		

The heat of reaction appears to be independent of the water sample size and also of whether sodium ion or lithium ion is present in solution. These results agree substantially with similar measurements made in connection with the calcium aluminates.[1]

The heat of reaction 4, −51,220 ± 11 cal./mole, resulted from five measurements, −51,230, −51,230, −51,220, −51,200 and −51,220.

Reaction 5 (the heat of mixing of approximately 5 ml. of the original acid solution with the final solution from reaction 4) required only two measurements to verify that its heat was nearly zero. The first measurement, −7.4 cal./mole, was conducted in the final solution from reaction 4; the second measurement, −5.7 cal./mole, was conducted in the final solution from reaction 12 of Table III. Thus, the rounded value for reaction 5 (and also reaction 13 of Table III) is −10 ± 10 cal./mole.

Reaction 6 represents the heat of formation of sodium aluminate plus aqueous hydrochloric acid from aluminum metal, sodium chloride and water. The heat of reaction was corrected to 298.15°K. using heat capacity data of King,[2] Kelley[7] and Rossini.[8] The heats of formation from the oxides (reaction 7) and from the elements (reaction 8) were obtained by substitution of literature values for sodium chloride and hydrochloric acid,[9] water and sodium oxide[10] and aluminum oxide.[11]

$$\tfrac{1}{2}\mathrm{Na_2O(c)} + \tfrac{1}{2}\mathrm{Al_2O_3}(\alpha) = \mathrm{NaAlO_2(c)}, \quad \Delta H_{298.15} = -20{,}890 \pm 780 \text{ cal./mole} \tag{7}$$

$$\mathrm{Na(c) + Al(c) + O_2(g) = NaAlO_2(c)}, \quad \Delta H_{298.15} = -270{,}840 \pm 170 \text{ cal./mole} \tag{8}$$

The free energy changes of these reactions, shown in Table IV, were evaluated using entropy data of Kerr, Johnston and Hallett,[12] King[2] and Kelley.[7]

$LiAlO_2$(c).—Table III shows skeleton equations of the reactions measured to obtain the heat of formation of lithium aluminate.

TABLE III

HEAT OF FORMATION OF $LiAlO_2$(c) (CAL./MOLE)

Mol. wt. = 65.92

	Reaction	$\Delta H_{303.15}$	Uncertainty
(9)	$\mathrm{Al(c) + 3H^+(sol) = Al^{+++}(sol) + 3/2\ H_2(g)}$	−127,050	±120
(10)	$\mathrm{LiCl(c) = Li^+(sol) + Cl^-(sol)}$	− 6,880	± 10
(11)	$\mathrm{14.731\ H_2O(l) = 14.731\ H_2O(sol)}$	− 1,200	± 20
(12)	$\mathrm{LiAlO_2(c) + 4H^+(sol) = Li^+(sol) + Al^{+++}(sol) + 2H_2O(sol)}$	− 46,000	± 50
(13)	$\mathrm{HCl\cdot 12.731\ H_2O(sol) = H^+(sol) + Cl^-(sol) + 12.731\ H_2O(sol)}$	− 10	± 10
(14)	$\mathrm{Al\ (c) + LiCl(c) + 14.731\ H_2O(l) = LiAlO_2(c) + HCl\cdot 12.731\ H_2O(sol) + 3/2\ H_2(g)}$	− 89,120	±140
	At 298.15°K., $\Delta H_{14} = -88{,}900 \pm 140$ cal./mole		

Reactions 9, 11 and 13 have been discussed as reactions 1, 3 and 5, respectively. The heat of reaction 10, −6,878 ± 3 cal./mole, is the mean of five measurements, −6,878, −6,876, −6,875, −6,879 and −6,882.

Five measurements of the heat of solution of lithium aluminate, −46,060, −45,960, −45,970, −45,970 and −46,060, yield a mean of −46,000 ± 46 cal./mole. Because of difficulty in preparing large amounts of the finely divided sample, two of the measurements (the second and fourth) were made with samples of one-half the theoretical size, measured consecutively in the same acid solution. Comparison with the other three measurements shows that the heat of solution is independent of sample size, within the limit of experimental error.

Reaction 14 was corrected to 298.15°K., using previously mentioned heat capacity data.[2,7,8] Heat of formation values from other sources[9-11] are used to evaluate reactions 15 and 16, the heats of

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(7) K. K. Kelley, U. S. Bur. Mines, Bulletin 477 (1950).

(8) F. D. Rossini, *J. Research Natl. Bur. Standards*, 4313 (1930).

(9) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, Natl. Bur. Standards Circular 500 (1952).

(10) J. P. Coughlin, U. S. Bur. Mines Bulletin 542 (1954).

(11) Heat of formation of Al_2O_3 (α,-corundum): $\Delta H_{298.15} = -400{,}500 \pm 200$ cal./mole. A. D. Mah, unpublished measurements, this Laboratory.

(12) E. C. Kerr, H. L. Johnston and N. C. Hallett, THIS JOURNAL, **72**, 4740 (1950).

TABLE IV

HEATS AND FREE ENERGIES OF FORMATION (KCAL./MOLE)

Substance	From the oxides $\Delta H_{298.15}$	$\Delta F^\circ_{298.15}$	From the elements $\Delta H_{298.15}$	$\Delta F^\circ_{298.15}$
$NaAlO_2(c)$	−20.89 ± 0.78	−21.58 ± 0.80	−270.84 ± 0.17	−255.60 ± 0.19
$LiAlO_2(c)$	−12.88 ± 1.03	−13.50 ± 1.03	−284.33 ± 0.21	−269.49 ± 0.22

formation of lithium aluminate from the component oxides and from the elements, respectively.

$$^1/_2Li_2O(c) + {}^1/_2Al_2O_3(\alpha) = LiAlO_2(c),\quad \Delta H_{298.15} = -12{,}880 \pm 1030 \text{ cal./mole} \quad (15)$$

$$Li(c) + Al(c) + O_2(g) = LiAlO_2(c),\quad \Delta H_{298.15} = -284{,}330 \pm 210 \text{ cal./mole} \quad (16)$$

Johnston and Bauer's[13] entropy value for lithium oxide is used, together with entropy data from sources,[2,7,12] to calculate the free energy data in Table IV.

Although no high temperature heat content and entropy increment data are available for these aluminates, the entropies of formation at 298.15°K. indicate that both substances should become increasingly stable with respect to their component oxides with increasing temperature.

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[13] H. L. Johnston and T. W. Bauer, THIS JOURNAL, **73**, 1119 (1951).

[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS EXPERIMENT STATION, REGION II, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heat Capacities at Low Temperatures and Entropies at 298.15° K. of Nickelous Oxide, Cobaltous Oxide and Cobalt Spinel

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RECEIVED DECEMBER 26, 1956

Heat capacities of nickelous oxide (NiO), cobaltous oxide (CoO) and cobalt spinel (Co_3O_4) were measured throughout the temperature range 51 to 298°K. The heat capacity of cobaltous oxide has a pronounced maximum at 287.3°K. The entropies at 298.15°K. are 9.08 ± 0.04, 12.66 ± 0.08 and 24.5 ± 0.2 cal./deg. mole, respectively.

This paper presents heat capacity measurements in the temperature range 50 to 298°K. and entropy values at 298.15°K. for crystalline nickelous oxide (NiO), cobaltous oxide (CoO) and cobalt spinel (Co_3O_4). No previous similar data exist for the cobalt compounds. Seltz, DeWitt and McDonald[1] have reported low temperature heat capacity data for nickelous oxide.

Materials.—Nickelous oxide[2] was prepared from reagent grade nickelous nitrate hexahydrate and nickelous sulfate hexahydrate. These materials were dissolved in water and precipitated as basic carbonate with ammonium hydroxide and carbon dioxide. The precipitate was heated slowly to 1000° where it was kept for nine days. Analysis showed 99.96% nickelous oxide, 0.05% cobaltous oxide, 0.01% sodium oxide, and 0.02% acid insoluble. Tests showed no calcium or sulfate. The X-ray diffraction pattern agreed with the ASTM catalog.

Cobaltous oxide was obtained from recrystallized, reagent grade cobaltous sulfate heptahydrate as the starting material. After heating slowly to 1000°, it was maintained at this temperature for nine days. Additional treatment involved heating for 16 hours at 1000° and cooling in nitrogen, followed by an additional six hours *in vacuo* at 1000° with cooling in nitrogen. Analysis showed 78.61% cobalt (theoretical, 78.65%). The X-ray pattern was identical with that in the ASTM catalog.

Recrystallized reagent grade cobalt sulfate heptahydrate was the starting material for preparing cobalt spinel. It was heated in air for 15 days at 850° and 16 hours at 900°, after which it was quenched to room temperature. At this point the product contained too much cobalt (73.71%). It was next heated for 16 hours at 720° and finally for 16 hours at 780°, followed by quenching to room temperature. Analysis of the final product gave 73.40% cobalt, as compared with the theoretical 73.42%. The X-ray diffraction pattern agreed with the ASTM catalog.

Heat Capacity Measurements and Results.—The heat capacity calorimeter has been described.[3] Results are given in defined calories (1 cal. = 4.1840 abs. joules). Weighings were reduced to vacuum and molecular weights were obtained using the 1954–55 Report on Atomic Weights.[4] Sample masses were 275.83 g. of nickelous oxide, 396.86 g. of cobaltous oxide and 161.23 g. of cobalt spinel.

The measurements are tabulated in Table I and plotted in Fig. 1. The heat capacity curves of nickelous oxide and cobalt spinel show a regular behavior over the measured range of temperature. A comparison of the heat capacities of nickel oxide with those of Seltz and co-workers[1] shows the present values to be lower. The difference is 2.0% at 75°K., becomes zero at 125°K., then increases again to 1.5% at 258°K., and finally decreases to 0.1% at 298°K.

Cobaltous oxide possesses a peak with the maximum at 287.3°K., at which point the heat capacity is greater than 17.6 cal./deg. mole. As may be seen in Fig. 1, abnormal heat capacities persist for a wide temperature range both above and below the maximum. At the highest measured temperature (307.6°K.) the heat capacity continues to decrease with increasing temperature. Results labeled (a) in Table I were obtained without temperature gaps. In the immediate neighborhood of the peak, runs with temperature rises of only about one degree

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[1] H. Seltz, B. J. DeWitt and H. J. McDonald, THIS JOURNAL, **62**, 88 (1940).

[2] All three substances were prepared by K. R. Bonnickson, Chemist, Minerals Thermodynamics Experiment Station, Region II, Bureau of Mines.

[3] K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686, 1946.

[4] E. Wichers, THIS JOURNAL, **78**, 3235 (1956).