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Heats of Formation of Cryolite and Sodium Fluoride

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Heat of solution measurements of cryolite, aluminum, sodium fluoride and sodium chloride were conducted at 303.15°K. in 4.360 *m* hydrochloric acid solution. Based upon these data the following heats of formation from the elements at 298.15°K. were derived: −784.8 kcal./mole for cryolite and −136.3 kcal./mole for sodium fluoride.

Introduction

In continuation of a program of measuring thermodynamic properties of substances of importance to aluminum metallurgy, this paper gives the heats of formation of cryolite and sodium fluoride. Recent publications from this Laboratory[1,2] presented low temperature heat capacities, entropies at 298.15°K.,[3] and high temperature heat contents for these substances and for anhydrous aluminum fluoride. Combination of these data with the present work permits evaluation of the free energies of formation of sodium fluoride and cryolite at temperatures from 0 to 1400°K.

Materials.—The cryolite sample consisted of hand-picked crystals of natural Greenland cryolite. It was a part of the sample used for low temperature heat-capacity measurements by King,[1] who reported the chemical analysis. In accordance with this analysis and in conformity with King, the composition is taken as $Na_{2.96}AlF_{5.96}$.

The sodium chloride and sodium fluoride were reagent-grade chemicals with negligible amounts of impurities. Analytical and heat-of-solution data for aluminum metal have been reported previously[4]; the two samples used had purities of 99.995 and 99.998%.

The $HCl \cdot 12.731H_2O$ solution (4.360 *m*) was prepared by diluting reagent grade concentrated acid and standardizing against sodium carbonate, as in previous work.[4]

The $HF \cdot 5.716H_2O$ solution also was prepared by diluting reagent grade concentrated acid. It was standardized against 1 *N* sodium hydroxide, which, in turn, had been standardized against the 4.360 *m* hydrochloric acid.

Methods and Results

The apparatus employed in the heat-of-solution measurements was that described by Southard,[5] with minor modifications by the author.[6] Further alterations were necessary for this work to protect the glass parts of the apparatus from attack by hydrofluoric acid. This was accomplished by coating the glass dewar with a thin layer of Tygon paint and eliminating the glass sample bulbs. The samples were placed in a bulb machined of lucite, sealed at the upper end with 0.25-inch tapered pipe threads to a hollow plastic tube, which extended out of the dewar through the calorimeter stirrer-shaft. The bottom of the bulb was closed with a tight-fitting hollow plastic stopper, which could be pushed out from above, at the appropriate time, with a lucite rod.

The results are expressed in defined calories (1 cal. = 4.1840 abs. joules), and all molecular weights are based on the 1954–55 Report on Atomic Weights.[7] Sample weights were corrected to vacuum, using the following densities: Al, 2.70; H_2O, 0.997; 4.360 *m* HCl, 1.062; $HF \cdot 5.716\ H_2O$, 1.055; NaCl, 2.49; NaF, 2.79; and Na_3AlF_6, 2.948. Sample weights used are 0.02 of the actual molal quantities expressed in equations 7 and 16; that is, 0.02000 mole of aluminum and sodium fluoride and equivalent amounts of the other materials.

The heat of solution measurements of cryolite and sodium fluoride include corrections for water impurities, based upon an assumed binding energy of 79.70 cal./g., equal to the heat of fusion of ice. The net corrections are 6 cal./mole for cryolite containing 0.06% water and −3 cal./mole for sodium fluoride containing 0.16% water. Other corrections, usually applied,[4] were negligible.

Cryolite.—Table I gives the skeleton equations for the reactions measured to obtain the heat of formation of $Na_{2.96}AlF_{5.96}(c)$. Reactions 1, 2, 3 and 4 were measured consecutively in the same acid solution; reactions 5 and 6 were measured consecutively in a second portion of the acid. Thus the final solution from reactions 1, 2, 3 and 4 and the final solution from reactions 5 and 6 are identical; it therefore follows that $\Delta H_7 = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 - \Delta H_5 - \Delta H_6$.

TABLE I

HEAT OF FORMATION OF $Na_{2.96}AlF_{5.96}(c)$ (CAL./MOLE)

Reaction	$\Delta H_{303.15}$
(1) $Al(c) + 3H^+(sol) = Al^{+++}(sol) + 3/2H_2(g)$	−127,050 ± 120
(2) $5.96(HF \cdot 5.716H_2O)(sol) = 5.96H^+(sol) + 5.96F^-(sol) + 34.067H_2O(sol)$	−4,750 ± 40
(3) $2.96NaCl(c) = 2.96Na^+(sol) + 2.96Cl^-(sol)$	+5,610 ± 10
(4) $3.617H_2O(l) = 3.617H_2O(sol)$	−290 ± 10
(5) $Na_{2.96}AlF_{5.96}(c) = 2.96Na^+(sol) + Al^{+++}(sol) + 5.96F^-(sol)$	+27,040 ± 50
(6) $2.96(HCl \cdot 12.731H_2O)(sol) = 2.96H^+(sol) + 2.96Cl^-(sol) + 37.684H_2O(sol)$	0 ± 10
(7) $Al(c) + 2.96NaCl(c) + 5.96(HF \cdot 5.716H_2O)(sol) + 3.617H_2O(l) = Na_{2.96}AlF_{5.96}(c) + 2.96(HCl \cdot 12.731H_2O)(sol) + 3/2H_2(g)$	−153,520 ± 140

At 298.15°K., $\Delta H_7 = -153{,}520 + 300 = -153{,}220 \pm 140$ cal./mole

Reaction 1 was discussed in an earlier paper.[4] The molal heat of solution of aluminum in 4.360 *m*

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(1) E. G. King, THIS JOURNAL, **79**, 2056 (1957).

(2) C. J. O'Brien and K. K. Kelley, *ibid.*, **79**, 5616 (1957).

(3) For definition of 25.00° as 298.15°K. see *Comité intern. poids et measures, procès-verbaux de séances de 1954*, **24**, T79 (1955).

(4) J. P. Coughlin, THIS JOURNAL, **78**, 5479 (1956).

(5) J. C. Southard, *Ind. Eng. Chem.*, **32**, 442 (1940).

(6) J. P. Coughlin, THIS JOURNAL, **77**, 868 (1955).

(7) E. Wichers, *ibid.*, **78**, 3235 (1956).

hydrochloric acid, including all corrections, is −127,050 ± 120 cal./mole at 303.15°K.

The data for reaction 2 (the heat of solution of $HF \cdot 5.716H_2O$ in 1936.7 g. of $AlCl_3 \cdot 725.4HCl \cdot 9.273H_2O$) are presented in Table II. According to Latimer,[8] the complex ion AlF_6^{---} is formed in solution by the addition of F^- to Al^{+++} in six distinct steps, diminishing in free energy of reaction from the first to the sixth fluoride ion added. The first five measurements in Table II show that the heat of reaction follows a similar trend. Corrections to the theoretical sample size of 14.6598 g. (corresponding to $Na_{2.96}AlF_{5.96}$) are based on runs 4 and 5. Run 5 shows the average heat of solution in the concentration range AlF_5^{--} to AlF_6^{---}; run 4 shows the heat of solution of HF in excess of the amount necessary to convert all of the Al^{+++} to AlF_6^{---}.

TABLE II

HEAT OF SOLUTION OF $HF \cdot 5.716H_2O$ (CAL./G.)

(Mol. wt. = 122.987)

Run no.	$HF \cdot 5.716H_2O$ (wt., g.) Added	In soln.	$\Delta H_{303.15}$ (cal./g.) Measured	Cor. to 14.6598 g.
1	5.4656	0	−10.83	....
2	5.3787	5.4656	− 4.87	....
3	3.9909	10.8443	− 3.18	....
4	2.7459	14.8500	− 2.63	....
5	2.2800	12.3075	− 2.95	....
6	14.8278	0	− 6.43	−6.47
7	14.6225	0	− 6.57	−6.56
8	14.6696	0	− 6.50	−6.51
9	14.6701	0	− 6.40	−6.41
10	14.6870	0	− 6.51	−6.52
11	14.6583	0	− 6.40	−6.40
			Av. (runs 6–11)	−6.48 ± 0.05

$\Delta H_{303.15}$ = −797 ± 6.1 cal./mole = −4750 ± 36 cal. (for 5.96 moles)

Six measurements were made of the heat of solution of sodium chloride in the final solutions from reaction 2, giving 1,894 ± 2 cal./mole as the mean of 1,891, 1,894, 1,894, 1,897, 1,891 and 1,894. Ignition loss of the sample was less than 0.01%.

Three measurements of reaction 4 (−81.2, −76.5 and −83.2 cal./mole) lead to an average of −80.3 cal./mole or −290 cal. for 3.617 moles. As this is in good agreement with previous heat of dilution measurements,[4,9] an uncertainty of ±10 cal. is assigned.

The heat of solution of cryolite, 27,040 ± 50 cal./mole, is the mean of six measurements, 27,020, 27,120, 27,080, 27,060, 27,000 and 26,990. Final solutions from this reaction were used for two measurements of the heat of reaction 6, 1.4 and −2.8 cal./mole, respectively. The average, 0 ± 10 cal./mole, agrees within the assigned limits with previous measurements of this type.[9]

Reaction 7 was corrected to 298.15°K. by means of heat capacity data taken from Kelley,[10] King,[11] Rossini[11] and Landolt–Börnstein.[12] Reaction 8, the heat of formation from the elements, was evaluated by substitution of heat of formation data from NBS Circ. 500[13]; the values for the hydrofluoric and hydrochloric acid solutions were obtained by graphical interpolation.

$$2.96Na(c) + Al(c) + 2.98F_2(g) = Na_{2.96}AlF_{5.96}(c) \qquad (8)$$

$$\Delta H_{298.15} = -779.11 \pm 0.71 \text{ kcal.}$$

Estimated uncertainties in the adopted values are ±100 cal./mole for NaCl(c) and $HF \cdot 5.716H_2O(sol)$ and ±50 cal./mole for $HCl \cdot 12 \cdot 731H_2O(sol)$.

A recent determination[14] of the heat of the reaction

$$3/2PbF_2(c) + Al(c) = 3/2Pb(c) + AlF_3(c) \qquad (9)$$

leads to a value of −355.6 kcal./mole for the heat of formation of aluminum fluoride, taking −158.5 kcal./mole as the heat of formation of lead fluoride. Assuming the heat of solid solution of excess aluminum fluoride in stoichiometric cryolite is zero, the heat of formation of cryolite from the elements, reaction 10, becomes −784.8 kcal./mole.

$$3Na(c) + Al(c) + 3F_2(g) = Na_3AlF_6(c) \qquad (10)$$

(It is of interest to note that if the sample of cryolite used in the measurements had been considered as stoichiometrically pure, the derived heat of formation would be −784.7 kcal./mole, a change of only 0.1 kcal./mole. The present result differs by over 25 kcal./mole from the value listed in NBS Circ. 500,[13] which depends upon data over 50 years old.)

Sodium Fluoride.—Table III gives the skeleton equations for the reactions studied to obtain the heat of formation of sodium fluoride. These measurements were made in an acid solution containing 0.5396 g. of aluminum, in order to utilize previous data.[9]

TABLE III

HEAT OF FORMATION OF NaF(c) (CAL./MOLE)

(Mol. wt. = 41.991)

Reaction	$\Delta H_{303.15}$
(11) $NaCl(c) = Na^+(sol) + Cl^-(sol)$	+1920 ± 10
(12) $7.015H_2O(l) = 7.015H_2O(sol)$	− 570 ± 10
(13) $HF \cdot 5.716H_2O(sol) = H^+(sol) + F^-(sol) + 5.716H_2O(sol)$	−1560 ± 30
(14) $NaF(c) = Na^+(sol) + F^-(sol)$	+1320 ± 40
(15) $HCl \cdot 12.731H_2O(sol) = H^+(sol) + Cl^-(sol) + 12.731H_2O(sol)$	0 ± 10
(16) $NaCl(c) + HF \cdot 5.716H_2O(sol) + 7.015H_2O(l) = NaF(c) + HCl \cdot 12.731H_2O(sol)$	−1530 ± 60
At 298.15°K., ΔH_{16} = −1410 ± 60 cal./mole	

Reactions 11 and 12 have been discussed previously in connection with the heat of formation of sodium aluminate.[9]

The heat of reaction 13 is the mean of six determinations, −1,560, −1,540, −1,560, −1,610 −1,580 and −1,520. Sample sizes ranged from 2.4306 to 2.5104 g., the theoretical size being 2.4597 g. Deviation of results from the mean was random with respect to sample size.

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[8] W. L. Latimer, "Oxidation Potentials," 2nd Ed., Prentice–Hall, Inc., New York, N. Y., 1952, p. 283.

[9] J. P. Coughlin, THIS JOURNAL, **79**, 2397 (1957).

[10] K. K. Kelley, U. S. Bur. Mines Bulletin 477, 1950.

[11] F. D. Rossini, *J. Research Natl. Bur. Standards*, **4**, 313 (1930).

[12] "Landolt–Börnstein Physikalisch-chemische Tabellen," Vol. III, 5th Ed., 3rd Supplement, 1936, p. 2282.

[13] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, NBS Circ. 500, 1952.

[14] P. Gross, C. Hayman and D. L. Levi, *Trans. Faraday Soc.*, **50**, 477 (1954).

Six measurements were made of the heat of solution of sodium fluoride, 1,300, 1,320, 1,350, 1,370, 1,280 and 1,280. Two measurements were made of reaction 15 (−3.5 and −5.1 cal./mole) to confirm that the heat is approximately zero, as previously reported.[9]

Heat-capacity data from the sources noted earlier[1,10–12] were used to correct ΔH_{16} to 298.15°K. Combination with heat of formation data[13] for NaCl(c), $HF.5{\cdot}716H_2O$(sol) and $HCl{\cdot}12{\cdot}731H_2O$(sol) led to a value of −136.3 ± 0.2 kcal./mole for the heat of formation of sodium fluoride from the elements at 298.15°K.

$$Na(c) + 1/2F_2(g) = NaF(c) \qquad (17)$$

This differs by 0.3 kcal./mole from the value chosen by Rossini and co-workers,[13] based upon older work.

Discussion

The heat of formation of aluminum fluoride (derived from the work of Gross and co-workers[14]) and the present data suffice for obtaining the heat of formation of cryolite from its constituent fluorides. (The author had hoped to check the value for aluminum fluoride; but this proved impossible with available apparatus, as no suitable solvent could be found.)

Combination of reactions 8 and 10 with the heats of formation of aluminum fluoride and sodium fluoride leads to reactions 18 and 19, the formation

$$2.96NaF(c) + AlF_3(c) = Na_{2.96}AlF_{5.96}(c), \quad \Delta H_{298.15} = -20.1 \text{ kcal./mole} \qquad (18)$$

$$3NaF(c) + AlF_3(c) = Na_3AlF_6(c), \quad \Delta H_{298.15} = -20.3 \text{ kcal./mole} \qquad (19)$$

of $Na_{2.96}AlF_{5.96}$(c) and of stoichiometric cryolite from the constituent fluorides. Application of King's[1] entropy data and O'Brien and Kelley's[2] high temperature heat content data to reaction 19 shows that the free energy of combination of the fluorides varies from −21.6 kcal./mole at 298° to −29.1 kcal./mole at 1400°K.

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The Structures of Lanthanum Dicarbide and Sesquicarbide by X-Ray and Neutron Diffraction

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Lanthanum dicarbide, with a structure of the calcium carbide type is body-centered tetragonal, $a = 3.934 \pm 0.002$ Å., $c = 6.572 \pm 0.003$ Å. The C–C distance of the C_2 group is 1.28 ± 0.02 Å., intermediate between double and triple bond C–C distances. Lanthanum sesquicarbide is body-centered cubic with the plutonium sesquicarbide ($D5_c$-type) structure, and a lattice constant between 8.803 and 8.819 Å. It also contains C_2 groups but with a C–C distance (1.32 ± 0.03 Å.) about that of a double bond. A possible relation between electron density and C–C distance is noted. Carbon positions in both structures were determined by neutron powder data, and were refined by a statistical method based on the least squares method.

Introduction

X-Ray powder data have shown that LaC_2 is isostructural with calcium carbide. The body-centered tetragonal cell contains two formula units; the already reported space group is D_{4h}^{17}–I 4/mmm.[1] There are a number of metal carbides with this structure, but in none has the C–C distance been determined accurately due to the relatively small X-ray scattering power of carbon. This distance is interesting due to its relationship to the acetylene ion, $C_2^{=}$.

The cubic sesquicarbides are related in that they also contain C_2 groups or ions. U_2C_3,[2] Pu_2C_3[3] and Ce_2C_3[4] have been reported previously. La_2C_3 was discovered in an examination of the La–C system.[5] The body-centered cell contains eight formula units, and the reported space group is T_d^6–I$\bar{4}$3d. There is only one metal parameter, and this has been well established for Pu_2C_3. From X-ray data the one carbon parameter can only be guessed, and the reported value for Pu_2C_3 leads to a C–C distance of 1.5 Å., which turns out to be considerably too long for lanthanum sesquicarbide. For reasons pointed out below, more data on several of these compounds would be of interest.

Preparation of Diffraction Samples.—The carbides used in this investigation were prepared from 99+% lanthanum and high purity graphite by arc melting under a helium atmosphere. Preparation, analyses and methods of handling are described fully elsewhere.[5]

X-Ray and neutron samples were obtained by crushing the carbide preparations in a hardened tool-steel mortar within a carefully flushed dry-box under a positive pressure of dry argon or helium. X-Ray capillary tubes were filled inside the dry-box, but were removed and sealed in air. This caused no contamination of the samples because of the inert atmosphere in the capillaries. Neutron diffraction samples were placed in special vanadium tubes and capped in the dry-box. Back-reflection camera samples were prepared in the dry-box by spreading the carbide on cellophane tape and sealing it with a second strip of tape. No appreciable oxidation of such samples was detected after 10 hours in air.

Lanthanum Dicarbide

Unit Cell and Density.—Accurate lattice constants for lanthanum dicarbide were obtained using a precision, self-focusing back-reflection

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(1) M. von Stackelberg, *Z. physik. Chem.*, **B9**, 437 (1930).

(2) M. W. Mallett, A. V. Gerds and D. A. Vaughan, *J. Electrochem. Soc.*, **98**, 505 (1951).

(3) W. H. Zachariasen, *Acta Cryst.*, **5**, 17 (1952).

(4) L. Brewer and O. Krikorian, *J. Electrochem. Soc.*, **103**, 38 (1956).

(5) F. H. Spedding, K. Gschneidner, Jr., and A. H. Daane, "The Lanthanum–Carbon System," to be published.