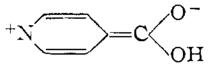
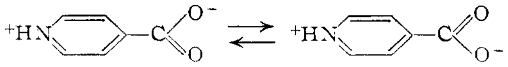
ties with the picolinic acid intensity. The observed violet shift of about 1700 cm.$^{-1}$ (*cf.* Fig. 3) which occurs for isonicotinic acid when the solution is changed from ethanol to water bears a close resemblance to the type of blue shift expected for an n-π^* transition,[14,28] but it is highly probable that the correct explanation for this blue shift is one that involves a discussion of π-electrons only. Kumler and Strait[21a] have pointed out in a discussion of the spectra of benzoic acid and *p*-aminobenzoic acid that resonance (migration of negative charge) between the carboxyl group and the ring is restricted whenever internal carboxyl resonance itself is enhanced by removal of the proton. Whereas, therefore, one expects some contribution from ionic resonance structures such as


IX (similar to VI)

in ethanol solutions, such structures will be restricted in water solution because of the added importance of the resonance


X

That is, one expects a greater migration of charge out of the ring in the neutral isonicotinic acid species than for the corresponding zwitterion species. The greater migration in the former case is a well-known explanation for the resulting shift of the π-absorption band to longer wave lengths.[21b] Since the shifts for picolinic and nicotinic acids are not so large, it can be assumed that the ionic structure IX is more important in determining the absorption by isonicotinic acid than is the corresponding structure VI for nicotinic acid (and picolinic acid). In the *ortho* and *meta*-positions the nitrogen atom undoubtedly restricts the degree of electron migration to the carboxyl group. A theoretical treatment of the perturbation effect of the carboxyl group when substituted on simple aromatic rings like benzene and pyridine is evidently very desirable.

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[28] G. J. Brealey and M. Kasha, THIS JOURNAL, **77**, 4462 (1955).

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

Low Temperature Heat Capacities and Entropies at 298.15° K. of Cryolite, Anhydrous Aluminum Fluoride and Sodium Fluoride

BY E. G. KING

RECEIVED NOVEMBER 28, 1956

Heat capacities of cryolite (Na_3AlF_6), sodium fluoride and aluminum fluoride were measured in the temperature range 51 to 298°K. All showed normal behavior. The 298.15°K. entropies are: cryolite, 57.0 ± 0.4 cal./deg. mole; sodium fluoride, 12.26 ± 0.07 cal./deg. mole; and aluminum fluoride, 15.89 ± 0.08 cal./deg. mole.

This paper reports the results of heat capacity measurements throughout the temperature range 51–298°K., with derived entropies, for cryolite and its constituent fluorides. Thermodynamic values for these substances are of importance in the usual electrolytic process for aluminum production. No similar data have been published previously.

Materials.—The cryolite, supplied by the Aluminum Company of America Research Laboratories, New Kensington, Pa., consisted of hand-picked crystals of natural Greenland cryolite. The analysis by ALCOA showed 32.76% sodium (theoretical, 32.85%) and 13.01% aluminum (theoretical, 12.85%). As impurities there were 0.036% potassium and 0.007% lithium. For the purpose of the present work, the substance was considered as $Na_{2.959}AlF_{5.959}$, and the heat-capacity results were corrected to stoichiometric composition. This correlation ranged from 0.1 to 0.2%.

The sodium fluoride was Mallinckrodt analytical reagent powder meeting A.C.S. specifications. No treatment of the sample was made other than heating to 700° immediately before use.

The aluminum fluoride was a vacuum-sublimed product, prepared especially for this work by the Reduction Research Laboratory, Kaiser Aluminum and Chemical Corp., Permanente, Calif. The sample analyzed 32.12% aluminum (theoretical, 32.13%). Impurities, measured spectrographically by the Kaiser Laboratories, were: Si, 0.008%; Fe, 0.008%; Mg, 0.005%; Na, 0.05%; Ti, 0.003%; and Ca, 0.06%. All other impurities were present in amounts less than 0.003%.

Measurements and Results.—The apparatus used for these measurements has been described.[1] Sample masses employed were: cryolite, 214.48 g.; sodium fluoride, 130.08 g.; and aluminum fluoride, 241.49 g.

The heat capacities are expressed in defined calories (1 defined calorie = 4.1840 absolute joules). The measured values are given in Table I. Molecular weights accord with the 1953 International Atomic Weights.[2]

All three compounds showed normal behavior over the entire measured temperature range. It is of interest to compare the heat capacity of cryolite with that of the stoichiometric summation of sodium and aluminum fluorides. Cryolite has 60% greater heat capacity at 50°K. However, the difference decreases rapidly with temperature, becoming 7% at 100°K., less than 0.2% at 200°K., and less than 0.2% for the entire range from 200 to 298.15°K.

Entropies at 298.15°K.—The entropy increments for the measured range, 51–298°K., were obtained by Simpson-rule integrations of C_p *vs.* log T plots.

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

[2] E. Wichers, THIS JOURNAL, **76**, 2033 (1954).

TABLE I

HEAT CAPACITIES (CAL./DEG.-MOLE)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
NaF (mol. wt., 41.991)					
54.01	1.659	114.61	6.434	216.14	10.08
58.57	2.025	124.46	7.007	225.80	10.27
62.80	2.380	135.98	7.606	235.96	10.44
67.29	2.770	145.74	8.060	245.66	10.57
71.81	3.165	155.77	8.460	256.40	10.73
76.33	3.555	165.84	8.815	266.20	10.91
80.98	3.955	175.84	9.124	276.20	10.97
85.79	4.355	186.05	9.413	287.15	11.09
95.40	5.110	195.79	9.650	295.86	11.17
105.04	5.808	205.89	9.882	298.15	(11.19)
AlF_3 (mol. wt., 83.98)					
53.65	1.774	114.53	7.268	215.91	14.48
56.69	2.013	124.39	8.131	226.20	15.02
57.89	2.110	135.56	9.077	235.93	15.50
61.01	2.380	145.35	9.879	245.55	15.92
65.62	2.782	155.75	10.68	256.18	16.39
70.32	3.206	165.58	11.38	266.31	16.80
74.88	3.623	175.81	12.08	276.22	17.19
82.19	4.304	185.93	12.75	286.59	17.54
86.30	4.685	195.84	13.35	296.10	17.88
94.60	5.463	206.14	13.93	298.15	(17.95)
104.82	6.404				
Na_3AlF_6 (mol. wt., 209.953)					
53.66	10.10	114.69	27.62	216.05	44.67
57.94	11.39	124.69	29.95	226.06	45.70
62.32	12.76	136.00	32.37	236.20	46.70
66.53	14.13	145.51	34.35	245.81	47.63
70.94	15.54	155.82	36.27	256.33	48.53
75.55	17.00	165.66	37.91	266.23	49.30
80.79	18.55	175.91	39.50	276.24	50.02
84.45	19.61	185.85	40.90	286.47	50.76
94.77	22.46	195.95	42.25	296.00	51.49
105.20	25.24	206.18	43.58	298.15	(51.60)

The curves were extrapolated below 51°K. by means of the following Debye and Einstein function sums, which fit the measured data within the limits of temperature and percentage of the heat capacity shown below

Na_3AlF_6: $D(144/T) + 4E(236/T) + 5E(568/T)$ (51–298°K., 1.7%)

NaF: $D(340/T) + E(391/T)$ (51–115°K., 0.2%)

AlF_3: $D(326/T) + E(385/T) + 2E(767/T)$ (51–298°K., 0.8%)

The entropy values are listed in Table II. The extrapolated portions of the total entropies at 298.15°K. are cryolite, 7.2%; sodium fluoride, 4.1%; and aluminum fluoride, 3.5%.

TABLE II

ENTROPIES AT 298.15°K. (CAL./DEG.-MOLE)

	Na_3AlF_6	NaF	AlF_3
0–51°K. (extrap.)	4.12	0.50	0.56
51–298.15°K.	52.86	11.76	15.33
$S^\circ_{298.15}$	57.0 ± 0.4	12.26 ± 0.07	15.89 ± 0.08

The entropy of formation of cryolite from sodium and aluminum fluorides is 4.3 ± 0.5 cal./deg. mole at 298.15° K.

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[CONTRIBUTION FROM THE WRIGHT AIR DEVELOPMENT CENTER]

Infrared Spectra of Cyclopentamethylenedialkylsilanes[1] in the 2–35–Region

BY GORDON D. OSHESKY AND FREEMAN F. BENTLEY

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The infrared absorption spectra of 21 cyclopentamethylenedialkylsilanes have been obtained from 2–35 μ and empirical assignments made for specific vibrations. The series begins with cyclopentamethylene-silane and ends with cyclpentamethylenedioctadecylsilane. Absorption bands at 10.93 to 11.00 and 20.20 to 20.85 μ are tentatively assigned to vibrations arising from the heterocyclic ring. All the observed absorption bands are given in a table showing their position and relative intensities.

This paper presents infrared absorption spectra of a series of cyclopentamethylenedialkylsilanes in the liquid state from 2 to 35 μ. This series of compounds was studied by this Laboratory for the purpose of correlating various physical properties with molecular structure.[2] This paper will deal solely with the infrared absorption bands of this and mainly with the tentative band assignment of the organosilicon ring vibration.

Experimental

Apparatus and Technique.—The infrared spectra in the 2 to 15 μ region were obtained with a Baird Associates, Model B, automatic recording spectrophotometer equipped with a sodium chloride prism. This instrument was calibrated to within ±0.05 μ by using ammonia and polystyrene. The liquid samples were recorded in a 0.028 mm. cell with sodium chloride windows. The thin capillary thicknesses were obtained by placing a drop of liquid between two rock salt plates, which were then fastened tightly together.

The spectra in the 15–35 μ region were obtained on a Perkin–Elmer Model 21, double beam recording spectrophotometer equipped with cesium bromide optics. This prism was calibrated by using atmospheric carbon dioxide and water vapor bands. The accuracy of the wave lengths as recorded here is probably better than ±0.05 μ, which in this region of the spectrum is equivalent to about ±1.5 cm.$^{-1}$. The liquid samples were measured in 0.510 and 0.053 mm. cells with cesium bromide windows. All measurements in the 2 to 35 μ region were made at 24.0 ± 0.5° and at a relative humidity of 35 ± 5%.

Due to insufficient sample the spectra of the diethyl and 2-ethylbutyl derivatives could not be obtained in the 15 to 35 μ region.

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(1) Opinions expressed are those of the authors and do not necessarily express the official opinions of the U. S. Air Force or the Wright Air Development Center.

(2) This series of compounds was prepared by Dr. Christ Tamborski, Dr. Harold Rosenberg and Mr. James Groves, and the details of their physical properties and preparation will be published elsewhere.