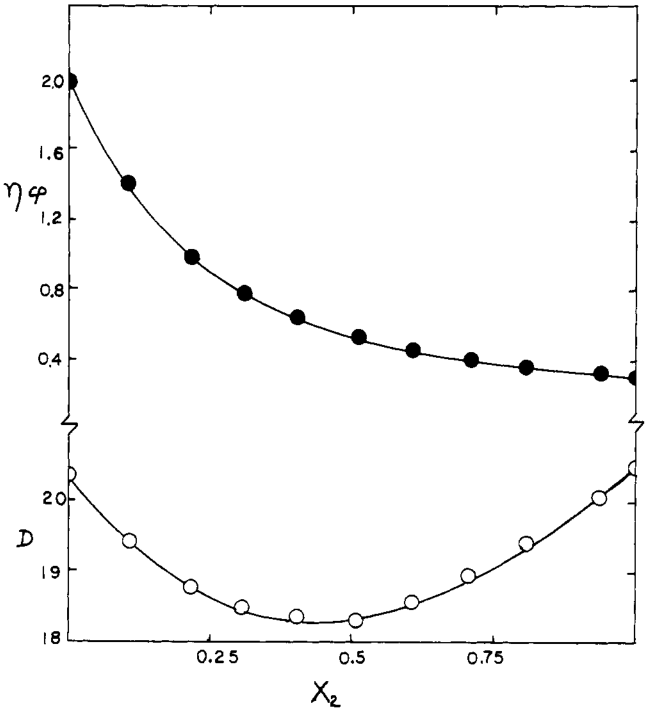

Figure 1. Dielectric constant and viscosity of acetone–1-propanol mixtures as a function of mole fraction composition

○ Dielectric constant

● Viscosity, centipoises

constant of the mixture consistent with the mixture rule. The structure breaking in hydrogen-bonded liquids, such as alcohols, is reflected as a remarkable decrease in both the dielectric constant and the viscosity. The relatively high decrease in the viscosity of 1-propanol on the initial addition of acetone, as seen in Figure 1, supports this view. The dielectric constant in acetone-*n*-hexane mixtures varies monotonically with the mole fraction composition. Evidence of changes in the intermolecular association can also be seen in the variation of Kirkwood's correlation factor, *g* (*9*), with composition. We calculated *g* by the method described by Oster (*12*). The correlation factor of acetone in *n*-hexane decreases from 1.12 in pure liquid to 0.99 in 40% acetone-60% *n*-hexane mixture. Further addition of *n*-hexane increases *g*. In binary mixtures of polar substances—e.g., acetone-1-propanol—it does not seem possible to calculate the correlation factor.

Acetone and 1-propanol are good solvents for several inorganic salts (*7, 13, 14*). It would be of interest to examine the conductance behavior of electrolytes in these two solvent systems to help single out the solvent's physical properties which affect Λ°.

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Low Temperature Heat Capacity and Entropy of Dipotassium Calcium Pyrophosphate at 10° to 310° K.

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The low temperature heat capacity of synthetic crystalline dipotassium calcium pyrophosphate, $K_2CaP_2O_7$, was measured over the temperature range 10° to 310° K. The calculated entropy at 298.15° K. is 60.91 cal. deg.$^{-1}$ mole^{-1} and the enthalpy is 9341 cal. per mole.

DIPOTASSIUM CALCIUM PYROPHOSPHATE, $K_2CaP_2O_7$, is relatively concentrated in both phosphorus and potassium, and its physical properties and ease of preparation make it a potentially useful fertilizer material. The optical properties and x-ray diffraction spectra of the crystalline material were measured by Brown *et al.* (*1*), and results of greenhouse tests of its agronomic value were reported by Lehr *et al.* (*5*). As part of a continuing program of determination of thermodynamic properties of compounds involved in fertilizer technology and in fertilizer-soil reactions, the low temperature heat capacity of dipotassium calcium pyrophosphate was measured over the range 10° to 310° K. and its entropy and enthalpy at 298.15° K. were calculated from the results.

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[1] Deceased.

MATERIALS AND APPARATUS

In the preparation of dipotassium calcium pyrophosphate by the reaction

$$KH_2PO_4 + K_3PO_4 + 2CaHPO_4 = 2K_2CaP_2O_7 + 2H_2O$$

a mixture of the calcium salt and a 10% excess of the potassium salts was heated on a hot plate for 20 hours. The cooled mixture was ground to pass 20-mesh and divided into 32 portions of about 30 grams each, and each portion was fused in a platinum dish in a pot furnace at 1180°.

Thirteen of the melts that microscopic examination showed to have the smallest amounts of occluded calcium pyrophosphate and only 0.1 to 0.5% of a glass phase were combined and ground to pass 40-mesh. In the grinding the last 5 or 10 grams of each melt appeared to be much harder than the bulk of the material, and this portion was discarded.

The composite was washed three times in 1200 ml. of water for 15 minutes and three times in 300 ml. of acetone for 2 minutes; the slime portion that did not settle in 3 or 4 minutes was discarded. Impurities in the air-dried product were estimated by petrographic techniques to be 0.05% calcium pyrophosphate and 0.4% glass phase. The glass phase was practically eliminated by grinding to pass 200-mesh and washing three times in 2500 ml. of water for 15 minutes and three times in 300 ml. of acetone, followed by air drying.

Table I. Observed Heat Capacity of Dipotassium Calcium Pyrophosphate, $K_2CaP_2O_7(c)$

(Cal. deg.$^{-1}$ mole^{-1})

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
10.21	0.178	103.1	26.80	194.5	41.72
11.48	0.217	104.5	27.10	198.1	42.13
11.78	0.212	108.4	27.92	199.0	42.21
12.82	0.289	109.6	28.16	202.5	42.66
13.61	0.386	112.0	28.68	202.7	42.67
15.18	0.578	115.7	29.42	203.9	42.79
16.36	0.758	116.9	29.66	206.9	43.27
18.59	1.140	119.6	30.20	210.0	43.49
20.72	1.596	123.2	30.87	210.5	43.56
21.73	1.832	124.8	31.16	213.6	43.92
24.36	2.545	126.9	31.56	216.8	44.24
25.17	2.782	130.8	32.26	220.3	44.65
26.85	3.275	131.9	32.46	226.2	45.29
29.58	4.203	133.9	32.82	228.2	45.48
30.47	4.503	137.9	33.48	233.4	46.06
34.97	6.136	138.6	33.58	236.2	46.31
35.68	6.393	141.6	34.09	240.5	46.78
41.00	8.394	143.9	34.51	244.0	47.13
42.16	8.820	146.2	34.82	247.5	47.47
46.67	10.51	149.0	35.30	251.0	47.84
48.83	11.30	150.9	35.63	254.6	48.16
51.86	12.41	153.5	36.05	257.9	48.49
53.82	13.09	156.6	36.52	261.8	48.84
55.33	13.60	158.0	36.74	265.5	49.20
56.02	13.85	160.6	37.13	269.2	49.53
58.15	14.56	164.4	37.69	273.0	49.91
62.00	15.87	165.1	37.78	275.3	50.08
63.63	16.41	167.6	38.14	277.7	50.34
68.07	17.79	171.2	38.64	281.0	50.61
70.02	18.35	171.4	38.67	283.6	50.82
73.99	19.48	174.6	39.11	284.6	50.95
76.65	20.25	175.7	39.27	287.8	51.23
79.86	21.20	178.2	39.60	289.2	51.30
80.42	21.36	179.8	39.82	291.0	51.53
82.09	21.81	181.7	40.06	294.5	51.78
83.89	22.31	183.1	40.23	294.6	51.80
87.24	23.18	184.9	40.48	298.2	52.09
89.40	23.71	186.7	40.72	300.8	52.29
91.02	24.11	188.6	40.99	301.2	52.34
94.17	24.82	189.9	41.12	304.5	52.59
96.13	25.27	190.6	41.20	306.3	52.75
97.43	25.56	192.1	41.42	307.1	52.82
101.2	26.40	193.5	41.59		

The final product was dried for 3 days at 95° and for 1 day at 105°. Chemical analysis showed CaO 19.43, K_2O 32.05, and P_2O_5 48.56% (stoichiometric, CaO 19.19, K_2O 32.24, P_2O_5 48.57%). Petrographic and x-ray examination showed the presence of a small amount of $Ca_2P_2O_7$ as a contaminating phase; the $Ca_2P_2O_7$ content was calculated to be 0.577% from the chemical analysis.

The low temperature calorimeter was that described by Egan *et al.* (*4*), and an automatic control system for the adiabatic shield was installed during the measurements on dipotassium calcium pyrophosphate. The measurements made with manual shield control in the ice and liquid nitrogen temperature regions in the first part of the measurements were repeated with the automatic control system. There was no difference between the results for the two series of measurements, both of which are given in Table I.

The defined calorie was taken as 4.1840 absolute joules, the ice point as 273.15° K. The heat capacities were corrected for curvature (*3*) and for the amount of calcium pyrophosphate present (*2*). Since small temperature differences were important, temperatures were read to four decimal places, but they were rounded to two decimal places in the final tabulation. The average deviation between the observed and the calculated values for heat capacity was 0.0112 cal. mole^{-1} deg.$^{-1}$ below 20° K. and 0.0155 cal. mole^{-1} deg.$^{-1}$ above 20° K.; this corresponds to an average deviation of 0.06% for all values above 20° K. The uncertainty in the heat capacity is estimated to be 0.1%.

Table II. Molal Thermodynamic Properties of Dipotassium Calcium Pyrophosphate, $K_2CaP_2O_7(c)$

T, °K.	C_p, Cal./° K.	$S°$, Cal./° K.	$H° - H_0°$, Cal.
10	0.1370	0.0433	0.3291
15	0.5465	0.1609	1.846
20	1.435	0.4289	6.610
25	2.731	0.8816	16.87
30	4.336	1.518	34.44
35	6.133	2.319	60.55
40	8.015	3.261	95.91
45	9.889	4.313	140.7
50	11.73	5.451	194.8
60	15.21	7.900	329.6
70	18.33	10.48	497.6
80	21.23	13.12	695.6
90	23.88	15.78	921.4
100	26.07	18.41	1171
110	28.30	21.00	1443
120	30.26	23.55	1736
130	32.11	26.04	2048
140	33.83	28.49	2378
150	35.48	30.88	2725
160	37.03	33.22	3087
170	38.48	35.51	3465
180	39.84	37.75	3857
190	41.14	39.94	4261
200	42.37	42.08	4679
210	43.52	44.17	5109
220	44.61	46.22	5549
230	45.68	48.23	6001
240	46.72	50.20	6463
250	47.72	52.12	6935
260	48.68	54.01	7417
270	49.61	55.87	7909
280	50.53	57.69	8409
290	51.40	59.48	8919
300	52.24	61.23	9437
273.15	49.91	56.45	8065
298.15	52.09	60.91	9341

The calorimeter charge was 98.8378 grams (vacuum) or 0.33627 mole of crystalline dipotassium calcium pyrophosphate (formula weight, 292.227) and 0.00224 mole of calcium pyrophosphate (formula weight, 254.103).

Observed molal heat capacities, corrected for the amount of calcium pyrophosphate present, are shown in Table I. The heat capacities at 1° intervals below 10° K. were read from a large-scale plot of the observed values of C_p/T *vs.* T^2 over the range 10° to 30° K. that was extrapolated smoothly to 0° K. The smoothed heat capacities and the corresponding entropy and enthalpy increments are shown in Table II.

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Enthalpy of Formation of Neptunium Dioxide

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The enthalpy of formation of neptunium dioxide has been determined by means of an oxygen bomb calorimeter and found to be $\Delta H^\circ_{f\ 298.15^\circ \mathrm{K.}}$ (NpO_2) = −256.7 ± 0.6 kcal. per mole.

OF THE MANY isotopes of neptunium, only Np^{237} has a sufficiently long half life to permit detailed studies of its properties. Only in recent years have sufficient amounts of this material been available for experimental use. Neptunium-237 is a by-product of plutonium production and is recovered and purified by solvent extraction and ion exchange methods. Fluorination of the dioxide followed by reduction with excess calcium in the presence of iodine (*7*) produces a metal of high purity. This paper describes the combustion of such metal in an oxygen bomb calorimeter to determine the enthalpy of formation of neptunium dioxide.

MATERIAL

The neptunium metal was in the form of pellets weighing 1.5 to 2 grams. In addition, Np wire was fabricated for use as a fuse (*9*). Analysis of the metal at this laboratory showed the following impurities: Pu^{238}, 0.02% (by radioassay); C, 0.0055%; H, 0.001%; N, 0.0034%; O, 0.0058%; Si, 0.02%. Thirty-six metallic elements were below the limit of detection by the spectrographic method used. A recasting of a portion of the metal increased the oxygen content to 0.015%. A metallographic examination revealed the presence of a very fine precipitate. An x-ray pattern showed only α-Np with no impurity lines. Mass spectrometer analysis showed essentially *m/e* of 237 with very small amounts of 235, 238, and 239.

The calculated composition of the material was (weight per cent): Np, 99.62; Pu, 0.02; NpC, 0.114; NpH_2, 0.119; NpO_2, 0.049; NpN, 0.061; Si, 0.02. For the recast sample the values were identical except for Np, now 99.54%, and NpO_2, which was increased to 0.126%.

Spectrographic analysis of the NpO_2 from which the metal was made showed small amounts of Al, Ca, and Si. This oxide was also used in the preparation of disks upon which the combustions were carried out.

METHODS AND RESULTS

The method involved the determination of the amount of heat evolved from the combustion of a weighed sample of neptunium metal in a bomb calorimeter at a known initial pressure of oxygen. The method and equipment have been described (*4, 5*). The energy equivalent of the calorimeter with 25 atm. of oxygen was 2390.0 ± 1.1 cal. per ° C. as determined with standard benzoic acid (NBS sample 39i). The calorie is the defined thermochemical calorie, equal to exactly 4.1840 absolute joules. Temperature measurements were made using a platinum resistance thermometer and a type G-2 Mueller bridge. They are believed accurate to 0.001° C. The 2 kg. of water used in the calorimeter were weighed to 0.01 gram.

Because of the neptunium alpha activity and the attendant health hazard the metal was handled through gloves in an enclosed box where it was weighed and loaded into the bomb. The Parr oxygen bomb screwed into an adapter in the floor of the box from the outside, so that the outside surface of the bomb remained uncontaminated. Although the top of the bomb was within the contaminated area of the box, it was protected by means of a molded disposable plastic cap which fitted snugly over the lid of the bomb. The gamma activity of the neptunium was not sufficient to be considered a hazard over the relatively short exposure times. The bomb was flushed and filled with oxygen in a ventilated hood. These precautions were sufficient to prevent contamination of the accessory apparatus.

The neptunium was burned as pellets on sintered disks of NpO_2 supported on a platinum platform weighing 20.8 grams. Two disks of NpO_2 each weighing 25 to 30 grams were used for each run. At room temperature α-Np is a hard (*Dph* ~ 355) brittle material of high density (20.45 grams per cc.). It proved difficult to drill holes through the pellets through which a fuse wire might be threaded. Such operations had to be performed in an inert atmosphere.

Ten-, 20-, and 30-mil diameter Np fuse wires were fabricated in addition to 10-mil magnesium and thorium wires. The 10-mil Np proved too brittle to be mounted on the electrical terminals. The 30-mil Np could not be ignited by any reasonable current flow. The magnesium wire would not ignite the Np. Two successful runs were made with the 20-mil Np and three with the thorium wire. In some cases the Np would not ignite but was heated by the fuse wire to a temperature where it would sustain oxidation over a period of 30 minutes or more. This unusual behavior