Summary

The dielectric constants of the vapors of trimethylene chloride and 1,1,2,2-tetrachloroethane have been measured and the results used to calculate the dipole moments of the two molecules, which show no variation with temperature over the range studied. Calculation of the internal energies of the molecules shows that the movable dipoles should oscillate in potential energy troughs in such a way as to give effective resultant moments not far from those observed and possessing a variation with temperature considerably smaller than that of ethylene chloride and, possibly, so small as to be undetectable in the temperature region studied.

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[CONTRIBUTION FROM FERTILIZER INVESTIGATIONS OF THE BUREAU OF CHEMISTRY AND SOILS, AND THE NATIONAL BUREAU OF STANDARDS]

Low Temperature Specific Heats. V. The Heat Capacity of Tricalcium Phosphate between 15 and 298°K.

BY J. C. SOUTHARD AND R. T. MILNER

A knowledge of the heat capacity of tricalcium phosphate was desired in connection with some phases of a phosphate investigation. Since no published data could be found, measurements were made on two crystalline forms of this substance in the apparatus previously described.[1]

The data are given in Tables I–III and shown in the figure. All results are expressed in calories per mole degree (one calorie = 4.1833 int. joules = 4.185 absolute joules). The errors are discussed in connection with the description of the apparatus. All weights are corrected to vacuum.

The two forms of tricalcium phosphate have

TABLE I

MOLAL HEAT CAPACITY OF α CALCIUM PHOSPHATE FROM 15 TO 285°K.

T, °K.	$Ca_3(PO_4)_2$ C_p cal./mole degree	T, °K.	$Ca_3(PO_4)_2$ C_p cal./mole degree	T, °K.	$Ca_3(PO_4)_2$ C_p cal./mole degree
15.27	0.391	107.43	25.79	199.61	43.37
18.03	.733	112.62	26.99	204.01	43.81
22.05	1.307	117.66	28.20	205.00	44.01
26.38	2.082	122.57	29.26	210.37	44.78
30.81	3.085	127.76	30.50	216.05	45.49
35.60	4.314	133.22	31.64	222.03	46.35
40.58	5.702	138.56	32.80	227.99	47.03
46.33	7.728	143.81	33.91	234.08	47.82
52.10	9.277	148.98	34.90	239.99	48.62
57.10	11.00	154.39	35.95	245.88	49.31
62.22	12.75	160.13	36.88	252.75	50.03
67.50	14.26	165.80	37.95	257.60	50.65
72.40	15.86	171.40	38.80	263.44	51.30
77.57	17.51	176.95	39.78	269.26	52.08
83.23	19.30	182.44	40.63	275.06	52.74
88.54	20.71	187.89	41.48	280.85	53.26
96.46	22.95	193.30	42.34	286.63	54.00
102.06	24.43	198.67	43.11		

TABLE II

MOLAL HEAT CAPACITY OF β CALCIUM PHOSPHATE (97.8% $Ca_3(PO_4)_2$) FROM 15 TO 300°K.

T, °K.	$Ca_3(PO_4)_2$ C_p cal./mole degree	T, °K.	$Ca_3(PO_4)_2$ C_p cal./mole degree	T, °K.	$Ca_3(PO_4)_2$ C_p cal./mole degree
15.26	0.310	73.02	15.89	190.26	41.69
17.90	.572	77.92	17.40	195.88	42.44
21.66	1.085	82.88	18.97	201.46	43.26
22.32	1.158	88.41	20.57	207.01	44.08
25.81	1.756	91.40	21.30	212.52	44.77
27.63	2.118	94.11	22.14	213.25	44.98
30.26	2.667	97.78	23.10	218.70	45.58
33.79	3.556	102.95	24.43	224.13	46.36
35.02	3.839	119.36	28.41	229.54	46.93
37.75	4.535	124.64	29.56	234.92	47.66
39.73	5.11	129.79	30.72	240.29	48.40
42.87	5.97	135.18	31.81	245.64	48.94
44.37	6.41	140.82	33.03	250.98	49.64
48.60	7.75	146.35	34.21	256.30	50.25
48.62	7.73	151.78	35.26	262.43	51.06
53.87	9.595	157.15	36.25	268.31	51.62
55.08	10.04	162.40	37.16	274.17	52.32
60.29	11.93	167.63	38.06	280.02	52.88
61.81	12.43	173.13	38.93	285.86	53.65
66.36	13.79	178.90	39.90	291.68	54.19
67.70	14.28	184.60	40.76	297.48	55.00
71.81	15.58				

TABLE III

MOLAL HEAT CAPACITIES OF β $Ca_8(PO_4)_2$ (CORRECTED FOR IMPURITIES) AT EVEN TEMPERATURES

T, °K.	$Ca_3(PO_4)_2$ C_p cal./mole degree	T, °K.	$Ca_3(PO_4)_2$ C_p cal./mole degree	T, °K.	$Ca_3(PO_4)_2$ C_p cal./mole degree
20	0.83	90	20.82	200	42.68
30	2.64	100	23.52	220	45.41
40	5.10	120	28.32	240	47.92
50	8.17	140	32.59	260	50.29
60	11.62	160	36.40	280	52.53
70	14.88	180	39.74	300	54.76
80	17.96				

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(1) Southard and Brickwedde, THIS JOURNAL, **55**, 4378 (1933).

been noted by Trömel.[2] The transition point was given by Trömel as between 1250 and 1500°.

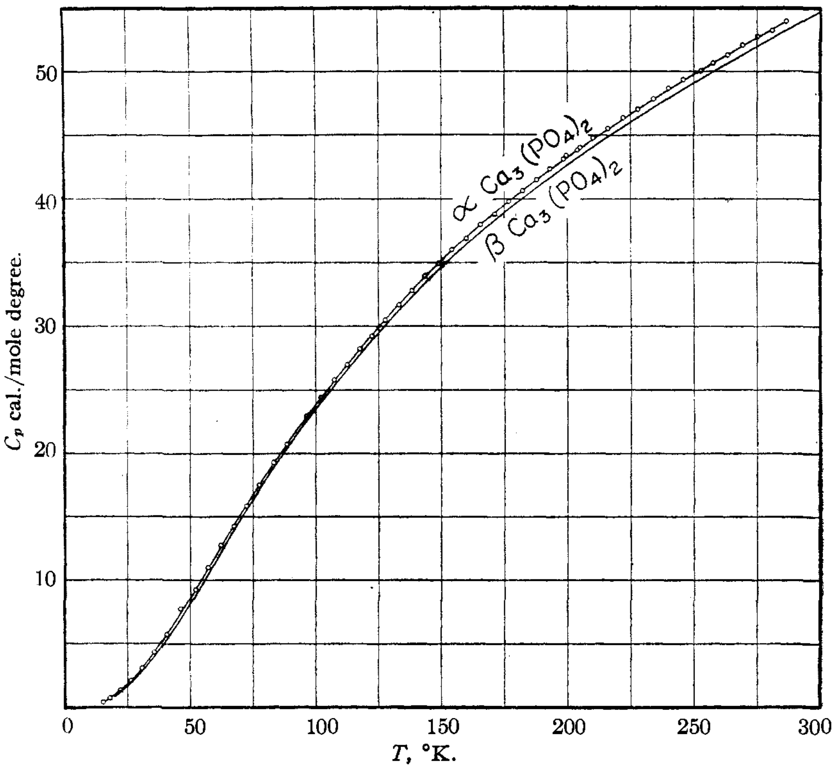

Fig. 1.—Heat capacities of tricalcium phosphates as a function of temperature in the range 15 to 290°K. The heat capacity of β tricalcium phosphate has been corrected from impurities in the sample.

The heat capacity of the α form, stable at higher temperatures, was determined on a sample prepared from very pure calcium hydroxide and phosphoric acid. This material was dried, heated to about 1400° for one hour and cooled quickly. It then exhibited the x-ray powder diffraction pattern which Trömel found for α-$Ca_3(PO_4)_2$. Chemical analysis showed less than 0.1% impurity. The sample used for the β form was made from sodium phosphate and calcium nitrate. It was first heated to 1400° for one hour, then held at 900° for an additional hour and allowed to cool slowly. The diffraction pattern showed it to be the β form. Chemical analysis showed that its composition, in mole per cent., was $Ca_3(PO_4)_2$ 97.8%, Na_3PO_4 2.1%, SiO_2 0.1%. A correction to the experimental results of about 1% was necessary because of the sodium phosphate and silica. Since there are no experimental data for the heat capacity of Na_3PO_4 it was necessary to estimate this from the heat capacity of α-$Ca_3(PO_4)_2$, making use of the known values in the analogous case, $CaCO_3$–Na_2CO_3.[3] Owing to this procedure the corrected heat capacity of the β form, Table III, may be in error by as much as 0.5%.

The entropy from 15 to 298°K. was determined by plotting the experimentally found molal heat capacity against log T and integrating graphically. Below about 25°K. the experimental points followed the curve $C_p = aT^3$ rather closely so that this relationship was used to extrapolate to 0°K. The results of the entropy calculations were as follows.

	$\alpha Ca_3(PO_4)_2$ cal/mole degree	$\beta Ca_3(PO_4)_2$ (corrected) cal./mole degree
$(S_{298.16} - S_{15°})$ graph	57.44 ± 0.12	56.29 ± 0.35
$(S_{15} - S_{0°})$ calcd.	0.14 ± .03	0.11 ± .03
$(S_{298.16} - S_{0°})$ total	57.58 ± .15	56.40 ± .38

There are insufficient data for a calculation of the free energy of formation of this salt.

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[2] Trömel, *Mitt. Kaiser-Wilhelm-Inst. Eisenforsch. Düsseldorf*, **14**, 25 (1932).

[3] Kelley, U. S. Bur. Mines *Bull.*, 350 (1932).