suspended from a plastic plug inside of a submarine which is fitted with an aluminum foil convection shield. The heater and resistance thermometer, made of the same lengths of wire as described above, were wound directly on the outer surface of the calorimeter. The stirrer and sample-breaking mechanism are the same as for the solution calorimeter. The calorimeter vessel was thoroughly flushed with hydrogen after it was filled, and a very slow stream was passed during the experiments to prevent the entry of air. The submarine was filled with Freon 114 to improve insulation, and it was cooled by injecting a stream of the liquid refrigerant when it was desired to cool the calorimeter. The thermal leakage modulus was 0.015/min., and the drift ranged from +0.015 to −0.005 deg./min. in the temperature range of this calorimeter, from 25 to 26.6°.

The cesium seemed to react completely within 10 seconds after breaking the sample bulb, but there was a lag of about 10 min., also found in the electrical calibration, before the temperature drift returned to the value characteristic of the calorimeter temperature. Neither the temperature drift nor the electrical calibrations gave any evidence of a heat effect from the reaction of the amalgam with impurities such as the oxide film which is presumably present on even the bright stainless steel surface.

Accessories.—The resistors of the heater circuit and the standard cell have been periodically compared with N.B.S. certified standards, as have the heaters themselves. Only the heaters show a measurable drift, which is small, however, compared with the accuracy required here. The limiting factor in the accuracy of the experiments described here is the reproducibility of the electrical calibrations. This can certainly be improved, although the exact source of the difficulty has not yet been established. The thermal leakage is also troublesome in the case of the amalgam calorimeter, but the large thermal leakage correction seems to be reproducible to about 0.0005 deg. per minute of "x" period.

LOS ANGELES, CAL.

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Thermodynamic Properties of Calcium Metaphosphate, 10 to 1400°K.

BY EDWARD P. EGAN, JR., AND ZACHARY T. WAKEFIELD

RECEIVED APRIL 9, 1956

The heat capacity of β-calcium metaphosphate crystals was measured over the range 10 to 306°K. The heat content, $H° - H_0°$, at 298.16°K. is 5715 cal. mole^{-1} and the entropy at 298.16°K. is 35.12 cal. deg.$^{-1}$ mole^{-1}. The heat contents of the β-crystalline and glassy forms of calcium metaphosphate were measured over the range 373 to 1370°K. and equations for the thermal properties of the materials were derived.

The thermodynamic properties of the calcium phosphates and other compounds of importance in the technology of phosphate fertilizers have for several years been the subject of a broad study.[1] As part of this study, measurements were made on calcium metaphosphate, the anhydride of monocalcium orthophosphate, in its β-crystalline and vitreous forms.

Materials and Methods.—Monocalcium phosphate monohydrate, twice recrystallized from phosphoric acid solution, was dehydrated by heating it to near constant weight at 250° and at 400°, and finally to constant weight at 750°. β-Calcium metaphosphate was the only phase detected in microscopic and X-ray examinations of the product. The chemical composition was 28.39% CaO and 71.22% P_2O_5, as compared with a theoretical composition of 28.32% CaO and 71.68% P_2O_5 for $Ca(PO_3)_2$ (formula weight, 198.03).

A method of promoting the development of crystallinity in the β-calcium metaphosphate was discovered too late for use in the present study. When the metaphosphate was heated for 1 to 2 hours at a temperature 5 to 10° below its melting point, growth of the crystals was pronounced. The resultant mass was lightly ground and digested in dilute hydrochloric acid to remove the small amount of glass phase. The product consisted of clean euhedral crystals.

Calcium metaphosphate glass was prepared by melting the crystalline metaphosphate at 1000° and allowing the melt to cool rapidly to room temperature. The melt was cooled within 30 minutes after it became molten, because phosphoric oxide is vaporized from molten calcium metaphosphate. The clear glass was crushed and the −20 + 100-mesh fraction was separated for measurements of its high temperature heat content.

The low and high temperature calorimeters have been described.[1]

One defined calorie was taken equal to 4.18331 international joules,[2] and 0° was taken to be 273.16°K.

Low Temperature Heat Capacity.—The observed heat capacities, $\Delta Q/\Delta T$, for the empty calorimeter and for the calorimeter filled with 90.9732 g. (vacuum) or 0.45939 mole of β-calcium metaphosphate were plotted, and arbitrary smooth curves were drawn through the experimental points. Values read at 5° intervals from the smooth curves were used in the calculation of curvature corrections from second differences.[3] Equations were fitted to the corrected heat capacities, a deviation plot was made, and the values calculated from the equations were corrected from the deviation plot. The observed molal heat capacities are listed in Table I. Temperatures were read to four decimal places and were so used in the calculations, since small differences were involved; the last two places were dropped in the compilation of Table I. The heat capacities at integral temperatures are shown in Table II.

The entropy at 298.16°K. is 35.12 ± 0.03 e.u., which is the sum of 0.03 e.u., obtained by Debye extrapolation ($\theta = 192$) between 0 and 10.26° K., and 35.09 e.u., obtained by graphical integration between 10.26 and 298.16°K. The graphical integration was checked by tabular integration[4] of C_p/T against T at 5° intervals. The heat content, $H^0 - H^0_0$, at 298.16°K., as derived from the integration of C_p against T, is 5715 cal. mole^{-1}. No correction was made for impurities. The derived entropy and heat content were assumed to represent the ideal state for the solid.

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[1] E. P. Egan, Jr., Z. T. Wakefield and K. L. Elmore, THIS JOURNAL, **72**, 2418 (1950); **73**, 5579, 5581 (1951); **78**, 1811 (1956).

[2] F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling and G. W. Vinal, *ibid.*, **74**, 2699 (1952).

[3] R. B. Scott, C. H. Meyers, R. D. Rands, Jr., F. G. Brickwedde and N. Bekkedahl, *J. Research Natl. Bur. Standards*, **35**, 39 (1945).

[4] Works Progress Administration, Mathematical Tables Project, "Tables of Lagrangian Interpolation Coefficients," Columbia University Press, New York, N. Y., 1944.

Table I

Heat Capacity of β-Calcium Metaphosphate, Cal. Deg.$^{-1}$ Mole^{-1}

Point[a]	T, °K.	ΔT	C_p	Point[a]	T, °K.	ΔT	C_p	Point[a]	T, °K.	ΔT	C_p
103	10.26	2.77	0.066	23	88.01	6.28	12.16	82	185.72	7.57	25.37
111	10.74	2.54	.712	67	91.18	7.10	12.70	48	186.01	6.06	25.41
104	14.46	5.57	.201	24	94.50	6.70	13.20	38	187.36	7.12	25.56
112	14.72	5.34	.214	68	98.04	6.63	13.80	83	192.44	6.80	26.09
105	19.83	5.10	.575	25	101.00	6.30	14.23	49	192.48	6.47	26.10
113	20.58	6.30	.664	69	104.48	6.26	14.81	8	196.75	3.35	26.44
106	24.87	4.95	1.110	26	107.14	5.97	15.19	84	198.75	5.95	26.71
114	26.67	5.87	1.397	70	110.60	5.96	15.75	85	199.01	5.07	26.71
107	30.38	6.04	1.858	71	112.05	6.39	15.95	9	201.74	6.62	26.96
115	32.32	5.46	2.236	27	113.32	6.42	16.12	86	205.11	7.12	27.31
108	38.12	9.43	3.119	72	116.97	6.16	16.71	10	208.28	6.51	27.59
116	38.49	6.90	3.296	28	119.60	6.14	17.06	87	211.82	6.30	27.97
117	45.26	6.65	4.513	73	123.08	6.05	17.61	11	214.74	6.41	28.17
109	46.13	6.57	4.532	29	125.94	6.54	17.98	88	218.45	6.91	28.56
118	51.26	5.34	5.621	74	129.45	6.68	18.51	12	221.10	6.31	28.74
110	52.76	6.70	5.795	30	132.36	6.30	18.88	89	225.30	6.79	29.17
52	54.27	6.63	5.969	75	136.15	6.72	19.45	13	227.36	6.22	29.30
50	55.04	4.31	6.132	31	138.68	6.34	19.73	90	232.05	6.70	29.71
59	55.54	5.91	6.232	76	142.91	6.79	20.35	14	233.55	6.14	29.82
119	56.24	4.62	6.560	32	145.18	6.66	20.60	15	239.65	6.07	30.35
53	57.58	3.99	6.626	41	145.69	3.19	20.63	17	251.50	6.07	31.34
51	59.12	3.86	6.945	77	149.67	6.72	21.22	93	251.92	7.54	31.29
60	61.40	5.80	7.388	42	150.85	7.12	21.31	18	257.60	6.14	31.81
54	61.77	4.38	7.459	33	152.09	6.45	21.46	94	259.58	7.79	31.89
55	66.30	4.70	8.318	78	156.46	6.86	22.06	19	263.71	6.07	32.28
61	67.18	5.76	8.473	43	158.18	7.53	22.21	95	266.68	6.41	32.43
56	71.14	4.98	9.184	34	158.77	6.90	22.27	96	273.68	7.60	32.97
62	72.99	5.85	9.504	79	163.69	7.61	22.93	98	281.08	5.62	33.50
57	75.66	4.04	9.975	44	164.99	6.09	23.09	99	286.37	4.96	33.86
63	78.07	4.31	10.42	45	169.28	7.42	23.57	100	291.92	6.14	34.25
58	79.58	3.80	10.69	80	171.20	2.50	23.80	101	298.04	6.08	34.68
65	80.15	4.27	10.78	46	173.62	7.40	24.07	6	300.28	6.18	34.86
64	81.76	3.07	11.08	81	178.68	7.05	24.63	102	304.09	6.03	35.08
22	82.46	4.82	11.17	47	179.74	6.17	24.75	7	305.92	5.11	35.24
66	84.96	5.35	11.65								

[a] Numbered in chronological order.

Table II

Heat Capacity of β-Calcium Metaphosphate at Integral Temperatures, Cal. Deg.$^{-1}$ Mole^{-1}

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
10	0.065	110	15.64	210	27.77
15	.239	115	16.40	215	28.23
20	.602	120	17.14	220	28.67
25	1.149	125	17.86	225	29.12
30	1.839	130	18.57	230	29.54
35	2.635	135	19.26	235	29.96
40	3.513	140	19.94	240	30.37
45	4.398	145	20.58	245	30.78
50	5.278	150	21.22	250	31.18
55	6.186	155	21.84	255	31.57
60	7.098	160	22.46	260	31.95
65	8.028	165	23.07	265	32.33
70	8.962	170	23.66	270	32.70
75	9.872	175	24.23	275	33.07
80	10.76	180	24.77	280	33.43
85	11.64	185	25.31	285	33.78
90	12.49	190	25.83	290	34.13
95	13.31	195	26.33	295	34.48
100	14.10	200	26.82	300	34.82
105	14.88	205	27.30	273.16	32.936
				298.16	34.693

The precision of the measurements was ±0.05% at temperatures above 30°K.; the deviation increased as the temperature was lowered below 30°K. and was ±7% at 10°K.

High Temperature Heat Content.—The heat contents above 298.16°K. of two samples of β-calcium metaphosphate crystals were measured alternately. About 8 g. (0.04 mole) of calcium metaphosphate filled each covered platinum–rhodium crucible. The heat contents were measured at 100° intervals to 1170°K., at about 5° intervals near the melting point (1250°K.), and then at 25° intervals to 1370°K.

The heat contents above 298.16°K. of two samples of the vitreous metaphosphate were measured similarly at 100° intervals to 1370°K. Each crucible was filled with about 8.5 g. of the crushed glass. The heat contents above 298.16°K. of a sample of synthetic sapphire were measured at 200° intervals as a check upon the reliability of the measurements. The platinum–platinum + 10% rhodium measuring thermocouple was checked at each temperature level against a couple certified by the National Bureau of Standards.

The observed heat contents above 298.16°K., in calories per gram, of the crucible plus metaphosphate less the observed heat contents of the empty crucible were converted to calories per mole. An equation was fitted to the observed heat contents by the method of Shomate,[5] the value for the heat capacity at 298.16°K. being taken from Table II. A deviation plot was made, and a smooth curve was drawn through the deviations from the derived equation. Heat contents at integral temperatures and smooth values at the observed temperatures were taken from the deviation curve. The observed heat contents are compared with the smoothed values in Tables III and IV. Smoothed values are not listed for temperatures above 1170°K., because the measured heat contents began to deviate noticeably from a smooth curve at about 1220°K.

TABLE III

OBSERVED HEAT CONTENT ABOVE 298.16°K. OF β-CALCIUM METAPHOSPHATE CRYSTALS, CAL. MOLE^{-1}

T, °K.	$H_T - H_{298.16}$ (obsd.)	Obsd. − smoothed	Dev., %
375.8	2,713	−255	..
376.2	2,965	− 16	0.54
475.9	7,307	180	..
475.8	7,163	41	.58
573.6	11,528	− 2	.02
573.4	11,498	− 24	.21
673.8	16,393	59	.36
673.6	16,322	1	.01
773.5	21,269	− 24	.11
774.7	21,225	−130	.61
873.7	26,389	− 37	.14
871.9	26,407	74	.28
971.8	31,622	40	.13
971.7	31,524	− 57	.18
1070.7	36,921	− 1	.00
1070.4	36,893	− 16	.04
1169.5	42,311	− 46	.11
1169.5	42,398	− 41	.10
1219.3	45,372		
1194.2	44,039	Av.	0.21
1194.2	43,964		
1228.9	46,182		
1229.1	46,135		
1234.1	46,593		
1238.8	47,134		
1243.6	48,050		
1248.4	49,389		
1248.4	49,225		
1253.0	52,239		
1268.4	54,131		
1293.1	56,010		
1318.1	57,583		
1341.9	59,427		
1366.9	61,123		
1223.8	45,832		
1223.8	45,762		

TABLE IV

OBSERVED HEAT CONTENT ABOVE 298.16°K. OF CALCIUM METAPHOSPHATE GLASS, CAL. MOLE^{-1}

T, °K.	$H_T - H_{298.16}$ (obsd.)	Obsd. − smoothed	Dev., %
373.3	2,965	−13	0.44
473.2	7,070	−11	.16
473.2	7,107	26	.37
573.6	11,631	30	.26
573.6	11,581	−20	.17
673.5	16,358	23	.14
673.7	16,374	35	.21
773.1	21,212	−30	.14
773.3	21,262	8	.04
873.6	26,348	−10	.04
873.6	26,389	29	.11
972.8	31,516	−49	.16
973.2	31,529	−54	.17
1068.9	36,807	39	.11
1173.8	42,536	−45	.11
1173.2	42,609	61	.14
1273.2	54,482		
1273.2	54,560	Av.	0.17
1372.9	61,360		
1373.0	61,430		

According to Hill, Faust and Reynolds,[6] the transition temperature of β- to α-calcium metaphosphate is 1239°K., the melting point of the metastable β-form is 1250°K., and the melting point of the α-form is 1257°K. They noted a marked tendency of β-calcium metaphosphate to persist in the region of the stable α-form. The α-form was not observed in the present study; attempts to prepare it in another study[7] resulted only in the formation of mixtures containing small amounts of α- with large amounts of β-calcium metaphosphate. No attempt was made in the present study to measure the heat of transition of β- to α-calcium metaphosphate.

With approach to 1220°K., the observed heat contents fell above an extrapolation of the smooth curve through the points below 1170°K., and the difference between the observed values and the extrapolated values increased up to 1260°K. From 1260 to 1370°K., the observed values fell on a smooth curve whose slope was greater than that of the curve for the lower range of temperature. A premelting or a transition heat effect, or a combination of both, may have set in at 1220°K. Samples quenched from a few degrees below the melting point, however, showed only a trace of glassy phase upon microscopic examination.

The observed heat content at 1370°K. was the same whether the melt was from crystals or glass. The material quenched from 1370°K. was a clear glass to the naked eye, but a microscopic examination showed areas of birefringence that suggested cryptocrystals. The quenched material was amorphous to X-rays. The observed heat content at 1370°K. differed from the heat content obtained through smooth extrapolation from 1170°K. by an amount corresponding to about 40% crystallization—a value incompatible with the slight crystallinity that was observed.

The heat of fusion of calcium metaphosphate at the melting point is taken as 19,820 cal. mole^{-1}—the average of two values (19,560 and 20,090 cal. mole^{-1}) calculated from tie-lines in the system $CaO–Al_2O_3–P_2O_5$ on which β-calcium metaphosphate is the stable phase.[7] A direct measurement

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[5] K. K. Kelley, Bur. Mines Bull. No. 476 (1949).

[6] W. L. Hill, G. T. Faust and D. S. Reynolds, *Am. J. Sci.*, **242**, 457, 542 (1944).

[7] P. E. Stone, E. P. Egan, Jr., and J. R. Lehr, *J. Am. Ceram. Soc.*, **39**, 89 (1956).

of the heat of fusion as the difference between the heats of solution of glass and crystals at 298.16°K. in a solution calorimeter, although desirable, was not made because of the near insolubility of crystalline calcium metaphosphate in acids of the moderate concentrations that could be used in the available solution calorimeter.

Since calcium metaphosphate glass does not crystallize readily, the observed heat contents above 298.16°K. for the glass do not include any heat of fusion, at least up to 1170°K. The small difference between the heat capacities of glass and crystals indicates that the heat of fusion is practically constant.

The smoothed heat content above 298.16°K., the heat capacity at high temperatures, the entropy above 298.16°K., and the free energy function for the crystals are listed in Table V at round values of absolute temperature. Corresponding values for the glass, not including the heat of fusion, are listed in Table VI, and those including the heat of fusion are listed in Table VII. The values of $(H^0 - H_0^0)_{298.16}$ and $S^0_{298.16}$, from the low-temperature data, are included in Table V to facilitate calculation of $(H^0 - H_0^0)_T$ and S^0_T at the listed temperatures.

TABLE V

THERMODYNAMIC PROPERTIES OF β-CALCIUM METAPHOSPHATE, CAL. MOLE^{-1}

T, °K.	C_p	$H_T - H_{298.16}$	$(H_T - H_{298.16})/T$	$S_T - S_{298.16}$	$-(F_T - F_{298.16})/T$
298.16	34.69	0	0	0	0
400	41.42	3,930	9.84	11.31	1.47
500	45.11	8,190	16.37	20.67	4.30
600	47.48	12,780	21.29	29.22	7.93
700	49.21	17,620	25.18	36.79	11.61
800	50.60	22,640	28.30	43.46	15.16
900	51.86	27,800	30.89	49.49	18.60
1000	52.87	33,100	33.10	55.03	21.93
1100	53.86	38,520	35.02	60.14	25.12
1200	54.81	44,040	36.70	64.85	28.15
1250.16 (m.p.)	55.27	46,820	37.46	67.06	29.60

298.16 $(H^0 - H_0^0) = 5715$ $S^0 = 35.12$

TABLE VI

THERMODYNAMIC PROPERTIES OF CALCIUM METAPHOSPHATE GLASS, CAL. MOLE^{-1} (NOT INCLUDING HEAT OF FUSION)

T, °K.	C_p	$H_T - H_{298.16}$	$(H_T - H_{298.16})/T$	$S_T - S_{298.16}$	$-(F_T - F_{298.16})/T$
298.16		0	0	0	0
400	41.45	4.030	10.08	11.58	1.50
500	45.15	8,260	16.52	20.62	4.10
600	47.47	12,840	21.40	29.22	7.82
700	49.15	17,630	25.18	36.71	11.53
800	50.49	22,600	28.25	43.42	15.17
900	51.63	27,730	30.81	49.47	18.66
1000	52.64	33,030	33.03	55.03	22.00
1100	53.58	38,480	34.98	60.14	25.16
1200	54.46	44,050	36.71	64.84	28.13
1250.16 (m.p.)	54.89	46,880	37.50	67.02	29.52
1300	55.31	49,500	38.08	69.00	30.92
1400[a]	56.12	55.000	39.29	73.18	33.89
1500[a]	56.91	61.000	40.67	77.37	36.70

[a] Extrapolated.

TABLE VII

THERMODYNAMIC PROPERTIES OF CALCIUM METAPHOSPHATE GLASS, CAL. MOLE^{-1} (INCLUDING HEAT OF FUSION)

T, °K.	$H_T - H_{298.16}$	$(H_T - H_{298.16})/T$	$S_T - S_{298.16}$	$-(F_T - F_{298.16})/T$
298.16	19,820	66.83	15.95	−50.88
400	23,860	59.65	27.27	−32.38
500	28,120	56.24	36.64	−19.60
600	32,710	54.52	45.19	− 9.33
700	37,560	53.66	52.76	− 0.90
800	42,560	53.20	59.42	6.22
900	47,710	53.01	65.43	12.42
1000	52,990	52.99	70.95	17.96
1100	58,400	53.09	76.04	22.95
1200	63,880	53.23	80.72	27.49
1250.16 (m.p.)	66,650	53.31	82.92	29.61
1300	69,270	53.29	85.05	31.76
1400[a]	74,960	53.54	89.17	35.63
1500[a]	80.710	53.81	93.08	39.27

[a] Extrapolated.

The heat capacity equation was obtained by differentiation of the heat content equation. The entropy equation was obtained from the heat capacity equation and corrections[5] based on the heat contents.

The free energy of fusion was assumed to be zero at the melting point, 1250°K. The free energy function of the glass, including the heat of fusion (Table VII), goes through zero at 705°K. It is not clear whether this phenomenon reflects the liquid-glass distinction discussed by Kauzmann[8] or whether an incorrect heat of fusion was assigned. Condon[9] discusses the dependence of a "fictive" temperature of glass on the thermal history and defines the temperature as that below which the energy relations are "frozen in" and the glass is not in true thermodynamic equilibrium with its surroundings.

In any event, there is an abrupt reversible change in the observed heat content of the metaphosphate glass between 1170 and 1260°K. There is not enough evidence to link this increase in heat content definitely to a fractional heat of crystallization. Furthermore, crystallization is in part a kinetic effect, and it is difficult to understand how the experimental conditions could be reproduced closely enough to place the observed points above 1260°K. on a smooth curve. The thermal behavior of calcium metaphosphate above 1220°K. remains obscure.

The derived equations relating the molal thermal functions to temperature are listed below.

Crystals:

$$H_T - H_{298.16} = 46.4756T + 3.847 \times 10^{-3}T^2 + 13.029 \times 10^5T^{-1} - 18{,}572\ (\pm 0.4\%;\ 298.16 \text{ to } 1250°\text{K.})$$

$$C_p = 46.48 + 7.694 \times 10^{-3}T - 13.029 \times 10^5T^{-2}$$

$$S_T - S_{298.16} = 107.014 \log T + 7.694 \times 10^{-3}T + 6.515 \times 10^5T^{-2} - 274.42$$

Glass (not including heat of fusion):

$$H_T - H_{298.16} = 46.9233T + 3.527 \times 10^{-3}T^2 + 13.257 \times 10^5T^{-1} - 18{,}750\ (\pm 0.4\%;\ 298.16 \text{ to } 1250°\text{K.})$$

$$C_p = 46.92 + 7.054 \times 10^{-3}T - 13.257 \times 10^5T^{-2}$$

$$S_T - S_{298.16} = 108.045 \log T + 7.054 \times 10^{-3}T + 6.628 \times 10^5T^{-2} - 276.91$$

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(8) W. Kauzmann, *Chem. Revs.*, **43**, 219 (1948).

(9) E. U. Condon, *Am. J. Phys.*, **22**, 132 (1954).

Fusion:

$$H_T - H_{298.16} = 0.448T - 0.32 \times 10^{-3}T^2 + 0.228 \times 10^5T^{-1} + 19{,}745$$

$$S_T - S_{298.16} = 1.0309 \log T - 0.64 \times 10^{-3}T + 0.114 \times 10^5T^{-2} + 13.46$$

Glass (including heat of fusion):

$$H_T - H_{298.16} = 46.923T + 3.527 \times 10^{-3}T^2 + 13.257 \times 10^5T^{-1} + 1170$$

$$S_T - S_{298.16} = 108.045 \log T + 7.054 \times 10^{-3}T + 6.628 \times 10^5T^{-2} - 260.96$$

Acknowledgment.—J. R. Lehr made the microscopic examination, J. P. Smith the X-ray examination and Inez J. Murphy the chemical analysis of the calcium metaphosphate.

WILSON DAM, ALABAMA

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

Pressure–Temperature Curves in Some Systems Containing Water and a Salt

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RECEIVED APRIL 13, 1956

A novel method for the determination of vapor pressures of saturated solutions has been applied to binary systems containing water and the salts LiF, NaF, KF, NaCl, KCl, RbCl, CsCl, $PbCl_2$, Li_2SO_4, Na_2SO_4, K_2SO_4, Tl_2SO_4, Na_2CO_3, K_2CO_3, $Na_2O \cdot 4B_2O_3$, $Na_4P_2O_7$, and $K_4P_2O_7$ at some or all of the temperatures 374, 400, 500, 600, and 700°

In this paper are presented a novel method for the determination of vapor pressures for the three-phase equilibrium gas + liquid + solid in binary systems containing water and a soluble salt, and numerous three-phase pressures so determined. In some of the solutions the solubility curve is continuous from ordinary temperatures to the melting point of the salt, and in some the solubility curve intersects the critical curve, giving rise to critical end-points. As can be seen from Fig. 1, with most of the salts studied the vapor pressure curves of the saturated solutions are continuous and pass through a point of maximum pressure. When at any temperature the pressure of steam is less than the three-phase pressure gas + liquid + solid, the salt is in a region in which only gas + solid is stable, and the salt will not be altered. But if the pressure is above the three-phase pressure, the salt will be in a region of gas + liquid, and it will deliquesce. In practice the salt is contained in a cylindrical crucible with a perforated bottom, so that the liquid formed will run out. Thus by varying the steam pressure at each temperature the vapor pressure of the saturated solution, the pressure above which the salt would deliquesce, could be located.

The apparatus is essentially that described by Morey and Hesselgesser.[1] Distilled water is pumped into a pressure line, which includes a pressure reservoir, a pressure gage and a pressure regulating apparatus, a bomb containing the charge and suitable valves. The purpose of the pressure reservoir, which has a volume of 2240 cc., is to increase the volume of the system so that each stroke of the pump does not have so much effect on the pressure. The pressure regulating device which controls the pump is a Baldwin fluid pressure cell, the sensitive elements of which are two Baldwin strain gages used in connection with a special Brown electronic indicating potentiometer. The apparatus was designed primarily for work at higher pressures and it was difficult to maintain pressures closer than ±25 p.s.i. Accordingly, most of the results are ±25 p.s.i., or 2 bars. Pressures were read on a 10-inch Bourdon type pressure gage which had been calibrated against a dead-weight gage. The temperature of the Nichrome-wound furnace was regulated by a Brown electronic indicating contact controller. The regulating thermocouple, either iron–constantan or chromel–alumel, was placed in a hole drilled in the cap of the bomb to the level of the top of the chamber. An auxiliary winding, controlled by a separate Variac, was so adjusted that the bottom of the bomb was a degree warmer than the top. Temperatures were determined by a platinum–platinum 10% rhodium couple placed in a position similar to that of the control couple.

The bomb is connected with the pressure line by a hollow plunger. The stem is long enough so that the cone joint connection is about 3 cm. above the top of the furnace. A suitable system of valves enables the bomb to be connected with the pressure line or to blow off to the air. At the end of the run the valve connecting the bomb to the pressure line is closed.

The bombs or pressure vessels most used in this work were those described by Morey and Hesselgesser.[1] In some of the work the closure was a flat silver washer used with a flat plunger. For most of the work a modified Bridgman closure was used. This closure makes use of the internal pressure to maintain the seal. The head of the plunger fits inside the chamber of the bomb. A follower washer made with a slight taper, held in place by the cap, fits over the stem of the plunger, and the lower 1/4 inch fits inside the chamber of the bomb. A washer 1/8-inch thick fits over the stem of the plunger and is compressed between the head of the plunger and the follower. The washers usually are of silver, but copper and aluminum washers have been used. The initial closure is made by screwing down the nut bearing on the top of the cap; the final closure, by the action of the pressure in the interior of the bomb. The area of the head of the plunger is 0.60 square inch, that of the silver washer, 0.30 square inch, so that the pressure on the washer is twice the internal pressure. This closure has never leaked, even when subjected to wide changes in pressure and temperature. Most of the bombs were made of Inconel X, but in some cases stainless steel was used.

The experimental results are summarized in Table I and shown in Fig. 1. In the figure the pressure–temperature curve of water is shown, extended as a broken curve beyond the critical temperature of water by extrapolation by means of a linear equation of log *p* *vs.* $1/T$, and plotting the points so obtained.

Table Ia includes those salts in which the solubility curve does not intersect the critical curve. Runs were made at 374, 400, 500, 600 and 700°. The curves are of different shapes, resembling each other only in possessing a temperature of maximum pressure. The equation[2] of this P–T curve is

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[1] G. W. Morey and J. M. Hesselgesser, *Am. J. Sci.*, Bowen Vol., 343 (1952).

[2] G. W. Morey, "Commentary on the Scientific Writings of J. Willard Gibbs," Vol. 1, Yale University Press, New Haven, Conn., p. 1936, p. 243.