[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Heat of Fusion and the Heat Capacities of Solid and Liquid White Phosphorus[1]

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The motive for this investigation has been the fact that liquid white phosphorus has an extraordinarily large molecular field strength or "internal pressure" and therefore its solutions in ordinary non-polar solvents show unusually large deviations from ideal behavior.[1a] Phosphorus is particularly interesting from our standpoint because it is so readily supercooled that the heat capacities for liquid and solid can be obtained through the same temperature range. Unfortunately, however, the difference in free energy between the solid and the supercooled liquid, from which the ideal solubility is calculated, has been subject to considerable uncertainty in view of the variation between the values reported by different observers.

The heat capacity of the solid in the region of room temperature has been given as 24.1 calories per mole by Desains,[2] 22.3 by Person,[3] 23.4 by Regnault,[4] 22.02 between 1° and 17° by Ewald.[5] For the liquid we have only 24.1 by Desains[2] and 25.2 by Person.[3] The heat of fusion is given as 670 cal. per mole by Desains,[2] 624 by Person,[3] 592 by Petterson,[6] 608 by Bridgman,[7] calculated from changes in volume on fusion at various pressures, and 615, calculated by Kelley[8] from the vapor pressure curves for the two phases.

One reason for the poor agreement between previous investigations lies in the fact that the heat of fusion is rather small so that the heat capacity of the container is large compared to that of the phosphorus. Temperature measurements must be made to an accuracy greater than is feasible with mercury thermometers. The procedure followed by Person was such as to allow appreciable heat loss while transferring the sample from the furnace to the calorimeter.

Preparation of Sample.—The phosphorus used in these determinations was prepared by the method of Hildebrand and Buehrer.[9] Care was taken to protect the phosphorus sample from the light during the heat capacity measurements.

Apparatus.—We used the method of mixtures. The phosphorus, sealed in a Pyrex tube, was brought to a constant temperature in a solid cylindrical copper block 8.5 cm. in diameter and 30 cm. high. The temperature of this block was determined by a copper–constantan thermocouple that had been carefully calibrated. The copper block was insulated from the heating coil by several layers of asbestos. Manual control of the heating current was sufficient in view of the high capacity of the furnace and consequent slow changes in its temperature. The heater was covered with several more layers of asbestos and, finally, by a cover of monel metal. A cylindrical radiation shield of sheet metal about 10 cm. away gave further insulation. The cylinder was supported on a movable arm so that it could be moved over the calorimeter immediately before dropping the tube, thus minimizing the radiation from the furnace to the calorimeter.

The calorimeter was a silvered, wide-mouthed pint vacuum flask whose inner surface was protected from breakage on dropping the tube of phosphorus by a screen of monel metal. The details of the construction and manipulation are available elsewhere and hence are not repeated here.[10] The temperature measurements were made on a Mueller bridge reading to 0.0001 ohm. The calorimeter temperatures were either 0° or approximately 25°. The lower temperature was necessary because of the difficulty of freezing liquid phosphorus at 25°. The heat given up to the calorimeter at 25° per gram of glass from initial temperatures ranging from 40 up to 104° was given with a maximum deviation of 0.2% by the equation

$$H_t - H_{25} = 0.1853(t - 25°) + 2.019 \times 10^{-4}(t - 25°)^2 - 7.080 \times 10^{-7}(t - 25°)^3 \quad (1)$$

The corresponding heat given to the calorimeter at 0° from initial temperatures between 25 and 36° was reproduced accurately by

(1) Condensed from the thesis for the Ph. D. degree by the junior author.

(1a) Hildebrand, "Solubility," Reinhold Pub. Corp., New York, N. Y., 1936, *cf.* pp. 147, 161.

(2) Desains, *Ann. chim. phys.*, [3] **22**, 432 (1848).

(3) Person, *ibid.*, **21**, 295 (1847).

(4) Regnault, *Pogg. Ann.*, **89**, 496 (1853).

(5) Ewald, *Ann. Physik*, [4] **44**, 1213 (1914).

(6) Petterson, *J. prakt. Chem.*, **24**, 129 (1881).

(7) Bridgman, *Phys. Rev.*, [2] **3**, 153 (1914).

(8) Kelley, *Bull. U. S. Bur. Mines*, **383**, 80 (1935).

(9) J. H. Hildebrand and T. F. Buehrer, THIS JOURNAL, **42**, 2213 (1920).

(10) M. A. Mosesman and Kenneth S. Pitzer, *ibid.*, **63**, 2348 (1941).

$$H_t - H_0 = 0.1742 + 1.987 \times 10^{-4}t^2 \quad (2)$$

The heat capacity of solid phosphorus was determined by six runs in which the initial temperatures ranged from 25 to 43° and the final temperature was 0°. Table I gives the results of these runs, corrected for the heat capacity of the glass in the capsule, together with the values calculated by the equation

$$H_t - H_0 = 21.46t + 1.436 \times 10^{-2}t^2 \quad (3)$$

TABLE I

SOLID PHOSPHORUS

t, °C.	$H_t - H_0$, (cal./mole) Measured	Calculated
25.00	544.8	545.6
31.79	697.0	696.8
35.47	780.2	779.4
39.69	872.8	873.7
42.79	944.7	944.7
44.2		976.8

The values for liquid phosphorus, supercooled to 25°, are given in Table II. The measured values were calculated by the equation

$$H_t - H_{25} = 24.19(t - 25°) - 5.954 \times 10^{-3}(t - 25°)^2 - 7.991 \times 10^{-6}(t - 25°)^3 \quad (4)$$

TABLE II

LIQUID PHOSPHORUS

t, °C.	$H_t - H_{25}$, (cal./mole) Measured	Calculated
48.87	573.7	573.8
50.50	611.6	611.6
73.53	1158	1159
74.32	1176	1177
74.54	1182	1182
97.14	1711	1711

Table III gives the four values of $H_t - H_0$ determined in the ice calorimeter in one column and in the next column the values of $H_t - H_{25}$ calculated from Eq. (4). The average of the differences of the values in the third column from those in the second is 1115.5 cal./mole.

TABLE III

PHOSPHORUS (LIQUID TO SOLID)

t, °C.	$H_t - H_0$ measured, cal./mole	$H_t - H_{25}$ (supercooled), calculated cal./mole	Diff.
57.09	1883	770	1113
59.02	1935	816	1119
59.92	1953	837	1116
60.04	1954	840	1114
		Average	1115.5

The heat of fusion and $(H_{25} - H_0)$ make up the 1115.5 cal. found in this way. Addition of 1115.5 to each of the $(H_t - H_{25})$ values given in Table II gives the results shown in the second column of Table IV compared to results calculated from the equation

$$H_t - H_0 = 506 + 24.48t - 4.761 \times 10^{-3}t^2 - 1.309 \times 10^{-t^3} \quad (5)$$

giving excellent agreement. All heats are given per mole of phosphorus.

TABLE IV

LIQUID TO SOLID PHOSPHORUS

t, °C.	$H_t - H_0$ measured, cal./mole	$H_t - H_0$, calculated, cal./mole	Diff., %
25.00	1115.5	1115	0.04
44.2		1578	.00
50.50	1727	1728	+ .05
57.09	1883	1882	− .05
59.02	1935	1933	− .1
59.92	1953	1954	+ .05
60.04	1954	1953	− .05
73.53	2275	2275	.00
74.32	2293	2294	+ .04
74.54	2298	2300	.09
97.14	2827	2827	.00

The melting point was taken as 44.2°.[8] $H_{44.2} - H_0$ was calculated from Eq. (3) for solid phosphorus and subtracted from $H_{44.2} - H_0$ for liquid to solid phosphorus calculated from Eq. (5) giving the heat of fusion as 601 ± 2 cal./mole.

The equations for the heat capacity of solid phosphorus derived from Eq. (3) are

$$C_p = 21.46 + 2.872 \times 10^{-2}t \text{ (per mole)} \quad (6)$$

or

$$c_p = 0.1731 + 2.316 \times 10^{-4}t \text{ (per gram)} \quad (7)$$

and for liquid phosphorus from equation (5)

$$C_p = 24.47 - 9.521 \times 10^{-3}t - 3.927 \times 10^{-5}t^2 \text{ (per mole)} \quad (8)$$

or

$$c_p = 0.1974 - 7.678 \times 10^{-5}t - 3.167 \times 10^{-7}t^2 \text{ (per gram)} \quad (9)$$

The equations for the solid are valid in the range from 0° to the melting point while the equations for the liquid should hold from 25 to 100°.

Summary

The molal heat capacity of solid white phosphorus, P_4, in the range 0–44.2° is given by

$$C_p = 21.46 + 2.872 \times 10^{-2}t$$

That of liquid phosphorus in the range 25–97° is

$$C_p = 24.47 - 9.521 \times 10^{-3}t - 3.927 \times 10^{-5}t^2$$

The heat of fusion is 601 cal./mole at the melting point, 44.2°.

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