THE FREE ENERGY OF FORMATION OF PHOSPHINE

By David H. Drummond

Received April 25, 1927 Published August 5, 1927

The elements that stand in the group between metals and non-metals have been studied very little from the standpoint of thermodynamics. Before 1923, no systematic study of the free energy of the compounds of silicon, phosphorus, boron, arsenic, antimony, tellurium and selenium had been made. The purpose of this investigation was to determine the free energy of formation of phosphine by the measurement of the thermal dissociation of the gas.

Experimental Part

Some preliminary experiments were made to determine the thermal decomposition of phosphine. It seemed probable that phosphine would decompose at low temperatures, since its homologs, arsine and stibine, do so. Some phosphine was passed through a glass tube which was heated near the center for a few minutes. The phosphine was then washed out with carbon dioxide and the ends of the tube closed off. When the tube was opened in a dark room a bright phosphorescence was apparent beyond the point where the tube had been heated. The gas is decomposed by heat and the phosphorus is condensed before it can recombine with the hydrogen.

If the temperature is kept slightly above the boiling point of phosphorus, equilibrium will result. If the gas is cooled quickly the phosphorus will condense before the recombination will have time to take place. The free energy of phosphine can, therefore, be determined by quickly cooling the gas after it has been heated and then determining the ratio of hydrogen to undecomposed phosphine.

The apparatus for the measurements consisted of a glass tube, enclosed in a muffle, through which dry phosphine was passed. The tube extended into a water-bath. On the end of the tube a potash bulb was placed, containing a saturated solution of copper sulfate. This tube absorbed the phosphine. The hydrogen was mixed with dry air at a T-joint and then passed through hot platinized asbestos. The water formed was

Table I

Degree of Decomposition of Phosphine

ΔPH_3, mg.	ΔH_2O, mg.	T, °C.	$\ln K$	I[a]	P, atm.
20.0	12.15	573	1.061	2.59	0.811
38.6	31.5	583	0.718	2.72	.812
17.6	19.9	593	.438	2.52	.811
28.15	32.45	603	.344	2.31	.812
21.0	25.85	613	.182	2.16	.812
35.15	27.05	578	.765	2.82	.825
6.9	7.45	608	.252	2.58	.855

[a] Mean value of I, 2.52.

absorbed in a calcium chloride tube. The temperature was controlled by hand to ±1°. Table I shows the results of these experiments.

Discussion

Solid white phosphorus at a temperature of 25° is the standard reference state for phosphorus. Since the measurements were made in the gaseous phase the free energy of fusion and vaporization must be known to calculate the standard free energy of formation.

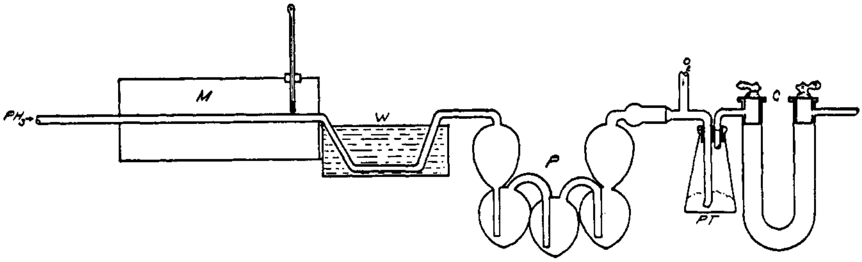

Fig. 1.—Diagram of apparatus. M, muffle; W, water bath; P, copper sulfate bulbs; P. T., platinized asbestos; C, drying tube.

The heat capacity of phosphorus as given by Richards and Jackson is 5.24 from 85°K. to 293°K. The value 5.4 at 298°K. is given by Kopp. Equation (1) fits these data fairly well.

$$Cp(P_1s) = 5.30 + 0.000341T \tag{1}$$

Because of lack of data it is necessary to assume that the law of Dulong and Petit holds for fused phosphorus. This is probably very near the truth since there is an increase in heat capacity after fusion. The heat capacity equation for fused phosphorus is

$$Cp(P_1l) = 6.10 + 0.000341T \tag{2}$$

Using the value 160.0 cal. for the heat of fusion of phosphorus[1] the equation for the free energy of fusion is

$$\Delta F = -70 - 0.8T\,lnT + 4.87T \tag{3}$$

For the standard free energy change in fusion this gives the value 13.1 cal.

Taking 12,600 cal.[2] for the heat of vaporization of phosphorus, and using the heat capacity equation for a quadri-atomic gas[3] the general free-energy equation for vaporization is

$$\Delta F^\circ(4P\,l, P_4\,g) = 58{,}871.7 + 15.4T\,ln\,T + 0.00033T^2 - 0.0000008T^3 - 203.7T \tag{4}$$

Equation (4) gives 6063 cal. for the standard free energy of vaporization of one gram atom of phosphorus. The entropy change in fusion and

---

[1] Landolt and Börnstein, "Tabellen," p. 1468.

[2] *Ibid.*, p. 1475.

[3] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, **1923**, p. 80.

vaporization can be calculated from the free-energy equation. The value 0.506 is obtained for the entropy change in fusion. The entropy change in vaporization is 25.5. Lewis and Randall[4] give for the entropy of phosphorus gas the value 35.95. Subtracting the entropy changes of vaporization and fusion, the value 9.95 entropy units is found for the standard entropy of phosphorus.

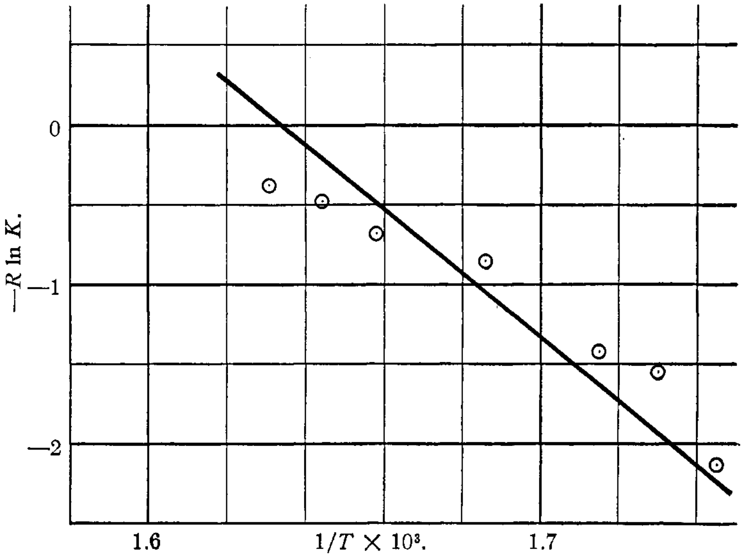

Fig. 2.

Taking —4900 cal.[5] as the standard heat of formation of phosphine, and subtracting the heats of vaporization and fusion, the value —17,660.5 cal. is obtained for the heat change in the reaction:

$$3/2H_2(g.) + {}^1/_4P_4(g.) = PH_3(g.) \qquad (5)$$

Using the heat-capacity equations[3] for the gases involved in the reaction, the general free energy equation is

$$\Delta F^\circ = -16{,}486.5 + 3.72T\,ln\,T + 0.0004T^2 + 0.0000007T^3 + IT \qquad (6)$$

The values of *ln K* given in Table I are calculated from equation (7) upon the assumption that the partial pressures of the gases are proportional to their mole fraction.

$$\Delta F^\circ = -RT\,ln\,\frac{P_{PH_3}}{(P_{H_2})^{3/2}\,(P_{P_4})^{1/4}} = -RT\,ln\,K \qquad (7)$$

The mean value of *I*, as shown in Table I, is 2.52. The free energy of formation of phosphine from hydrogen and solid phosphorus at 298°K., as calculated from equations (3), (4) and (6), is —3296.0 cal.

The entropy change in the reaction as calculated from the free energy

---

[4] Ref. 3, p. 464.

[5] Ref. 1, p. 1491.

equation is —27.72. This value gives for the standard entropy of phosphine the value 52.4 entropy units.

If $-R \ln K$ is plotted against $1/T$, the slope of the curve is ΔH. This was done on a large scale plot between the limits 573°K. and 613°K. The points were somewhat scattered. A line drawn through the means of these points had a slope of —20,200 as compared with the value —19,711 cal., calculated from the equation for the heat of reaction.

In conclusion the author wishes to thank Dr. R. K. McAlpine for his kind help and encouragement in this investigation. Acknowledgment is also due to Mr. L. D. Anderson of the Riverton High School for his kindness in lending some of the apparatus used in these experiments.

Summary

1. The equations have been worked out for the free-energy change of fusion and vaporization of white phosphorus. The standard free energies of these changes have been calculated.

2. The dissociation of phosphine has been measured in the temperature interval 573°K. to 613°K. From this the free energy of formation of phosphine has been calculated.

3. The entropy change of vaporization and fusion and the standard entropy of phosphorus have been calculated. The standard entropy of phosphine has been calculated.

RIVERTON, WYOMING

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF MACDONALD COLLEGE]

DISSOCIATION PRESSURES OF AMMONIUM ORTHOPHOSPHATES[1]

BY T. E. WARREN

RECEIVED APRIL 28, 1927 PUBLISHED AUGUST 5, 1927

Recent developments in the manufacture of ammonia[2] and phosphoric acid[3] have demonstrated the possibility of the commercial use of ammonium phosphate as a fertilizer. As such it contains two of the fundamental plant nutrients in readily available form.[4]

The most economical starting state for ammonia is the gaseous and for phosphoric acid a concentrated solution, the latter because the heat of reaction is sufficient to dry the product. The various reactions of ammonia gas with phosphoric acid have been the subject of the following experiments made by the author.

[1] From a thesis submitted in partial fulfilment of the requirements for the degree of M. Sc. in McGill University.

[2] Brown, *Trans. Am. Electrochem. Soc.*, **48,** 175–182 (1925).

[3] Jacob, *ibid.*, **48,** 125–133 (1925).

[4] Allison, *Soil Science*, **5,** 1–80 (1918).