

From this equation the free energy of formation of hydrogen molecules from atoms can be calculated.

The following table gives the degree of dissociation (p_1) of hydrogen at 1 atm. pressure at various (absolute) temperatures.

TABLE XI.

Degree of Dissociation of Hydrogen at Atmospheric Pressure.

T. °K.	p_1 atm.	T. °K.	p_1 atm.
293° (20° C.)	5.4×10^{-46}	2900°	0.236
		3100	0.441
500	1.7×10^{-25}	3300	0.666
1000	5.8×10^{-11}	3500	0.840
1500	4.49×10^{-8}	3700	0.933
2000	1.30×10^{-3}	3900	0.973
2300	0.0121	4100	0.988
2500	0.0394	4500	0.9962
2700	0.106	5000	0.99981

I wish here to acknowledge the valuable assistance of Mr. E. Q. Adams, Mr. S. P. Sweetser, Mr. H. Huthsteiner, and Mr. G. S. Meikle, who have carried out most of the experimental work involved in this investigation.

RESEARCH LABORATORY,
GENERAL ELECTRIC COMPANY,
April 23, 1912.

THE DISSOCIATION PRESSURES OF PHOSPHONIUM BROMIDE AND IODIDE.

By F. M. G. JOHNSON.

Received April 27, 1912.

The dissociation pressures of phosphonium chloride have been investigated by Tammann,¹ but for the bromide and iodide only the temperatures at which the dissociation pressures are one atmosphere appear to have been determined.² These two substances have therefore been made the subject of this investigation.

The salts were prepared by passing PH_3 into tubes containing the liquefied acid cooled by CO_2 and ether. The PH_3 was obtained by the action of KOH solution on PH_4I . The gas was bubbled through KOH solution and then passed through a U tube surrounded by solid CO_2 . The halogen acids were prepared by the method used by McIntosh and Steele,³ but were not dried by P_2O_5 . Both salts appeared as white powders which in time changed to large colorless crystals.

The method employed for the measurement of the pressures was similar in principle to that used in former work of this nature.⁴ The apparatus,

¹ *Arch. néerl.*, 244 (1901). *Z. Elektrochem.*, 8, 158 (1902).

² Abegg, *Handbuch*, 3, III, 398.

³ *Phil. Trans. Roy. Soc., (A)*, 205, 99. *Z. physik. Chem.*, 55, 129 (1906).

⁴ *Z. physik. Chem.*, 61, 457 (1908); 65, 36 (1908). *THIS JOURNAL*, 31, 1138 (1909); 33, 777 (1911).

which has been somewhat modified, is shown in Fig. 1. The tube containing the phosphonium salt was first cooled by means of CO_2 and ether, and the whole apparatus evacuated with a mercury pump. At the same time the tube containing the Al_2O_3 was heated to remove moisture.

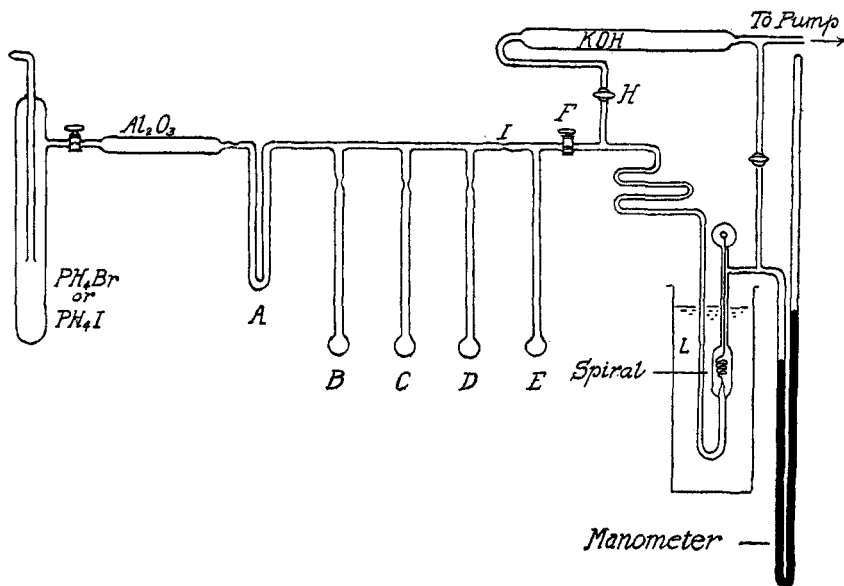


Fig. 1.

(The Al_2O_3 was employed as a drying agent. Its usefulness for this purpose will be discussed later.) Taps H and F were then closed, the U tube A was surrounded by the CO_2 and ether mixture, while the phosphonium salt was allowed to warm up to the temperature of the room. It was thus slowly sublimed through the Al_2O_3 , which removed moisture, into A . The Al_2O_3 tube was sealed off and the salt fractionally sublimed by means of the tubes B , C , D , and finally led into E which was sealed from the rest of the apparatus at I . For measurements at temperatures below that of the room the salt was allowed to remain in E . For higher temperatures it was sublimed into K which was then sealed at L . For low temperatures a bath of ether in a Dewar flask was employed, the temperature being raised or lowered by the addition of suitable quantities of warm or cold ether. At 0° melting snow was used. Temperatures above that of the room were obtained by means of a metal water bath heated with a Bunsen flame, and furnished with a thermo-regulator capable of keeping the temperature constant to within a small fraction of a degree. The glass spiral was sensitive to a pressure change of 1 mm. Hg.

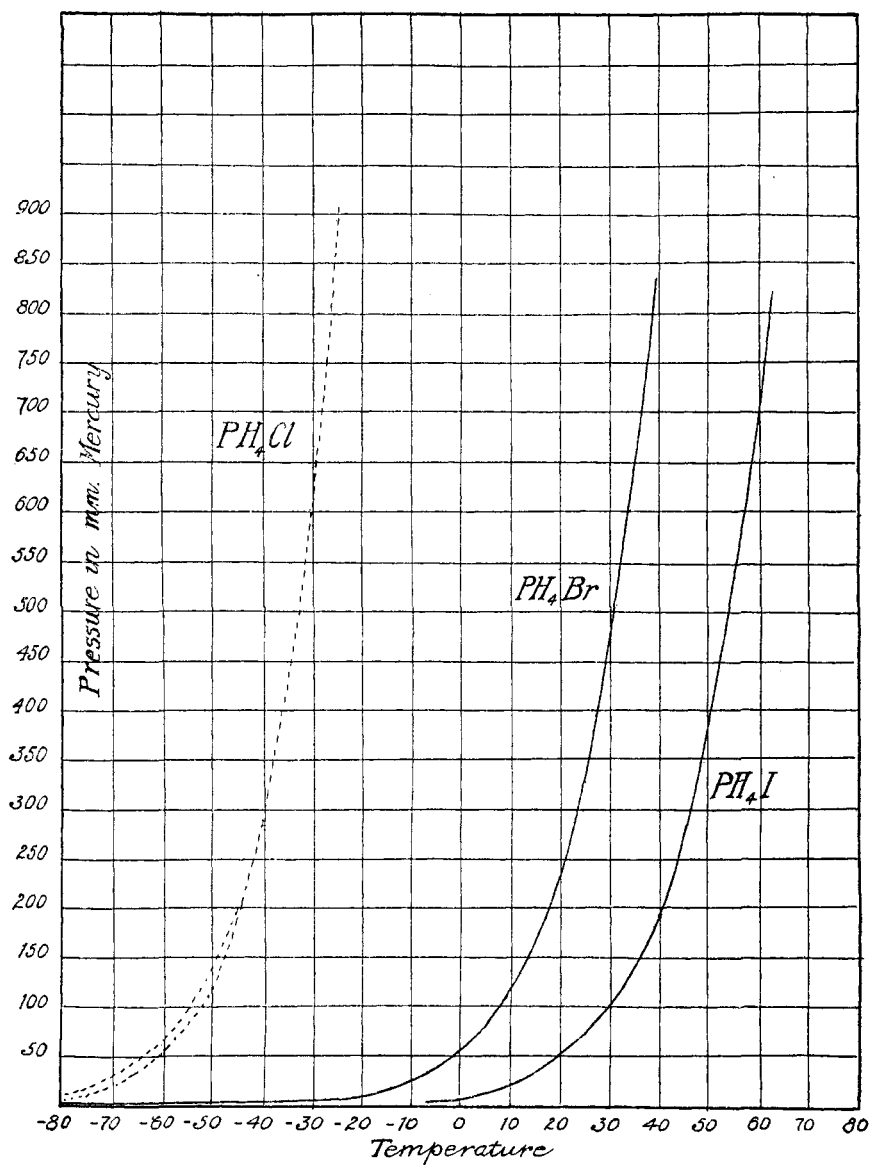


Fig. 2.

The following are the results obtained:

PH ₄ Br.			
Temp.	Press. in mm. Hg.	Temp.	Press. in mm. Hg.
-80°	1	6.4°	91
-50	3	6.8	93
-36	4	7.5	101
-24	8	9.8	118
-14.2	17	11.0	126
- 9.8	25	14.4	159
- 8.0	30	19.0	222
- 4.8	37	20.5	250
0	56	23.0	291
1.4	63	27.6	396
2.0	65	31.6	507
4.6	80	34.3	602
5.2	83	38.8	794
PH ₄ I.			
0°	8	42.2°	231
11.4	24	43.6	286
15.0	32	47.0	309
18.5	47	48.8	348
22.0	57	51.8	417
24.4	74	52.2	426
31.4	117	56.2	535
34.2	141	56.4	536
34.4	144	56.8	557
40.2	206	59.8	651
40.4	207	61.0	708

The curves obtained are shown in Fig. 2. The dotted curve shows the values obtained by Tammann for phosphonium chloride. Below -41° this salt exists in two modifications, crystallin and amorphous, the former being the unstable form with the higher dissociation pressures. A similar occurrence was not observed in the case of either the bromide or iodide.

From the curves, PH₄Br and PH₄I have dissociation pressures of 1 atmosphere at 38° and 62°, respectively.

Although it is probable that all three salts are practically completely dissociated in the state of vapor the only one investigated is PH₄Cl.¹ No comparisons of the heats of dissociation can be made. An investigation leading to the necessary data is being undertaken.

McGILL UNIVERSITY, MONTREAL.

THE MIXED CRYSTALS OF AMMONIUM CHLORIDE WITH NICKEL, COBALT AND COPPER CHLORIDES.

By H. W. FOOTE.

Received April 24, 1912.

The fact that ammonium chloride can crystallize from solutions con-

¹ Briner, *J. chim. phys.*, 4, 476 (1906).