[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Heat of Vaporization of Hydrogen Fluoride

BY J. H. SIMONS AND J. W. BOUKNIGHT

The heat of vaporization of hydrogen fluoride, as calculated from the vapor pressure measurements of Simons,[1] is 6025 calories for one apparent molecular weight of the gas; and this value is approximately constant over a range of temperature. It is difficult to reconcile this fact with the results of surface tension measurements of the present authors[2] and the equilibrium between HF and H_6F_6 with a heat of dissociation of about 40,000 calories per mole of H_6F_6, as determined by Simons and Hildebrand.[3] The surface tension measurements indicate that the liquid is probably composed of molecules of H_6F_6. The heat of vaporization was determined experimentally in this investigation to ascertain whether or not it would be equal to the calculated value or differ from it by an amount equal to the heat of dissociation.

Apparatus

The apparatus is shown in the diagram. It consisted essentially of a pure silver vessel, called a vaporizer, which screwed tightly into a copper plug cemented into the ground cover of a silvered Dewar vessel. To reduce the heat conduction the connection between the copper plug and the copper outlet tube was made with a small piece of thin walled silver tube silver-soldered to both copper pieces. The copper outlet tube was connected by means of silver-plated brass screw connections to three absorption tubes. These tubes were made of copper and contained finely ground sodium fluoride. They could be removed separately and weighed. The space between the silver vaporizer and the walls of the Dewar vessel could be evacuated by means of a vacuum pumping system connected through the cover of the Dewar. The heating element consisted of a piece of copper tubing wound with asbestos-covered wire, which fitted as a plug into a well in the bottom of the vaporizer. A ten-junction copper–constantan thermocouple was shellacked to a glass ring that fitted the outside of the vaporizer. The electrical leads came through cement seals in the cover of the Dewar. The Dewar vessel was located in a hand-operated air thermostat. The outside ends of the thermocouples were located in the box near the copper outlet tube. It was possible to keep the temperature of the thermostat about a degree above that inside the Dewar. This prevented the liquid from condensing in the outlet tube but at the same time reduced the conduction of heat into the Dewar through the metal wires and tube.

Experimental Procedure

The hydrogen fluoride was prepared by the method of Simons.[1] It was condensed directly into the vaporizer, which had been removed from the rest of the apparatus and placed in a freezing mixture. The outlet of the generator was a small copper tube that fitted inside the outlet tube of the silver vaporizer. Special precautions were taken to ensure that no water vapor entered the vaporizer during the condensation.

The vaporizer was screwed into place and the Dewar assembled. The space inside

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(1) Simons, THIS JOURNAL, **46**, 2179 (1924).

(2) *Ibid.*, **54**, 129 (1932).

(3) Simons and Hildebrand, *ibid.*, **46**, 2183 (1924).

the Dewar was evacuated. When temperature equilibrium had been established with the liquid at its boiling point and the air thermostat at about a degree higher in temperature, the liquid was allowed to vaporize into the absorption tubes. By weighing the absorption tubes before and after a known length of time the amount of vaporization due to heat leak into the Dewar was determined. The actual determination was made by finding the gain in weight of the absorption tubes for a known amount of energy supplied to the heating element in a given time. This was then corrected for the vaporization due to heat leak. This correction factor was determined for every run.

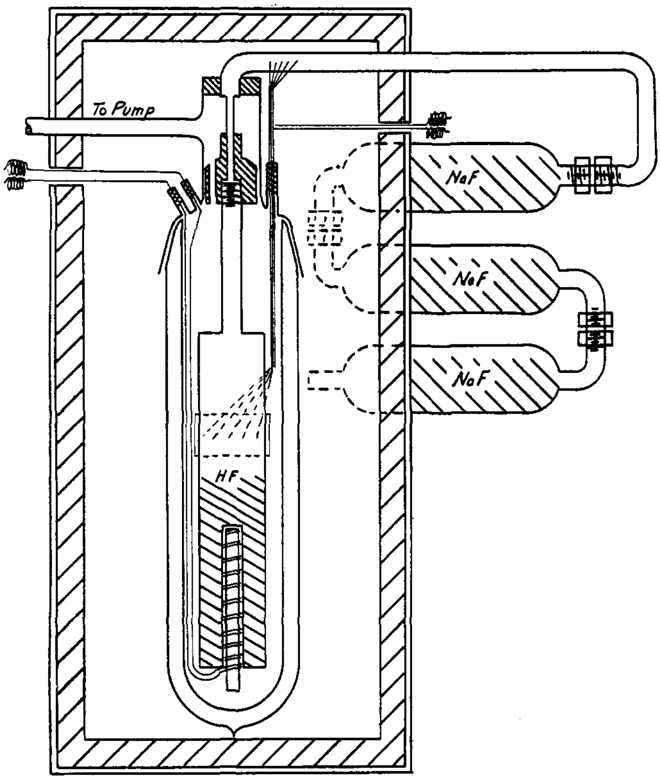

Fig. 1.

Results and Discussion

The results are shown in the table. The calculated value of the heat of vaporization per gram was obtained by dividing Simons' value of the molar heat of vaporization by the apparent molecular weight determined in the vapor density determinations of Simons and Hildebrand.

The fact that the experimental values agree closely with the calculated value indicates that the actual heat of vaporization does not involve the heat of dissociation of the polymer. The agreement does, however, confirm the molecular weight determinations of Simons and Hildebrand.

HEAT OF VAPORIZATION OF HYDROGEN FLUORIDE

Duration of run, min.	Energy input volts	amp.	Weight HF vaporized, g.	Correction,[a] g. HF	Heat of vaporization, cal.
76	2.08	0.145	3.4850	0.4630	109
62	2.09	.145	4.4331	1.2200	84
37	2.53	.175	2.4444	0.3901	114
41	2.62	.185	4.2252	.6540	80
20	2.46	.175	1.7732	.3188	85
17	2.83	.200	1.4280	.2713	119
The above runs represent preliminary work					
Barometric pressure 750 mm.				Average	98
30	2.88	0.200	2.4759	0.0762	103
30	2.52	.175	2.1602	.1875	96
30	2.15	.150	1.5765	.1754	99
30	1.806	.125	1.2395	.1952	93
30	1.57	.110	0.9883	.1952	94
29.25	2.14	.150	1.4279	.0815	100
Barometric pressure 748 mm.				Average	97.5

Calculated heat of vaporization per gram = 6025/63.36 = 95.

[a] This correction factor is obtained experimentally. It is the amount of hydrogen fluoride vaporized by the heat leak for the same time as the duration of the run.

Summary

The heat of vaporization of hydrogen fluoride has been determined experimentally and found to agree with the value calculated from the vapor pressure and vapor density measurements.

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Notes

A Method for the Preparation of Telluric Acid

BY L. I. GILBERTSON

Gutbier, and Gutbier and Wagenknecht,[1] prepared tellurates by the oxidation of tellurium or tellurous oxide with 15% hydrogen peroxide in solution of strong alkalies. Schluck[2] oxidized tellurium with 60% hydrogen peroxide to form telluric acid.

The oxidation of tellurium and tellurous oxide is accomplished readily in sulfuric acid solution by 30% hydrogen peroxide. Best oxidation is obtained when a mixture of two volumes of 30% hydrogen peroxide with one volume of concentrated sulfuric acid (the mixture being prepared at 0°) is refluxed with the sample. The active oxidizing agent is permonosulfuric acid.[3]

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(1) Gutbier, *Z. anorg. Chem.*, **42**, 174 (1904); Gutbier and Wagenknecht, *ibid.*, **40**, 260 (1904).

(2) Schluck, *Monatsh.*, **37**, 489 (1916).

(3) *Northwest Science*, **6**, No. 3, 108–109 (1932).