

which is sensitive to one part of mercury in 2 million parts of solution, and which by isothermal concentration at room temperature detects 1 part of mercuric ion per billion.

CLEVELAND, OHIO

[CONTRIBUTION FROM THE BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

THE VAPOR PRESSURES OF SOLID AND LIQUID CYANOGEN¹

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Previous Investigations

The vapor-pressure measurements of liquid cyanogen by Faraday² and by Chappuis and Riviére³ cannot be considered very exact, as the purity of their material is uncertain, and precise thermometry had not been developed. A more extensive investigation has been made by J. W. Terwen⁴ who measured vapor pressures of solid cyanogen to the triple point and liquid cyanogen to the critical temperature. Care was taken to obtain a very high purity of cyanogen and a sensitive platinum-resistance thermometer was used, but the low-temperature bath had a drift upward of 1° in five minutes at -70°. The drift was less at higher temperatures. Since the thermal conductivity of the solid is low there is some uncertainty as to the lag in temperature between the outer parts of the vapor-pressure bulb and the resistance thermometer at the center.

Preparation of Cyanogen

About 300 g. of c. p. mercuric cyanide was heated to 400° in a Pyrex flask which had previously been evacuated. The cyanogen evolved was passed through a tube containing phosphorus pentoxide and condensed in a bulb immersed in liquid air. With the bulb in liquid air, a small pressure on the manometer indicated some non-condensable gas, probably nitrogen, which was removed by a mercury-diffusion pump. The cyanogen was melted and frozen and the permanent gas pumped off until there was no residual pressure in liquid air. A preliminary set of measurements was made on the solid in the course of which it was observed that when the material was melted and then cooled to -89° there was a residual pressure of several centimeters above the vapor pressure of cyanogen. This residual gas was condensable in liquid air, which indicated that it was carbon dioxide. The most probable source of carbon dioxide is carbonate in the mercuric cyanide. Terwen⁴ reported difficulty in removing nitrogen. It seems more plausible that carbon dioxide was one of the impurities in his gas. To remove this residual gas we fractionated the solid cyanogen at -88° to -92° until the pressure did not exceed 2 mm., that is, the vapor pressure of cyanogen, upon complete transfer of the

¹ Published by permission of the Director of the Bureau of Mines, U. S. Department of the Interior.

² Faraday, *Phil. Mag.*, [1] **135**, 155 (1845).

³ Chappuis and Riviére, *Compt. rend.*, **104**, 1504 (1887).

⁴ Terwen, *Z. physik. Chem.*, **91**, 469 (1916).

solid (3 cc.) from one bulb to another where the volume above the solid was not over 10 cc. The impurity was thus completely removed unless solid solutions were formed, which is very improbable. The purity of the final product is attested by the fact that for the highest vapor pressures measured, the observed vapor pressure before and after distilling more than two-thirds of the liquid from the vapor-pressure bulb differed by less than 1 mm., which is less than one part in 1400.

Apparatus

The temperature measurements were obtained with a spade-type, platinum-resistance thermometer which had been carefully calibrated at the ice and steam points and at the boiling points of naphthalene and oxygen. The Henning⁵ equation, evaluated from these points, using Henning's values for the fixed points, checked the observed points for carbon dioxide to less than 0.01°. The writers wish to thank Dr. A. G. Loomis and Mr. J. E. Walters for their supervision and aid in the construction and calibration of the thermometer.

The Leeds and Northrup-Mueller type of bridge used had been calibrated by the Bureau of Standards.

The low-temperature cryostat was a modification of that used by Henning⁶ further developed by Loomis and Walters of the Cryogenic Laboratory of the Bureau of Mines. A detailed description of this cryostat⁷ was given at the meeting of the American Chemical Society at Washington, D. C., April, 1924, and is to be published soon. A 3-liter glass Dewar vessel was substituted for the metal liquid-air reservoir.⁸ In these experiments the cryostat was maintained by hand regulation to within $\pm 0.005^\circ$.

A Gaertner cathetometer with cast-iron track was used in reading the heights of the mercury in the manometer arms. This instrument was calibrated against a Geneva Society standard meter bar of Invar and showed at 20° an error of 0.1 mm., evenly distributed over a total scale range of 700 mm.

TABLE I
THE VAPOR PRESSURES OF SOLID AND LIQUID CYANOGEN^a

T° Abs. ^b	A. Solid		T° Abs.	B. Liquid	
	P Obs.	P Calcd.		P Obs.	P Calcd.
179.94	1.7	1.72	245.93	572.6	572.5
190.7	5.65	5.84	247.91	629.8	629.8
191.25	6.48	6.19	251.77	754.0	753.9
199.05	12.79	13.78	255.35	886.4	886.4
203.86	22.29	21.88	258.26	1007.4	1006.5
212.41	47.53	47.28	260.03	1086.4	1085.8
224.08	123.2	123.2	261.82	1171.5	1170.2
230.27	196.7	196.8	263.40	1250.7	1249.2
237.82	336.4	336.9	265.97	1387.4	1386.6
239.92	390.9	388.9	265.98	1388.4	1387.5
240.79	412.9	412.5	273.10	1828.8

^a Pressures are given in millimeters of mercury reduced to 0° C. at sea level and 45° latitude.

^b 0° C. = 273.1° Abs.

⁵ Henning, *Z. Physik*, **23**, 95 (1924).

⁶ Henning, *Z. Instrumentenkunde*, **33**, 33 (1913).

⁷ Loomis and Walters, *THIS JOURNAL*, **47**, 2302 (1925).

⁸ This modification was first used by Mr. Frank Porter of the Cryogenic Laboratory of the Bureau of Mines.

Vapor pressures of the solid phase of cyanogen are given in Table I-A, and are shown graphically by the lower curve of Fig. 1. Col. 3 of Table I-A gives vapor pressures for temperatures at which observations were made, calculated by the following equation.

$$\log P^{\text{mm.}} = -(1695.122/T) + 9.65530 \quad (1)$$

The latent heat of sublimation calculated by the approximate Clapeyron equation, $L(\text{cal. per mole}) = (2.303 R/M)(T_1 T_2)/(T_2 - T_1) \log(P_2/P_1)$, is 7750 cal. per mole.

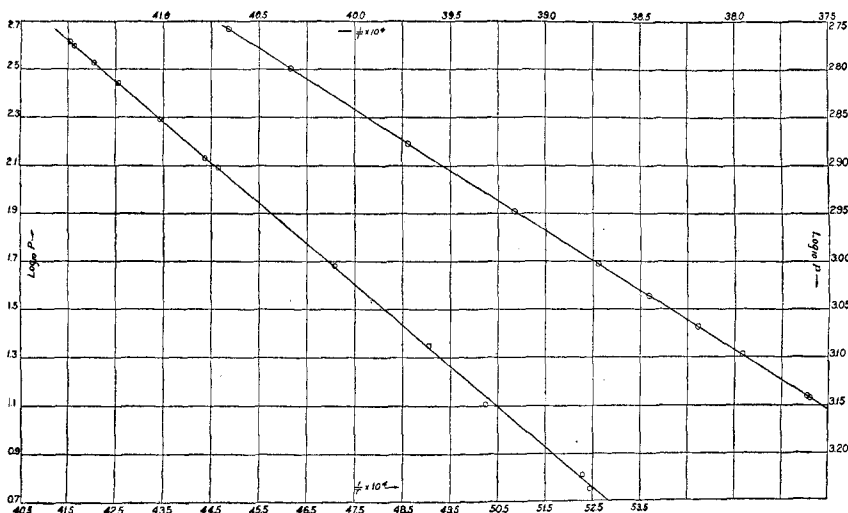


Fig. 1.

In the case of the liquid phase of cyanogen, the vapor pressures were measured up to about 700 mm., as were those of the solid phase; that is, with the long arm of the manometer under constant evacuation with a mercury-diffusion pump. Above this pressure, the long arm of the manometer was opened to atmospheric pressure and the true vapor pressure was obtained by reading the barometer and manometer simultaneously. In this way, vapor pressures of the liquid phase were extended to about 1400 mm.

The data on the liquid phase of cyanogen are given in Table I-B, and are shown graphically by the upper curve of Fig. 1. Col. 3 of Table I-B gives the vapor pressures of liquid cyanogen calculated by the following equation.

$$\log P^{\text{mm.}} = -(1818.554/T) - 5.0813 \log T + 22.30083 \quad (2)$$

From this equation, the normal boiling point is found to be 251.94° Abs. or -21.17° C.

The latent heat of vaporization has been calculated by means of the approximate Clapeyron equation given above. The values so calculated are given in Table II.

TABLE II
LATENT HEATS OF VAPORIZATION

L , cal. per mole	5823	5772	5722	5671	5621	5564 (extrapolated)
T° Abs.	247.5	252.5	257.5	262.5	267.5	273.1

The latent heat of vaporization, expressed as a function of the temperature, is given by the equation

$$L \text{ (cal. per g. mole)} = 8331 - 10.133 T \quad (3)$$

At the normal boiling point (251.94° Abs.), the latent heat of vaporization is equal to 5778 cal. per gram-mole.

Solving the vapor-pressure equations for the solid and for the liquid simultaneously, the triple point is found to be 245.20° Abs. or -27.90° C., at a vapor pressure of 552.2 mm.

The heat of vaporization of liquid cyanogen at the melting point (245.20° Abs.) is equal to 5846 cal. per gram-mole from the above equation. Subtracting this value from the latent heat of sublimation, 7750 cal. per gram-mole, gives 1904 cal. per gram-mole for the latent heat of fusion of cyanogen at the triple point.

Discussion of Results

Terwen's vapor pressures for solid and liquid cyanogen in the range which we covered are slightly higher throughout and showed a discontinuity in the region 245.6° to 246.8° which must be accounted for by experimental error in Terwen's measurement.

Chappuis⁹ obtained three determinations of the heat of vaporization at 0° C. calorimetrically, namely, 5376.8, 5382 and 5409.6 cal. per gram mole. Equation 3 gives 5564 cal. per gram-mole at 0° C.

Summary

1. Vapor pressures of cyanogen were measured from -93° to the triple point for the solid, and from the triple point to -7° C. for the liquid.
2. Equations derived for the solid and the liquid are, respectively $P^{\text{mm.}} = (-1695.122/T) + 9.65530$, and $\log P^{\text{mm.}} = (-1818.554/T) - 5.0813 \log T + 22.30083$.
3. The triple point of cyanogen has been calculated to be 245.20° Abs. or -27.90° C. at a vapor pressure of 552.2 mm. The normal boiling point of the liquid has been determined to be 251.94° Abs. or -21.17° C.
4. The heats of sublimation, vaporization and fusion have been calculated.

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⁹ Chappuis, *Ann. chim. phys.*, [6] 15, 517 (1888).