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## THE VAPOR PRESSURES OF SOLID AND LIQUID HYDROGEN CYANIDE<sup>1</sup>

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There is but one investigation on the vapor pressure of pure liquid hydrogen cyanide recorded in the literature,<sup>2</sup> with the exception of a few isolated attempts at determining the boiling point. A painstaking search failed to reveal any references on the vapor pressures of solid hydrogen cyanide. It was to supply this deficiency of data that the following investigation was begun.

### Experimental Part

**Preparation of Hydrogen Cyanide.**—The hydrogen cyanide was prepared by dropping dil. (1 : 1) sulfuric acid upon pulverized potassium cyanide. The hydrogen cyanide evolved was passed through two tubes of phosphorus pentoxide and then condensed in a glass bulb immersed in liquid air. The hydrogen cyanide was melted and frozen and any permanent gas pumped off until there was no residual pressure in liquid air. The material was then fractionated several times until, before and after a fractionation, it showed no change in vapor pressure at the ice point. Since the pressure at the ice point is over 260 mm., this was very good evidence as to the purity of the hydrogen cyanide.

**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 the boiling points of naphthane and oxygen. The Henning equation,<sup>3</sup> evaluated from these points,

<sup>1</sup> Published by permission of the Director, Bureau of Mines.

<sup>2</sup> Hara and Shinozaki, *J. Chem. Ind.* (Japan), **26**, 884 (1923); *C. A.*, **18**, 2624 (1924).

<sup>3</sup> Henning, *Z. Physik*, **23**, 95 (1924).

checked the observed carbon dioxide point to less than  $0.01^\circ$ . This thermometer was the same as that used in the investigation of the vapor pressures of cyanogen.<sup>4</sup>

The cryostat employed was that used in the previously mentioned paper on cyanogen.

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

The Gaertner cathetometer with cast iron track was also that reported in the previously mentioned work on cyanogen.

Pressures are given in millimeters of mercury reduced to  $0^\circ\text{C}$ . at sea level and  $45^\circ$  latitude.

TABLE I  
THE VAPOR PRESSURES OF SOLID AND LIQUID HYDROGEN CYANIDE

Temp., °K.	Pressure, mm. (corr.)			Temp., °K.	Pressure, mm. (corr.)		
	Obs.	Calcd.	$P_{\text{obs.}} - P_{\text{calcd.}}$		Obs.	Calcd.	$P_{\text{obs.}} - P_{\text{calcd.}}$
SOLID				LIQUID, CONT.			
243.70	50.24	48.66	+1.58	279.93	359.11	357.84	+1.27
253.40	95.49	95.49	0.00	285.30	448.93	448.20	0.73
257.95	128.78	128.75	.03	289.77	538.35	537.14	1.21
LIQUID				294.53	647.87	647.17	0.70
265.08	183.08	183.26	-0.18	297.67	729.04	729.65	-0.61
273.10	264.39	265.42	-1.03	298.67	757.27	757.78	-.51
276.11	303.71	303.42	+ .29	300.42	807.23	808.71	-1.48
				300.42	807.88	808.90	-1.02

The vapor pressures of the solid phase are given in Table I. Col. 3 of the table gives vapor pressures for the temperatures at which observations were made, calculated by the following equation.

$$\log_{10} P_{(\text{mm.})} = 9.33902 - (1864.8/T) \quad (1)$$

The latent heat of sublimation, calculated by the approximate Clapeyron equation:

$$L \text{ (Cals./g.)} = [2303 R/M] [T_1 T_2 / (T_2 - T_1)] [\log_{10} (P_2/P_1)]$$

is 316.13 calories per gram, where  $M$  is the molecular weight,  $P_2$  and  $P_1$  are the vapor pressures corresponding to the absolute temperatures  $T_2$  and  $T_1$ , respectively.

The vapor pressures of the liquid phase of hydrogen cyanide were measured up to about 700 mm., in the same manner as were those of the solid phase, that is, with the long arm of the manometer under constant evacuation with a mercury-vapor pump. Above this pressure the long arm of the manometer was opened to atmospheric pressure and the true vapor pressures were obtained by reading the barometer and manometer simultaneously. In this way vapor pressures of the liquid were extended to over 800 mm.

The data on the liquid phase of hydrogen cyanide are given in Table I. Col. 3 of this table gives the vapor pressures of the liquid hydrogen

<sup>4</sup> Perry and Bardwell, THIS JOURNAL, 47, 2629 (1925).

cyanide calculated by the following equation which was obtained by the method of least squares.

$$\text{Log}_{10} P_{(\text{mm.})} = 7.744603 - (1453.063/T) \quad (2)$$

From this equation, the normal boiling point is 298.75°K. or 25.65°C.

The latent heat of vaporization has been calculated by means of the approximate Clapeyron equation given above to be 246.84 calories per gram at the normal boiling point.

Solving the vapor-pressure equations for the solid and for the liquid simultaneously the triple point is found to be 258.24°K. or -14.86°C. at a vapor pressure of 131.16 mm.

By subtracting the latent heat of vaporization of liquid cyanide at the triple point 258.24°K., equal to 246.84 calories per gram, from the latent heat of sublimation, 316.13 calories per gram, the value 69.29 calories per gram is obtained for the latent heat of fusion of hydrogen cyanide at the triple point.

### Discussion of Results

The following results of Hara and Shinozaki were obtained from the abstract of their article. At 288.98° and 309.78°K. they found vapor pressures of 519.4 and 1128.4 mm., respectively, as compared with our values of 520.42 and 1132.3 mm., calculated by Equation 2 above.

It is seen that the values of Hara and Shinozaki are both slightly lower than those of the present paper. Further comment cannot be made since their original article is not available.

The following values for the heats of vaporization of hydrogen cyanide obtained by Hara and Shinozaki by means of the approximate Clapeyron equation, 246.4 cal. at 273.1°K., 245.5 cal. at 293.1°K., and 244.5 cal. at 318.1°K., may be compared with the one value of 246.84 cal./g. at the normal boiling point 298.75°K.

The boiling point was determined by Hara and Shinozaki to be 298.8°K. which is very close to that obtained in the present investigation, 298.75°K.

Hara and Shinozaki did not study the vapor pressures of the solid phase of hydrogen cyanide, so that no comparison of data may be made.

Other values of the boiling point obtained by previous investigators are 26.5°<sup>(5)</sup>, 25°<sup>(6)</sup> and 26.1°C.<sup>(7)</sup>

The melting points are variously given as -15°<sup>(5)</sup> and -12°C.<sup>(6)</sup> etc., which may be compared with the value from the present work of -14.86°C.

### Summary

1. Vapor pressures of hydrogen cyanide were measured from -30.4° to the triple point for the solid and from the triple point to +27.32° for the liquid. The equations derived from the experimental data are, for

<sup>5</sup> Gay-Lussac, *Ann. chim.*, **95**, 156 (1815).

<sup>6</sup> Nef, *Ann.*, **287**, 295 (1895).

<sup>7</sup> Gautier, *Ann. chim.*, [4] **17**, 115 (1869).

the solid and liquid, respectively,  $\log_{10} P_{(\text{mm.})} = 9.33902 - (1864.8/T)$ ;  $\log_{10} P_{(\text{mm.})} = 7.744603 - (1453.063/T)$ .

2. The triple point of hydrogen cyanide has been calculated to be 658.24°K. or -14.86°C. at a vapor pressure of 131.16 mm. The normal boiling point is 298.75°K. or +25.65°C.

3. The latent heats of sublimation, fusion and evaporation are 316.13, 69.29 and 246.84 calories per gram, respectively.

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## THE INFLUENCE OF CITRATES ON THE PRECIPITATION OF BARIUM SULFATE

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In 1858 Spiller<sup>1</sup> reported that in the course of an investigation he attempted to precipitate barium phosphate from a solution containing alum, citric acid, sodium phosphate and ammonia but obtained no precipitate, which led him to investigate the cause of the sulfuric acid and barium salt existing together in the same solution. He concluded that this peculiar condition was due to the formation of a soluble double salt by the citrate. This solution could only be prepared by adding the barium salt to a mixture of the sulfate and citrate and after preparation the barium sulfate could be precipitated in a "peculiar flocculent condition" by barium nitrate in excess, hydrochloric, acetic, tartaric, or oxalic acid or by heating.

A similar case was noted by Scheerer<sup>2</sup> who found that when sodium metaphosphate was treated with hydrochloric acid, barium chloride added and the mixture shaken until the barium metaphosphate dissolved, no precipitate of barium sulfate was formed on the addition of dil. sulfuric acid. Cases<sup>3</sup> have also been found of the simultaneous presence of barium and sulfates in dilute solution, in certain mineral waters.

The influence of citrates on the solubility and precipitation of certain other salts has also been studied<sup>4</sup> by Lea, Warrington, Teodossiu and Mains, as well as the influence of different substances on the solubility and precipitation of barium sulfate<sup>5</sup> by Gil-

<sup>1</sup> Spiller, *J. Chem. Soc.*, [I] 10, 110 (1858).

<sup>2</sup> Scheerer, *Chem. Gaz.*, 17, 57 (1859).

<sup>3</sup> Anon., *J. Chem. Soc.*, [I] 25, 923 (1872). Carles, *J. Pharm.*, [6] 13, 562 (1901).

<sup>4</sup> Lea, *J. Chem. Soc.*, [I] 27, 964 (1874). Warrington, *ibid.*, 28, 993 (1875). Teodossiu, *Bull. soc. chim. România*, 3, 9 (1921); Mains, *J. Assoc. Official Agr. Chem.*, 4, 235 (1920).

<sup>5</sup> Gilkowsky, *J. Chem. Soc.*, [I] 25, 1113 (1872). Lucion and Tauber, *Chem.-Ztg.*, 12, 427, 477 (1888). Fraps, *Am. Chem. J.*, 27, 288 (1902). Kernot, *Rend. accad. sci. Napoli*, (iii) 15, 155 (1909). Johnson and Adams, *THIS JOURNAL*, 33, 829 (1911). Karaoglanow, *Z. anal. Chem.*, 56, 225 (1917). Weiser, *J. Phys. Chem.*, 21, 314 (1917); 23, 205 (1919).