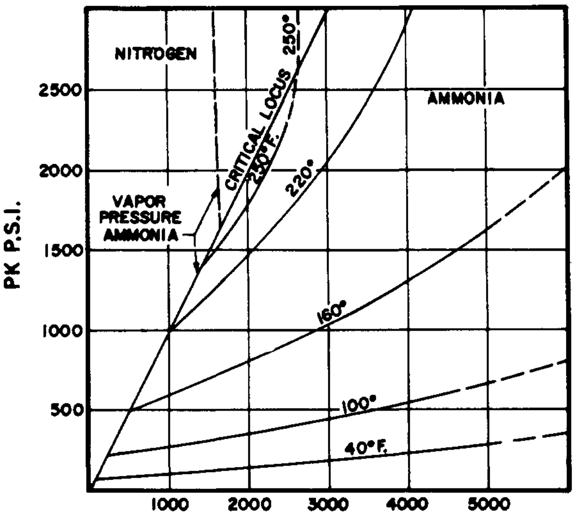

Figure 3. Equilibrium ratios for ammonia in the nitrogen-ammonia system

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Vapor Pressure and Boiling Point of Titanium Tetrachloride

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The published information on the volatility of titanium tetrachloride has consisted mainly of only three vapor pressure studies, one by Arii (*1*), one by Schäfer and Zeppernick (*14*), and one embodied in an equation by Dreisbach (*5*), based upon data obtained over the pressure range of about 100 to 760 mm. of mercury on material of high and tested purity. With widely varying degrees of precision, there are a number of measurements of the boiling point at ordinary pressures. Not all of this information is in satisfactory agreement. As a consequence, the vapor pressure has been redetermined over the temperature range from 90° to 142° C.

EXPERIMENTAL

Material. The original titanium tetrachloride was water-white and obtained from the Fisher Scientific Co., Pittsburgh, Pa., as the "purified" grade. It was further purified by fractionation in an isothermal, 1-cm. diameter, 120-cm. long column packed with 1/8-inch glass helices. A center cut was taken that came over at a constant temperature, within less than 0.1° C. Considerable care was taken to see that the titanium tetrachloride was stored and handled only in closed systems and only in glassware that had been carefully dried. However, in the transfer of the purified titanium tetrachloride from the distillation column to the vapor pressure measuring equipment, there was an instant of slight exposure to ordinary air as the 1-liter collection flask was shifted from one apparatus to another. After the transfer, to counteract any trace of water contamination, a front-end fraction was distilled off and discarded, after which a fraction was distilled into the vapor pressure measuring equipment.

Equipment and Procedure. The vapor pressures were measured in a modified Gillespie (*7*) still. The changes consisted of substituting Teflon plug-valves for the glass stopcocks, permitting the elimination of all stopcock grease; constructing the entire assembly as one closed, dry system; and using separate liquid- and vapor-sample traps similar to those of Thornton (*15*).

The pressure was regulated by a vacuum pump, a controlled leak of dry air into a surge reservoir, and a Cartesian manostat (*8*). The pressure was read to 0.3 mm. on a mercury manometer by means of a cathetometer. The readings were corrected to standard conditions, which include 0° C. The equilibrium temperature was measured in the Gillespie-type still with a 5-junction iron-constantan thermopile. It was calibrated to 0.01° C. by measuring the vapor pressure of water in the same still, with additional calibration points for the melting points of pure benzoic acid at 122.36° C. and of camphor at 172.98° C.

RESULTS AND DISCUSSION

The experimental results on the vapor pressure of titanium tetrachloride, in millimeters of mercury at 0° C., are presented in Table I, along with the predictions by Equation 1. The average deviation is 2.32 mm. of mercury.

A comparison was made between these results, those of Arii (*1*) and of Schäfer and Zeppernick (*14*), and the equation of Dreisbach (*5*). The vapor pressures of Arii were in all cases

Table I. Vapor Pressure of Titanium Tetrachloride

Temp., ° C.	Pressure, Mm. Hg (0° C.) Obsd.	Pressure, Mm. Hg (0° C.) Calcd. (Eq. 1)	Temp., ° C.	Pressure, Mm. Hg (0° C.) Obsd.	Pressure, Mm. Hg (0° C.) Calcd. (Eq. 1)
90.54	189.1	191.2	129.44	634.7	631.8
97.09	236.1	238.9	129.82	643.6	638.4
103.89	288.6	298.0	133.45	701.7	703.7
116.29	434.8	435.6	133.97	713.5	713.5
116.55	439.8	438.9	134.10	716.0	716.0
119.79	482.6	482.3	136.25	756.6	757.6
122.73	525.4	524.5	139.07	814.5	815.0
123.94	535.4	542.7	141.61	870.1	869.6
125.63	571.9	569.0			

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Table II. Selected Values of the Boiling Point of Titanium Tetrachloride

Investigators	B.P., °C.	Pressure, Mm. Hg	B.P., °C. at 760 Mm. Hg
Arii (*1*)	Equation		135.8
Biltz and Meinecke (*2*)	136.5	761	136.4
Bond and Beach (*3*)	136.0	750	136.5
Bond and Stephens (*4*)	136.1	752	136.5
Dreisbach (*5*)	Equation		136.51
Emich (*6*)	134.8	735	136.1
Hildebrand and Carter (*10*)	135.6–.8	758	135.8
Nasu (*11*)	135.7	760	135.7
Pierre (*12*)	136.0	762.3	135.9
Sagawa (*13*)	135.77	749.6	136.30
Sagawa (*13*)	135.03	745.1	135.79
Schäfer and Zeppernick (*14*)	135.5	739.6	136.5
Schäfer and Zeppernick (*14*)	Equation 2[a]		135.9
Thorpe (*17*)	136.35	753.3	136.69
Thorpe (*16*)	136.03	752.6	136.41
Average, including all values			136.2
Average of values above 136.0° C.			136.4

[a] Schäfer and Zeppernick (*14*) obtained two equations, a simple one predicting 132.7° and a more elaborate one predicting 136.5° C.

higher than the rest, particularly at low pressures. He employed a static system, so it appears that a residual gas pressure was present. The present results and those of Schäfer and Zeppernick do not overlap, but together form, from 40° to 142° C., a set of vapor pressure data that is in close agreement with the equation of Dreisbach. The entire set of both groups was fitted by Grandage (*9*) on an electronic computer to an Antoine equation by the method of Willingham (*18*). The result is Equation 1.

$$\log_{10} P_{\text{mm Hg}} = 6.79094 - \frac{1348.56}{t^\circ\text{C.} + 208.52} \qquad (1)$$

The normal boiling point calculated by Equation 1 is 136.37° C., perhaps more appropriately given as 136.4 ±0.1° C. Equation 1 agrees well with that of Dreisbach, within less than 1% on the average for calculated pressures. The data of Schäfer and Zeppernick (*14*), treated by themselves for comparative purposes, led to Equation 2, an Antoine equation obtained by Grandage (*9*).

$$\log_{10} P_{\text{mm Hg}} = 6.82271 - \frac{1360.26}{t^\circ\text{C.} + 209.15} \qquad (2)$$

The various reported values for the boiling point of titanium tetrachloride are pertinent information. In Table II are listed all values reported to 0.1° C. or better, for which the accompanying pressure was also given. Using Equation 1, the reported values were corrected to 760 mm. of mercury. The average of all these corrected boiling points is 136.2° C. If the probability that the true value is above 136.0° C. is accepted, and hence all values below that are omitted, the average is 136.4° C. The net result is consistent with Equation 1.

The latent heats of vaporization were calculated from the basic form of the Clausius-Clapeyron equation. For this calculation, the *dp/dt* values in millimeters of mercury per °C. were calculated from the derived Antoine equation, and the necessary vapor compressibility factors were calculated with the procedure and vapor densities provided by Dreisbach (*5*). The slight corrections for liquid volumes were included, using the data of Sagawa (*13*). The results in gram-calories per gram-mole are 10,160 at 20°C., 10,060 at 25° C., 9950 at 30° C., 9620 at 50° C., 8820 at 100° C., and 8280 at 136.4° C. These values are consistent with those of Dreisbach (*5*) within about 1%.

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CORRECTION

In "Isobaric Vapor-Liquid Equilibria for the Ternary System Acetone-Benzene-Chlorobenzene" [K. W. Free and H. P. Hutchison, J. CHEM. ENG. DATA **4,** 193 (1959)] a method was given for testing the thermodynamic consistency of ternary vapor liquid equilibrium data. It was also suggested that, in the absence of heat of mixing data, the expression

$$\sum \frac{\partial x_i}{\partial x_1} \log \gamma_i + \sum x_i \frac{\partial \log \gamma_i}{\partial x_i}$$

could be integrated graphically from one pure component to another by using the experimental results. The magnitude of the result was to be a measure of the thermodynamic inconsistency. This suggestion is incorrect because the result should be zero regardless of the relationship between the γ's and x's provided $\log \gamma_i = 0$ where $x_i = 1$.

Therefore, the method given can be used only along isothermals, unless heat of mixing data are available. However, the thermodynamic consistency of the acetone-benzene-chlorobenzene data in the article has been checked by the method of Li and Lu [J. C. M. Li and B. C.-Y. Lu, *Can. J. Chem. Eng.* **37,** 117 (1959)] applied to groups of near-isothermal points. The results indicated that the ternary data are consistent.

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