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.

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

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*).

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

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%.

LITERATURE CITED

(1) Arii, Kimio, *Bull. Inst. Phys. Chem. Research* (*Tokyo*) **8,** 714 (1929); *Sci. Repts. Tohoku Imp. Univ., First Ser.* **22,** 182 (1933).

(2) Biltz, Wilhelm, Meinecke, Erich, *Z. anorg. u. allgem. Chem.* **131,** 1 (1923).

(3) Bond, P. A., Beach, H. T., *J. Am. Chem. Soc.* **48,** 348 (1926).

(4) Bond, P. A., Stephens, W. R., *Ibid.*, **51,** 2910 (1929).

(5) Dreisbach, R. R., "Physical Properties of Chemical Compounds," Dow Chemical Co., 1952. Sheet No. Inorg. 8, August 20, 1953.

(6) Emich, F., *Monatsh. Chem.* **25,** 907 (1904).

(7) Gillespie, D. T. C., *Ind. Eng. Chem., Anal. Ed.* **18,** 575 (1946).

(8) Gilmont, Roger, *Anal. Chem.* **23,** 147 (1951).

(9) Grandage, A. H. E., private communication, Institute of Statistics, N. C. State College, Raleigh, N. C.

(10) Hildebrand, J. H., Carter, J. M., *J. Am. Chem. Soc* **54,** 3592 (1932).

(11) Nasu, Nobuyuki, *Bull. Chem. Soc. Japan* **8,** 392 (1933); Sci. Repts, Tohoku Imp. Univ., First Ser. **22,** 986 (1933).

(12) Pierre, Isidore, *Ann. chim. et phys.*, Ser. 3, **20,** 5 (1847).

(13) Sagawa, Tatsushiro, *Sci. Repts, Tohoku Imp. Univ., First Ser.* **22,** 959 (1933).

(14) Schäfer, Harald, Zeppernick, Friedrich, *A. anorg. u. allgem. Chem.* **272,** 274 (1953).

(15) Thornton, J. D., *J. Appl. Chem.* **1,** 237 (1951).

(16) Thorpe, T. E., *J. Chem. Soc.* **37T,** 327 (1880).

(17) *Ibid.*, **47T,** 108 (1885).

(18) Willingham, G. B., Taylor, W. J., Pignocco, J. M., Rossini, F. D., *J. Research Natl. Bur. Standards* **35,** 219 (1945). Equation 8 on page 235 is in error. Place a minus sign before α, β, γ.

RECEIVED for review January 5, 1959. Accepted June 25, 1959.

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.

K. W. FREE
H. P. HUTCHISON