BOILING POINT CURVES OF THE BINARY SYSTEMS, $TiCl_4$-CCl_4, $TiCl_4$-$SiCl_4$ and $TiCl_4$-$SnCl_4$.

By Nobuyuki NASU.

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Synopsis.

Boiling point curves of these binary mixtures have been determined by a newly designed apparatus which serves well in the treatment of such fuming liquids as these chlorides. The analytical method of these mixtures have also been contrived in such a manner that it can be prevented decomposition of titanium tetrachloride by the use of ethyl ether as a defending material from fuming.

Introduction.

In previous to this work the author has determined the freezing point curves of these binary mixtures for the study of the nature of titanium tetrachloride⁽¹⁾; this paper being the continuation of that work. Among the systems previously studied $TiCl_4$-$SbCl_5$ has been purposely omitted, due to the fact that the antimony pentachloride decomposes into trichloride and chlorine under the pressure of one atmosphere before it reaches to the boiling point.

Experimental.

1. **Apparatus and Procedure.** Samples used in this experiment were the same as that has been used in the investigation of the freezing point curve. The apparatus used for the measurement of the boiling points of fuming chlorides is shown in Fig 1. In Fig. 1, B is a boiling vessel connected with an equilibrium chamber E. At the base of E capillary tube P is equipped. T is a normal thermometer inserted into the mixture which is boiling and C is a cooler at which the vapour condenses and fills E, overflowing and returning the liquid into the boiling liquid. V is a tube through which vapour passes to the condenser. Boiling tube B is well wrapped with cloths to avoid the vapour from condensing. Short capillaries whose one end is sealed by fusing are inserted into the boiling chamber B, and by these capillaries the constant boiling is assumed. F is an electric furnace, and D is a Dewer vessel whose inner side is not silvered. The upper end of C is connected to a chamber containing P_2O_5. The extremity of capillary P is introduced into a drying chamber G, in which a

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(1) This Bulletin, **8** (1933), 195.

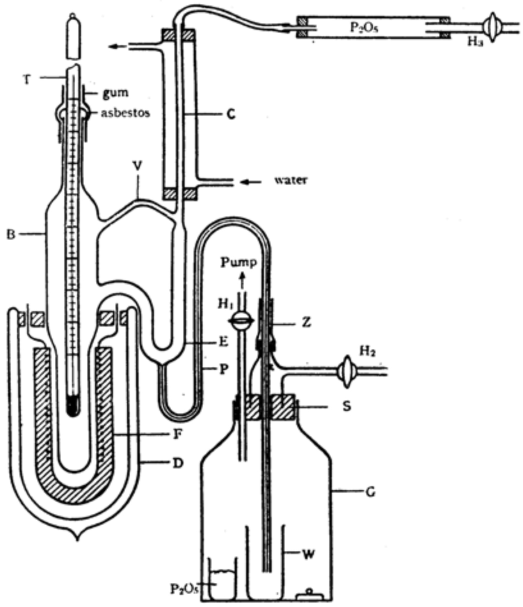

Fig. 1. Apparatus for Boiling Point Curve Measurement.

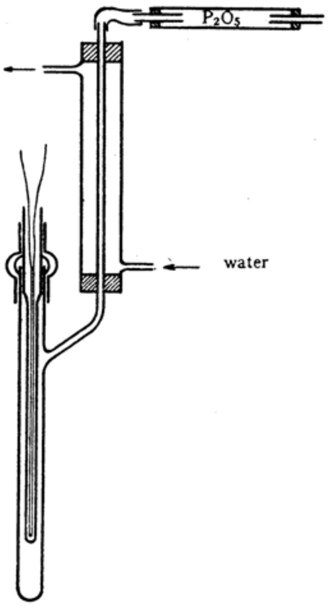

Fig. 2. Boiling Point Apparatus for the Liquid Condensed from Vapour.

weighing bottle W, its lid, and a vessel containing P_2O_5 are placed. Tubes provided with cocks H_1 and H_2 are tightly fit into the gum stopper S. G and S are movable up and down by sliding a gum tube Z along the capillary tube P. H_1 is connected to a cenco-pump and H_2 to air drying tube.

Before starting the experiment the whole apparatus is evacuated through H_1 by the cenco-pump and then filled with the dried air. By repeating this procedure the moisture in the whole apparatus is expelled, then the known quantities of chlorides are introduced into the boiling vessel from the upper end of C by the same method(2) as used in determining the freezing point curve. When these preparations were completed the chlorides are heated by a furnace F, and after the reading of thermometer T becomes constant by boiling for long time, F with D are quickly removed for the purpose of stopping the boiling of the liquid. After the liquid in E was cooled, the air is introduced into this chamber through the air-hole H_3 and this liquid is siphoned out into the vessel W, which is quickly covered with the lid at the removel of S from G; then this condensed chloride is weighed. The atmospheric pressure is always read when the boiling temperature becomes constant.

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(2) loc. cit.

2. Determination of the Compositions of Boiling Liquid and of Vapour which are in Equilibrim with Each Other. For the determination of the composition of vapour which is in equilibrium with boiling liquid, it is sufficient to know the composition of the liquid condensed in the equilibrium chamber E.

(a). $TiCl_4$-CCl_4. The composition of the condensed liquid was determined by the direct chemical analysis. To the chloride in the vessel W ethyl ether was introduced little by little through a capillary. After the chloride became dark yellow and not fuming, it was introduced, a small amount at a time, into a beaker containing water; the surface of the water being covered with small quantity of ether. In so doing every portion of the titanium tetrachloride in this dark yellow solution of chlorides with ether was dissolved into water, making a pale yellow solution, while on the other hand a little portion of the titanium tetrachloride was decomposed into smoke by hydrolysis, but since it was held in the layer between water and ether, no smoke was come out into the air from the solution. The smoke was soon dissolved into the solution by stirring. Carbon tetrachloride in the dark yellow solution remained undissolved at the bottom of the beaker, containing a small portion of titanium tetrachloride. A very small part of titanium tetrachloride, which was seemed to be remained in ether over the solution and in carbon tetrachloride, were washed by large quantity of water, and this water was added to the solution. Finally, carbon tetrachloride and ether were expelled by warming this solution, from which titanium hydroxide was precipitated by the addition of ammonia to the solution. The precipitate thus obtained was filtered, ignited in a porcelain crucible, and then weighed in terms of dioxide. From the weight of this titanium dioxide the compositions of the condensed liquid and of the boiling iquid were calculated.

(b). $TiCl_4$-$SiCl_4$. The chemical analysis was carried out as in the preceeding experiment in determining the composition of condensed liquid in this system. Ethyl ether was also used as a defending material from fuming produced from titanium tetrachloride. In this case a large part of silicon tetrachloride was decomposed into meta-silicic acid, titanium tetrachloride with the remaining portion of silicon tetrachloride dissolving into water under the cover of ether. After diluting this solution with a large quantity of water, these chlorides were decomposed and were precipitated by the addition of ammonia. All the precipitate was placed in a platinum crucible, added sufficient quantities of concentrated sulphuric acid and hydrofluoric acid solution, and by warming this mixture of precipitate and the acids all the silicon was drived away as fluoride. Lastly, titanium hydroxide was precipitated with ammonia from this solution, and it was then ignited in porcelain crucible and weighed in terms of dioxide. Compositions of both condensed and boiling liquid were calculated as before.

(c). $TiCl_4$–$SnCl_4$. If an ordinary chemical analysis were carried on in this system it should be obtained a mixture of oxides of both titanium and tin. According to the literature(3) the separation of tin from titanium could be made by heating this mixture of oxides in the atmosphere of hydrogen, reducing the oxide of tin to metallic state, and treating it with hydrochloric acid. But according to the author's point of view this method is far from application, because, firstly, it is very difficult to grind this ignited mixture of oxides to the extent of such powder as the oxide of tin can be reduced merely with hydrogen, and secondly it is doubtful that only the oxide of tin is reduced to the metallic state, and not the oxide of titanium even to its some oxide of lower grade, though not to metallic titanium. If this lower oxide of titanium is soluble in hydrochloric acid the above referred method of analysis will be evidently in error. On account of these reasons the direct chemical analysis was not carried on, but the following method was adopted.

With a boiling vessel, unconnecting equilibrium chamber E, the boiling points of the mixed chlorides of this system were determined. In this case correction for small quantity of vapour and condensed liquid was neglected owing to the smallness of their value. The results obtained were shown as the lower part of the curve in Fig. 5. The boiling points of this system were determined in the usual manner as before with an apparatus shown in Fig. 1 and the boiling point of liquid condensed in the equilibrium chamber E was measured by a small boiling vessel shown in Fig. 2, then from the boiling point-composition curve stated above the composition of the condensed liquid was determined. In this case corrections were neglected as before.

Results.

Values obtained from the above experiment were corrected for atmospheric pressure at which the mixtures of chlorides were boiling. Results obtained are tabulated in Tables 1, 2 and 3 and illustrated diagrammatically in Figs. 3, 4 and 5. In all these three systems there appears neither maxima nor minima in their boiling point curve. The distances between the liquid curve and the vapour curve are the widest in the system of $TiCl_4$–$SiCl_4$ and are the narrowest in the system of $TiCl_4$–$SnCl_4$.

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(3) A. Hilger and H. Haas, *Ber.*, **23** (1890), 458.

In conclusion the writer wishes to express his hearty thanks to Prof. K. Iwasé for his direction and encouragement throughout this work.

Table 1. $TiCl_4$–CCl_4

No.	$TiCl_4$ gr.	CCl_4 gr.	Bar. press. mm.	Boiling point °C		Condensed liq. Mol % CCl_4	Boiling liq. Mol % CCl_4
				Reading of thermometer	Corrected for bar. press.		
1	0.0000	39.4625	761.6	76.6	76.6	100.00	100.00
2	5.2032	47.4510	762.6	79.3	79.2	99.33	90.24
3	13.8888	50.6400	762.7	84.2	84.1	98.68	78.84
4	17.2610	39.4625	748.0	89.0	89.4	97.50	68.73
5	32.8169	41.5104	765.3	93.8	93.6	95.16	55.73
6	40.9935	32.9508	763.9	100.5	100.3	91.60	43.00
7	43.4450	26.9161	764.4	106.2	106.0	88.51	36.56
8	43.5075	15.8450	758.8	116.6	116.7	78.65	24.19
9	50.5261	10.8182	748.6	124.5	124.0	54.40	15.11
10	60.5059	6.6747	763.3	129.6	129.5	29.17	8.36
11	61.2737	1.5823	764.4	134.3	134.1	10.03	1.97
12	32.4380	0.0000	765.1	135.3	135.7	0.00	0.00

Table 2. $TiCl_4$–$SiCl_4$

No.	$TiCl_4$ gr.	$SiCl_4$ gr.	Bar. press. mm.	Boiling point °C		Condensed liq. Mol % $SiCl_4$	Boiling liq. Mol % $SiCl_4$
				Reading of thermometer	Corrected for bar. press.		
1	0.0000	63.4568	746.0	56.6	57.1	100.00	100.00
2	17.3610	63.4568	753.3	63.2	63.5	98.21	77.66
3	34.4798	53.4016	753.1	75.1	75.4	96.96	59.18
4	51.4768	44.3443	758.5	81.2	81.3	95.62	43.55
5	51.8970	29.7980	760.5	90.5	90.5	86.98	32.14
6	67.7980	21.4148	760.3	106.5	106.5	74.51	19.62
7	51.9060	9.3876	758.6	118.0	118.1	58.91	8.23
8	51.8820	6.7036	757.8	124.8	124.9	45.12	5.45
9	51.8820	2.9049	759.3	130.1	130.1	20.92	2.15
10	34.4380	0.0000	765.1	135.5	135.7	0.00	0.00

Table 3. $TiCl_4$–$SnCl_4$

a. Liquid

No.	$TiCl_4$ gr.	$SnCl_4$ gr.	Bar. press. mm.	Boiling point °C		Mol % $SnCl_4$
				Reading of thermometer	Corrected for bar. press.	
1	0.0000	47.3456	749.1	115.3	115.8	100.00
2	3.4462	,,	748.8	116.7	117.2	90.91
3	6.8900	,,	748.8	118.0	118.6	83.35
4	10.3338	,,	748.6	119.4	119.9	76.94
5	13.7746	,,	748.6	120.4	120.9	71.45
6	17.2150	,,	748.7	121.4	121.9	66.70
7	20.6548	,,	748.7	122.3	122.8	62.54
8	24.0946	,,	748.7	123.0	123.5	58.87
9	27.5344	,,	748.7	123.6	124.1	55.60
10	30.9742	,,	748.7	123.9	124.4	52.68
11	34.4164	,,	749.2	124.6	125.1	50.05
12	34.4380	44.3056	752.3	125.1	125.4	48.37
13	,,	39.8766	,,	125.5	125.8	45.75
14	,,	35.4476	,,	126.1	126.4	42.84
15	,,	31.0168	,,	126.8	127.1	39.61
16	,,	26.5896	,,	127.6	127.9	36.02
17	,,	22.1606	,,	128.6	128.9	31.94
18	,,	17.7290	,,	129.4	129.7	27.29
19	,,	13.2974	,,	130.7	131.0	21.97
20	,,	8.8658	,,	131.9	132.2	15.79
21	,,	4.4342	,,	133.7	134.0	8.57
22	,,	0.0000	756.1	135.5	135.7	0.00

b. Vapour

No.	Boiling liquid			Condensed liquid			
	Bar. press. mm.	Boiling point °C		Bar. press. mm.	Boiling point °C		Mol % $SnCl_4$
		Reading of thermometer	Corrected for bar. press.		Reading of pyrometer	Corrected for bar. press.	
1	753.2	117.2	117.5	753.2	115.4	116.1	98.5
2	751.0	118.5	118.9	751.0	115.8	116.2	97.5
3	752.2	120.1	120.4	752.2	116.2	116.5	95.5
4	752.3	120.3	120.6	752.3	116.7	117.1	92.0
5	751.3	121.6	122.0	751.3	117.6	118.0	86.5
6	751.0	123.2	123.6	751.0	118.4	118.8	82.8
7	751.5	124.2	124.6	751.5	119.1	119.5	78.5
8	756.5	125.2	125.4	756.5	120.1	120.4	74.0
9	754.0	125.7	126.0	754.0	120.9	121.2	69.0
10	753.3	127.2	127.5	753.3	122.0	122.3	64.0

b. Vapour—(*Concluded*)

No.	Boiling liquid			Condensed liquid			
	Bar. press. mm.	Boiling point °C		Bar. press. mm.	Boiling point °C		Mol % $SnCl_4$
		Reading of thermometer	Corrected for bar. press.		Reading for pyrometer	Corrected for bar. press.	
11	753.3	129.2	129.5	753.3	124.0	124.3	54.0
12	753.8	130.7	131.0	753.8	126.6	126.9	40.5
13	754.0	132.5	132.8	754.0	128.6	128.9	31.5
14	754.0	133.6	133.9	754.0	130.5	130.8	22.5
15	752.3	134.8	135.2	752.3	132.6	132.9	12.5
16	752.3	135.1	135.5	752.3	134.3	134.6	5.0

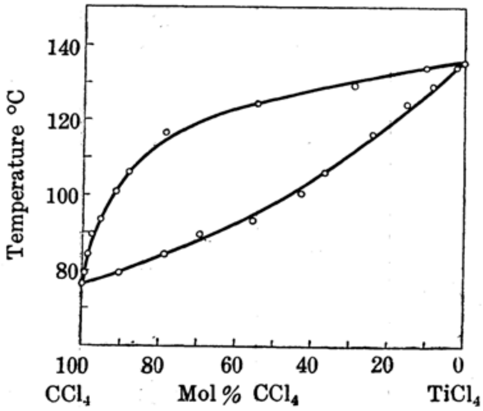

Fig. 3. Boiling Point Curve of the System $TiCl_4$-CCl_4.

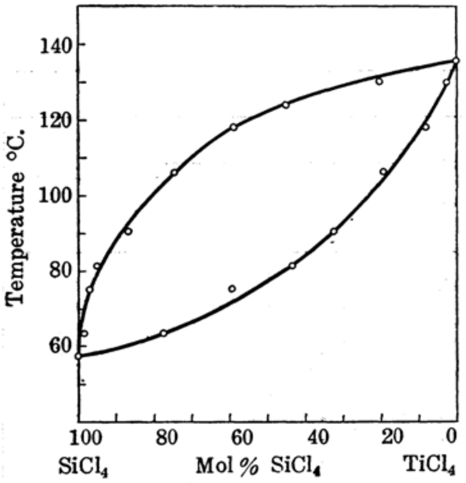

Fig. 4. Boiling Point Curve of the System $TiCl_4$-$SiCl_4$.

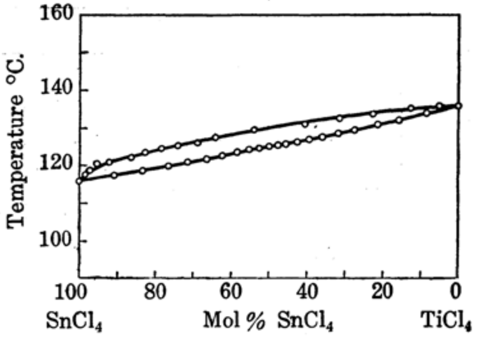

Fig. 5. Boiling Point Curve of the System $TiCl_4$-$SnCl_4$.

Summary.

1. An apparatus has been devised in which a capillary is introduced into a drying chamber at which the condensed liquid is siphoned out into a weighing bottle.

2. Analytical methods of the mixtures have also been contrived in which ethyl ether is used to prevent titanium tetrachloride from fuming out.

3. By using this apparatus and applying this analytical method, boiling point curves of the mixtures have been determined.

The Research Institute for Iron,
Steel and Other Metals.
Tohoku Imperial University, Sendai.