FREEZING POINT CURVES OF BINARY MIXTURES: $TiCl_4$-$SiCl_4$, $TiCl_4$-CCl_4, $TiCl_4$-$SnCl_4$ AND $TiCl_4$-$SbCl_5$.

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Synopsis.

Freezing point curves of binary mixtures, $TiCl_4$-$SiCl_4$, $TiCl_4$-$SnCl_4$, $TiCl_4$-CCl_4, and $TiCl_4$-$SbCl_5$ have been determined by the methods of both total and differential thermal analyses. In the system $TiCl_4$-$SiCl_4$ an eutectic point lies on the position almost 100% of $SiCl_4$, and with the mixtures $TiCl_4$-CCl_4 and $TiCl_4$-$SbCl_5$ a simple eutectic system has been shown, while the mixture $TiCl_4$-$SnCl_4$ shows a simple solid solution.

Introduction.

Titanium tetrachloride can be prepared from titanium dioxide which is usually found in the iron sand. Consequently the investigation of

titanium tetrachloride has very profound interest with the industrial application of the iron sand. The present author has intended as a first attempt to investigate the freezing point curves of the binary mixtures of liquid chlorides containing titanium tetrachloride.

Experimental Method.

1. Sampling of the Chlorides avoiding those from Decomposition. It will be difficult to prepare mixtures of known composition, which is extremely smoky in the presence of wet atmosphere, such as, those chlorides (excepting carbon tetrachloride), by weighing them with a balance. There is also a method of measurement by which these can be distillated in a measuring apparatus which is kept in vacuum, but then this will be of greatly complicated in such a case as to determine the freezing point curve. Hence in the present experiment the volumes of these chlorides have been measured with burettes avoiding them contact with moisture, and calculated the composition of these mixtures from their density. All these chlorides were purified by the distillation before use. Stocked chlorides were kept in flasks each of which has a side tube as shown in Fig. 1 A, and when those were used, dried air were let in from the tube avoiding the contact of moisture with chlorides. When the chlorides were let into a burette from the stocked flask through a long mouthed funnel inserted into a tube *a* shown in Fig. 1, dry air was sent from the tube *b* letting it out from the funnel, avoiding the contact of moisture with the chlorides, and taking the lid *c* off to allow the chlorides into the burette. After the chlorides were let into the burette, the lid *c*, being replaced the funnel being removed and the tube *a* was closed, at the same time, sending of the dry air from *b* was ceased. *d* in Fig. 1 and *d'* in Fig. 2 are gum stoppers whose surfaces are previously attacked by the chloride vapour for a sufficiently long time to avoid chlorides from being contaminated. Two grooves are dug on the stop-cock as shown in the figure and mercury is poured in them to protect the chlorides from

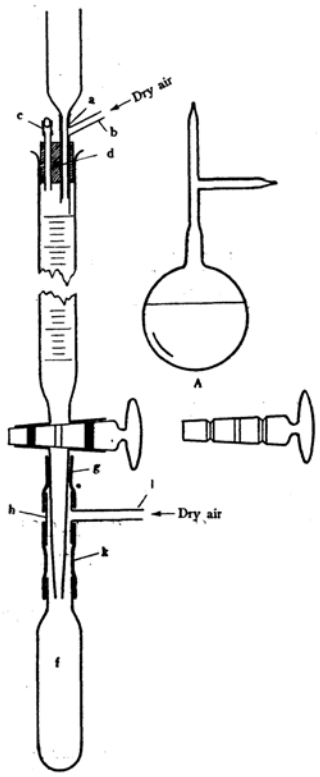

Fig. 1.

the moisture and to keep it movable. Although the boundary between the mercury and the chlorides became brownish black due to the contamination of the mercury during the experiment, the phenomenon was simply confined in the boundary; hence, the chlorides in the burette were able to keep their original purity. The purity was further assured by discording the first small quantity of chlorides into *f*, before measuring the chlorides out from the burette into the apparatus. *g* and *k* are gum tubes and *h* is made of glass. The measuring of the chlorides into the apparatus was consisted of lowering *g*, *h* and *k* downwards, passing the dry air very slowly from tube *l*, connecting the side tube *m* in Fig 2 with rubber tube *k*, at the same time *f* is removed and while opening the lid *n* allowing the air coming out, the desired quantity of the chlorides was measured into the apparatus. When the measurement was completed, *m* is removed from *k*, letting the dry air pass through from *n*, and *m* is quickly covered up, and finally the air supply from *n* was discontinued. *f* is re-set into *k*, at the same time letting the dry air cease to come from *l*. When carbon tetrachloride was used, an usual burette was employed, as it does not fume in the wet air. Since the data available in the literature relating to the density of these chlorides are very meagre, the density of these chlorides was calculated by the interpolation of several values in the literature. The references on the value adopted are as follows; the density of titanium tetrachloride from T. Sagawa,[1] a member of our institute, of silicon tetrachloride from T. E. Thorpe,[2] O. Ruff, and C. Albert,[3] of carbon tetrachloride from T. E. Thorpe[4] and Joseph,[5] of stannic chloride from Young and Fortey,[6] of antimony tetrachloride from A. Haagen,[7] O. Ruff, and W. Plato.[8]

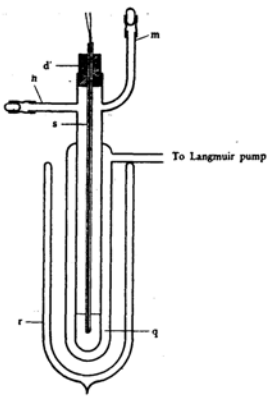

Fig. 2.

2. Thermal Analyses. The cooling velocity is regulated by the pressure at the space *q* in Fig. 2 to which Langmuir pump is connected. *r* is a Dewar vessel containing liquid nitrogen or mixture of solid carbon

(1) T. Sagawa, *Kinzoku no Kenkyū*, **9** (1932), 189.
(2) T. E. Thorpe, *J. Chem. Soc.*, **37** (1880), 327.
(3) O. Ruff, C. Albert, *Ber.*, **38** (1905), 2222.
(4) T. E. Thorpe, *Trans. Chem. Soc.*, **37** (1880), 141.
(5) Joseph, *Trans. Chem. Soc.*, **107** (1915), 1.
(6) Young & Fortey, *J. Chem. Soc.*, **81** (1902), 783.
(7) A. Haagen, *Pogg. Ann.*, **131** (1867), 122.
(8) O. Ruff & W. Plato, *Ber.*, **37** (1904), 679.

dioxide and ether. *s* is a protecting glass tube in which one junction of the copper-constantan thermocouple is inserted, and the other junction is inserted in the melting ice. The temperature was read by a pyrometer. The copper-constantan thermocouple was previously calibrated by the melting points of pure chlorobenzene, chloroform, ethyl acetate, toluene, ethyl ether, and mercury, and also by the boiling point of liquid nitrogen. On the differential thermal analysis the mixture of the desired composition was prepared firstly in the flask shown in Fig. 3 with the burette shown in Fig. 1, and then about 0.05 c.c. of the mixture was introduced into the glass tube whose diameter is 3 mm. shown in Fig. 4. The purpose of using such a small quantity of chloride was to make the uniform temperature at the extremity of the thermocouple. In Fig. 4 *t* is a copper block, 3 cm. in diameter and 4 cm. in length, into which two glass tubes are inserted; the one contains chloride, and the other water. In the tube containing chloride two junctions, each end of the temperature measurement thermocouple and of the differential thermal analysis, are inserted. These two junctions are inserted respectively into two capillaries which are placed symmetrically about the inner wall of the tube containing chloride. Two wires of the junction are insulated with the oxide coating on the copper wire made by the Bunsen burner. When the differential thermal analysis was carried on the copper block was previously dipped in liquid nitrogen, solidifying both the chloride and the neutral matter (water), and they were then taken out in the air, and finally the heating curves were drawn from the readings of a galvanometer. The velocity of the heating was about 0.4° per minute.

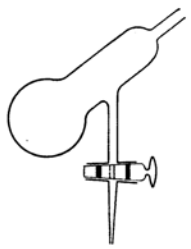

Fig. 3.

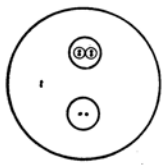

Fig. 4.

In the case of the total thermal analysis the solidus points on both sides of the eutectic point in the system $TiCl_4$-CCl_4 were indicated slightly lower temperature on the cooling curve and somewhat higher temperature on the heating curves. The similar phenomena were observed on the antimony pentachloride rich-side in the system $TiCl_4$-$SbCl_5$; consequently in both diagrams the mean values of these temperatures were adopted. Curves of the thermal analyses were shown in Figs. 9 and 10, and the results were tabulated and illustrated diagramatically in next paragraph.

Results of Experiment.

(1) **$TiCl_4$-$SiCl_4$.** When the cooling curve of the total thermal analysis was taken in this system, the eutectic flat did not appears until the

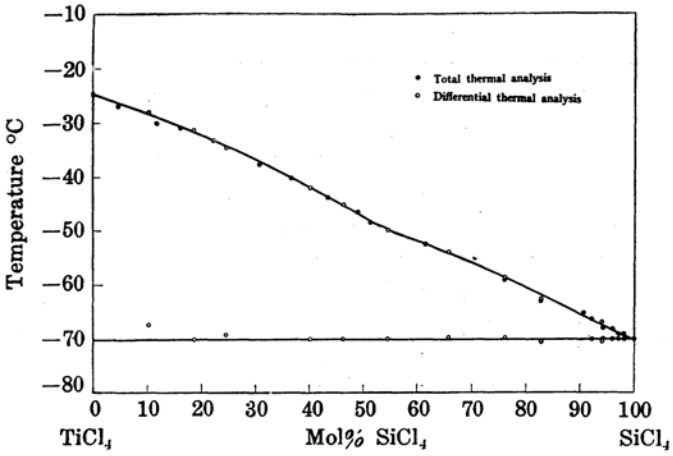

Fig. 5. Freezing point curve of the mixture: $TiCl_4$—$SiCl_4$.

1. $TiCl_4$-$SiCl_4$

Table 1. Total Thermal Analysis (Cooling Curves)

No.	Temp.	$TiCl_4$		$SiCl_4$		Mol% $SiCl_4$	Liquidus point —°C	Eutectic point —°C
		s.g.	c.c.	s.g.	c.c.			
1	15.4	1.7354	5.0	1.4927	0.0	0.0	24.8	—
2	15.5	1.7352	,,	1.4926	0.25	4.6	27.0	—
3	15.3	1.7356	,,	1.4928	0.7	11.9	30.3	—
4	15.5	1.7353	,,	1.4926	1.0	16.2	31.0	—
5	15.8	1.7346	,,	1.4924	1.5	22.4	33.4	—
6	14.2	1.7376	,,	1.4937	2.3	30.6	37.6	—
7	14.5	1.7370	,,	1.4935	3.0	36.6	40.4	—
8	15.1	1.7360	,,	1.4930	4.0	43.5	43.9	—
9	13.2	1.7393	,,	1.4946	5.0	49.0	46.7	—
10	12.1	1.7410	,,	1.4755	5.5	51.3	48.7	—
11	12.2	1.7408	3.0	1.4954	5.0	61.5	52.6	—
12	12 5	1.7403	2.0	1.4952	,,	70.6	55.2	—
13	13.5	1.7386	1.5	1.4943	,,	76.2	59.3	—
14	16.5	1.7336	1.0	1.4918	,,	82.8	63.3	—
15	15.4	1.7352	0.5	1.4927	,,	90.6	65.3	—
16	14.8	1.7364	0.4	1.4932	,,	92.3	66.8	70.3
17	15.9	1.7346	0.3	1.4923	,,	94.1	68.3	70.3
18	14.1	1.7376	0.2	1.4938	,,	96.0	68.3	70.3
19	13 2	1.7391	0.15	1.4946	,,	97.0	69.3	70.3
20	15.1	1.7359	0.1	1.4930	,,	98.0	69.3	70.3
21	15.1	1.7359	0.0	1.4930	,,	100.0	70.4	—

Table 2. Differential Thermal Analysis (Heating Curves)

No.	Temp.	$TiCl_4$		$SiCl_4$		Mol% $SiCl_4$	Liquidus point —°C	Eutectic point —°C
		s.g.	c.c.	s.g.	c c.			
22	12.5	1.7403	5.0	1.4952	0.6	10.3	28.0	67.3
23	13.0	1.7394	,,	1.4948	1.2	18.7	31.4	70.3
24	13.4	1.7388	,,	1.4944	1.7	24.6	34.6	69.3
25	13.5	1.7386	,,	1.4943	3.5	40.2	42.0	70.3
26	12.5	1.7303	,,	1.4952	4.5	46.3	45.3	70.3
27	12.8	1.7398	4.0	1.4949	5.0	54.5	50.4	70.3
28	13.2	1.7391	2.5	1.4946	,,	65.8	54.2	70.3
29	13.4	1.7388	1.5	1.4944	,,	76.2	58.9	70.3
30	13.8	1.7381	1.0	1.4941	,,	82.8	60.3	70.9
31	13.5	1.7386	0.3	1.4943	,,	94.1	66.6	70.9

mixture contained a quite large quantity of $SiCl_4$, say 90.6 Mol % $SiCl_4$. In the case of the differential thermal analysis the eutectic points were observed until the mixtures contained as small quantity of $SiCl_4$ as 10.3 Mol %. In both analyses this eutectic point was perfectly equal to the freezing point of pure $SiCl_4$. Liquidus curve descends, as shown in Fig. 5, gradually from 100% $TiCl_4$ to 100% $SiCl_4$. In another words in this system when a mixture freezes, $TiCl_4$ crystallizes out firstly, and until all the $TiCl_4$ freezes out, the crystallization of $SiCl_4$ does not begin.

(2) **$TiCl_4$-CCl_4.** In this system both the liquidus and the eutectic point appeared distinctly, as shown in Fig. 6, even in the case of the

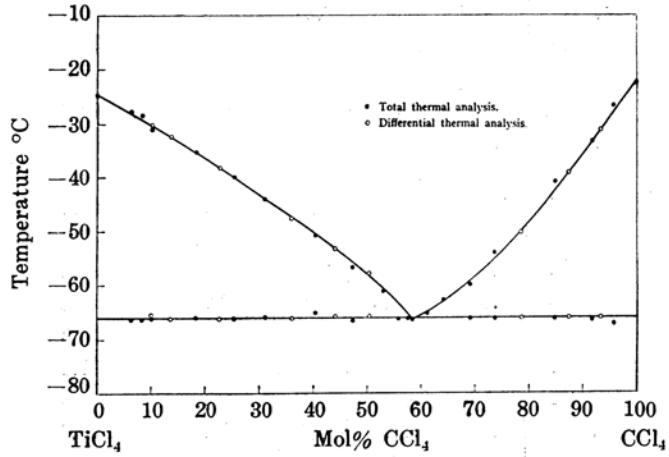

Fig. 6. Freezing point curve of the mixture: $TiCl_4$—CCl_4.

total thermal analysis; but the eutectic point found to be somewhat higher temperature in the heating curves than that of the cooling. This difference grew greater and greater as the composition of the mixture remote from the eutectic point, as shown in Table 3; hence in the figure mean values have been plotted. Perhaps these abnormalities can be removed if small quantity of the sample is used. In the case of the differential thermal analysis, therefore, small quantities of the samples were employed as described before, and almost definite eutectic temperature was observed.

2. $TiCl_4$-CCl_4

Table 3. Total Thermal Analysis (Cooling Curves)

No.	Temp.	$TiCl_4$		CCl_4		Mol % CCl_4	Liquidus point —°C	Eutectic point —°C		
		s.g.	c.c.	s.g.	c.c.			Cooling	Heating	Mean
1	16.0	1.7344	5.0	1.5817	0.0	0.0	24.8	—	—	—
2	16.1	1.7341	,,	1.5816	0.3	6.3	27.6	75.2	57.3	66.3
3	16.5	1.7336	,,	1.5813	0.4	8.3	28.5	75.2	57.3	66.3
4	16.8	1.7331	,,	1.5810	0.5	10.1	31.0	74.0	58.0	66.0
5	17.9	1.7311	,,	1.5801	1.0	18.4	35.4	74.0	58.0	66.0
6	18.2	1.7308	,,	1.5799	1.5	25.3	40.0	73.5	59.0	66.1
7	17.6	1.7318	,,	1.5804	2.0	31.0	44.3	73.0	59.3	65.8
8	18.1	1.7309	,,	1.5800	3.0	40.3	50.7	70.2	59.8	65.0
9	19.0	1.7294	,,	1.5793	4.0	47.4	56.7	68.8	64.3	66.6
10	20.8	1.7264	,,	1.5778	5.0	53.0	61.1	66.8	—	—
11	21.3	1.7256	,,	1.5774	5.6	55.8	—	66.3	—	—
12	21.8	1.7247	,,	1.5770	6.5	57.5	—	66.3	—	—
13	23.9	1.7211	4.0	1.5753	5.0	58.5	—	66.5	—	—
14	22.8	1.7230	5.0	1.5762	7.0	61.2	65.3	67.8	—	—
15	23.0	1.7227	5.0	1.5960	8.0	64.4	62.8	67.8	—	—
16	24.5	1.7202	2.5	1.5748	5.0	69.3	60.3	69.3	63.2	66.3
17	24.2	1.7207	2.0	1.5750	,,	73.8	54.2	70.2	62.3	66.3
18	25.9	1.7178	1.0	1.5736	,,	85.0	41.3	72.0	60.6	66.3
19	25.2	1.7190	0.5	1.5742	,,	91.9	33.4	73.0	60.0	66.5
20	26.5	1.7168	0.25	1.5732	,,	95.8	26.9	75.2	59.3	67.3
21	26.4	1.7170	0.0	1.5733	,,	100.0	22.9	—	—	—

Table 4. Differential Thermal Analysis (Heating Curves)

No.	Temp.	$TiCl_4$		CCl_4		Mol% CCl_4	Liquidus point —°C	Eutectic point —°C
		s.g.	c.c.	s.g.	c.c.			
22	11.2	1.7424	5.0	1.5856	0.5	10.1	30.4	65.7
23	11.5	1.7420	,,	1.5854	0.7	13.6	32.4	66.3
24	12.5	1.7403	,,	1.5845	1.3	22.6	38.2	66.3
25	10.5	1.7436	,,	1.5862	2.5	35.9	47.6	66.1
26	12.3	1.7406	,,	1.5847	3.5	44.0	53.2	65.9
27	12.5	1.7403	,,	1.5846	4.5	50.3	58.1	65.9
28	12.8	1.7398	1.5	1.5843	5.0	78.9	50.2	66.1
29	12.7	1.7400	0.8	1.5844	,,	87.5	39.4	66.2
30	12.7	1.7400	0.4	1.5844	,,	93.4	31.4	66.1

(3) **$TiCl_4$-$SnCl_4$.** In this system, as shown by the cooling curves in Fig. 12, while the primary crystallization points were observed distinctly, the eutectic flat did not appear at all. From this fact it is to be assumed that this system is to form the solid solution; but in spite of this prospect, the decision as to whether this system would form the solid solution or not seemed inadequate merely by the total thermal analysis. Only when the differential thermal analysis was taken it was able to decide that all the mixtures in this system, whatever was the composition, would form the solid solution. In Fig. 7 liquidus points from cooling curves of the total thermal analysis and the solidus points from heating curves of the differential thermal analysis were plotted.

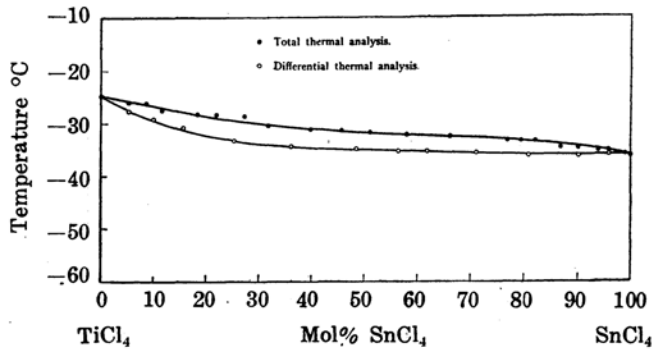

Fig. 7. Freezing point curve of the mixture: $TiCl_4$—$SnCl_4$.

3. $TiCl_4$-$SnCl_4$

Table 5. Total Thermal Analysis (Cooling Curves)

No.	Temp.	$TiCl_4$		$SnSl_4$		Mol% $SnCl_4$	Liquidus point —°C
		s.g.	c.c.	s.g.	c.c.		
1	26.7	1.7165	5.0	2.2088	0	0.0	24.8
2	26.8	1.7164	,,	2.2085	0.3	5.3	26.0
3	26.6	1.7167	,,	2.2090	0.5	8.6	27.1
4	27.1	1.7158	,,	2.2078	0.7	11.6	27.5
5	26.5	1.7168	,,	2.2093	1.2	18.4	28.3
6	26.4	1.7170	,,	2.2096	1.5	22.0	28.4
7	25.5	1.7185	,,	2.2119	2.0	27.3	28.6
8	25.4	1.7187	,,	2.2121	2.5	31.9	30.5
9	25.8	1.7180	,,	2.2111	3.5	39.6	31.2
10	25.7	1.7181	,,	2.2114	4.5	45.8	31.3
11	25.1	1.7192	,,	2.2129	5.5	50.8	31.6
12	24.2	1.7208	3.4	2.2152	5.0	58.0	32.2
13	23.8	1.7214	2.4	2.2163	,,	66.1	32.5
14	23.2	1.7240	1.4	2.2224	,,	77.0	33.4
15	22.4	1.7237	1.2	2.2199	,,	79.6	33.4
16	22.0	1.7244	1.0	2.2210	,,	82.4	34.4
17	20.0	1.7278	0.7	2.2262	,,	87.0	34.7
18	18.0	1.7311	0.5	2.2315	,,	90.4	34.8
19	19.5	1.7286	0.3	2,2275	,,	94.0	35.2
20	19.5	1.7286	0.2	2.2275	,,	95.9	35.4
21	19.3	1.7889	0.05	2.2280	,,	98.9	35.8
22	19.4	1.7287	0.0	2.2278	,,	100.0	36.2

Table 6. Differential Thermal Analysis (Heating Curves)

No.	Temp.	$TiCl_4$		$SnCl_4$		Mol% $SnCl_4$	Solidus point —°C
		s.g.	c.c.	s.g.	c.c.		
23	11.0	1.7428	5.0	2.2497	0.3	5.3	27.9
24	11 2	1.7424	,,	2.2492	0.6	10.1	29.4
25	12.5	1.7403	,,	2.2458	1.0	15.8	30.8
26	13.0	1.7394	,,	2.2445	1.8	25.3	33.4
27	13.5	1.7386	,,	2.2432	3.0	36.1	34.4
28	12.5	1.7403	,,	2.2458	5.0	48.5	34.8
29	12.4	1.7404	3.65	2.2461	5.0	56.3	35.4
30	13.4	1.7388	2.9	2.2434	,,	61.8	35.4
31	12.8	1.7398	1.9	2.2450	,,	71.2	35.6
32	13.0	1.7394	1.1	2.2445	,,	81.0	36.1
33	12.0	1.7411	0.5	2.2472	,,	90.4	36.4
34	14.2	1.7374	0.2	2.2414	,,	96.0	35.9

(4) **$TiCl_4$-$SnCl_5$.** From the results of the total and the differential thermal analyses, it has been found that the eutectic could be observed regularly in this system. But when cooling and heating curves of total thermal analysis were drawn the eutectic temperature varied only on the $SbCl_5$ rich side.

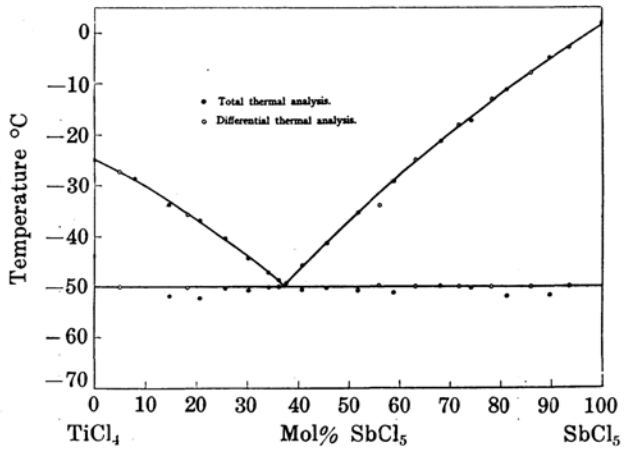

Fig. 8. Freezing point curve of the mixture: $TiCl_4 - SbCl_5$.

4. $TiCl_4$-$SbCl_5$

Table 7. Total Thermal Analysis (Cooling Curves)

No.	Temp.	$TiCl_4$		$SbCl_5$		Mol% $SbCl_5$	Liquidus point —°C	Eutectic point —°C		
		s.g.	c.c.	s.g.	c.c.			Cooling	Heating	Mean
1	26.1	1.7176	5.0	2.3325	0.0	0.0	24.8	—	—	—
2	26.0	1.7177	,,	2.3327	0.5	7.9	28.7	—	—	—
3	26.2	1.7174	,,	2.3322	1.0	14.7	33.8	51.6	—	—
4	26.1	1.7175	,,	2.3324	1.5	20.5	36.8	52.2	—	—
5	25.8	1.7180	,,	2.3331	2.0	25.6	40.4	50 2	—	—
6	25.5	1.7185	,,	2.3338	2.5	30.1	44.4	50.6	—	—
7	25.6	1.7184	,,	2.3336	3.0	34.1	47.2	50.2	—	—
8	25.8	1.7180	,,	2.3331	3.3	36.3	48.7	50.0	—	—
9	25.7	1.7182	,,	2.3335	3.5	37.6	—	49.2	—	—
10	26.0	1.7177	,,	2.3327	4.0	40.8	45.7	50.7	—	—
11	25.6	1.7184	,,	2.3336	5.0	46.3	41.4	50.2	—	—
12	25.8	1.7180	4.0	2.3331	5.0	51.9	35.4	50.7	—	—
13	25.6	1.7184	3.0	2.3336	,,	59.0	29.4	51.2	—	—
14	25.7	1.7182	2.0	2.3334	,,	68.3	21.3	53.2	46.2	49.7
15	25.8	1.7180	1.5	2.3331	,,	74.2	17.3	52.7	47.7	50.2
16	25.8	1.7180	1.0	2.3331	,,	81.2	11.3	57.8	45.2	51.9
17	25.5	1.7185	0.5	2.3338	,,	89.6	5.0	59.3	43.8	51.7
18	25.4	1.7187	0.0	2.3340	,,	100.0	+ 2.0	—	—	—

Table 8. Differential Thermal Analysis (Heating Curves)

No.	Temp.	$TiCl_4$		$SbCl_5$		Mol% $SbCl_5$	Liquidus point —°C	Eutectic point —°C
		s.g.	c.c.	s.g.	c.c.			
19	12.5	1.7403	5.0	2.3627	0.3	4.9	27.3	50.0
20	12.3	1.7406	,,	2.3631	1.3	18.3	35.8	50.2
21	12.4	1.7404	3.5	2.3629	5.0	56.0	34.0	49.8
22	12.3	1.7406	2.5	2.3631	,,	63.3	25.1	50.2
23	12.3	1.7406	1.7	2.3631	,,	71.7	18.1	50.0
24	12.4	1.7404	1.2	2.3629	,,	78.2	13.1	50.0
25	12.5	1.7403	0.7	2.3627	,,	86.0	8.0	50.2
26	12.5	1.7403	0.3	2.3627	,,	93.5	3.0	50.0

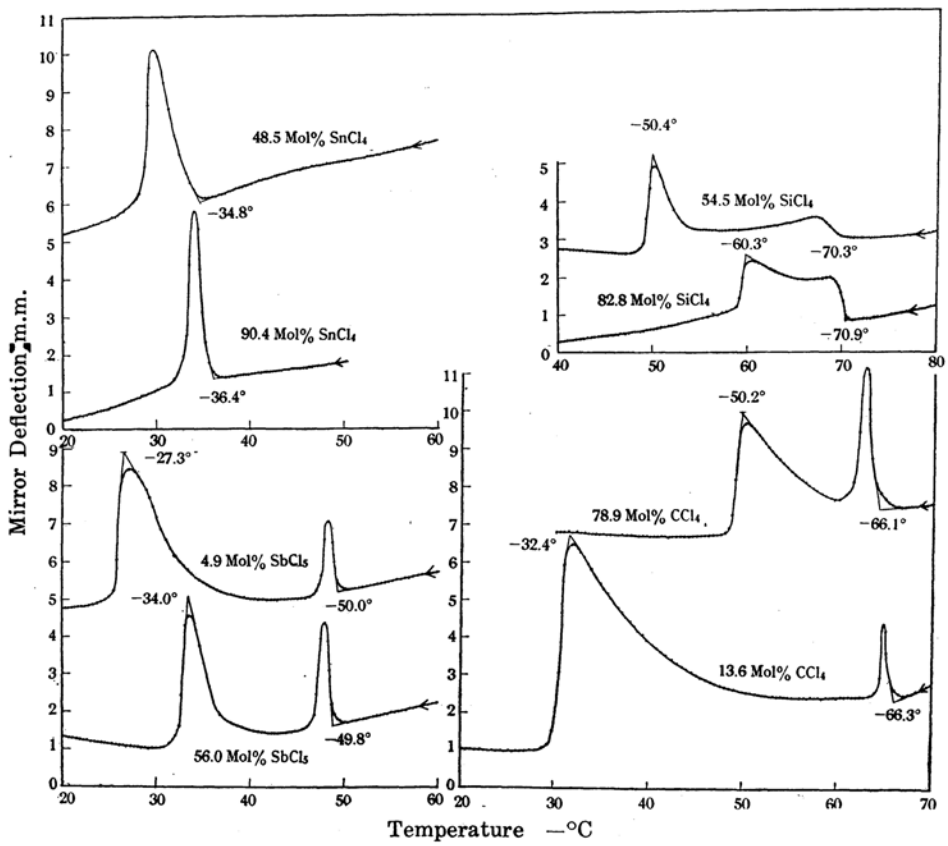

Fig. 9. Differential Thermal Analysis (Heating Curves).

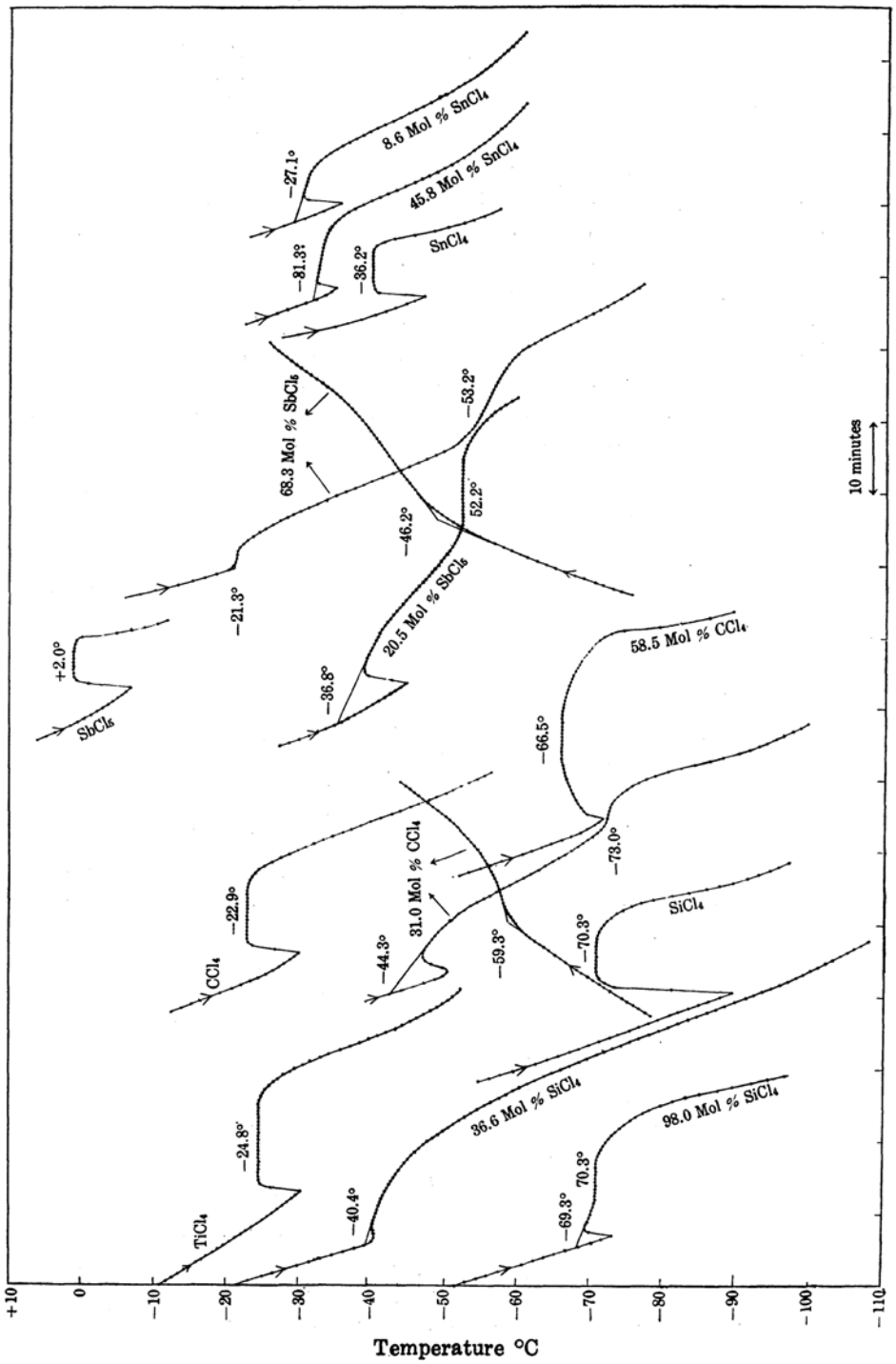

Fig. 10. Total Thermal Analysis.

As almost all of the cooling curves shows the supercooling of samples, primary crystallization points were decided by the back extrapolation method as shown in Fig. 10. In the case of the differential thermal analysis the points of intersection of the curves were taken as the required points.

In conclusion the present writer wishes to express his hearty thanks to Prof. Dr. K. Iwasé for his kind guidance, and thanks are also due to Mr. T. Okamura for his valuable advice.

Summary.

1. The apparatus was devised for the measurement of the liquids which smokes in the wet atmosphere without letting them smoke.

2. Using the apparatus described above the freezing point curves of the mixtures, $TiCl_4$-$SiCl_4$, $TiCl_4$-CCl_4, $TiCl_4$-$SnCl_4$, and $TiCl_4$-$SbCl_5$ were determined.

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