ON THE HEATS OF FUSION OF TITANIUM TETRACHLORIDE, CARBON TETRACHLORIDE, AND ANTIMONY PENTACHLORIDE.

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The present writer recently determined the freezing point curves of the binary systems of titanium tetrachloride, carbon tetrachloride, and antimony pentachloride, but he did not carry out his experiment with the solutions sufficiently dilute to calculate the heats of fusion of these chlorides. Hence the freezing points of these systems were determined again with sufficiently dilute solutions and the heats of fusion were calculated by the following formula:

$$\ln\frac{N}{N'} = \frac{Q}{R}\left\{\frac{1}{T'} - \frac{1}{T}\right\}^{(1)},$$

where T and T' are the freezing points of the solutions with the concentrations N and N', respectively. It must be mentioned here that the above formula is applicable only to the case where the two components do not form a solid solution.

Experimental.

The apparatus used was exactly the same as described in the previous paper.[2] In the present experiment, a mixture of solid carbon dioxide and ether was used as a cooling agent, and since a small quantity of solute had to be accurately measured, a special burette, in which 0.01 c.c. corresponded to 2 mm. in length, was used. An example of cooling curves is shown in Fig. 1.

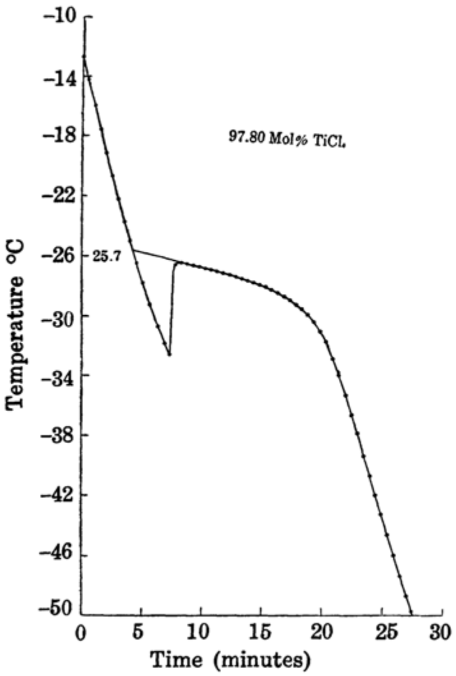

Fig. 1. An Example of Cooling Curves ($TiCl_4$—CCl_4)

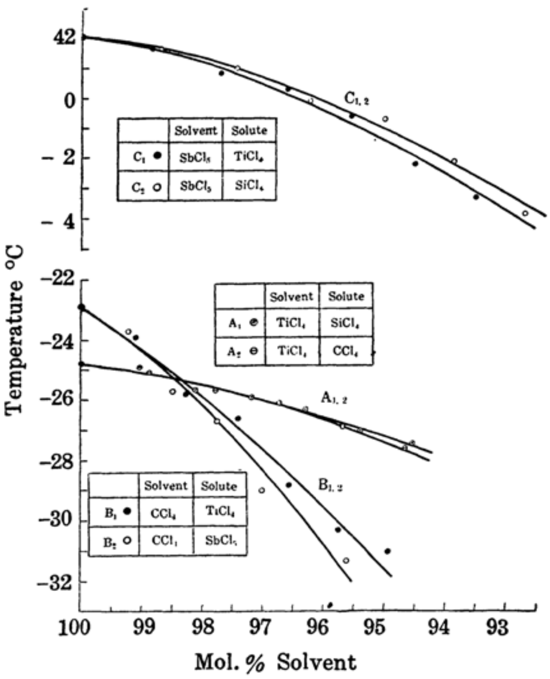

Fig. 2.

(1) S. Mitsukuri and A. Nakatsuchi, *Sci. Rep.*, **15** (1926), 50.
(2) This Bulletin, **8** (1933), 195.

(1) $TiCl_4$. The freezing point-concentration curves of the solution containing $SiCl_4$ and CCl_4 as the solute respectively are marked with $A_{1,2}$ in Fig. 2, and the $\frac{1}{T}$—ln N curve is almost straight as shown by $A_{1,2}$ in Fig. 3. The heat of fusion Q was calculated by taking two points on this straight line, which was drawn by the method of the least square. The values of Q corresponding to two solutes $SiCl_4$ and CCl_4 were found to be 2520 and 2350 cal./mol. respectively, the mean of which is 2440 cal./mol. or 12.90 cal./gr.

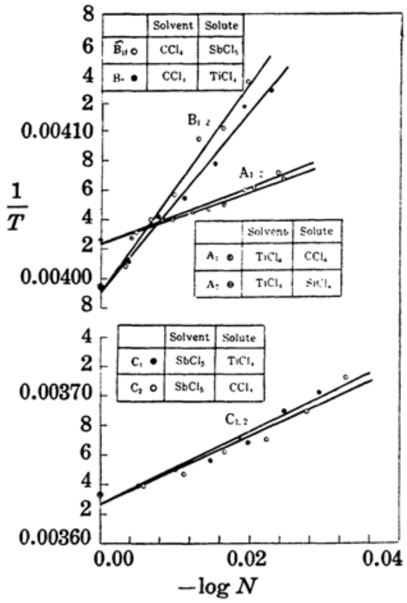

Fig. 3.

The formula for the depression of freezing point is applicable, as stated before, only when one of the two components does not show any solubility in the other in solid state. In the determination of the freezing point diagram of the system $TiCl_4$–$SiCl_4$, it was not ascertained whether the solid $TiCl_4$ is soluble in $SiCl_4$ or CCl_4, the lowest concentration used in the former investigation being 10.3 mol. % for $SiCl_4$ and 6.3 mol.% for CCl_4. Hence in order to confirm this point, a differential thermal analysis was carried out. In the system $TiCl_4$–CCl_4, the eutectic horizontal could be traced up to 2.2 mol. %, but in the system $TiCl_4$–$SiCl_4$, the same line could not be detected below the concentration of 10.3 mol. % $SiCl_4$. Again, the reaction time of eutectic obtained in the former experiment is plotted against the temperature as shown in Fig. 4 and 5 from which it is concluded that the system $TiCl_4$–$SiCl_4$ or $TiCl_4$–CCl_4 does not form solid solution on $TiCl_4$-rich side. The formula of the freezing point depression can thus be applied to the calculation of the heat of fusion of the compounds.

(2) CCl_4. The heat of fusion of CCl_4 was likewise calculated from the data obtained from dilute solutions containing CCl_4 as the solvent and $TiCl_4$ and $SbCl_5$ as the solute, respectively. The results are shown in Table 2 and by curves $B_{1,2}$ in Fig. 2 and 3. The values calculated from the above results for CCl_4, $TiCl_4$ and $SbCl_5$ being used as the solute, are respectively 740 and 630 cal./mol., thus giving the mean value of 680 cal./mol. or 4.40

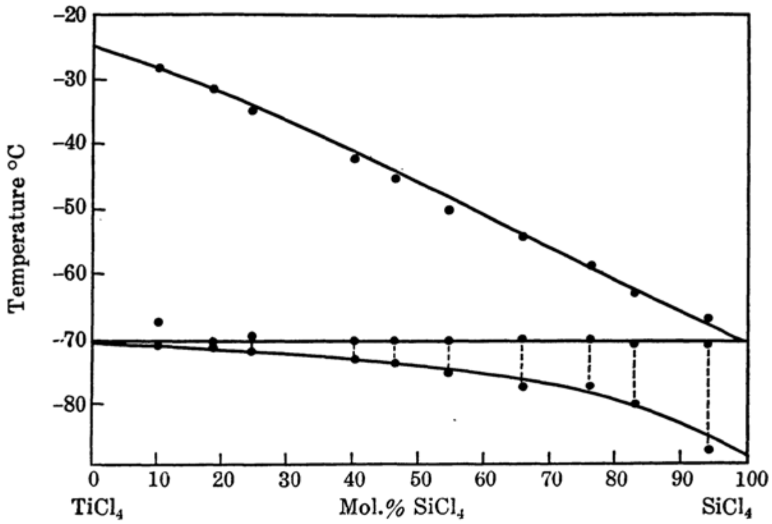

Fig. 4. $TiCl_4$-$SiCl_4$.

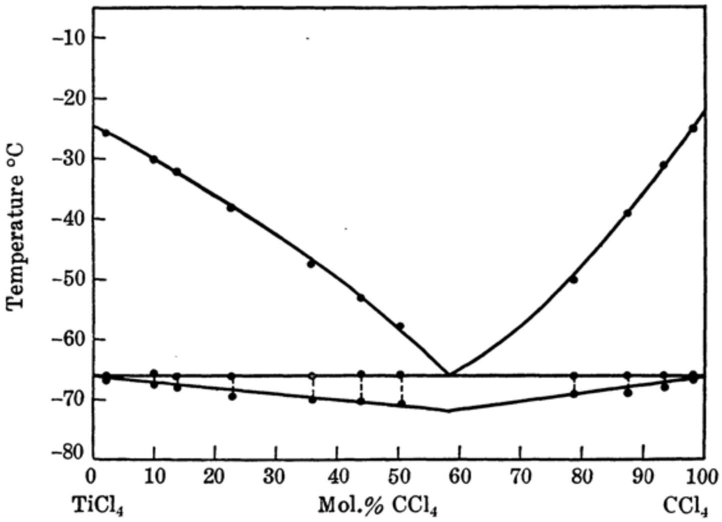

Fig. 5. $TiCl_4$-CCl_4.

cal./gr. It is also necessary to confirm if solid carbon tetrachloride is soluble in $TiCl_4$ or $SbCl_5$.

In the system CCl_4–$TiCl_4$, the eutectic horizontal can be traced down to 1.79% $TiCl_4$ by a differential thermal analysis as shown in Table 4. It is found from Fig. 5 that in the system CCl_4–$TiCl_4$ no solution seems to exist on CCl_4-rich side.

In the former investigation, the freezing point curve of the system CCl_4–$SbCl_5$ was not determined, and hence the question as to the existence of solid solution on CCl_4-rich side remains untouched ; but from the concordant results in the calculation of the heats of fusion of CCl_4 from the data obtained with $TiCl_4$ or $SbCl_5$ as the solutes, it is concluded that solid CCl_4 has no solubility in $SbCl_5$.

(3) **$SbCl_5$.** In this case $TiCl_4$ and CCl_4 were used as solutes. The results of experiments are given in Table 3 and shown by curves $C_{1,2}$ in Fig. 2 and 3. The heats of fusion of $SbCl_5$ calculated from the data obtained with $TiCl_4$ and CCl_4 as the solutes are 1870 and 1970 cal./mol. respectively, the mean value being 1920 cal./mol. or 6.40 cal./gr. It was also confirmed that in the system $SbCl_5$–$TiCl_4$, solution in solid phase does not exist at all (Fig. 6).

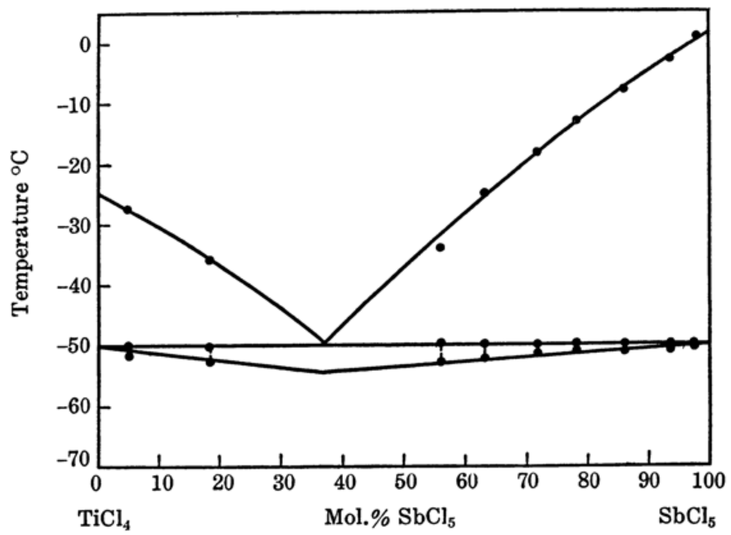

Fig. 6. $TiCl_4$–$SbCl_5$.

Although the freezing point curves of the system $SbCl_5$–CCl_4 was not determined in the recent investigation as stated in paragraph (2), it is apparent from the concordant result in the calculation of the heats of fusion of $SbCl_5$ from the cases where $TiCl_4$ and CCl_4 are used as solutes respectively that it can be assumed that solid $SbCl_5$ has no solubility in these two compounds.

The heats of fusion of three chlorides obtained by the present writer and those by previous workers are put together in Table 5 for comparison.

Table 1.

(A) Solvent : $TiCl_4$; Solute : $SiCl_4$

Mol. % $TiCl_4$ 100 N	Beginning of freezing point.		$\frac{1}{T}$	$-\log N$
	$-°C$	T		
100.00	24.8	248.4	0.004026	0.00000
99.05	24.9	248.3	0.004027	0.00415
98.12	25.7	247.5	0.004040	0.00825
97.20	25.9	247.3	0.004044	0.01233
96.30	26.3	246.9	0.004050	0.01637
95.42	27.0	246.2	0.004062	0.02036
94.55	27.4	245.8	0.004068	0 02434

$Q = 2520$ cal./mol.

(B) Solvent : $TiCl_4$; Solute : CCl_4

Mol. % $TiCl_4$ 100 N	Beginning of freezing point.		$\frac{1}{T}$	$-\log N$
	$-°C$	T		
100.00	24.8	248.4	0.004026	0.00000
98.89	25.1	248.1	0.004031	0.00485
97.80	25.7	247.5	0.004040	0.00966
96.74	26.1	247.1	0.004047	0.01439
95.69	26.9	246.3	0.004060	0.01913
94.68	27.6	245.6	0.004072	0.02374

$Q = 2350$ cal./mol. mean $Q = 2440$ cal./mol. or 12.90 cal./gr.

Table 2. (C) Solvent : CCl_4 ; Solute : $TiCl_4$

Mol. % CCl_4 100 N	Beginning of freezing point.		$\frac{1}{T}$	$-\log N$
	$-°C$	T		
100.00	22.9	250.3	0.003995	0.00000
99.12	23.9	249.3	0.004011	0.00384
98.26	25.8	247.4	0.004042	0.00762
97.41	26.6	246.6	0.004055	0.01140
96.57	28.0	245.2	0.004078	0.01516
95.75	30.3	242.9	0.004117	0.01886
94.94	31.0	242.2	0.004128	0.02225

$Q = 740$ cal./mol.

(D) Solvent : CCl_4 ; Solute : $SbCl_5$

Mol. % CCl_4 100 N	Beginning of freezing point.		$\frac{1}{T}$	$-\log N$
	$-$°C	T		
100.00	22.9	250.3	0.003995	0.00000
99.24	23.7	249.5	0.004008	0.00331
98.50	25.7	247.5	0.004040	0.00656
97.76	26.7	246.5	0.004057	0.00984
97.04	29.0	244.2	0.004095	0.01305
96.32	29.4	243.8	0.004102	0.01628
95.62	31.3	241.9	0.004134	0.01945

$Q = 630$ cal./mol. mean $Q = 680$ cal./mol. or 4.40 cal./gr.

Table 3. (E) Solvent : $SbCl_5$; Solute : $TiCl_4$

Mol. % $SbCl_5$ 100 N	Beginning of freezing point.		$\frac{1}{T}$	$-\log N$
	°C	T		
100.00	2.0	275.2	0.003634	0.00000
98.85	1.6	274.8	0.003939	0.00512
97.73	0.8	274.0	0.003650	0.00997
96.64	0.3	273.5	0.003656	0.01484
95.57	$-$0.6	272.6	0.003668	0.01968
94.53	$-$2.2	271.0	0.003690	0.02443
93.51	$-$3.3	269.4	0.003705	0.02914

$Q = 1870$ cal./mol.

(F) Solvent : $SbCl_5$; Solute : CCl_4

Mol. % $SbCl_5$ 100 N	Beginning of freezing point.		$\frac{1}{T}$	$-\log N$
	°C	T		
100.00	2.0	275.2	0.003634	0.00000
98.71	1.6	274.8	0.003639	0.00564
97.45	1.0	274.2	0.003647	0.01122
96.23	0.1	273.1	0.003662	0.01669
95.03	0.7	272.5	0.003670	0.02214
93.87	$-$2.1	271.1	0.003689	0.02747
92.73	$-$3.8	269.4	0.003712	0.03278

$Q = 1970$ cal./mol. mean $Q = 1920$ cal./mol. or 6.40 cal./gr.

Table 4.

Results of the differential thermal analysis.

System	Concentration	Liquidus point °C	Eutectic point °C
$TiCl_4-CCl_4$	2.20 mol. % CCl_4.	−25.5	−65.5
$TiCl_4-CCl_4$	1.74 mol. % $TiCl_4$.	−25.4	−66.0
$TiCl_4-SbCl_5$	97.73 mol. % $SbCl_5$.	1.4	−50.9

Table 5. Heat of fusion (cal. per gram)

	$TiCl_4$	CCl_4	$SbCl_5$
Values obtained by the author	12.90	4.40	6.40
Those by previous workers	11.70(3)	4.20(3)	8.18(4)

As is found from Table 5, the heats of fusion of $TiCl_4$ and CCl_4 obtained by the present writer and those determined calorimetrically by previous workers are in good agreement, but in the case of $SbCl_5$, the discrepancy is considerable. The origin of the values, 8.18 cal./gr. adopted by W. Herz is not given in his paper, and hence the exact method of determination can not be known.

Summary.

The heats of fusion of $TiCl_4$, CCl_4, and $SbCl_5$ were calculated from the data of the depression of freezing point in dilute solutions. The heats of fusion of $TiCl_4$, CCl_4 and $SbCl_5$ were found 12.90, 4.40, and 6.40 cals. per gram respectively. These values were in a close agreement with those observed by previous investigators.

In conclusion the writer wishes to express his hearty thanks to Prof. K. Honda, the President of the Tôhoku Imperial University and to Prof. K. Iwasé for their kind guidances during the course of this work.

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(3) W. H. Latimer, *J. Am. Chem. Soc.*, **44** (1922), 90.
(4) W. Herz, *Z. anorg. allgem. Chem.*, **170** (1928), 237.