PHASE EQUILIBRIUM OF $SbCl_3$-HCl-H_2O SYSTEM①

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ABSTRACT

Phase equilibrium of the $SbCl_3$-HCl-H_2O system and the temperature effect on the distillation rate of As and recovery of Sb in distillation process have been studied. The phase diagrams of temperature-concentration and Y-X (Y: composition of gaseous phase, X: compostion of liquid phase) diagrams of the $SbCl_3$-HCl-H_2O system with 4, 8, 12 mol/L HCl have experimentally been measured. From the results obtained, a rectification method to prepare high purity $SbCl_3$ from aqueous solution has been proposed.

Key words: antimony trichloride hydrochloric acid phase equilibrium rectification

1 INTRODUCTION

Preparation of high purity compounds from aqueous solution is mainly the separation of hard-to-separate impurities in the system. It is difficult to separate those impurities from aqueous solution by ordinary methods. Rectification method can effectively answer the purpose. This method has been used in analytical chemistry and chemical engineering. It should be studied in the case of preparing high purity metallurgical chemical products.

It is based on phase diagrams to prepare high purity antimony compounds by rectification method. The diagram of the $SbCl_3$-HCl-H_2O ternary system at 20 C and the $AsCl_3$-$SbCl_3$ melt system had been worked out[1,2] and the phase equilibrium of the Sb (Ⅲ)-$MeCl^-$-H_2O system at room temperature was also studied[3]. In this paper, the phase equilibrium of the $SbCl_3$-HCl-H_2O system at elevated temperatures has been studied. A rectification method to prepare high purity $SbCl_3$ from aqueous solution has been proposed.

2 EXPERIMENTAL

2.1 *Laboratory Equipment*

It is a set of glass instruments as shown in Fig. 1.

2.2 *Experimental Method*

By Othmer method, the compositions of gaseous and liquid phase and boiling points of HCl solution with certain concentrations of $SbCl_3$ were determined. The concentrations of HCl solution used were 4, 8, 12 mol/L, respectively. The solutions were heated to boiling point until equilibrium. The boiling points were determined by standard thermometer (accuracy: ± 0.2 C). Gaseous and liquid phases were collected from condenser and reaction vessel, respectively to determine the percentage compositions of $SbCl_3$, HCl and H_2O. From these re-

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sults, the phase diagrams were constructed.

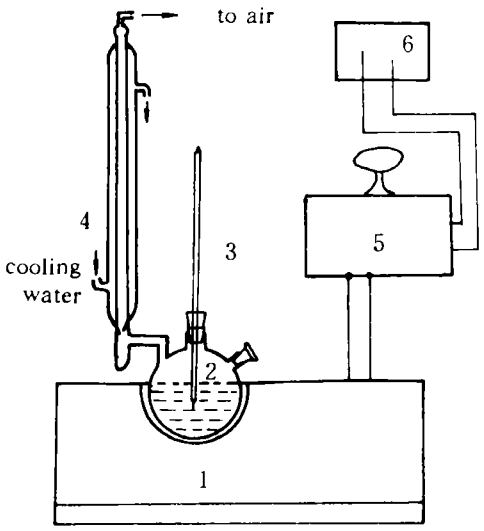

Fig. 1 Apparatus of phase diagram determination by Othmer method

1—heating device; 2—reaction vessel; 3—thermometer; 4—cooling tube; 5—transposition voltmeter; 6—alternating current power source

In distillation system, the percentage of As elimination and Sb recovery from the soluton containing $AsCl_3$ and $SbCl_3$ at a series of temperatures were determined.

2.3 *Analytical Method*

The percentages of Sb and Cl^- in the solutiion were determined by $KBrO_3$ titration method and $AgNO_3$-KSCN precipitation titration method, respectively. The H_2O in the system was determined by the subtraction method.

3 RESULTS AND DISCUSSION

3.1 *Temperature-Concentration Diagrams*

According to the experimental data, temperature concentration diagrams in 4, 8 and 12 mol/L HCl media were worked out, as shown in Figs. 2, 3 and 4, respectively (pressure 101.3 KPa, $SbCl_3$ as a component, $HCl+H_2O$ as another component).

From Figs. 2～4, it is known that boiling point temperature changes with the concentrations of the various components in both gaseous and liquid phase. In the upper

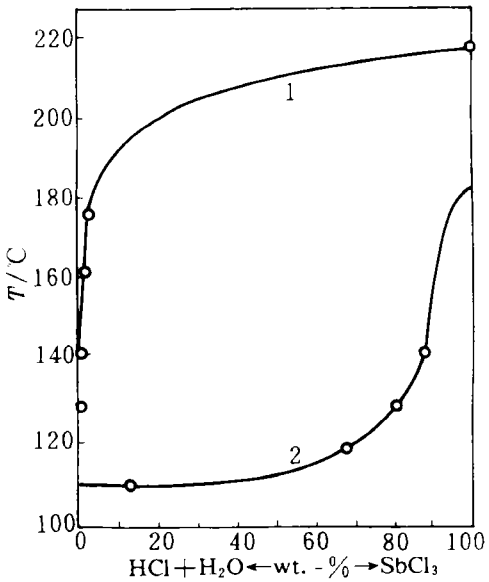

Fig. 2 Temperature-concentration diagram in 4 mol/L HCl medium

1—gaseous phase curve; 2—liquid phase curve

curves, the larger the percentage of $SbCl_3$ in the gaseous phase, the higher the boiling point temperature. In the lower curves, the little the percentage of $HCl+H_2O$ in the liquid phase, the higher the boiling point temperature. Comparing several temperature concentration curves, we know that the lower the concentration of HCl, the slower changes the boiling point temperature with raising percentage of $SbCl_3$ in gaseous phase under 180 C, that is, $SbCl_3$ is not easily evaporated out from liquid phase; but above 180 C the more rapid changes the boiling point temperature with raising percentage of $HCl+H_2O$, that is, $HCl+H_2O$ is easily evaporated out from liquid phase so that it can be evoparated out thoroughly. This changing tendency provides the key from

controlling temperature in rectification.

3.2 *Y—X Diagrams*

According to experimental data, Y—X diagrams in 4, 8 and 12 mol/L HCl media were worked out, as shown in Figs. 5, 6 and 7 respectively.

From Figs. 5 ~ 7, the relationship between compositions of gaseous and liquid phase at pressure 101.3 KPa can be determined. In Y—X curves, the relative evaporation ratio (α) in various acidities can be

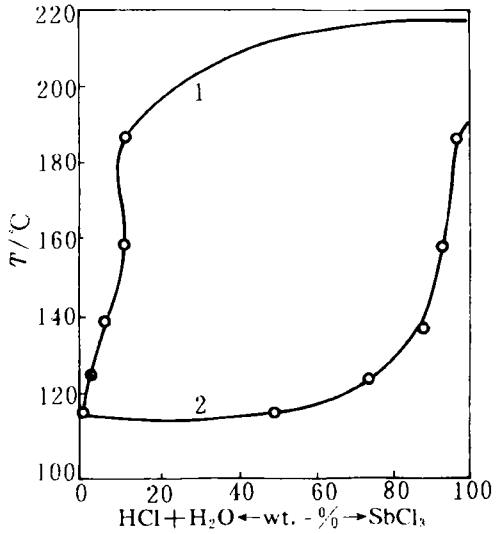

Fig. 3 Temperature-concentration diagram in 8 mol/L HCl medium
1—gaseous phase curve; 2—liquid phase curve

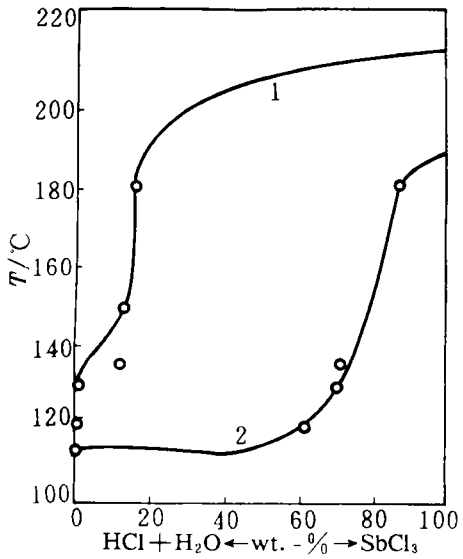

Fig. 4 Temperature-concentration diagram in 12 mol/L medium
1—gaseous phase curve; 2—liquid phase curve

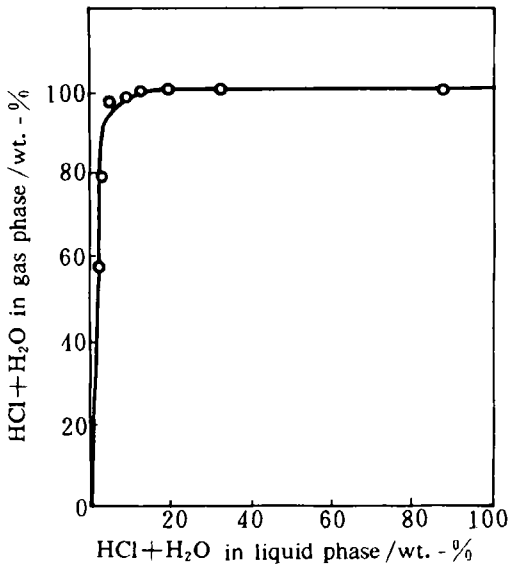

Fig. 5 Y—X diagram of the $SbCl_3$-HCl-H_2O system with 4 mol/L HCl

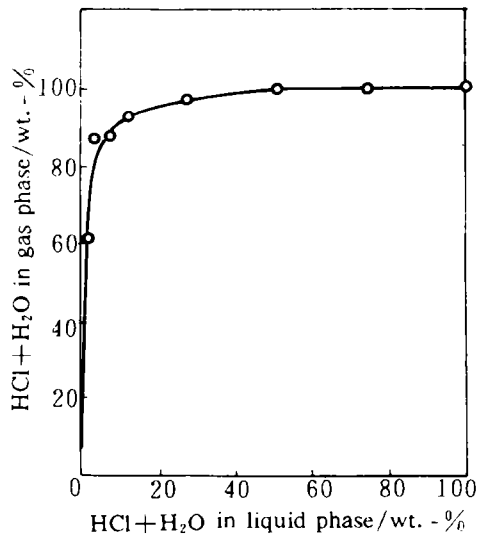

Fig. 6 Y—X diagram of the $SbCl_3$-HCl-H_2O system with 8 mol/L HCl

expressed as:

$$\alpha = Y_a X_b / (Y_b X_a)$$

where a and b represent two kinds of components. Generally, a varies with change in temperature. But the average value(a_m) in certain temperature range can be treated as a constant. In Y—X diagrams, the benter the curve, the larger the a_m value. Comparing several Y—X curves in various acidities, the lower the acidity, the benter the curve, the larger the a_m value, the more easily the volatile component is seperated from the system. This provides a basis for selecting acidity in rectification.

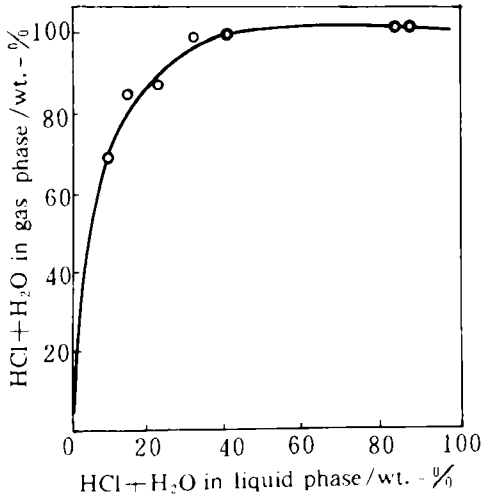

Fig. 7 Y—X diagram of the $SbCl_3$-HCl-H_2O system with 12 mol/L HCl

In Y—X diagrams, the number of theoretical column plate can be calculated by diagrammatic method. This can be used to design the rectification column. Morever, minimum refluxing ratio and heating condition can also be calculated by using Y—X diagrams.

3.3 *Temperature Effect in Distillation*

In order to estimate the conditons to seperate the volatile components, such as $AsCl_3$, from $SbCl_3$ by distillation, the percentage of As distilled and Sb recovered at a series of temperatures were determined. The results are shown in Table 1. And the boiling points of various metal chlorides are shown in Table 2[4].

Table 1 Temperature effects in distillation system

Temperature /℃	111	122	126	134	145	155	165
As distilling /%	4.92	63.07	69.52	92.29	95.12	95.82	96.58
Sb recovery /%	99.87	99.44	99.40	98.91	95.60	92.69	91.44

Table 2 Boiling points of various metal chlorides

Metal Chlorides	$SnCl_4$	$AsCl_3$	$TiCl_4$	$AlCl_3$	$GaCl_3$	$SbCl_3$	$HgCl_2$	$FeCl_3$
Boiling point/℃	113	130	136	180	200	220	304	309
Metal chlorides	$BiCl_3$	$ZnCl_2$	$PbCl_2$	$CaCl_2$	$NiCl_2$	$FeCl_2$	$CoCl_2$	$MnCl_2$
Boiling point/℃	441	732	954	967	987	1026	1050	1110

From Table 1 the percentage of As distilled in the distillation system increases with temperature so that almost all of $AsCl_3$ can be distilled out at high temperature; Sb can be leached in HCl solution and remain in the solution with high percentage. From Table 2 it can be estimated that in the distillation system, the metal chlorides wiht lower boiling points than that of $SbCl_3$ can be distilled out partly or thoroughly together with HCl and H_2O; those metal chlorides with higher boiling points than that of $SbCl_3$ are left in the solution or residue.

4 PREPARATION OF HIGH PURITY $SbCl_3$

Based on the investigation of $SbCl_3$-HCl-H_2O phase diagram, the preparation of

high purity $SbCl_3$ was studied from the flue dust containing As and Sb. The flowsheet is shown as Fig. 8.

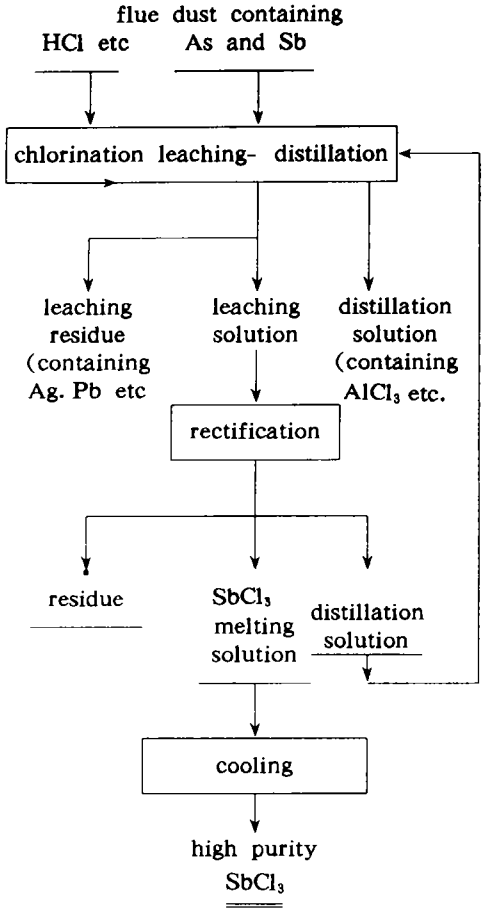

Fig. 8 The flowsheet of preparation of high purity $SbCl_3$

According to Fig. 8, the flue dust containing As and Sb is first leached and distilled with HCl solution in the appropriate conditions at about 110 ℃. A part of $AsCl_3$ is distilled out with HCl and H_2O. $SbCl_3$ and other metal chlorides are dissolved in the leaching solution. Some metals can not be leached by HCl solution and are left in the residue. Then from the leaching solution, high purity $SbCl_3$ can be prepared by rectification method. The rectification column is maintained in a temperature range of 120～220 ℃. The exiting temperature for distilling $AsCl_3$, HCl and H_2O is about 120 ℃, and for $SbCl_3$ is about 220 ℃. $SbCl_3$ melt solution was cooled to room temperature to obtain high purity $SbCl_3$.

5 CONCLUSIONS

(1) The phase diagrams of temperature-concentration and Y—X of the $SbCl_3$-HCl-H_2O system with 4, 8, 12 mol/L HCl have been measured. And in distillation system the temperature effect on distillation rate of As and recovery rate of Sb have been determined.

(2) Based on the phase equilibrium study and concerned data, a distillation-rectification method for preparation of high purity $SbCl_3$ from flue dust containing As and Sb has been proposed. This method has many advantages such as simple flowsheet and equipment, low pollution and high purity product.

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