THERMODYNAMIC EQUILIBRIUM OF Sb-Cl-H_2O SYSTEM ①

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ABSTRACT According to the law of conservation of mass and the law of simultaneous equilibrium, logarithm concentration-pH(lg$C$-pH) diagrams of Sb(Ⅲ)-Cl-H_2O system have been made for the first time. The effect of Sb and Cl on stabilization zone of each solid phase was studied and discussed. The results show that the pH of complete hydrolysis and complete dechloride are decreasing with the toal concentration of Cl in the system C^0_{Cl} and the toal concentration of Sb in the system C^0_{Sb} decrease, C^0_{Cl} and C^0_{Sb} has little effect on Sb_2O_3-solution equilibrium, but they have prominent effect on the equilibrium of SbOCl-solution and $Sb_5O_4Cl_2$-solution. Using the figures we can choose some technology parameters of hydrolyzing and eliminate chloride process in theory. The pH of hydrolysis completely is approximately 0.5 and the pH of dechloride completely is above 7.

Key words antimony chloride thermodynamic equilibrium logarithm concentration-pH diagrams

1 INTRODUCTION

The thermodynamic equilibrium of Sb(Ⅲ)-Cl-H_2O system was studied firstly by Vam Bemmelen and his collaborators. Sabaneff and Lea had studied the hydrolysis problem of antimony trichloride too. However these studies are preparatory and qualitative, they hadn't obtained fixed quantitative equilibrium relation of each substance in hydrolysis process[1]. Fu Chongyue[2] had studied thermodynamic equilibrium of Sb_2S_3-Cl-H_2O system, it wasn't considered that the equilibrium of $Sb_4O_5Cl_2$ and solution in their study. Duan Xuechen[3] had studied the phase equilibrium of $SbCl_3$-HCl-H_2O system to prepare high purity $SbCl_3$. Tang Motang[4] had studied specially the relationship of total concentration of antimony $[Sb]_T$ and total concentration of chloride $[Cl^-]_T$, and that of $[Sb]_T$ and other metallic ion concentration in Sb(Ⅲ)-Cl-H_2O system, however the relation of pH and the stabilization zone of each solid phase matter had not been studied. The antimony trichloride hydrolysis process is very complex because there are some intermediate products of solid phase matter in the process. People will be concerned practically about the stabilization zone of each solid matter in solution, however, it was not reported in predecessor's studies. In the present paper, the mathematical model was established according to the law of conservation of mass and the law of simultaneous equilibrium, the lg$C$-pH diagrams of Sb(Ⅲ)-Cl-H_2O system have been made, and the stabilization zone of each solid phase in different pH value at normal temperature was studied and discussed.

2 REACTION EQUATIONS AND MATHEMATICS MODEL

2.1 Reaction Equations

The Sb(Ⅲ)-Cl-H_2O system is a very complex system because there are some complex ions of Sb^{3+} with Cl^- and Sb^{3+} with OH^- except the ion of Sb^{3+}, Cl^-, OH^- *etc* in the solution, and maybe there are some solid products such as SbOCl, $Sb_4O_5Cl_2$, Sb_2O_3 and $Sb(OH)_3$ at higher pH. Though Sb^{3+} ion is only exists at high

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acidity and is hard to see under other conditions, we adopt reaction equation based on Sb^{3+} for sake of calculation in following. Activity was replaced by concentration on the calculation because of lack of activity coefficient. There are four kinds of element, twenty one kinds of chemical matter and involving four numbers of multiphase equilibrium of solution-solid such as solution-SbOCl, solution-$Sb_4O_5Cl_2$, solution-Sb_2O_3 and solution-$Sb(OH)_3$ in the system. So we can divide this system into four parts to study, then overlap the four diagrams into one of this system.

In the $\lg C$-pH diagrams, there is only one solid matter that can stably exist at each pH value except the triple point. There are 18 kinds of matter in the reaction system for someone solution-solid equilibrium, therefore the number of independent reaction is 18− 4= 14.

The independent reactions of this system can be expressed as follows, where (s) indicates solid and (l) indicates liquid:

1) Reaction of water dissociation

$$H_2O = H^+ + OH^- \qquad K_w = [H^+][OH^-] \tag{1}$$

2) Reactions of Sb^{3+}, Cl^- and their complex ions

$$Sb^{3+} + nCl^- = SbCl_n^{(3-n)} \quad (n = 1, 2, \cdots, 6)$$

$$\beta_n = \frac{[SbCl_n^{(3-n)}]}{[Sb^{3+}][Cl^-]^n} \tag{2}$$

3) Reactions of Sb^{3+}, OH^- and their complex ions

$$Sb^{3+} + mOH^- = Sb(OH)_m^{(3-m)} \quad (m = 1, 2, 3, 4)$$

$$\beta'_m = \frac{[Sb(OH)_m^{(3-m)}]}{[Sb^{3+}][OH^-]^m} \tag{3}$$

4) Other reactions in this system

$$Sb^{3+} + Cl^- + H_2O = SbOCl(s) + 2H^+$$

$$K_1 = \frac{[H^+]^2}{[Sb^{3+}][Cl^-]} \tag{4}$$

$$Sb^{3+} + H_2O = SbO^+ + 2H^+$$

$$K_2 = \frac{[H^+]^2[SbO^+]}{[Sb^{3+}]} \tag{5}$$

$$Sb^{3+} + 2H_2O = SbO_2^- + 4H^+$$

$$K_3 = \frac{[H^+]^4[SbO_2^-]}{[Sb^{3+}]} \tag{6}$$

$$4Sb^{3+} + 2Cl^- + 5H_2O = Sb_4O_5Cl_2(s) + 10H^+$$

$$K_4 = \frac{[H^+]^{10}}{[Sb^{3+}]^4[Cl^-]^2} \tag{7}$$

$$2Sb^{3+} + 3H_2O = Sb_2O_3(s) + 6H^+$$

$$K_5 = \frac{[H^+]^6}{[Sb^{3+}]^2} \tag{8}$$

$$Sb^{3+} + 3OH^- = Sb(OH)_3(s)$$

$$K_{sp} = [Sb^{3+}][OH^-]^3 \tag{9}$$

2.2 Selection of thermodynamics data

The Gibbs free energies of Sb^{3+}, SbOCl and $Sb_4O_5Cl_2$ are selected from reference [5]. The complex constants of Sb^{3+} with Cl^- and Sb^{3+} with OH^- are from reference [6]. The Gibbs free energies of others are from reference [7]. Some thermodynamics data are listed in Table 1 and Table 2 as following.

Table 1 Complex constants of Sb^{3+} with Cl^- and Sb^{3+} with OH^- complex ions at 298 K

Complex constants	$\lg\beta_1$	$\lg\beta_2$	$\lg\beta_3$	$\lg\beta_4$	$\lg\beta_5$	$\lg\beta_6$
Sb^{3+}-Cl^-	2.26	3.49	4.18	4.72	4.7	4.10
Sb^{3+}-OH^-	–	24.3	36.7	38.3	–	–

2.3 Mathematical model

According to the law of simultaneous equilibrium and the law of conservation of mass, some equations of ion concentration in the solution deduced from reactions above can be expressed as follows.

1) The total concentration of Sb^{3+}-Cl^- complex $[SbCl]_T$:

Table 2 Gibbs free energy of some matters at 298 K

Matters	H_2O	OH^-	Cl^-	Sb^{3+}	SbO^+	SbO_2^-	SbOCl	$Sb_4O_5Cl_2$	Sb_2O_3
$\Delta G^\ominus$/kJ·mol^{-1}	−273.178	−157.293	−131.056	69.467	−175.64	−339.74	−335.908	−1349.533	−626.604

$$[SbCl]_T = \sum_{n=1}^{6}[SbCl_n^{(3-n)}] = \sum_{n=1}^{6}\beta_n[Sb^{3+}][Cl^-]^n = [Sb^{3+}]\sum_{n=1}^{6}\beta_n[Cl^-]^n \quad (10)$$

2) The total concentration of Sb^{3+}-OH^- complex $[SbOH]_T$:

$$[SbOH]_T = \sum_{m=1}^{4}[SbOH_m^{(3-m)}] = \sum_{m=1}^{4}\beta'_m[Sb^{3+}][OH^-]^m = [Sb^{3+}]\sum_{m=1}^{4}\beta'_m[OH^-]^m \quad (11)$$

3) The total concentration of Sb^{3+} $[Sb^{3+}]_T$:

$$[Sb^{3+}]_T = [Sb^{3+}] + [SbCl]_T + [SbOH]_T + [SbO^+] + [SbO_2^-] = [Sb^{3+}] + [Sb^{3+}]\sum_{n=1}^{6}\beta_n[Cl^-]^n + [Sb^{3+}]\sum_{m=1}^{4}\beta'_m[OH^-]^m + K_2\frac{[Sb^{3+}]}{[H^+]^2} + K_3\frac{[Sb^{3+}]}{[H^+]^4} = [Sb^{3+}]\{1 + \sum_{n=1}^{6}\beta_n[Cl^-]^n + \sum_{m=1}^{4}\beta'_m[OH^-]^m + \frac{K_2}{[H^+]^2} + \frac{K_3}{[H^+]^4}\} \quad (12)$$

4) The total concentration of Cl^- $[Cl^-]_T$:

$$[Cl^-]_T = [Cl^-] + [Sb^{3+}]\sum_{n=1}^{6}n\beta_n[Cl^-]^n \quad (13)$$

There are six relationship equations and eight variates for a solid-solution equilibrium according to the reactions above, thus the degree of freedom is 8 − 6 = 2. If we consider it in phase rule, the degree of freedom $f = c - p + 2 = 4 - 2 + 2 = 4$, so f is 2 when it is at constant temperature and constant pressure. In the predecessor's calculation, the total concentration of some ions is always fixed, but every total concentration is variable with pH in the system. So it was incorrect if we would suppose some concentration is fixed. In order to solve these equations, we supposed that the total quantity of Sb (III) (concentration) and the total quantities of Cl (concentration) are fixed, and supposed they are C^0_{Sb} and C^0_{Cl}. Therefore it is added a stoichiometry equation for each solid-solution equilibrium, and there are seven equations and eight variates and the f is 1. So we can solve these equations if the pH is given.

(1) Solution-SbOCl equilibrium

Because 1 mol SbOCl needs 1 mol Cl^- and 1 mol Sb^{3+} according to equation (4), then $[Cl^-]_T$ is

$$[Cl^-]_T = C^0_{Cl} - C^0_{Sb} + [Sb^{3+}]_T$$

$[Sb^{3+}]$ in the solution is

$$[Sb^{3+}] = \frac{[H^+]^2}{K_1[Cl^-]}$$

The two equations above are substituted into (12), (13) and adjusted, then we get an equation as following:

$$\frac{[H^+]^2}{K_1}\{\sum_{n=1}^{6}(1-n)\beta_n[Cl^-]^n + \sum_{m=1}^{4}\beta'_m[OH^-]^m + \frac{K_2}{[H^+]^2} + \frac{K_3}{[H^+]^4} + 1\} - [Cl^-]^2 + (C^0_{Cl} - C^0_{Sb})[Cl^-] = 0 \quad (14)$$

Under the initial condition as above, we can get $[Cl^-]$ if pH is given, then substitute $[Cl^-]$, $[Sb^{3+}]$ and $[H^+]$ into (10) ~ (13) we can get $[SbCl]_T$, $[SbOH]_T$, $[Sb^{3+}]_T$ and $[Cl^-]_T$.

(2) Solution-$Sb_4O_5Cl_2$ equilibrium

Because 1 mol $Sb_4O_5Cl_2$ needs 2 mol Cl^- and 4 mol Sb^{3+} according to equation (7), then $[Cl^-]_T$ is:

$$[Cl^-]_T = C^0_{Cl} - 0.5C^0_{Sb} + 0.5[Sb^{3+}]_T$$

$[Sb^{3+}]$ in the solution is:

$$[Sb^{3+}] = \frac{[H^+]^{5/2}}{K_4^{1/4}[Cl^-]^{1/2}}$$

The two equations above are substituted into (12), (13) and adjusted, then we get an equation as following:

$$\frac{[H^+]^{5/2}}{2K_4^{1/2}[Cl]^{1/2}}\{\sum_{n=1}^{6}(1-n)\beta_n[Cl^-]^n + \sum_{m=1}^{4}\beta'_m[OH^-]^m + \frac{K_2}{[H^+]^2} + \frac{K_3}{[H^+]^4} + 1\} - [Cl^-] + (C^0_{Cl} - 0.5C^0_{Sb}) = 0 \quad (15)$$

Under the initial condition as above, we can get $[Cl^-]$ if pH is given, then substitute $[Cl^-]$, $[Sb^{3+}]$ and $[H^+]$ into (10) ~ (13) we can get $[SbCl]_T$, $[SbOH]_T$, $[Sb^{3+}]_T$ and $[Cl^-]_T$.

(3) Solution-Sb_2O_3 equilibrium

Because 1 mol Sb_2O_3 only needs 2 mol Sb^{3+} according to equation (8), then $[Cl^-]_T$ is:

$$[Cl^-]_T = C^0_{Cl}$$

$[Sb^{3+}]$ in the solution is

$$[Sb^{3+}] = \frac{[H^+]^3}{K_5^{1/2}}$$

The two equations above are substituted into (12), (13) and adjusted, then we get an equation as following:

$$[Cl^-] + \frac{[H^+]^3}{K_5^{1/2}} \sum_{n=1}^{6} n\beta_n [Cl^-]^n - C^0_{Cl} = 0 \quad (16)$$

Under the initial condition as above, we can get $[Cl^-]$ if pH is given, then substitute $[Cl^-]$, $[Sb^{3+}]$ and $[H^+]$ into (10) ~ (13) we can get $[SbCl]_T$, $[SbOH]_T$, $[Sb^{3+}]_T$ and $[Cl^-]_T$.

(4) Solution-$Sb(OH)_3$ equilibrium

Because 1 mol $Sb(OH)_3$ only needs 1 mol Sb^{3+} according to equation (9), then $[Cl^-]_T$ is

$$[Cl^-]_T = C^0_{Cl}$$

$[Sb^{3+}]$ in the solution is

$$[Sb^{3+}] = \frac{K_{sp}}{[OH^-]^3}$$

The two equations above are substituted into (12), (13) and adjusted, then we get an equation as following:

$$[Cl^-] + \frac{K_{sp}}{[OH^-]^3} \sum_{n=1}^{6} n\beta_n [Cl^-]^n - C^0_{Cl} = 0 \quad (17)$$

Under the initial condition as above, we can get $[Cl^-]$ if pH is given, then substitute $[Cl^-]$, $[Sb^{3+}]$ and $[H^+]$ into (10) ~ (13) we can get $[SbCl]_T$, $[SbOH]_T$, $[Sb^{3+}]_T$ and $[Cl^-]_T$.

3 RESULTS AND ANALYSIS

Initial condition C^0_{Sb} and C^0_{Cl} are given, the $\lg C$-pH diagram of SbOCl-solution equilibrium is calculated by solving equation (14) and (12), they are shown in Fig. 1. It is stabilization zone of SbOCl on the curve above, and the below is solution zone. It is shown that the C^0_{Sb} and C^0_{Cl} have important effects on stabilization zone of SbOCl in Fig. 1. The diagrams of $Sb_4O_5Cl_2$, Sb_2O_3 and $Sb(OH)_3$ will be calculated in the same way. We can get the stabilization zone diagram of these solid matters at different pH by overlapping them which have same initial condition.

The overlapped diagram of C^0_{Sb} = 1.0 mol/L, C^0_{Cl} = 3.0 mol/L and C^0_{Sb} = 0.1 mol/L, C^0_{Cl} = 0.3 mol/L is shown in Fig. 2. It is seen that the pH of hydrolysis is low when C^0_{Sb} and C^0_{Cl} are low, which is useful for eliminating foreign matter, but it can increase the quantity of waste water. The pH of hydrolysis completely is approximately 0.5 when C^0_{Sb} is 0.1 mol/L, which is in the range of pH in practical hydrolysis. It is commonly adding 10 times water in practical hydrolysis, which is correspond to the result of calculation. SbOCl is not stable when C^0_{Sb} < 1 mol/L and pH > 1, but the stabilization zone of $Sb_4O_5Cl_2$ is wide. When pH > 7, it is stabilization zone of Sb_2O_3. $Sb(OH)_3(s)$ does not exist if there is Cl^- in the solution.

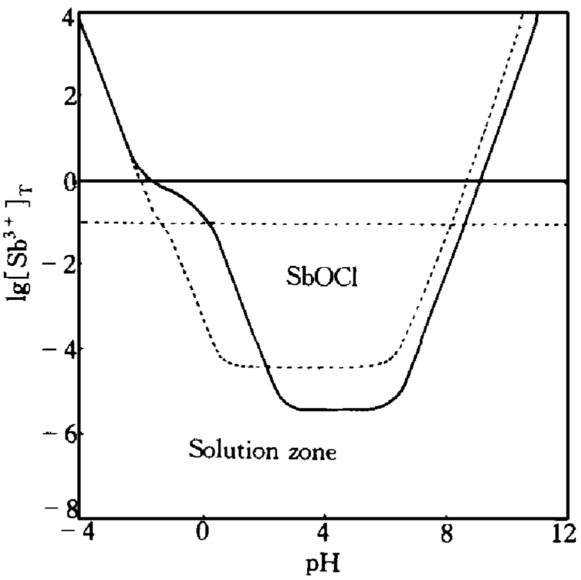

Fig. 1 lg$C$-pH diagram of SbOCl-solution

——— C^0_{Sb} = 1.0 mol/L, C^0_{Cl} = 3.0 mol/L;

…… C^0_{Sb} = 0.1 mol/L, C^0_{Cl} = 0.3 mol/L

There are many complex ions and other ions in the solution as discussed above. In order to study and research which ions are dominating at some pH, we calculated the lg$C$-pH curves of Sb^{3+}, SbO^+, SbO_2^- and all of complex ions and overlapped them in stabilization zones and get the diagram of ion equilibrium as shown in Fig. 3, which is calculated that total concentration of $SbCl_3$ is 1 mol/L. [Sb^{3+}] is higher when pH < 0, but it is so few that it may be neglect when pH > 0. The dominating ions are complex ions of Sb^{3+} with Cl^- when pH is from 0 to 3. So [Cl^-] is the major factor to effect hydrolysis. When pH < 3, SbO^+ is an another major ion. SbO_2^- is dominating ion when pH > 7. When pH > 10, [SbO_2^-] is increasing over 10~ 6 mol/L, which means Sb_2O_3 begin to be dissolved. Although Sb^{3+} and OH^- maybe react to complex ions, their concentration are so few that they have little effect on this system.

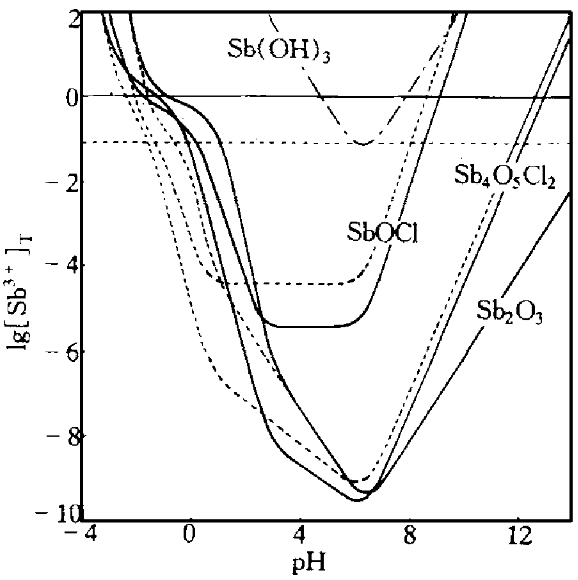

Fig. 2 lg$C$-pH diagram of Sb(III)-Cl-H$_2$O system

———C^0_{Sb} = 1.0 mol/L, C^0_{Cl} = 3.0 mol/L;

……—C^0_{Sb} = 0.1 mol/L, C^0_{Cl} = 0.3 mol/L

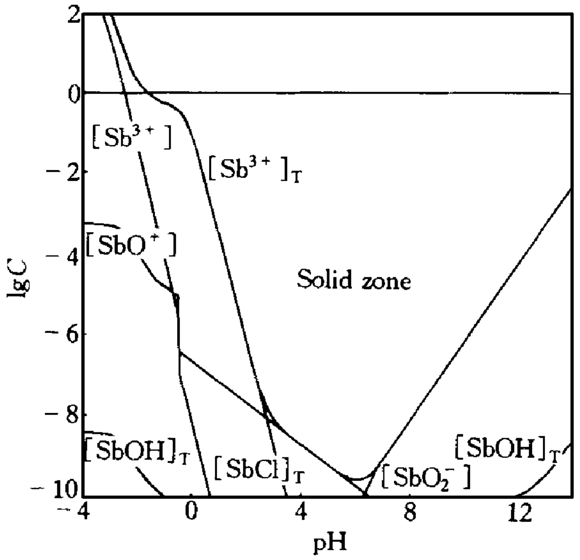

Fig. 3 Ion equilibrium of Sb(III)-Cl-H$_2$O system

C^0_{Sb} = 1.0 mol/L, C^0_{Cl} = 3.0 mol/L

Fig. 4 shows the effect of concentration of Cl^-. The pH of complete hydrolysis and complete dechloride are decreasing with C^0_{Cl} decrease. C^0_{Cl} has smaller effect on Sb_2O_3-solution equilibrium, and when pH > 4 the effect is little. But C^0_{Cl} has prominent effect to the equilibrium of SbOCl-solution and $Sb_5O_4Cl_2$-solution. The stabilization zone of SbOCl is enlarging with C^0_{Cl} decreasing.

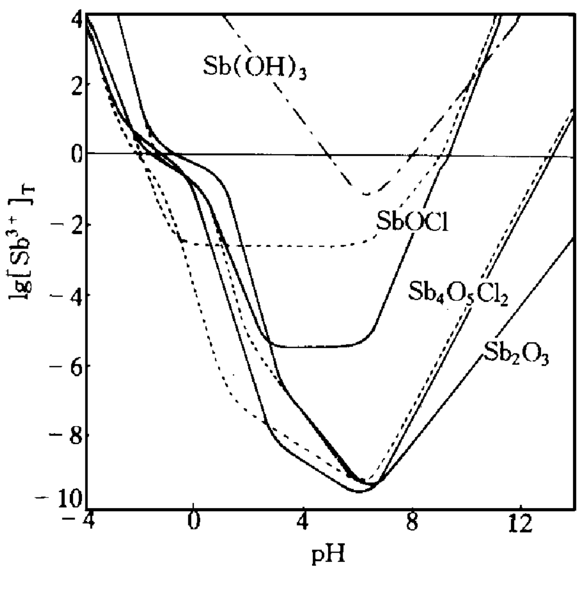

Fig. 4 Effect of C^0_{Cl} on hydrolysis process of Sb(III)-Cl-H$_2$O system

———C^0_{Sb} = 1.0 mol/L, C^0_{Cl} = 3.0 mol/L;

……—C^0_{Sb} = 1.0 mol/L, C^0_{Cl} = 1.0 mol/L

Fig. 5 shows the effect of C^0_{Sb}. The pH of complete hydrolysis and complete dechloride are decreasing with C^0_{Sb} decrease too. C^0_{Sb} has effect on equilibrium of SbOCl-solution and $Sb_4O_5Cl_2$-solution, but has little effect on Sb_2O_3-solution equilibrium. By the diagrams above, the process of dechloride in produce Sb_2O_3 is mainly process of transfer $Sb_4O_5Cl_2$ to Sb_2O_3. When pH > 5, the C^0_{Sb} and C^0_{Cl} have little effect on Sb_2O_3-solution equilibrium, but C^0_{Cl} is the major factor to effect $Sb_4O_5Cl_2$-solution equilibrium.

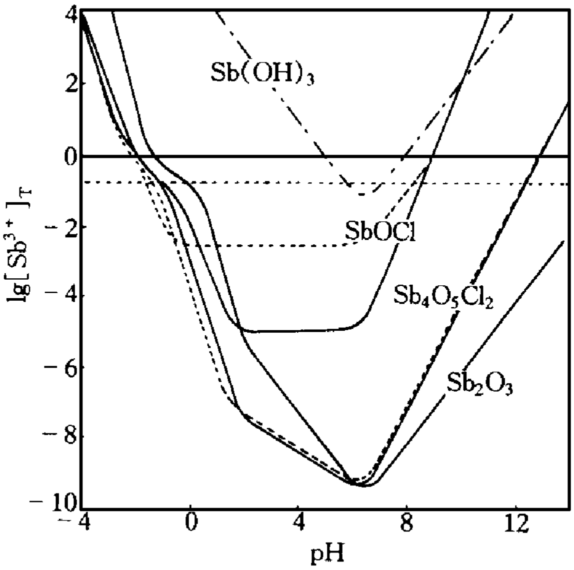

Fig. 5 Effect of C^0_{Sb} on hydrolysis process of Sb(Ⅲ)-Cl-H$_2$O system

——C^0_{Sb}= 1.0 mol/L, C^0_{Cl}= 1.0 mol/L;
……C^0_{Sb}= 0.3 mol/L, C^0_{Cl}= 1.0 mol/L

The effect of C^0_{Cl} on pH of complete dechloride is shown in Fig. 6. The pH of dechloride is low when C^0_{Cl} is low, and it increases with C^0_{Cl} increasing. The pH of dechloride is 6 when C^0_{Cl} is 1 mol/L, and it is increased to 6.7 when C^0_{Cl} is increased to 3 mol/L. The pH has some change when C^0_{Cl} is low, but it has little change when C^0_{Cl} is high.

4 CONCLUSIONS

(1) It is studied that the effect of pH, Sb^{3+}, Cl^- on the stabilization zone of solid matter in Sb(Ⅲ)-Cl-H$_2$O system and on the process of producing Sb_2O_3 by hydrometallurgy.

(2) Using the diagrams shown in the paper, the technology parameters of process of hydrolysis and dechloride in producing Sb_2O_3 by hydrometallurgy will be simply and obviously selected in the initiation. The results of calculation are similar to that of the practical process.

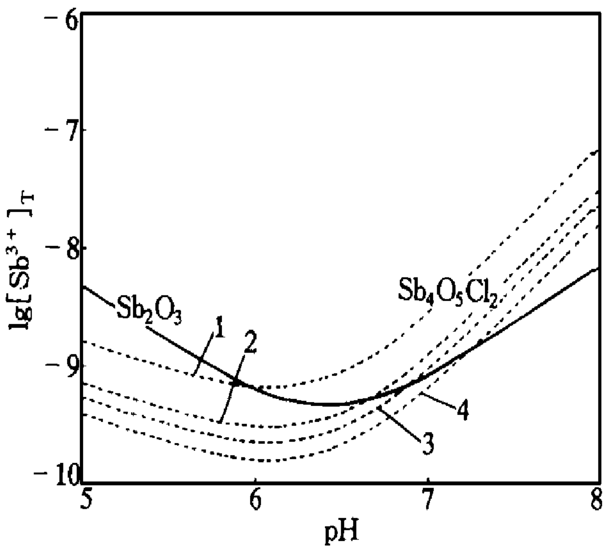

Fig. 6 Selection of pH in decholoride process

——Sb_2O_3; ……$Sb_4O_5Cl_2$
1—C^0_{Sb}= 1.0 mol/L, C^0_{Cl}= 1.0 mol/L;
2—C^0_{Sb}= 1.0 mol/L, C^0_{Cl}= 3.0 mol/L;
3—C^0_{Sb}= 1.0 mol/L, C^0_{Cl}= 5.0 mol/L;
4—C^0_{Sb}= 1.0 mol/L, C^0_{Cl}= 10.0 mol/L

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