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Thermodynamic calculation of Sn(IV)-NH^{4+}-Cl^--H_2O system①

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Abstract: According to the principles of simultaneous equilibrium and electronic charge neutrality, the thermodynamics of Sn(IV)-NH^{4+}-Cl^--H_2O system under normal condition was calculated. Relation between all sorts of complex of Sn^{4+} and pH was plotted. Based on thermodynamics analysis and calculation, some experiments were done to validate the relation between the total concentration of tin ion and pH in this system. The results suggest that the total concentration of ammonium and pH are the most important factors which determine whether $(NH_4)_2SnCl_6$ or $Sn(OH)_4$ exists in this system. Results further suggest when contnet of HCl is more than 6 mol/L, Sn^{4+} in this system will be also precipitated in the form of $(NH_4)_2SnCl_6$. These results lay the solid theory foundation to prepare pure $(NH_4)_2SnCl_6$, a promising substitution for $SnCl_4 \cdot 5H_2O$ to prepare antimony doped tin oxide(ATO) and indium tin oxide(ITO), from the tinny material.

Key words: thermodynamic calculation; Sn(IV)-NH^{4+}-Cl^--H_2O; $(NH_4)_2SnCl_6$
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1 INTRODUCTION

Antimony doped tin oxide, for short ATO, with excellent conductivity performance, is a kind of metal oxide powders. Due to its wide application, the preparation and application are abroad in the world.

At present, tin compounds such as $SnCl_4 \cdot 5H_2O$, SnO_2 and $Sn(OH)_4$ are usually used to prepare ATO powders[1-8]. All these stannic compounds are prepared by pure, expensive tin; furthermore, $SnCl_4$ is very easy to volatilize, which causes hard measurement; in addition, using SnO_2 or $SnO_2 \cdot 2H_2O$ to prepare ATO demand for rigorous condition. Therefore, finding a more inexpensive, more applicable stannic compound to substitute $SnCl_4 \cdot 5H_2O$ for preparing ATO becomes more significant. Unfortunately, there are few researches and thermodynamic plots in the system of $SnCl_4$-NH4Cl-HCl-H_2O in open literatures.

Using Computing-Exponential-Equations method, Tang et al[9-13] have ever carried out the thermodynamics researches of Sb(Ⅲ)-Cl^--H_2O and Zn(Ⅱ)-NH_3 systems. To the system of Sn(IV)-NH^{4+}-Cl^--H_2O, however, nothing has been done yet. So, based on thermodynamics analysis to the system of Sn(Ⅳ)-NH^{4+}-Cl^--H_2O, the thermodynamics relationship plots have been constructed in the paper. These results show that the $SnCl_4$ in this system can be precipitated in the form of $(NH_4)_2SnCl_6$ at high acidity condition, which provides the theory basement for using stannic material to prepare pure $(NH_4)_2SnCl_6$.

2 SPECIES AND THERMODYNAMICS EQUILIBRIA

2.1 Species in this system

Species existing in this system are as follows:
$SnCl_i^{4-i}$ $(i=0, 1, 2, 3, 4, 5, 6)$, $Sn(OH)_j^{4-j}$ $(j=1, 2, 3, 4)$, NH_4OH; NH_4^+; NH_4Cl_{aq}; H^+; OH^-; $HCl_{(aq)}$, Cl^-.

2.2 Thermodynamic equilibria and corresponding data of species in this system

There exist some chloride complex equilibria in this system as follows.

$$Sn^{4+} + iCl^- \rightleftharpoons SnCl_i^{4-i} \quad (i=1-6)$$

$$[SnCl_i^{4-i}] = [Sn^{4+}] \cdot \beta_i \cdot [Cl^-]^i \tag{1}$$

$$Sn^{4+} + jH_2O \rightleftharpoons Sn(OH)_j^{4-j} + jH^+ \quad (j=1-4)$$

$$[Sn(OH)_j^{4-j}] = [Sn^{4+}] \cdot \exp\left(\frac{-\Delta G_j}{2.303RT} + j\,pH\right) \tag{2}$$

Under high acidity condition these equilibria give priority to the homeostasis of $(NH_4)_2SnCl_6(s)$ with the solution:

$$(NH_4)SnCl_{6(s)} \rightleftharpoons 2NH_4^+ + SnCl_6^{2-}$$

Based on this equilibrium, we can determine the liberation stannic ionic concentration in this system:

$$[Sn^{4+}] = \frac{K_{sp}}{\beta_6 \cdot [NH_4^+]^2 \cdot [Cl^-]^6} \tag{3}$$

Under low acidity condition, the homeostasis give priority to the equilibrium as

$$Sn^{4+} + 4OH^- \rightleftharpoons Sn(OH)_3(s) \tag{4}$$

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We can also determine the liberation stannic ionic concentration by this equilibrium

$$[Sn^{4+}] = \frac{K_{sp}}{[OH^-]^4} \quad (5)$$

There still exists other chemistry equilibria in this system:

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$[OH^-] = \frac{K_{sp}}{[H^+]} = \exp(-32.37 + 2.303\text{pH}) \quad (6)$$

$$NH_4Cl(aq) \rightleftharpoons NH_4^+ + Cl^-$$

$$[NH_4Cl_{(aq)}] = 10^{3.15\times10^{-3}}[NH_4^+][Cl^-] \quad (7)$$

The complex equilibria stable constants and standard Gibbs free energies[14] of relation species are lined in Tables 1 and 2, respectively.

Table 1 Complex constant of Sn^{4+} with Cl^- and Sn^{4+} with OH^- ($T = 298$ K)

Species	$\lg\beta_i$	Species	$\lg\beta_j$
$SnCl^{3+}$	0.62[14]	$Sn(OH)^{3+}$	0.49[14]
$SnCl_2^{2+}$	1.38[14]	$Sn(OH)_2^{2+}$	0.30[14]
$SnCl_3^+$	2.09[14]	$Sn(OH)_3^+$	0.58[14]
$SnCl_4$	2.42[14]	$SnOH_{4(aq)}$	2.61[14]
$SnCl_5^-$	2.81[14]	$SnCl_6^{2-}$	4.00[15]

Table 2 Gibbs free energy of substances concerned at 298 K ($J\cdot mol^{-1}$)

Species	$\Delta_f G_r^T$	Species	$\Delta_f G_r^T$
$SnCl^{3+}$	−132 208	$Sn(OH)^{3+}$	−152 603
$SnCl_2^{2+}$	−267 718	$Sn(OH)_2^{2+}$	−311 586
$SnCl_3^+$	−402 941	$Sn(OH)_3^+$	−474 506
$SnCl_4$	−535 995	$Sn(OH)_{4(aq)}$	−643 989
$SnCl_5^-$	−669 392	Sn^{4+}	2 500[13]
$SnCl_6^{2-}$	−807 355	OH^-	−157 898[13]
H_2O	−238 098[13]	Cl^-	−131 170[13]
NH_4^+	−79 800		

2.3 Thermodynamic simultaneous equations

2.3.1 Mass equilibria

According to the principle of simultaneous equilibrium, the following equations can be formed as follow.

1) Stannic mass equation

$$[Sn^{4+}]_T = [Sn^{4+}] + \sum_{i=1}^{6}[SnCl_i^{4-i}] + \sum_{j=1}^{4}[Sn(OH)_j^{4-j}] \quad (8)$$

2) Chloride mass equation

$$[Cl^-]_T = [Cl^-] + \sum_{i=1}^{6} i\cdot[SnCl_i^{4-i}] + [HCl_{(aq)}] + [NH_4Cl_{(aq)}] \quad (9)$$

3) Ammoniac mass equation

$$[NH_4^+]_T = [NH_4^+] + [NH_4Cl_{(aq)}] \quad (10)$$

2.3.2 Electric charge equilibria

According to the principle of electronic charge neutrality, the electric charge equilibria equation can be formed as

$$4[Sn^{4+}] + [H^+] + [NH_4^+] = [Cl^-]_T + [OH]^- \quad (11)$$

where $[Sn^{4+}]$, $[Sn^{4+}]_T$, $[Cl^-]$, $[Cl^-]_T$, $[NH^{4+}]$ and $[NH_4^+]_T$ are, respectively, concentration (mol/L) of liberation stannic ion, sum stannic ion, liberation chloride ion, sum chloride, liberation ammonium, and sum ammonium for simple $[N]_T$.

Under high acidity condition, liberation stannic ironic concentration is determined by equilibrium of $(NH_4)_2SnCl_6$ with the solution; while at low acidity, its concentration is determined by the equilibrium of $Sn(OH)_4$ with the solution. In Eqns. (8)−(11), there exist five unknown value such as $[Sn^{4+}]_T$, $[Cl^-]$, pH, $[Cl^-]_T$ and $[NH_4^+]_T$, only fix everyone of them, the rest can be obtained by solving the simultaneous equations.

2.3 Determination of K_{sp} of $(NH_4)_2SnCl_6$

The value of K_{sp} is key to solving this simultaneous equation, but unfortunately, its value could not be found from the present literature, neither for the value of $\Delta_f G_i^T$ and $\Delta_f G_i^T$. Here an approximate way is used to calculate this value as follow.

Put a quantitative $(NH_4)_2SnCl_6$ into a cup of quantitative distilled water, when it reaches the equilibrium point, there exist those homeostasis in this solution.

$$(NH_4)_2SnCl_6 = 2NH_4^+ + SnCl_6^{2-}$$

$$K_{sp} = [SnCl_6^{2-}]\cdot[NH_4^+]^2 \quad (12)$$

Using the stannic ion chloride complex equilibria, we can obtain

$$[Sn^{4+}] = \frac{K'_6\cdot K'_5\cdot K'_4\cdot K'_3\cdot K'_2\cdot K'_1\cdot[SnCl_6^{2-}]}{[Cl^-]^6}$$

Based on the definition of Step by Step Dissociation Equilibrium, and the fact that 100 parts of water can dissolve 33.3 parts of $(NH_4)_2SnCl_6$[15], combining those above relation equations, we can gain equations as

$$[Sn^{4+}]_T = [SnCl_6^{2-}]\cdot\Big(1 + \frac{K'_1}{[Cl^-]} + \frac{K'_2\cdot K'_1}{[Cl^-]^2} + \frac{K'_3\cdot K'_2\cdot K'_1}{[Cl^-]^3} + \frac{K'_4\cdot K'_3\cdot K'_2\cdot K'_1}{[Cl^-]^4} + \frac{K'_5\cdot K'_4\cdot K'_3\cdot K'_2\cdot K'_1}{[Cl^-]^5} +$$

$$\frac{K'_6 \cdot K'_5 \cdot K'_4 \cdot K'_3 \cdot K'_2 \cdot K'_1}{[\mathrm{Cl}^-]^6}) \quad (13)$$

$$[\mathrm{Cl}^-]_T = [\mathrm{Cl}^-] + [\mathrm{SnCl}_6^{2-}] \cdot (6 + \frac{K'_1}{[\mathrm{Cl}^-]} + \frac{2 \cdot K'_2 \cdot K'_1}{[\mathrm{Cl}^-]^2} + \frac{3 \cdot K'_3 \cdot K'_2 \cdot K'_1}{[\mathrm{Cl}^-]^3} + \frac{4 \cdot K'_4 \cdot K'_3 \cdot K'_2 \cdot K'_1}{[\mathrm{Cl}^-]^4} + \frac{5 \cdot K'_5 \cdot K'_4 \cdot K'_3 \cdot K'_2 \cdot K'_1}{[\mathrm{Cl}^-]^5}) \quad (14)$$

To solve this simultaneous equation, the concentration of $SnCl_6^-$ can be got, then the value of K_{sp} can be obtained.

3 RESULTS AND DISSCUSION

3.1 Thermodynamic relation plot at high acidity

Under high acidity condition, $(NH_4)_2SnCl_6$ is in equilibrium with the solution, the concentration of liberation stannic ion can be obtained from equation (3). After determining the concentration of NH^{4+}, this simultaneous equation can be solved to obtain Fig. 1 − Fig. 3.

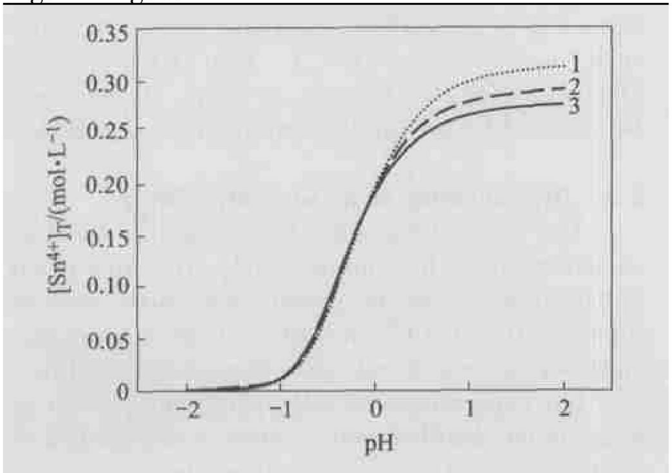

Fig. 1 Theoretical relation between $[Sn^{4+}]_T$ and pH under high acidity condition
1 —$[N]_T$= 3 mol/L; 2 —$[N]_T$= 3.5 mol/L; 3 —$[N]_T$= 4 mol/L

It can be seen from Figs. 1 − 3 that, under high acidity condition the total stannic concentration will go to a relative low value (zero). The cause is that solid phase of $(NH_4)_2SnCl_6$ is formed in this system. When changing the total ammonium concentration from 3 to 4 mol/L, the effect of total chloride concentration is nearly unchangeable.

3.2 Thermodynamic plots at low acidity condition

Under low acidity condition, all the stannic ion is, respectively, kept equilibrium with $Sn(OH)_4$. The concentration of liberation stannic ion is determined by Eqn. (4), when the total ammonium concentration is fixed, this simultaneous equation can be solved, and the results are shown in Figs. 4 to 6.

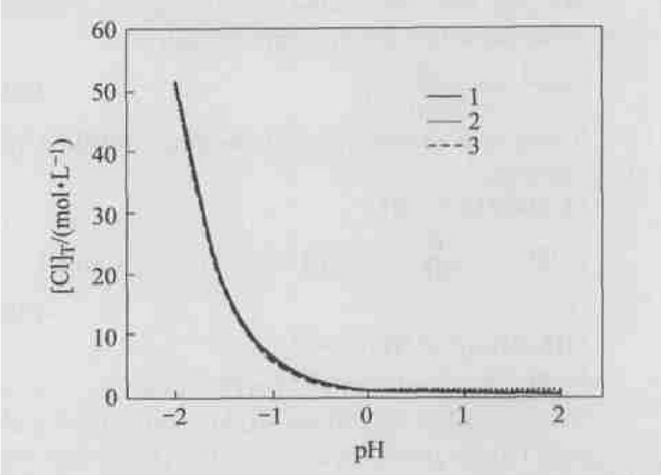

Fig. 2 Theoretical relation between $[Cl^-]_T$ and pH under high acidity condition
1 —$[N]_T$= 3 mol/L; 2 —$[N]_T$= 3.5 mol/L; 3 —$[N]_T$= 4 mol/L

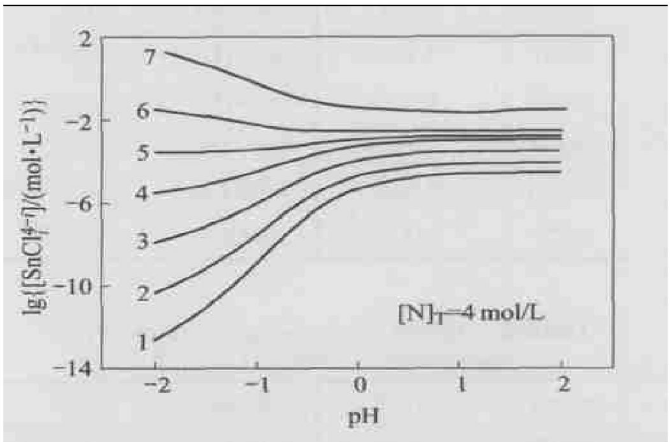

Fig. 3 Theoretical relation between complex constants of Sn^{4+} and pH under high acidity condition
1 —Sn^{4+}; 2 —$SnCl^{3+}$; 3 —$SnCl_2^{2+}$; 4 —$SnCl^{3+}$; 5 —$SnCl_4$; 6 —$SnCl_5^-$; 7 —$SnCl_6^{2-}$

From Figs. 4 to Fig. 6, it can seen that with the decline of acidity, the total concentration of tin is sharply gone to zero when pH is equal to 0.8. During this cause, the total concentration of chloride in this system shows the same change rules.

3.3 Synthesis of two thermodynamic plots

With the changing of pH, two solid phase, $(NH_4)_2SnCl_6(s)$ and $Sn(OH)_4$, will appear respectively in Sn(Ⅳ)-NH_4^+-Cl^--H_2O system. The cross point is the coexisting point of these two solid phase; elevating value of pH from this point, all the stannic ion is, respectively, in equilibrium with $Sn(OH)_4$; otherwise, all the stannic ion is, respectively, in equilibrium with $(NH_4)_2SnCl_6(s)$. Fig. 7 shows the synthesis plot of the two plots.

From Fig. 7, it can be seen that in this system,

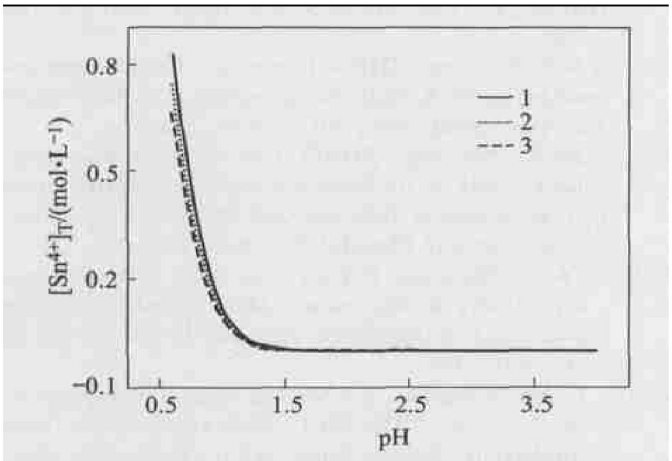

Fig. 4 Theoretical relation between $[Sn^{4+}]_T$ and pH under low acidity condition
1—$[N]_T$= 3 mol/L; 2—$[N]_T$= 3.5 mol/L; 3—$[N]_T$= 4 mol/L

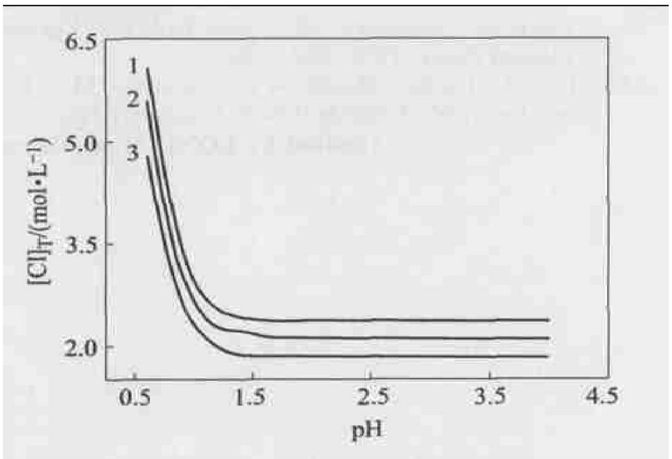

Fig. 5 Theoretical relation between $[Cl^-]_T$ and pH in low acidity condition
1—$[N]_T$= 3 mol/L; 2—$[N]_T$= 3.5 mol/L; 3—$[N]_T$= 4 mol/L

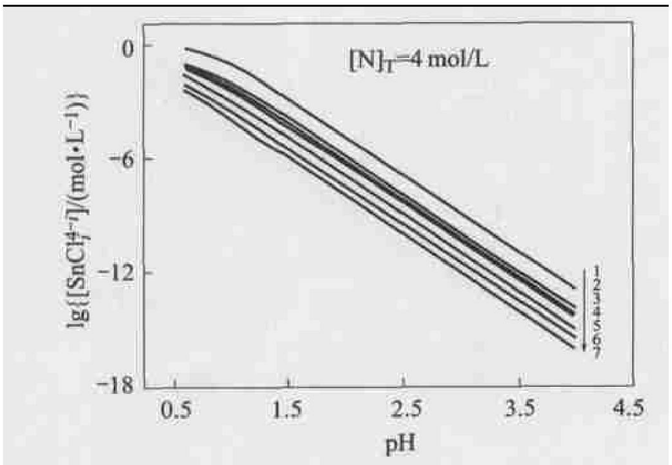

Fig. 6 Theoretical relation between complex constants of Sn^{4+} and pH in low acidity condition
1—Sn^{4+}; 2—$SnCl^{3+}$; 3—$SnCl_2^{2+}$; 4—$SnCl^{3+}$; 5—$SnCl_4$; 6—$SnCl^{5-}$; 7—$SnCl_6^{2-}$

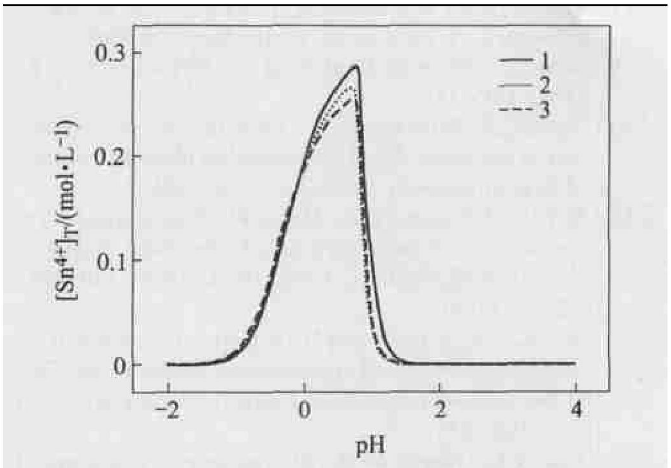

Fig. 7 Comprehensive theoretical relation between $[Sn^{4+}]_T$ and pH in this system
1—$[N]_T$= 3 mol/L; 2—$[N]_T$= 3.5 mol/L; 3—$[N]_T$= 4 mol/L

the concentration of total stannic ions reaches the maximum when pH is equal to 0.8; when pH< 0.8, the concentration of total stannic ions decline sharply because of formation of $(NH_4)_2SnCl_{6(s)}$:

$$SnCl_i^{4-i} + 2NH_4Cl = (NH_4)_2SnCl_6\downarrow + (i-4)Cl^-$$

When pH> 0.8, the concentration of total stannic ions also decline sharply, because $Sn(OH)_{4(s)}$ forms.

4 CONCLUSIONS

1) The value of pH and the total concentration of ammonium are the most important factors which affect the total concentration of stannic ions; when pH = 0.8, the total concentration of stannic ions reaches the maximum, otherwise, with the incline or decline of pH, the total concentration of stannic ions declines sharply because of the formation of solid phase of $(NH_4)_2SnCl_6$ or $Sn(OH)_4$.

2) When changing the total concentration of ammonium, the total concentration of stannic ion seems little change. Only when the point of pH equals to 0.8, can it show some effects; with increasing total ammonium concentration, the total concentration of stannic ion inclines gradually.

3) The effects of chloride concentration accord to the total concentration of ammonium.

4) When pH< −1, this system suits for preparing $(NH_4)_2SnCl_6$, while pH> 1.5, this system suits for preparing $Sn(OH)_4$.

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