[Article ID] 1003- 6326(2001)01- 0150- 04

A new look at φ-pH diagram (II)①

——All-equilibrium φ-pH diagram for M-ligand-H_2O system

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[Abstract] A new viewpoint on metal complex system was proposed on traditional M-ligand-H_2O system φ-pH diagrams. Simultaneous equilibrium principle and activity term method were used to plot all-equilibrium φ-pH diagrams for M-ligand-H_2O systems based on the thermochemical database developed. The mathematical and computer algorithms were described with the Cu-NH_3-H_2O system as an example. More quantitative information on real hydrometallurgical processes can be obtained from these diagrams compared with the conventional Pourbaix φ-pH diagram.

[Key words] activity term method; simultaneous equilibrium; metal-ligand-H_2O system; nonlinear equation group
[CLC number] TF111.1 **[Document code]** A

1 INTRODUCTION

The study of metal-ligand system is always the topic of metallurgy researchers. Osseo-Asare[1] tried to compile a general program to plot φ-pH diagram for Metal-NH_3-H_2O system, however, the plotted diagram deviates from practical solution due to its assumptions, which leads to the enlargement of aqueous phase stable area. Fu et al[2,3] and Luo[4,5] proposed a series methods to plot such simultaneous φ-pH diagram.

In the previous paper, the algorithm for plotting all-equilibrium diagram of M-H_2O system was described. In this paper, a new viewpoint is set on the metal-ligand system φ-pH diagram, whose triple points and invariant points are discussed in detail; and on the base of previous work[6,7], a new general program is compiled to plot metal-ligand system φ-pH diagram.

2 ANALYSIS OF POURBAIX DIAGRAM FOR Cu-NH_3-H_2O SYSTEM

Fig. 1 is the Pourbaix diagram of Cu-NH_3-H_2O system. From the diagram, it can be seen that due to the introduction of ligand NH_3, the stable regions of solid Cu_2O and CuO are divided into two parts by $Cu(NH_3)_n$, and Cu_2O or CuO will dissolve in certain φ and pH range, at higher pH value they will reprecipitate. It shows that the possible triple points for two solid phases and aqueous phase will probably be more than 2. At the same time, points a and b identify some identical metal-bearing information, that is, the same stable solid phases Cu_2O, Cu and predominant Cu-bearing aqueous species $Cu(NH_3)^{2+}$; however, it can be seen that the two points are different, the difference lies in the different ligand species. As to point a, the predominant ligand species is NH_4^+ and it is $NH_3(a)$ for point b. So in order to get all possible triple point, it is not enough only to know the information of metal-bearing species, but also very important to know about the predominant ligand-bearing species.

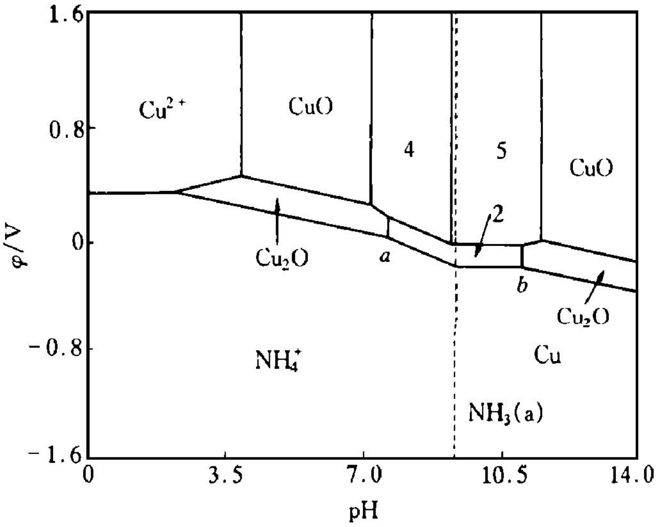

Fig. 1 Pourbaix diagram of Cu-NH_3-H_2O system at 298 K
$[NH_3 + NH_4^+] = 5$ mol/L; $a_i = 1$ mol/L; 2—$Cu(NH_3)_2^+$; 4—$Cu(NH_3)_4^{2+}$; 5—$Cu(NH_3)_5^{2+}$

3 ALGORITHM FOR M-L-H_2O SYSTEM ALL-EQUILIBRIUM φ-pH DIAGRAM

3.1 Phase rule analysis

① **[Foundation item]** Project (98053306) supported by the Doctorate Fund of the State Education Ministry of China
[Received date] 2000- 01- 13; **[Accepted date]** 2000- 06- 15

The phase rule analysis is similar to the M-H$_2$O system, but another dependent component ligand is included. At the same time we fix the total concentration of ligand as $[L]_T$, so the phase rule accords to the following expression under certain temperature and pressure:

$$f = 3 - \Phi \quad (1)$$

where f is the number of freedom degrees, Φ is the number of phases.

In the stable area of aqueous solution, $\Phi = 1$, so freedom degrees number is 2, that means no solid phase precipitate with certain $[M]_T$ and $[L]_T$ within some φ and pH range. The solid-aqueous phase equilibrium line exists between one solid and aqueous phase, so the freedom degrees number is 1. Triple point exists among two solid phases and aqueous phase, the freedom degree number is 0. On the base of activity term method proposed in the previous papers[6,7], a new computation method of calculating the simultaneous equilibrium for M-ligand-H$_2$O system is proposed and described below.

3.2 Simultaneous equilibrium for M-L-H$_2$O system

3.2.1 Solid-aqueous solution equilibrium

Here solid phase is defined as $M_{si}L_{sj}$ (such as Cu_2O, CuCl, element H and O are omitted), metal aqueous species $M_{ai}L_{aj}$ (including metal complex and single metal ion), ligand species $H_{ci}L_{cj}$ (such as NH_3, NH_4^+, CNO^-, CN^-, HCNO(a)).

Suppose at a point (φ, pH) the most stable solid phase species and ligand species are $M_{sm}L_{sl}$(s) and $H_{ch}L_{cl}$, the base reaction for $M_{sm}L_{sl}$ is,

$$M + l_{sm}L + w_{sm}H_2O + m_{sm}H^+ + n_{sm}e \rightleftharpoons r_{sm}M_{sm}L_{sl} \quad (2)$$

For $H_{ch}L_{cl}$ it is

$$L + w_{cl}H_2O + m_{cl}H^+ + n_{cl}e \rightleftharpoons r_{cl}H_{ch}L_{cl} \quad (3)$$

As to any metal-bearing aqueous species $M_{ai}L_{aj}$, the base reaction is

$$M + l_{ai}L + w_{ai}H_2O + m_{ai}H^+ + n_{ai}e \rightleftharpoons r_{ai}M_{ai}L_{aj} \quad (4)$$

(4) − (2) − l_{ai} × (3), get

$$r_{sm}M_sL_s(s) + lH_{ch}L_{cl} + wH_2O + mH^+ + ne \rightleftharpoons r_{ai}M_{ai}L_{aj} \quad (5)$$

The concentration of $M_{ai}L_{aj}$ can be calculated by

$$[M_{ai}L_{aj}] = \exp[(A_i\mathrm{pH} + B_i\varphi + C_i + D_i\lg[H_cL_c])/r_{ai} \times \ln 10] \quad (6)$$

where $A_i = f(A_{ai}, A_s, A_{cl})$, $B_i = f(B_{ai}, B_s, B_{cl})$, $C_i = f(C_{ai}, C_s, C_{cl})$, $D_i = f(D_{ai}, D_s, D_{cl})$, $f(x_1, x_2, x_3) = x_1 - x_2 - l_{ai} \times x_3$

At given total metal concentration and total ligand concentration, we can get

$$\sum_i m_i [M_{ai}L_{aj}] = [M]_T \quad (7)$$

$$\sum_i l_i [M_{ai}L_{aj}] + \sum_j l_j [H_{ci}H_{cj}] = [L]_T \quad (8)$$

It can be solved via Eqns. (6) ~ (8) since there are only three independent variables.

3.2.2 Equilibrium of aqueous species

At any point (φ, pH) in the stable area of aqueous solution, suppose that metal aqueous species $M_{am}L_{al}$ whose concentration is $[M_{am}]$ and ligand species $H_{ch}L_{cl}$ are predominant, the base reaction for the two species is

$$M + l_{am}L + w_{am}H_2O + m_{am}H^+ + n_{am}e \rightleftharpoons r_{am}M_{am}L_{al} \quad (9)$$

Then all the other aqueous species are in equilibrium with $M_{am}L_{am}$ and $H_{ch}L_{cl}$ as:

$$r_{am}M_{am}L_{al} + l_{cl}H_{ch}L_{cl} + w_{ai}H_2O + m_{ai}H^+ + n_{ai}e \rightleftharpoons r_{ai}M_{ai}L_{al} \quad (10)$$

The concentration of M_aL_a(a) can be expressed as

$$[M_{ai}L_{al}] = \exp\{(A\mathrm{pH} + B\varphi + C + D\lg[H_{ch}L_{cl}] + \lg[M_{am}]^{r_{am}}/r_{ai} \times \ln 10\} \quad (11)$$

Through Eqns. (7) and (8) the solution for $\lg[H_{ch}L_{cl}]$ and $\lg[M_{am}]^{r_{am}}_{cal}$ can be calculated.

In order to determine if the point belong to the stable area of aqueous solution, it should be made sure that no solid will form.

As to any solid species $M_{si}L_{sj}$, we get

$$r_{am}M_{am}L_{am} + l_{cl}H_{ch}L_{cl} + w_{si}H_2O + m_{si}H^+ + n_{si}e \rightleftharpoons r_{si}M_{si}L_{sj} \quad (12)$$

The theoretical value of $\lg[M_{am}]^{r_{am}}$ that solid M_sL_s will not form can be calculated according to

$$\lg[M_{am}]^{r_{am}}_{theo} = -(A\mathrm{pH} + B\varphi + C + D\lg[H_{ch}L_{cl}])/r_{si} \times \ln 10 \quad (13)$$

If $\lg[M_{am}]^{r_{am}}_{theo} > \lg[M_{am}]^{r_{am}}_{cal}$, no M_sL_s forms, otherwise the point belongs to the stable area of solid phase instead of solution.

3.2.3 Analysis of possible triple point and invariant point

According to phase rule analysis, the possible triple points are ("+" is used to express the information of point for simplification, as to solid phase, the activity term is maximal, as to aqueous species, the concentration is maximal):

1) Two solid phases + one M-bearing + one L-bearing aqueous species. The aqueous solution satisfies Eqns. (14) and (15)

$$\sum m_i [M_{ai}L_{aj}] = [M]_T \quad (14)$$

$$\sum l_j [M_{ai}L_{aj}] + \sum l_j [H_{ci}L_{cj}] = [L]_T \quad (15)$$

2) Three solid + one ligand species. The concentration of L-bearing species still satisfies Eqn. (14) and the concentration of M-bearing species satisfies the following inequation:

$$\sum m_{ai} [M_{ai}L_{aj}] < [M]_T \quad (16)$$

As discussed above, due to the inclusion of ligand, the stability of ligand is very important to equilibrium. So different from M-H$_2$O system, the following invariant points should be worked out so as to plot a complete φ-pH diagram. All possible invariant points are as follows.

1) One solid phase + two metal aqueous species + one metal-free ligand-bearing species. The total concentration of M-bearing and L-bearing satisfies Eqns. (14) and (15).

2) One solid phase + one M-bearing aqueous species + two metal-free ligand-bearing species. The total concentration of M-bearing and L-bearing satisfies Eqns. (14) and (15).

3) One solid + three metal-free ligand-bearing species. The total concentration of M-bearing species and L-bearing species satisfy inequation (16) and Eqn. (15).

4) Two solid phases + one metal aqueous species + one metal-free ligand-bearing species. The total concentration of M-bearing species and L-bearing satisfies Eqns. (14) and (15).

5) Two solid phases + two L-bearing species. The total concentration of M-bearing species and L-bearing satisfies inequation (16) and Eqn. (15), respectively.

6) Two M-bearing aqueous species + two metal-free ligand-bearing species and no solid phase forms. The total concentration of M-bearing and L-bearing satisfies Eqns. (14) and (15).

7) Three M-bearing aqueous species and no solid phase forms. The total concentration of M-bearing and L-bearing satisfies Eqns. (14) and (15).

8) Three metal-free ligand-bearing aqueous species + one metal aqueous species and no solid phase forms. The total concentration of M-bearing species and L-bearing species satisfy Eqns. (14) and (15).

By solving all the triple points and invariant points with the method described in the previous paper, all the solid-aqueous equilibrium lines and invariant lines can be determined. Joining all the invariant lines and solving the solid-aqueous equilibrium lines a all-equilibrium diagram can be completed.

4 ALGORITHM FOR SOLVING NON-LINEAR EQUATIONS GROUP

4.1 Algorithm procedure

In the previous paper, arithmetic-geometric method is used to solve nonlinear equations. Though it proves to be very efficient, some changes must be made when it is used to solve M-ligand-H_2O system nonlinear equations for M-ligand-H_2O system.

Assume that the concentration of any aqueous species $M_iL_jH_kO_o$ ($i \geqslant 0$) is c_i, atom number for metal is m_i and for ligand l_j, then

$$[M]_T = \sum m_i c_i = \prod \left(\frac{m_i c_i}{d_i} \right)^{d_i} \quad (17)$$

For ligand,

$$[L]_T = \sum l_j c_i = \prod \left(\frac{l_i c_i}{d_i} \right)^{d'_i} \quad (18)$$

where $d_i = \dfrac{m_i c_i}{\sum m_j c_j}$, $d'_i = \dfrac{l_i c_i}{\sum l_j c_j}$.

We can get a simplified formula

$$\lg[M]_T = \left(\sum \frac{d_i}{r_i} A_i \right) pH + \left(\sum \frac{d_i}{r_i} B_i \right) \varphi + \sum \frac{d_i}{r_i} C_i - \sum d_i \lg \left(\frac{d_i}{m_i} \right) \quad (19)$$

$$\lg[L]_T = \left(\sum \frac{d'_i}{r_i} A_i \right) pH + \left(\sum \frac{d'_i}{r_i} B_i \right) \varphi + \sum \frac{d'_i}{r_i} C_i - \sum d_i \lg \left(\frac{d'_i}{l_i} \right) \quad (20)$$

Thus linear equations shown in (7) and (8) represent linear equations in the logarithmic space. Then the equations can be easily solved to get triple points and invariant points.

4.2 Determination of initial values

Arithmetic-geometric method to solve nonlinear equations is very efficient, however only one solution is obtained once a time. In the previous paper, it is concluded that for M-H_2O system, there will be possible two solutions for two solid phases in equilibrium with aqueous phase. Due to the introduction of ligand species, it is easily concluded that there will be over two solutions to solve the nonlinear equations. It can be seen from Fig. 1 that the triple points between Cu_2O, Cu and aqueous phases are 3. So in order to obtain all the possible solutions for all the possible triple points and invariant points, the initial guess for solving nonlinear equations is very important. Considering the triple points for Cu_2O, Cu and aqueous phase, every M-bearing aqueous species and metal-free ligand-bearing species are given the opportunity to be the only predominant species so as to get different initial guess values.

5 APPLICATION AND EXAMPLES

Many authors have plotted the φ-pH diagram for Cu-NH_3-H_2O system[2~5], in which simultaneous principle was used to calculate the equilibrium. To some extent it reflects the truth of the system, however, there are still some limitations.

A series of diagrams for Cu-NH_3-H_2O system is replotted, as shown in Figs. 2~4, according to the computation method described above. From Figs. 2~4, the following conclusions and differences that any other references did not point out can be got:

1) The solid-aqueous equilibrium line shows curvilinear rather than linear, especially near the area where two aqueous species has the same concentration, which is quite different from traditional φ-pH diagram.

2) With the increase of $[NH_3]_T/[Cu]$, the stable area of solid phase such as Cu_2O and CuO become small or even disappears.

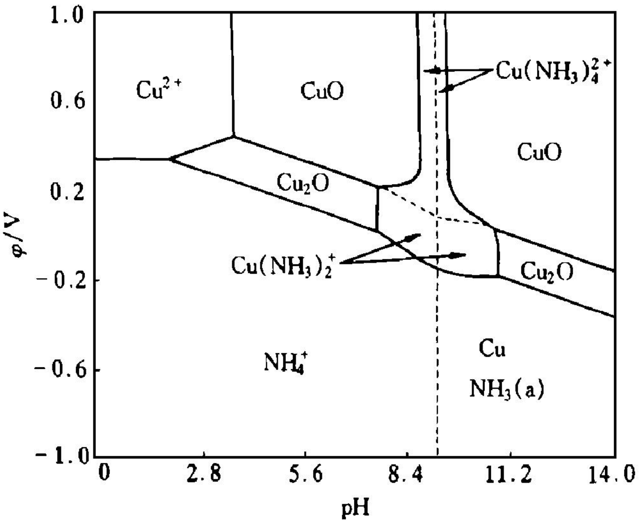

Fig. 2 All-equilibrium diagram of Cu-NH_3-H_2O system ($[Cu]_T$= 1 mol/L, $[NH_3]_T$= 5 mol/L)

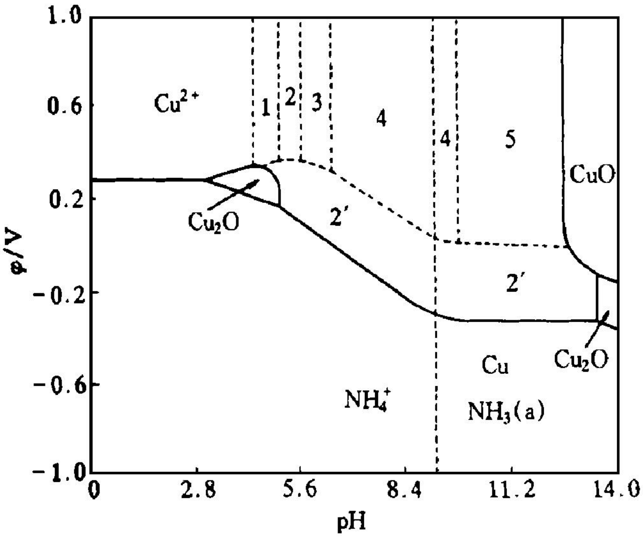

Fig. 3 All-equilibrium diagram of Cu-NH_3-H_2O system ($[Cu]_T$= 0.01 mol/L; $[NH_3]_T$= 5 mol/L)
1 —$Cu(NH_3)^{2+}$; 2 —$Cu(NH_3)_2^{2+}$; 3 —$Cu(NH_3)_3^{2+}$;
4 —$Cu(NH_3)_4^{2+}$; 5 —$Cu(NH_3)_5^{2+}$

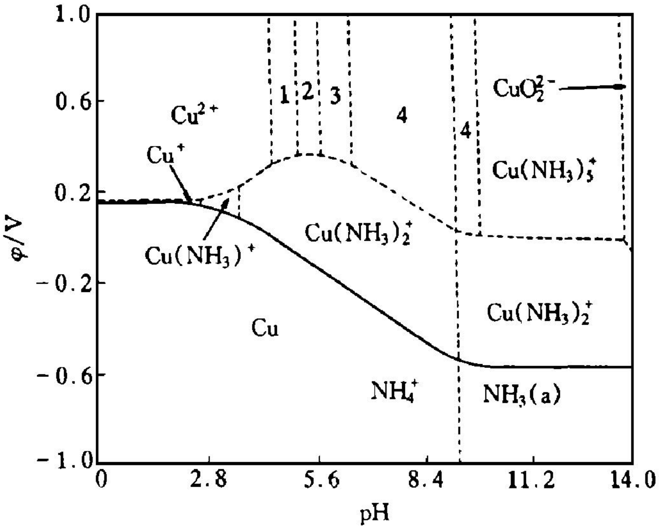

Fig. 4 All-equilibrium diagram of Cu-NH_3-H_2O system ($[Cu]_T$= 10^{-6} mol/L; $[NH_3]_T$= 5 mol/L)
1 —$Cu(NH_3)^{2+}$; 2 —$Cu(NH_3)_2^{2+}$;
3 —$Cu(NH_3)_3^{2+}$; 4 —$Cu(NH_3)_4^{2+}$

3) The equilibrium lines between aqueous species (dot line in the figures) which are rarely studied are plotted. Only all the equilibrium lines are worked out, can we get a complete diagram and compile a general program to plot any other all-equilibrium φ-pH diagram for M-lignand-H_2O system.

4) Due to the introduction of NH_3, the stable area of Cu_2O and CuO are divided into two parts. The corresponding triple points are over 3. No references pointed out the triple points at right side of coordinate axis.

5) Ref. [4] pointed out that the difference at high pH value appears as a result of inclusion of CuO_2^{2-} and $HCuO_2^-$. In fact, near the invariant line of NH_4^+ and NH_3, the difference is caused by Cu-$(NH_3)_2^+$ who shares the concentration of $[Cu]_T$. The concentration of CuO_2^{2-} and $HCuO_2^-$ is quite low.

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(Edited by LONG Huai-zhong)