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A new look at φ pH diagram (I)

——All-equilibrium φ pH diagram for M-H₂O system^①

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[Abstract] A new viewpoint of computer program pourbaix diagram was proposed on traditional φ pH diagrams. All equilibrium principle and activity term method were used to plot φ pH diagrams for M-H₂O systems based on the thermochemical database developed. And a new method——arithmetic-geometric method is used to solve nonlinear equations group. The calculation procedure is proved to be efficient and convergent. The method seldom depends on artificial intervention and can extend to multi-component all equilibrium φ pH diagrams such as M-ligand-H₂O system.

[Key words] Pourbaix diagram; activity term method; all-equilibrium; nonlinear equation group; M-H₂O system

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1 INTRODUCTION

Pourbaix diagram has been widely used in many fields since 1960s. The computation procedure is considerably tedious and complicated. So computer algorithm has been the research topic for many years. And until now, there have been several famous software systems which are able to finish this work. They are mainly: Thermo Calc (Thermochemical data bank for equilibrium and phase diagram calculations), Sweden; Thermo data, France; FACT (Facility for analysis of chemical thermodynamics), Canada; HSC, Finland; MTDATA (Metallurgical and thermodynamical data), United Kingdom; THERDAS, German; CSIRO/ Monash, Australia, etc. The up-to-date information about them can be browsed on Internet.

However, traditional Pourbaix diagram is limited due to: 1) presupposing the activity of all possible species; 2) not considering the simultaneous equilibrium for all the aqueous species.

In fact, the aqueous phase is uniform. According to minimum Gibbs energy principle, all the species coexist are in equilibrium. The diagram presents a stable region of solution instead of regions of individual species. Only the concentration of total metal can be known. It leads to the extension of the stable area of aqueous phase. This situation will become especially severe for M-ligand-H₂O system.

FU et al^[1,2] introduced simultaneous equilibrium principles into the plotting of φ pH diagram for Cu-NH₃-H₂O and Cu-Cl⁻-H₂O systems. With the new idea, all the equilibria are taken into account simultaneously. The newly plotted diagram represents the equilibrium area between solid and aqueous phases in-

stead of area of individual dissolved species. Many researchers^[3,4] extends this method to other metal-ligand system. WANG^[5] have established a generalized program to plot such diagram with this method. All the works made a great contribution to the thermodynamic study of metal-ligand system. However, there are still limitations for plotting the φ pH diagrams. First, the equilibrium of aqueous species is not clear. Second, the plot procedure still depends on experience instead of on certain judgement. Third, mathematics aspects are seldom considered for the solution of nonlinear equations so that some deficiency may happen inevitably. And last, most of the program can not solve the equilibrium between the solid phase containing ligand such as CuCl(s), Ni(CN)₂(s) and aqueous phase.

In this series of papers, a new viewpoint on φ pH is proposed. Simultaneous equilibrium principle is used to plot M-H₂O and M-ligand-H₂O system φ pH diagram. This kind of diagram represents the reality of practical solution better compared to traditional φ pH diagram and it also improves and makes up for the deficiency pointed out above. A general system is programmed on microcomputer. Only inputting little information the system will automatic index the data from thermochemical database, and a complete all-equilibrium diagram is obtained.

2 ALGORITHM FOR M-H₂O ALL-EQUILIBRIUM φ pH DIAGRAM

2.1 Phase rule analysis

All-equilibrium φ pH diagrams accord strictly with phase rule principle.

The phase rule presented in the conventional

form is

$$f = 2 - \Phi + C \quad (1)$$

where f is the number of freedom degrees, Φ is the number of phases and C is the number of independent components.

As to $M-H_2O$ system, there are four independent components, M , H , O and electron. Fixing the parameters temperature, pressure and the total concentration of metal-bearing aqueous species $[M]_T$, so Eqn.(1) can be simplified as

$$f = 3 - \Phi \quad (2)$$

In the stable area of aqueous solution, $\Phi=1$, so freedom degrees number is 2, that means no solid phase precipitates within certain φ and pH range. The solid-solution equilibrium line exists between one solid and one aqueous phases, so the freedom degrees number is 1. Triple point exists among two solid phases and one aqueous phase with $[M]_T$ or three solid phases with total metal aqueous species concentration less than $[M]_T$, the freedom degree number is zero. On the basis of activity term method proposed in the previous paper^[6], a new computation method of calculating the simultaneous equilibrium is proposed.

2.2 Analysis of Pourbaix φ pH diagram for Cu H_2O system

Although traditional Pourbaix diagram is limited to some extent, there is still much useful information. Fig.1 is the Pourbaix diagram of Cu H_2O system.

Fig.1 Pourbaix φ pH diagram for Cu H_2O system
($a_i = 10^{-6}$ mol/L, $T = 298$ K)

From Fig.1, the following conclusions can be obtained: 1) solid phases as Cu, Cu_2O , CuO are in equilibrium with aqueous species at points a , b , c , d , e ; 2) as to triple points such as points a and e , which represents two equilibrium points between Cu, Cu_2O and aqueous phase, it means that there are two

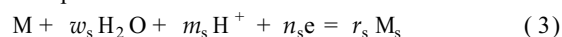
solutions with the equilibrium; 3) there is equilibrium lines between points a and b , while it is not so between points e and b . It can be explained that the predominant aqueous species is different. Points a and b have the same aqueous species Cu^{2+} while the predominant aqueous species for point e is CuO_2^{2-} . Therefore it is important to identify the aqueous species in equilibrium; 4) there is no predominant aqueous species between points c and e . In fact, there is equilibrium line between these two points. It is the point d that connects them. It means on the point d that the activity of two aqueous species $HCuO_2^-$ and CuO_2^{2-} are equal. It is an invariant point with zero freedom degree number.

The diagram undoubtedly provides the theoretical basis for the following algorithm.

2.3 Simultaneous equilibrium principle for M H_2O system

2.3.1 Equilibrium between solid-aqueous phases

Suppose the most stable solid phase is M_s (whose activity term is maximal), the base reaction for M_s can be expressed as



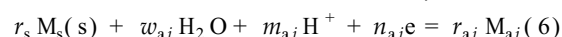
The activity term is^[3]

$$\lg(a_{M_s})^{r_s} = A_s pH + B_s \varphi + C_s \quad (4)$$

As to any possible metal-bearing aqueous species M_{ai}

$$\lg(a_{M_{ai}})^{r_{ai}} = A_{ai} pH + B_{ai} \varphi + C_{ai} \quad (5)$$

All the aqueous species are in equilibrium with solid phase M_s , subtracting the base reaction for M_s , the reaction can be written as a new one,



From Eqns.(4) ~ (6) we can calculate the concentration of M_{ai} (here activity coefficient is neglected),

$$[M_{ai}] = \exp\{[(A_{ai} - A_s) pH + (B_{ai} - B_s) \varphi + (C_{ai} - C_s) / r_{ai} \times \ln 10]\} \quad (7)$$

Fix the total metal concentration,

$$\sum_i m_i [M_{ai}] = [M]_T \quad (8)$$

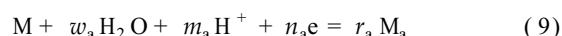
where m_i is the atom number of M_{ai} .

Presuppose φ or pH, corresponding pH or φ value can be obtained via Eqn.(8).

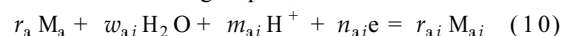
2.3.2 Equilibrium of aqueous species without no solid phase

Compared to the equilibrium between solid phase and aqueous phase, the equilibrium for aqueous species shows a little different.

At any specific point (φ , pH) in the stable area of aqueous solution, suppose all metal aqueous species M_{ai} are in equilibrium with M_a , the base reaction for M_a is,



As to M_{ai} , subtracting Eqn.(9),



The concentration of M_{ai} can be expressed as the function of φ , pH and $[M_a]$

$$[M_{ai}] = \exp\{[(A_{ai} - A_a)]pH + (B_{ai} - B_a)\varphi + (C_{ai} - C_a) + \lg([M_a])^{r_a}\} / r_a \times \ln 10 \quad (11)$$

$\lg([M_a])^{r_a}$ can be calculated by solving Eqn. (8) since there is only one variable at specific point (φ , pH).

In order to determine if the point belongs to the stable area of aqueous solution, it is necessary to make sure that no solid phases form.

As to any solid phase M_{sj} , the following expression can be written as

$$r_a M_a + w_{sj} H_2O + m_{sj} H^+ + n_{sj} e = r_{sj} M_{sj} \quad (12)$$

The theoretical value for $\lg([M_a])^{r_a}$ that solid M_{sj} will not form can be calculated according to the following equation:

$$\lg([M_a])_{\text{theo}}^{r_a} = -[(A_{sj} - A_a)]pH + (B_{sj} - B_a)\varphi + (C_{sj} - C_a) / r_{sj} \times \ln 10 \quad (13)$$

If $\lg([M_a])_{\text{theo}}^{r_a} > \lg([M_a])_{\text{cal}}^{r_a}$, then no M_{sj} forms, otherwise the point belongs to the stable area of M_{sj} .

2.4 Computation method

2.4.1 Analysis of triple point and invariant point

From Fig. 1, it can be concluded that on the solid-solid equilibrium line, there would be two terminal points, triple points or boundary points. It means that if two solid phases are in equilibrium with aqueous phase, there are possible 0, 1 or 2 triple points. This can also be proved mathematically. It is well known, the exponential function is monotonic increasing or decreasing. Therefore, there will be one or two solution for Eqn. (8). Both points b and c in Fig. 1 are triple points for Cu_2O , CuO and aqueous phase. Points a and e are for Cu , Cu_2O and aqueous phase. That also shows that solid phase is possibly in equilibrium with different solution constituents. So how to determine the solid-aqueous phase equilibrium lines is especially important. For example points a and c can not be taken as the direction of solid-aqueous equilibrium line. Therefore, it must be pointed out that at this triple point which metal aqueous phase species is predominant, that is, its concentration is maximal. Cu^{2+} is predominant at points a and b . At point c HCuO_2^- is predominant and at point e CuO_2^{2-} is predominant. A solid-aqueous phase line exists between points a and b , while no line between points c and e . According to above analysis and phase rule, the possible triple points are as follows.

1) Two solid phases are in equilibrium with aqueous phase in which one metal aqueous species is predominant (the concentration is maximal). The

predominant metal aqueous species is used to identify definite triple points, i.e., point a or e from Fig. 1.

2) Three solid phases with maximal activity term are in equilibrium under the condition that the calculated total metal concentration is less than the given concentration $[M]_T$.

On the other hand, there exists a definite solid-aqueous equilibrium line between c and e . Another kind of special points—invariant points should be solved. When one solid is in equilibrium with aqueous phase, at a special point, the atom concentration of two aqueous species is equal and maximal. The invariant points are not triple points. Since an extra constraint is included, the freedom degree number is still 0. All possible invariant points are: 1) one solid phase with maximal activity term is in equilibrium with aqueous phase and two aqueous species with the same concentration are predominant. 2) three aqueous species with the same atom concentration are predominant and no solid phase forms.

By above analysis, the key problem is to work out all the triple points and invariant points.

2.4.2 Calculation of triple point

1) The triple point exists between two solid phases M_{sp} , M_{sq} and aqueous solution. A new equation can be obtained via Eqns. (3) and (4), such as

$$(A_{sp} - A_{sq})pH + (B_{sp} - B_{sq})\varphi + (C_{sp} - C_{sq}) = 0 \quad (14)$$

The triple point coordinate can be obtained by solving Eqns. (7), (8) and (14). At the same time it should be made certain if the activity term of M_{sp} , M_{sq} is maximal via Eqn. (4). If not the point is not stable triple point.

2) The triple point exists between three solid phases M_{sp} , M_{sq} and M_{sr} . Two new equations can be obtained:

$$(A_{sp} - A_{sq})pH + (B_{sp} - B_{sq})\varphi + (C_{sp} - C_{sq}) = 0 \quad (15)$$

$$(A_{sr} - A_{sq})pH + (B_{sr} - B_{sq})\varphi + (C_{sr} - C_{sq}) = 0 \quad (16)$$

The pH and φ can be calculated via Eqns. (15) and (16). At the same time it should be checked out if it satisfies the following expression at the point.

$$\sum m_i [M_{ai}] < [M]_T \quad (17)$$

If so the point is stable triple point.

2.4.3 Calculation of invariant points

1) One solid is equilibrium with aqueous phase and the concentration of two metal aqueous species is equal and maximal. According to Eqn. (6), the following relations can be got for solid phase M_{ap} and M_{aq} :

$$m_{ap} [M_{ap}] = m_{ap} \exp[(A_{ap}pH + B_{ap}\varphi + C_{ap}) / r_{ap} \times \ln 10] \quad (18)$$

$$m_{aq} [M_{aq}] = m_{aq} \exp[(A_{aq}pH + B_{aq}\varphi + C_{aq}) / r_{aq} \times \ln 10] \quad (19)$$

$$m_{ap}[M_{ap}] = m_{aq}[M_{aq}] \quad (20)$$

We can get a new equation through Eqns. (18) ~ (20) .

$$\begin{aligned} & (A_{ap}/r_{ap} - A_{aq}/r_{aq}) \text{pH} + \\ & (B_{ap}/r_{ap} - B_{aq}/r_{aq}) \varphi + (C_{ap}/r_{ap} - \\ & C_{aq}/r_{aq}) + \lg(m_{ap}/m_{aq}) = 0 \quad (21) \end{aligned}$$

Solving Eqns. (20) and (7) we can get such point as d .

At point d , Cu_2O is in equilibrium with aqueous phase and at the same time the concentration of HCuO_2^- and CuO_2^{2-} is equal and maximal .

2) Three metal aqueous species with same concentration are predominant . According to Eqn. (12) , three metal aqueous species are supposed to be M_{ap} , M_{aq} , M_{ar} , then

$$m_{ap}[M_{ap}] = m_{ap} \exp \left[\frac{A_{ap}}{r_{ap}} + \frac{B_{ap}}{r_{ap}} + \frac{C_{ap}}{r_{ap}} + \lg([M_a]) / r_{ap} \times \ln 10 \right] \quad (22)$$

$$m_{aq}[M_{aq}] = m_{aq} \exp \left[\frac{A_{aq}}{r_{aq}} + \frac{B_{aq}}{r_{aq}} + \frac{C_{aq}}{r_{aq}} + \lg([M_a]) / r_{aq} \times \ln 10 \right] \quad (23)$$

$$m_{ar}[M_{ar}] = m_{ar} \exp \left[\frac{A_{ar}}{r_{ar}} + \frac{B_{ar}}{r_{ar}} + \frac{C_{ar}}{r_{ar}} + \lg([M_a]) / r_{ar} \times \ln 10 \right] \quad (24)$$

$$m_{ap}[M_{ap}] = m_{aq}[M_{aq}] = m_{ar}[M_{ar}] \quad (25)$$

Two new independent equations through Eqns. (22) ~ (25) can be expressed as

$$\begin{aligned} & (A_{ap}/r_{ap} - A_{aq}/r_{aq}) \text{pH} + \\ & (B_{ap}/r_{ap} - B_{aq}/r_{aq}) \varphi + (C_{ap}/r_{ap} - C_{aq}/r_{aq}) + \\ & (D_{ap}/r_{ap} - D_{aq}/r_{aq}) + \lg(m_{ap}/m_{aq}) = 0 \quad (26) \end{aligned}$$

$$\begin{aligned} & (A_{ar}/r_{ar} - A_{aq}/r_{aq}) \text{pH} + (B_{ar}/r_{ar} - \\ & B_{aq}/r_{aq}) \varphi + (C_{ar}/r_{ar} - C_{aq}/r_{aq}) + \\ & (D_{ar}/r_{ar} - D_{aq}/r_{aq}) + \lg(m_{ar}/m_{aq}) = 0 \quad (27) \end{aligned}$$

Then such type of invariant points can be solved via Eqns. (26) ~ (28) .

According to above analysis and reasoning , all possible triple points and invariant points can be calculated . The problem is how to solve the nonlinear equations group . So a new method is proposed , which proves to be an efficient and easily convergent .

3 ALGORITHM FOR SOLVING NON-LINEAR EQUATIONS GROUP

3.1 Algorithm description

Up to now , Newton Raphson method is generally accepted as the most popular one to solve chemical equilibrium . An important characteristic of this method is that it converges to solution faster than any other method if the initial guess is fairly close to the true solution ; otherwise the method will fail to converge . Furthermore , the computation of the Jacobian matrix is quite cumbersome especially for exponential function , which is easy to overflow . These limitations have motivated researcher to develop new computational for equilibrium computations . Ben^[7] proposed arithmetic-geometric method to solve chemical equilibrium problems . The advantage of the method

is its ability to recast the conservation equations as linear equations in the logarithmic space , in which the equilibrium constant expression are readily linearized . And it is barely affected by the initial guess and converges very quickly . This method is introduced and subjected to a little change to solve the above equilibrium problems .

For the sake of mathematical solution , it would be beneficial if the nonlinear equations are recast in a linear form . The arithmetic-geometric method allows this transformation to take place . It is well known that it is not so difficult to solve a set of linear equations since the solution is unique if it exists .

Suppose for variable U_1 , U_2 , ... , U_N ,

$$U_1 + U_2 + \dots + U_N = \left[\frac{U_1}{d_1} \right]^{d_1} \left[\frac{U_2}{d_2} \right]^{d_2} \dots \left[\frac{U_N}{d_N} \right]^{d_N} \quad (28)$$

In a condensed form

$$\sum_{j=1}^N U_j = \prod_{j=1}^N \left[\frac{U_j}{d_j} \right]^{d_j} \quad (29)$$

where $d_i = U_i / \sum_{j=1}^N U_j$.

Suppose the concentration of any aqueous species is M_{ai} whose concentration is $[M_{ai}]$ and atom number is m_i , Eqn. (7) can be rewritten as

$$[M]_T = \sum m_i [M_{ai}] = \prod \left[\frac{m_i [M_{ai}] d_i}{d_i} \right] \quad (30)$$

where $d_i = m_i [M_{ai}] / \sum m_i [M_{ai}]$.

Taking the logarithm of Eqn. (29) and combining Eqn. (7) , a new equation can be obtained :

$$\begin{aligned} & \left[\sum \frac{d_{ai}}{r_{ai}} A_{ai} \right] \text{pH} + \left[\sum \frac{d_{ai}}{r_{ai}} B_{ai} \right] \varphi + \\ & \left[\sum \frac{d_{ai}}{r_{ai}} C_{ai} \right] - \sum d_{ai} \lg \left[\frac{d_{ai}}{b_{ai}} \right] = \lg [M]_T \quad (31) \end{aligned}$$

Thus a nonlinear equation shown in Eqn. (8) represents a linear equation in the logarithmic space . Then the equation can be solved .

The method is also iterative . However it proves to be efficient and good convergence . In general several iterative times is enough . For more , it is barely affected by initial values .

3.2 Determination of initial value

Arithmetic-geometric method proves to be an efficient method to solve chemical equilibrium problems . The method is barely affected by the initial guess and can converge very quickly . However , as discussed above , the possible triple point between two solid phases and aqueous phase is possibly more than one . So it is very important to determine the initial value in order to obtain all possible solution . Taking the Cu_2O , Cu and aqueous phase triple point as an example , every metal bearing aqueous species M_{ai} are given to have the opportunity to be the only species ,

so the following expression can be got:

$$\lg[M]_T = \lg(m_i[M_{ai}]) = A_i \text{pH} + B_i \varphi + C_i \quad (32)$$

According to Eqns.(14) and (32), a set of initial values for (φ , pH) can be got. And then solve the nonlinear Eqns.(8) and (14) with arithmetic-geometric method and the true solution can be worked out. Then according to the solved solution, it is necessary to determine which metal aqueous species is really predominant and if the activity term of the two solid phases is maximal. Thus we can get the point a as well as point e .

4 APPLICATIONS AND EXAMPLES

The Pb-H₂O system is taken as an example to illustrate the new method. Fig.2 is traditional Pourbaix diagram with the activity of all aqueous species 10^{-4} mol/L. The thermodynamic data are from Ref. [5]. There are four solid phases, Pb, PbO, Pb₃O₄, PbO₂, and seven aqueous species Pb²⁺, PbOH⁺, H₂PbO₂(a), Pb(OH)₃⁻, Pb₃(OH)₄²⁺, Pb₄(OH)₄²⁺, Pb₆(OH)₈⁴⁺. It should be noted that some of Pb-bearing species are multi-atomic, so the concentration of two aqueous species are equal that means the equality of the atom concentration, for example $[PbOH^+] = 4 \cdot [Pb_4(OH)_4^{2+}]$.

Fig.2 Traditional Pourbaix diagram for Pb-H₂O system
($a_i = 10^{-4}$ mol/L)

The dot lines show that two aqueous species are predominant. It does not mean that only one species exists in the identified aqueous area, it only shows that the concentration of one aqueous species is maximal.

From Figs.2, 3, it can be seen there is great difference between traditional φ pH diagram and all-equilibrium φ pH diagram. The stable area of solid

Fig.3 All-equilibrium φ pH diagram for Pb-H₂O system with $[Pb]_T = 10^{-4}$ mol/L

phase of traditional φ pH diagram is larger than that of all-equilibrium φ pH diagram, some solid phase such as PbO will disappear. And on the other hand, solid-aqueous equilibrium line shows curvilinear rather than linear. Especially at the border of two aqueous species with equal concentration, the curvature is reasonably great, which can be seen from the stable area of Pb₃O₄.

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