APPLICATION OF "THREE-STEP METHOD" IN CALCULATION OF CONDITIONAL POTENTIAL AND PRECIPITATION SOLUBILITY IN ANALYTICAL CHEMISTRY

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ABSTRACT

According to the teaching experience, for the important and difficult knowledge "calculation of conditional potential" and "calculation of precipitation solubility" in analytical chemistry, a three-step method is summarized to solve the above problems. It aims to help students master the problem-solving method so as to solve all the similar problems and improve their scientific thinking ability. *[African Journal of Chemical Education—AJCE 13(1), January 2023]*

INTRODUCTION

Analytical chemistry is one of the important means to study substances and their changes. Its theories and methods are not only the basis of chemistry, but also the basis of biology, geology, environment and other disciplines. The purpose of this course in college is to enable students to establish an accurate concept of "quantity" and master the basic theories, principles and experimental techniques related to this, so as to lay a solid foundation for subsequent courses and scientific research.

In the course of many years of teaching "Analytical Chemistry" in normal university, the author has carefully analyzed the key and difficult knowledge and extracted the rules behind them, then summarized some methods that are easy for students to master. Through the transition from "teaching knowledge" to "teaching method", the students' learning abilities can be improved [1, 2], and students are able to draw inferences from one example and learn by analogy on the basis of mastering the method. For example, "three-step methods" have been summarized for calculating conditional potential and precipitation solubility.

1 "THREE-STEP METHOD" TO CALCULATE CONDITIONAL POTENTIAL

The oxidation/reduction capacity of oxidized/reduced forms of a substance can be judged by the electrode potential. The electrode potential of reversible pairs can be calculated using Nernst equation.

$$E_{Ox/Red} = E^{\theta}_{Ox/Red} + \frac{0.059}{n} \lg \frac{a_{Ox}}{a_{Red}} \ (1)$$

a_{Ox} is the activity of the oxidized form, a_{Red} is the activity of the reduced form, T=298K, n is the number of electrons transferred in the half-reaction.

Usually, the effect of ionic strength is ignored, and the equilibrium concentrations of oxidized/ reduced forms are used instead of activity, and the influence of ionic strength is not discussed in this paper.

$$E_{Ox/Red} = E^{\theta}_{Ox/Red} + \frac{0.059}{n} \lg \frac{[Ox]}{[Red]} \ (2)$$

For the irreversible electric pair, the electrode potential can be estimated by the results of Nernst equation. When the Nernst equation is applied to the calculation, the changes of the oxidized and reduced forms should be considered, or the effects of side reactions should be taken into account.

$[Ox]=c_{Ox}/\alpha_{Ox}$ (3), $[Red]=c_{Red}/\alpha_{Red}$ (4)

c_{Ox}, c_{Red} are the analytical concentrations of the oxidized and reduced forms, respectively. α_{Ox}, α_{Red} are the side reaction coefficients of the oxidized and reduced forms respectively.

Substitute Equation (3) and (4) into Equation (2):

$$E_{Ox/Red} = E^{\theta}_{Ox/Red} + \frac{0.059}{n} \lg \frac{c_{Ox}/\alpha_{Ox}}{c_{Red}/\alpha_{Red}} \ (5)$$

When $c_{Ox} = c_{Red} = 1 mol \cdot L^{-1}$,

$$E^{\theta'}{}_{Ox/Red} = E^{\theta}{}_{Ox/Red} + \frac{0.059}{n} \lg \frac{\alpha_{Red}}{\alpha_{Ox}} \ (6)$$

$E^{\theta'}_{Ox/Red}$ is called the conditional potential [3]. Then the Nernst equation becomes the following form:

$$E_{Ox/Red} = E^{\theta'}_{Ox/Red} + \frac{0.059}{n} \lg \frac{c_{Ox}}{c_{Red}} \quad (7)$$

The value of the conditional potential is not only related to the standard electrode potential E^{θ}, but also to the side reaction coefficient. Therefore, the conditional potential is not only affected by the temperature, but also by the acidity of the solution, the concentration of complexing agent and other factors. It is constant only when the conditions are certain, and the conditional potential is also named. The calculation of conditional potential can help students to understand the meaning of conditioned potential and the factors that affect conditioned potential. Based on years of analytical chemistry teaching experience, the author found that the calculation of conditional potential is a difficult point for students to learn for many reasons. For example, some students have a poor grasp of the Nernst equation itself, while others confuse conditional potential with standard electrode potential and some other concepts learned in inorganic chemistry. In order to help students master this difficult content, the "three-step method" for calculating conditional potentials has been summarized. Students can solve all kinds of problems in calculating conditional potentials as long as they follow these three steps. The specific application examples of the three-step method are shown in Table 1.

Table 1 Three-step method to calculate conditional potential

	Effect of precipitation formation on conditional potential	Effect of complex formation on conditional potential	Effect of acidity on conditional potential
	Example: Calculate the conditional potential of the Cu^{2+}/Cu^{+} couple in the presence of I^{-}	Example: Calculate the conditional potential of the Fe^{3+}/Fe^{2+} couple in the presence of F^{-}	Example: Investigating the effect of acidity on the H$_3$AsO$_4$/HAsO$_2$ redox couple
Step 1 Write the Nernst equation in terms of the half-reaction	half-reaction: $Cu^{2+} + e^{-} \Leftrightarrow Cu^{+}$ Nernst equation: $E = E^{\theta}_{Cu^{2+}/Cu^{+}} + 0.059\lg \frac{[Cu^{2+}]}{[Cu^{+}]}$	half-reaction: $Fe^{3+} + e^{-} \Leftrightarrow Fe^{2+}$ Nernst equation: $E = E^{\theta}_{Fe^{3+}/Fe^{2+}} + 0.059\lg \frac{[Fe^{3+}]}{[Fe^{2+}]}$	half-reaction: $H_3AsO_4 + 2H^{+} + 2e^{-} \Leftrightarrow HAsO_2 + 2H_2O$ Nernst equation: $E_{H_3AsO_4/\ HAsO_2} = E^{\theta}_{H_3AsO_4/\ HAsO_2} + \frac{0.059}{2}\lg \frac{[H_3AsO_4][H^{+}]^2}{[HAsO_2]}$
Step 2 Replace the equilibrium concentrations of oxidized/reduced forms in the Nernst equation with the analytical concentrations	Cu^{2+} has no side reactions, so $[Cu^{2+}] = c_{Cu^{2+}}$ (1) Cu^{+} has a side reaction: Cu^{+} + I$^{—}$= CuI↓, $[Cu^{+}][I^{—}]= K_{sp'CuI'}$, so $[Cu^{+}]=Ksp/[I^{—}]$ (2) Substitute equations (1) and (2) into Nernst equation, and get: $E = E^{\theta}_{Cu^{2+}/Cu^{+}} + 0.059\lg \frac{c_{Cu^{2+}}}{Ksp/[I^{-}]}$	Fe^{2+} has no side reactions, so $[Fe^{2+}] = c_{Fe^{2+}}$ (1) Fe^{3+} undergoes the following side reaction: Fe^{3+} + F$^{—}$ = FeF^{2+}, FeF^{2+} + F$^{—}$ = FeF$_2^{+}$, FeF$_2^{+}$ + F$^{—}$= FeF$_3$ According to the definition of the side reaction coefficient, $\alpha_{Fe^{3+}(F^{-})} = \frac{[Fe^{3+}]+[FeF^{2+}]+[FeF_2^{+}]+[FeF_3]}{[Fe^{3+}]} = \frac{c_{Fe^{3+}}}{[Fe^{3+}]}$ therefore $[Fe^{3+}] = \frac{c_{Fe^{3+}}}{\alpha_{Fe^{3+}(F^{-})}}$ (2) Substitute equations (1) and (2) into Nernst equation, and get: $E = E^{\theta}_{Fe^{3+}/Fe^{2+}} + 0.059\lg \frac{c_{Fe^{3+}}/\alpha_{Fe^{3+}(F^{-})}}{c_{Fe^{2+}}}$	Because H$_3$AsO$_4$ is triprotic acid, the distribution fraction of H$_3$AsO$_4$ is $\delta_{H_3AsO_4} = \frac{[H_3AsO_4]}{[H_3AsO_4] + [H_2AsO_4^{-}] + [HAsO_4^{2-}] + [AsO_4^{3-}]}$ $= \frac{[H_3AsO_4]}{c_{H_3AsO_4}}$ hence $[H_3AsO_4] = c_{H_3AsO_4}\delta_{H_3AsO_4}$ (1) similarly $[HAsO_2] = c_{HAsO_2}\delta_{HAsO_2}$ (2) Substitute equations (1) and (2) into Nernst equation, and get: $E = E^{\theta}_{H_3AsO_4/HAsO_2} + \frac{0.059}{2}\lg \frac{C_{H_3AsO_4}\delta_{H_3AsO_4}[H^{+}]^2}{C_{H_3AsO_4}\delta_{HAsO_2}}$
Step 3 According to the algorithm of	According to the rules of the logarithmic algorithm, the following formula is obtained	According to the rules of the logarithmic algorithm, the following formula is obtained	According to the rules of the logarithmic algorithm, the following formula is obtained

logarithm, the term containing analytical concentrations is separated out alone and the sum of the other two terms is the conditional potential	$E = E^{\theta}_{Cu^{2+}/Cu^{+}} + 0.059\lg([I^{-}]/Ksp) + 0.059\lg c_{Cu^{2+}}$ Add the first two items on the right of the equal sign to get the conditional potential $E^{\theta'} = E^{\theta}_{Cu^{2+}/Cu^{+}} + 0.059\lg(^{-}\square I/Ksp)$	$E = E^{\theta}_{Fe^{3+}/Fe^{2+}} + 0.059\lg\frac{1}{\alpha_{Fe^{3+}(F^{-})}} + 0.059\lg\frac{c_{Fe^{3+}}}{c_{Fe^{2+}}}$ Add the first two items on the right of the equal sign to get the conditional potential $E^{\theta'} = E^{\theta}_{Fe^{3+}/Fe^{2+}} + 0.059\lg\frac{1}{\alpha_{Fe^{3+}(F^{-})}}$	$E = E^{\theta}_{H_3AsO_4/HAsO_2} + \frac{0.059}{2}\lg\frac{[H^{+}]^{2}\delta_{H_3AsO_4}}{\delta_{HAsO_2}} + \frac{0.059}{2}\lg\frac{C_{H_3AsO_4}}{C_{HAsO_2}}$ Add the first two items on the right of the equal sign to get the conditional potential $E^{\theta'} = E^{\theta}_{H_3AsO_4/HAsO_2} + \frac{0.059}{2}\lg\frac{[H^{+}]^{2}\delta_{H_3AsO_4}}{\delta_{HAsO_2}}$

It can be seen from the above table that when calculating the conditional potential in the three-step method, the first step must be to write the Nernst equation correctly, which is the basis of the three-step method. Write the equilibrium concentration of the oxidized form on the numerator of the logarithmic term and write the equilibrium concentration of the reduced form on the denominator, that is $E_{Ox/Red} = E^{\theta}_{Ox/Red} + \frac{0.059}{n}\lg\frac{[Ox]}{[Red]}$. If there are H^+ and OH^- in the half-reaction, then $[H^+]$ and $[OH^-]$ also appear in the Nernst equation. The second step is the "key step", in which the transition from the equilibrium concentration to the analytical concentration should be completed. First, write down the side reactions of oxidized and reduced forms: the formation of precipitation, the occurrence of complexation reactions, the occurrence of acid dissociation or basic dissociation, and so on.

Then according to the definition formula of solubility product constant Ksp, the definition formula of the side reaction coefficient and distribution fraction, the mathematical relationships between the equilibrium concentrations of the oxidized and reduced forms and their analytical concentrations are deduced. The equilibrium concentrations are expressed by the expressions containing the analytical concentrations, and then they are substituted into the Nernst equation to obtain the following formula $E_{Ox/Red} = E^{\theta}_{Ox/Red} + \frac{0.059}{n}\lg\frac{c_{Ox}/\alpha_{Ox}}{c_{Red}/\alpha_{Red}}$ or $E_{Ox/Red} = E^{\theta}_{Ox/Red} + \frac{0.059}{n}\lg\frac{c_{Ox}\cdot\delta_{Ox}}{c_{Red}\cdot\delta_{Red}}$ (Here, take those containing side reaction coefficients and distribution fraction s as examples, and other examples containing Ksp are shown in Table 1). The difficulty of this step mainly involves the side reaction coefficient mentioned in the chapter of complexometric titration and the distribution fraction mentioned in the chapter of acid-base titration. If these two important concepts are not mastered well, the conditional potential cannot be calculated correctly. In other words, the calculation of conditional potential is actually a comprehensive application of the knowledge learned from acid-base equilibrium, complexation equilibrium, precipitation dissolution equilibrium and oxidation-reduction equilibrium. In the third step, according to the algorithm of logarithm, separate out the term containing analytical concentrations alone (that is $E_{Ox/Red} = E^{\theta}_{Ox/Red} + \frac{0.059}{n}\lg\frac{\alpha_{Red}}{\alpha_{Ox}} + \frac{0.059}{n}\lg\frac{c_{Ox}}{c_{Red}}$ or $E_{Ox/Red} = E^{\theta}_{Ox/Red} + \frac{0.059}{n}\lg\frac{\delta_{Ox}}{\delta_{Red}} + \frac{0.059}{n}\lg\frac{c_{Ox}}{c_{Red}}$) and the sum of the other two terms on the right of the equal sign is the conditional potential $E^{\theta'}{}_{Ox/Red} = E^{\theta}{}_{Ox/Red} + \frac{0.059}{n}\lg\frac{\alpha_{Red}}{\alpha_{Ox}}$ or $E^{\theta'}{}_{Ox/Red} = E^{\theta}{}_{Ox/Red} + \frac{0.059}{n}\lg\frac{\delta_{Ox}}{\delta_{Red}}$. The second term on the right of the equal sign includes the effects of various external conditions on the potential, so the sum of the two terms is called the conditional potential.

2 "THREE-STEP METHOD" TO CALCULATE THE SOLUBILITY OF PRECIPITATES

The second typical case is for another important point of knowledge "solubility calculation", the "three-step method" was also summarized to calculate the solubility of the precipitation under various conditions. Table 2 demonstrates how to apply the three-step method to calculate the effects of common ion effect, acid effect and complex effect on solubility.

Table 2 Three-step method to calculate solubility

	Common Ion Effect e.g. Add excess SO_4^{2-} to the Ba^{2+} solution until [SO_4^{2-}] = 0.01mol·L^{-1}, calculate the solubility of $BaSO_4$ in this case.	Acid Effect e.g. Calculate the solubility of CaC_2O_4 at pH=2	Complex Effect e.g. Calculate the solubility of AgCl in 0.10 mol·L^{-1}Cl$^-$.
Step 1 Write down the precipitation-dissolution equilibrium (main reaction), side reactions, and the relationship between the equilibrium concentration of configurational ions and the solubility S	$BaSO_4(s) \Leftrightarrow Ba^{2+} + SO_4^{2-}$ $S \quad 0.01 + S$ [Ba^{2+}] is equal to solubility S, and [SO_4^{2-}] is equal to 0.01+S.	$CaC_2O_4(s) \Leftrightarrow Ca^{2+} + C_2O_4^{2-}$ $S \quad \Updownarrow H^+$ $HC_2O_4^-$ $H_2C_2O_4$ $[C_2O_4^{2-}] + [HC_2O_4^-] + [H_2C_2O_4]$ $= [(C_2O_4^{2-})'] = S$ The main reaction is the dissolution of CaC_2O_4 to produce Ca^{2+} and $C_2O_4^{2-}$, and the side reaction is the combination reaction of $C_2O_4^{2-}$ and H^+ (acid effect). [Ca^{2+}] is equal to the solubility S. Due to the occurrence of side reactions, [($C_2O_4^{2-}$)'] is equal to S, but [$C_2O_4^{2-}$] isn't equal to S.	$AgCl(s) \Leftrightarrow Cl^- + Ag^+$ $0.1 + S \quad \Updownarrow Cl^-$ $AgCl, AgCl_2^-, \ldots$ $[Ag^+] + [AgCl] + [AgCl_2^-] + [AgCl_3^{2-}] + [AgCl_4^{3-}]$ $= [(Ag^+)'] = S$ The main reaction is the dissolution of AgCl to produce Ag^+ and Cl^-, and the side reaction is the complexation effect occurring between Ag^+ and Cl^-. The [Cl^-] is equal to 0.1+S (common ion effect) and because of the side reaction, [(Ag^+)'] is equal to the solubility S but [Ag^+] is not equal to S.

Step 2 According to the definition of the solubility product constant Ksp and the relationship between the equilibrium concentration of configurational ions and the solubility S, a set of equations is created	$\begin{cases} [Ba^{2+}] = S & (1) \\ [SO_4^{2-}] = 0.01 + S \approx 0.01 & (2) \\ K_{sp} = [Ba^{2+}][SO_4^{2-}] & (3) \end{cases}$	$\begin{cases} [Ca^{2+}] = S & (1) \\ [(C_2O_4^{2-})'] = S & (2) \\ K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = [Ca^{2+}]\dfrac{[(C_2O_4^{2-})']}{\alpha_{C_2O_4^{2-}(H^+)}} & (3) \end{cases}$	$\begin{cases} [Cl^-] = 0.1 + S \approx 0.1 & (1) \\ [(Ag^+)'] = S & (2) \\ K_{sp} = [Cl^-][Ag^+] = [Cl^-]\dfrac{[(Ag^+)']}{\alpha_{Ag^+(Cl^-)}} & (3) \end{cases}$
Step 3 The solubility S is calculated by solving the system of equations	Substitute equations (1) and (2) into equation (3) to obtain the formula for S: $S = \dfrac{K_{sp}}{0.01}$	Substitute equations (1) and (2) into equation (3) to obtain the formula for S $S = \sqrt{K_{sp}\alpha_{C_2O_4^{2-}(H^+)}}$	Substitute equations (1) and (2) into equation (3) to obtain the formula for S $S = \dfrac{Ksp \cdot \alpha_{Ag^+(Cl^-)}}{0.10}$

It can be seen from Table 2 that the solubility is calculated according to the "three-step method": the first step is to write the main reaction and side reactions, which is the basis of the three-step method. To calculate the solubility correctly, it is necessary to know all the reactions that occur in the system. It is important to note that when a side reaction occurs, such as an acid effect, $[C_2O_4^{2-}]$ is no longer equal to solubility S, but $[(C_2O_4^{2-})']$ (= $[C_2O_4^{2-}]+[HC_2O_4^{-}]+[H_2C_2O_4]$, the total concentration of all the oxalate species in equilibrium, i.e. analysis concentration of all the oxalate species) is equal to solubility S. The same is true when a complexation effect occurs, where $[Ag^+]$ is not equal to S, but $[(Ag^+)']$ (= $[Ag^+]+[AgCl]+[AgCl_2^+]+[AgCl_3^{2+}]+[AgCl_4^{3+}]$, the total concentration of all the Ag^+ species in equilibrium) is equal to the solubility S. In the second step, a system of equations is established based on the definition of solubility product and the relationship between the equilibrium concentration of constitutive ions and solubility S. This step is the core of the three-step method and the step where the difficulties are concentrated.

The thing to note in this step is that the third equation for K_{sp} should not be written as an equation for the conditional solubility product constant K'_{sp} [3]. K_{sp} is constantly equal to the equilibrium concentration of the configurational cation multiplied by the equilibrium concentration of the configurational anion. In contrast, K'_{sp} is equal to product of the analysis concentration of the configurational cation and anion and it varies with the composition of the solution. Therefore, when calculating solubility, it is recommended to use K_{sp} instead of K'_{sp}. Since the relationship between the equilibrium concentration of the configurational ion and the analytical concentration is involved in this step, the concept of the side reaction coefficient is used again. In the third step, the formula for solubility is obtained by substituting the first and second equations into the third equation. In this step, the coefficients of the side reactions involved need to be calculated correctly. Regarding the formula of S, it can be briefly summarized that when there is a common ion effect, the formula of S is in the form of fraction; when there is no common ion effect, only acid or complex effect, the formula of S exists in the form of a square root $\sqrt{K_{sp} \cdot \alpha}$, where α represents coefficient of the side reaction.

For the above two important points of knowledge, we have summarized and taught students the three-step method, so that they can solve the same type of problem on the basis of mastering the method. By learning these methods, students are actually taught to see the essence through the phenomena and find the regularity behind the complicated apparent phenomena. This is beneficial to the development of chemistry students' ability to think logically and summarize inductively [4,5].

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