

Comprehensive Analysis of Acid-Base Equilibria Using MBE, CBE, and PBE *

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1 Acid-Base Reactions and Equilibria in Solution

1.1 Ion Activity and Activity Coefficient

It is known that chemical reactions in solution are related to the activity of reactants and products. The activity of an ion refers to its effective concentration in chemical reactions. Due to electrostatic interactions between ions in solution, their free movement and reactivity are thus affected, causing discrepancies between their effective and actual concentrations. If c_i denotes the equilibrium concentration of ion i (usually represented as $[i]$) and a_i denotes the activity, then their relationship can be expressed as:

$$a_i = \gamma_i c_i \quad (1)$$

The proportionality constant γ_i is called the activity coefficient of ion i , which reflects the deviation between a real solution and an ideal solution. For strong electrolyte solutions, when the solution concentration is extremely dilute, the distance between ions becomes quite large, making their mutual force negligible. At this point, they can be considered as an ideal solution, and the ion's activity coefficient can be regarded as 1, i.e., $a_i = c_i$.

Currently, there is no good quantitative method for calculating the activity coefficient of ions in high-concentration electrolyte solutions due to the complexity of the situation. However, for dilute solutions ($\leq 0.1 \text{ mol} \cdot \text{L}^{-1}$), the Debye-Hückel equation can be used:

$$-\log \gamma_i = \frac{0.51 z_i^2 \sqrt{I}}{1 + B a_i \sqrt{I}} \quad (2)$$

*MBE = Material Balance Equation, CBE = Charge Balance Equation, PBE = Proton Balance Equation

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where z_i is the charge of ion i , B is a constant (equal to 0.00328 at 25°C), a_i is the ion volume parameter, approximately equal to the effective radius of the hydrated ion in pm (10^{-12} m), and I is the ionic strength of the solution. When the ionic strength is small, the size of the hydrated ion can be ignored, and the activity coefficient can be calculated using the Debye-Hückel limiting law:

$$-\log \gamma_i = 0.51 z_i^2 \sqrt{I} \quad (3)$$

This formula can also be used for approximate calculations.

The ionic strength I is related to the concentration of various ions in the solution and their charges. The ionic strength of a dilute solution can be calculated as follows:

$$I = \frac{1}{2} \sum_i c_i z_i^2 \quad (4)$$

1.2 Acid-Base Reactions and Equilibrium Constants in Solution

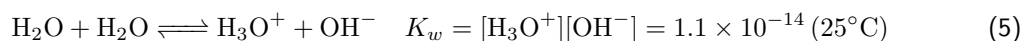
According to Bronsted's proton theory, any substance that can donate protons is an acid, and any substance that can accept protons is a base. Substances that can both donate and accept protons are amphiprotic species. (For instance, H_2O is an amphiprotic specie because it can donate a proton to form OH^- and accept a proton to form H_3O^+ .) Acid-base reactions are the process of proton exchange between acids and bases.

Acid	Base	Conjugate Base/Acid
HCl	H_2O	Cl^-
H_2SO_4	H_2O	HSO_4^-
H_3PO_4	H_2O	$H_2PO_4^-$
H_2CO_3	H_2O	HCO_3^-
H_2O	NH_3	OH^-
H_2O	HS^-	OH^-

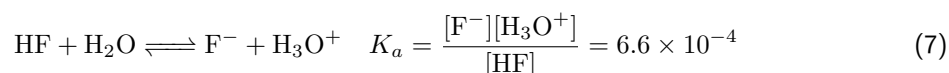
Table 1: Common Bronsted acids and bases

The following types of reactions are considered acid-base reactions in solution:

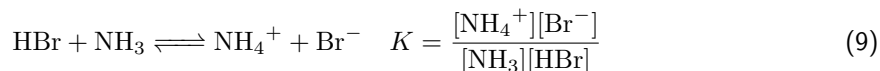
1. **Proton Transfer Between Solvent Molecules:** Also known as autoprotolysis, such as:



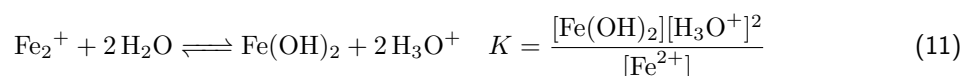
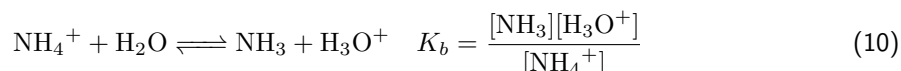
2. **Dissociation of Acid-Base Solutes:** The dissociation of acids or bases in solvent molecules, e.g.,



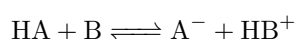
3. **Neutralization Reactions:** Usually the reverse of dissociation reactions, commonly used in acid-base titration:



4. **Hydrolysis Reactions:** Typical of weak acids and bases, where a weak acid or base dissociates slightly in water, such as:



In the previous discussion, the expression of the equilibrium constant of the reaction was represented by the equilibrium concentrations of the relevant components. In fact, it can also be expressed using activities or a combination of concentrations and activities. Suppose the chemical reaction in the solution is:



When both reactants and products are expressed in terms of activities, the equilibrium constant is:

$$K^\circ = \frac{a_{A^-} a_{HB^+}}{a_B a_{HA}}$$

This K° is called the **thermodynamic constant**, and its value depends on the temperature.

If all components are expressed in terms of equilibrium concentrations, then:

$$K = \frac{[A^-][HB^+]}{[B][HA]}$$

This equilibrium constant K is called the **concentration constant**. The relationship between K° and K is:

$$K^\circ = \frac{a_{A^-} a_{HB^+}}{[A^-][HB^+]} \cdot \frac{[B][HA]}{a_B a_{HA}} = K \cdot \frac{\gamma_{A^-} \gamma_{HB^+}}{\gamma_B \gamma_{HA}}$$

It can be seen that the concentration constant is not only related to temperature but also to the ionic strength of the solution. The concentration constant is only constant when both temperature and ionic strength are fixed.

If HB^+ is expressed in terms of activity and other components in terms of concentration, the equilibrium constant expression for the above reaction is:

$$K_{\text{mix}} = \frac{[A^-] a_{HB^+}}{[B][HA]}$$

This K_{mix} is called the mixed constant. Obviously, K_{mix} is also related to temperature and ionic strength. In practical work, since the activities of H^+ or OH^- can be easily measured using a pH meter, they are often expressed in terms of activities, while other relevant components are mostly expressed in terms of concentrations. In this case, it is more convenient to use the mixed constant for calculations.

In the treatment of acid-base equilibrium in analytical chemistry, since the solution concentration is generally small, the effect of ionic strength is usually ignored, and the activity constant is used instead of the concentration constant for related calculations. This approach can meet the requirements of general work, but when more precise calculations are needed, such as calculating the pH of standard buffer solutions, the effect of ionic strength on chemical equilibrium should be considered.

2 Material Balance, Charge Balance, and Proton Balance

The expression of the acid-base equilibrium constant is the basic relationship for acid-base equilibrium calculations. However, relying solely on this relationship to handle acid-base equilibrium problems can often encounter difficulties. It becomes much easier if other equilibrium relationships present in the solution are considered. The following are some commonly used equilibria.

2.1 MBE: Material Balance Equation

Material balance refers to the total concentration (i.e., analytical concentration c) of a given substance in a chemical equilibrium system being equal to the sum of the equilibrium concentrations of all relevant species. The mathematical expression is called the material balance equation (MBE). For example, the material balance for a solution with concentration c of H_3PO_4 is:

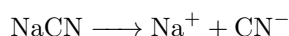
$$[H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] = c$$

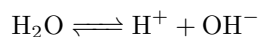
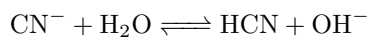
Similarly, for a solution with concentration c of Na_2SO_4 , the material balance equations related to Na^+ and SO_4^{2-} can be written as:

$$[Na^+] = 2c, \quad [SO_4^{2-}] + [HSO_4^-] + [H_2SO_4] = c$$

2.2 CBE: Charge Balance Equation

Since the solution is electrically neutral, the amount of positive charge carried by cations in the same solution should equal the amount of negative charge carried by anions. This is known as charge balance. The expression considering the charge numbers and concentrations of various ions is called the charge balance equation (CBE). For example, in a solution with concentration c of $NaCN$, the following reactions occur:

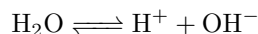
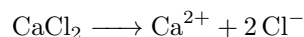




Thus, the amount of positive charge carried by cations in the solution is $[\text{H}^+] + [\text{Na}^+]$, and the amount of negative charge carried by anions is $[\text{CN}^-] + [\text{OH}^-]$. Since the solution is electrically neutral, they are equal:

$$[\text{H}^+] + c = [\text{CN}^-] + [\text{OH}^-]$$

For a solution with concentration c of CaCl_2 , based on the following reactions:



The cations in the solution are Ca^{2+} and H^+ , and the anions are Cl^- and OH^- . Since Ca^{2+} carries two positive charges, the charge balance equation should multiply $[\text{Ca}^{2+}]$ by 2 to ensure that the units of charge amounts represented by the ion concentrations are the same. Therefore, the charge balance equation is:

$$[\text{H}^+] + 2[\text{Ca}^{2+}] = [\text{OH}^-] + [\text{Cl}^-]$$

2.3 PBE: Proton Balance Equation

According to the proton theory of acids and bases, the essence of acid-base reactions is the transfer of protons. The result of acid-base reactions in the solution is that some substances lose protons, and some substances gain protons. Clearly, the amount of protons gained by substances (i.e., bases) should equal the amount of protons lost by substances (i.e., acids). This is known as proton balance. The expression considering the number of protons gained or lost and the concentrations of relevant components is called the proton balance equation (PBE).

Since there are often multiple acid-base components in the solution, it is necessary to know which components gain protons and which lose protons when writing the proton balance equation. When determining who gains or loses protons, some acid-base components are usually chosen as reference levels (reference level or zero level). Compared to these reference levels, components with fewer protons are the proton-losing products, and those with more protons are the proton-gaining products. The reference level is usually chosen as the original acid-base components or the acid-base components that are present in large amounts and directly related to proton transfer in the solution. It is worth noting that for the same substance, only one species can be chosen as the reference level. Additionally, when dealing with polyprotic acids and bases, some components may transfer more than one proton, and a corresponding coefficient should be multiplied in front of the equilibrium concentration representing the amount of protons.

For example, consider an aqueous solution of $(\text{NH}_4)\text{HPO}_4$. Using NH_3 , HPO_4^{2-} , and H_2O as reference levels, the proton-gaining products are H_3PO_4 , H_2PO_4^- , and H^+ , and the proton-losing products are NH_3 , PO_4^{3-} , and OH^- . The proton balance equation is:

$$[\text{H}^+] + [\text{H}_2\text{PO}_4^-] + 2[\text{H}_3\text{PO}_4] = [\text{OH}^-] + [\text{PO}_4^{3-}] + [\text{NH}_3]$$

Sometimes, when acid-base components dissolve in water, significant acid-base reactions occur, and the main acid-base components present in the solution are no longer the original acid-base components. In this case, the original acid-base components can still be used as reference levels, and the amount of protons gained or lost remains equal. For example, in a solution with concentration c of Na_2S , the original acid-base components S^{2-} and H_2O can be chosen as the proton reference levels. Thus, the proton-gaining products are H^+ , HS^- , and H_2S , and the proton-losing product is OH^- . The proton balance equation is:

$$[\text{H}^+] + [\text{HS}^-] + 2[\text{H}_2\text{S}] = [\text{OH}^-]$$

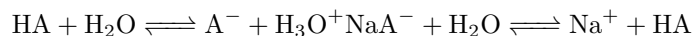
For acid-base conjugate systems, they can be regarded as mixtures of weak acids with strong bases or strong acids with weak bases. Therefore, the proton reference levels can be chosen as the corresponding weak acids with strong bases or strong acids with weak bases. For example, in a solution of 0.2 mol/L NaAc and 0.1 mol/L HAc , the proton reference levels can be chosen as NaOH (0.2 mol/L, i.e., strong base), HAc , and H_2O , or HCl (0.1 mol/L, i.e., strong acid), Ac^- , and H_2O . The proton balance equation is:

$$[\text{Na}^+] + [\text{H}^+] = [\text{Ac}^-] + [\text{OH}^-]$$

3 Deduction of the Henderson-Hasselbalch Equation with MBE and CBE

The Henderson-Hasselbalch equation is a widely used formula in buffer solution equilibrium calculations. It is derived from the material balance equation (MBE) and charge balance equation (CBE) for a weak acid solution. The derivation process is as follows:

Consider a buffer solution containing a weak acid HA and its conjugate base A^- . The dissociation reaction of HA is:



Let $[HA] = c_a$ and $[A^-] = c_b$. From the Material Balance Equation we have:

$$[Na^+] = c_a[HA] + [A^-] = c_a + c_b$$

From the Charge Balance Equation we have:

$$[Na^+] + [H^+] = [A^-] + [OH^-]$$

Cross multiplying the above two equations, we get:

$$[A^-] = c_b + [H^+] - [OH^-] \quad [HA] = c_a - [H^+] + [OH^-]$$

Substitute the above two equations into the equilibrium constant expression:

$$K = \frac{[A^-][H^+]}{[HA]} = \frac{c_b + [H^+] - [OH^-][H^+]}{c_a - [H^+] + [OH^-]}$$

As $[H^+]$ and $[OH^-]$ are negligible compared to c_a and c_b , the equation can be simplified to:

$$K = \frac{c_b[H^+]}{c_a}$$

And therefore, the Henderson-Hasselbalch equation is derived:

$$pH = pK + \log \frac{[A^-]}{[HA]}$$

And that also explains why the Henderson-Hasselbalch equation is only applicable to weak acid solutions. Since the dissociation of weak acids is incomplete, the concentrations of HA and A^- are not significantly affected by the presence of H^+ and OH^- .

4 Code Implementation

Now that we have discussed the basic principles of acid-base equilibrium calculations, and the material balance, charge balance, and proton balance equations. From any two of the MBE, CBE, and PBE, the equilibrium concentrations of all relevant components in the solution can be calculated.

4.1 Material Balance Equation

```
class Acid:
    def __init__(self, Ka=None, pKa=None, charge=None, conc=None):
        self.pKa = np.array([pKa] if pKa else -np.log10(Ka), dtype=float)
        self.pKa.sort()
        self.Ka = 10**(-self.pKa)
        self.charge = np.arange(charge, charge - len(self.Ka) - 1, -1)
        self.conc = conc

    def alpha(self, pH):
        h3o = 10**(-np.array([pH] if isinstance(pH, (int, float)) else pH, dtype=float))
        h3o_pow = h3o**np.arange(len(self.Ka) + 1)[::-1]
        Ka_prod = np.cumprod(np.append(1., self.Ka))
        h3o_Ka = h3o_pow * Ka_prod
        den = h3o_Ka.sum(axis=1) if len(h3o.shape) > 1 else h3o_Ka.sum()
        return h3o_Ka / den.reshape(-1, 1) if len(h3o.shape) > 1 else h3o_Ka / den
```

The above code defines a class `Acid` that can be used to calculate the dissociation of acids. The `alpha` method calculates the degree of dissociation of the acid at a given pH value.

It is related to the MBE as the sum of the equilibrium concentrations of all relevant species should equal to 1. This is a very important constraint in the calculation of the equilibrium concentrations of all relevant species.

4.2 Charge Balance Equation

```
def ChargeBalance(acid, pH):
    Kw = 1.1e-14
    h3o = 10**(-pH)
    oh = Kw / h3o
    alpha = acid.alpha(pH)
    pos = h3o + sum(alpha[acid.charge > 0] * acid.conc * acid.charge[acid.charge > 0])
    neg = oh + sum(alpha[acid.charge < 0] * acid.conc * abs(acid.charge[acid.charge < 0]))
    return pos, neg
```

The above code defines a basic function `ChargeBalance` that calculates the positive and negative charges in the solution at a given pH value. With this code, we can plot the charge balance curve of a solution. Here we use $(\text{NH}_4)_3(\text{PO}_4)$ as an example.

The positive charges can be calculated as:

$$P = [\text{H}^+] + 3[\text{NH}_4^+]$$

The negative charges can be calculated as:

$$N = [\text{OH}^-] + 3 \times [\text{PO}_4^{3-}] + 2 \times [\text{HPO}_4^{2-}] + [\text{H}_2\text{PO}_4^-]$$

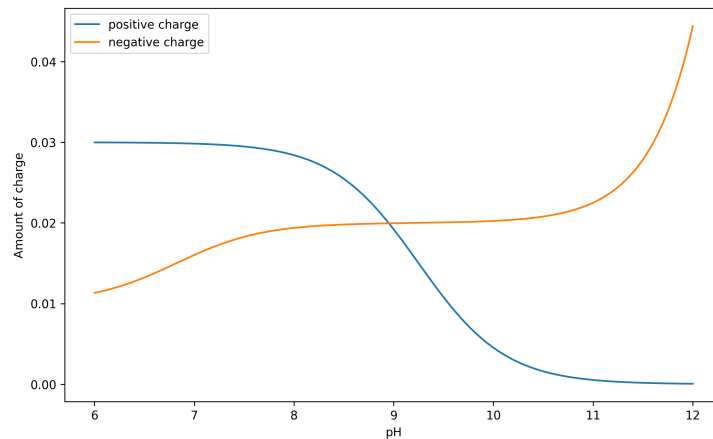


Figure 1: Charge balance curve of $(\text{NH}_4)_3(\text{PO}_4)$

From the above figures (1 and 5), we can see that the positive and negative charges are equal at the isoelectric point, which is the point where the solution is electrically neutral.

Therefore we can use a minimization algorithm to find the isoelectric point of the solution. For example, we can use the `scipy.optimize.minimize` function to find the pH value where the absolute charge balance error is minimized. I have used the Nelder-Mead method to find the isoelectric point of $(\text{NH}_4)_3(\text{PO}_4)$.

$$\begin{aligned} &\text{minimize} \quad f(x) = \text{abs}(P - N) \\ &\text{subject to} \quad 0 \leq x \leq 14 \end{aligned} \tag{12}$$

Below is the code implementation of the `CBE_calc` class that calculates the isoelectric point of a solution.

```
class CBE_calc:
    def __init__(self, *species, Kw=1.01e-14):
        ...

    def Charge_diff(self, pH):
        ...
```

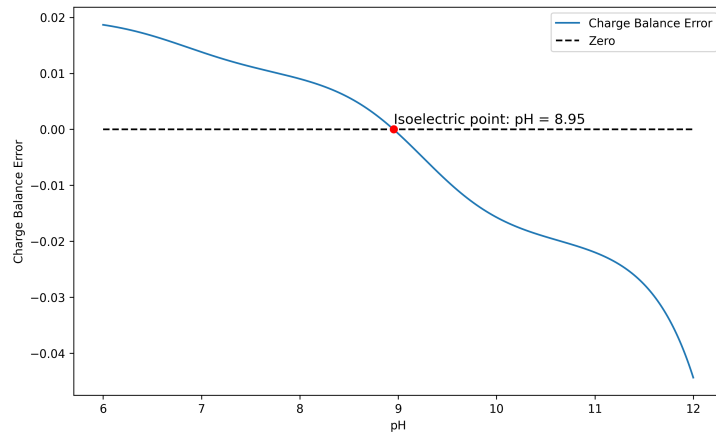


Figure 2: Charge balance error curve of $(\text{NH}_4)_3(\text{PO}_4)$, the error is calculated as the difference between the positive and negative charges

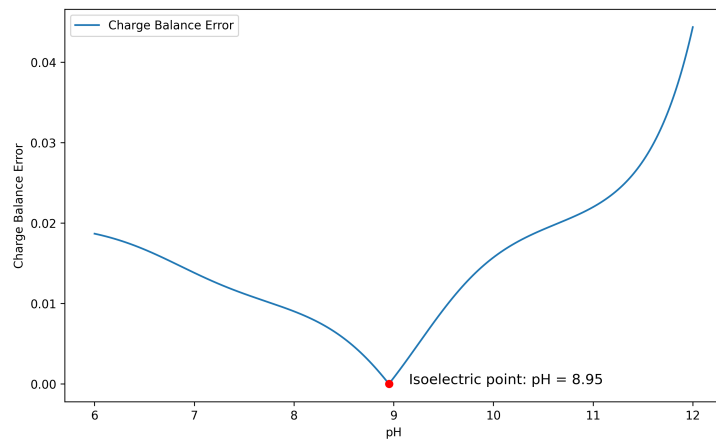


Figure 3: Absolute charge balance error curve of $(\text{NH}_4)_3(\text{PO}_4)$, the error is calculated as the absolute difference between the positive and negative charges

```
def pH_calc(self, start=7.0, method='Nelder-Mead', tol=1e-5):
    result = minimize(self.Charge_diff, start, method=method, tol=tol)
    self.pH = result.x[0] if result.x.size == 1 else result.x
```

4.3 Proton Balance Equation

The same calculation method of the charge balance equation can be used to calculate the proton balance equation. However, the Proton Balance Equation is more complex than the Charge Balance Equation, as it involves the dissociation of acids and bases. Proton Balance Equation requires a reference level to determine which components gain or lose protons.

For instance, still using $(\text{NH}_4)_3(\text{PO}_4)$ as an example, the proton balance equation can be written as:

1. using NH_4^+ , PO_4^{3-} and H_2O as reference
2. Proton gaining products: H_3PO_4 , H_2PO_4^- , H^+
3. Proton losing products: NH_3 , OH^-

$$\text{Gain} = [\text{H}^+] + [\text{H}_2\text{PO}_4^-] + 2 \times [\text{H}_3\text{PO}_4]$$

$$\text{Loss} = [\text{NH}_3] + [\text{OH}^-] + 3 \times [\text{PO}_4^{3-}]$$

Figure 5 shows the gain and loss proton curves of $(\text{NH}_4)_3(\text{PO}_4)$, and Figure 5 shows the proton balance error curve of $(\text{NH}_4)_3(\text{PO}_4)$. The isoprotonic point is the point where the gain and loss protons are equal. We can see that PBE calculation gives the same result as CBE calculation.

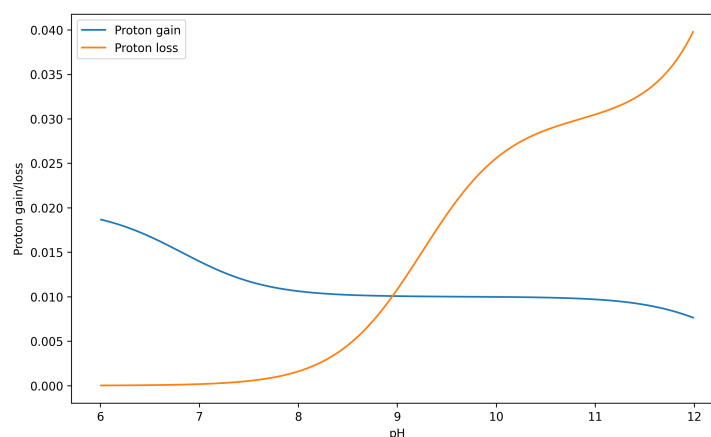


Figure 4: Proton balance curve of $(\text{NH}_4)_3(\text{PO}_4)$

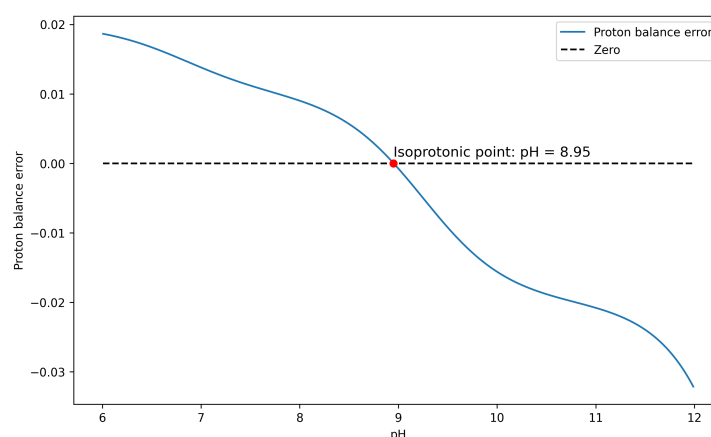


Figure 5: Proton balance error curve of $(\text{NH}_4)_3(\text{PO}_4)$, the error is calculated as the difference between the proton gaining and losing products

5 Conclusion

In this paper, we have explored the fundamental principles of acid-base equilibrium calculations, focusing on the Material Balance Equation (MBE), Charge Balance Equation (CBE), and Proton Balance Equation (PBE). These equations are essential tools for understanding and predicting the behavior of acid-base systems in solution.

We demonstrated the derivation and application of these equations through various examples, including the calculation of equilibrium constants and the use of the Henderson-Hasselbalch equation for buffer solutions. Additionally, we implemented Python code to calculate the dissociation of acids and the charge balance in solutions, providing a practical approach to solving complex equilibrium problems.

The graphical analysis of $(\text{NH}_4)_3(\text{PO}_4)$ using CBE and PBE highlighted the importance of these equations in identifying the isoelectric point, where the solution is electrically neutral. Both CBE and PBE calculations yielded consistent results, underscoring their reliability in acid-base equilibrium studies.

Overall, the integration of theoretical principles with computational tools offers a comprehensive framework for analyzing acid-base equilibria, facilitating more accurate and efficient solutions to chemical equilibrium problems.

Code Availability

The codes and data used in this paper are available on GitHub at [Github.com/Eric-xin/pH_Calculation](https://github.com/Eric-xin/pH_Calculation). The code is written in Python and can be run in any Python environment with the required libraries installed. Jupyter notebooks are also provided for interactive exploration of the calculations and results.

References

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