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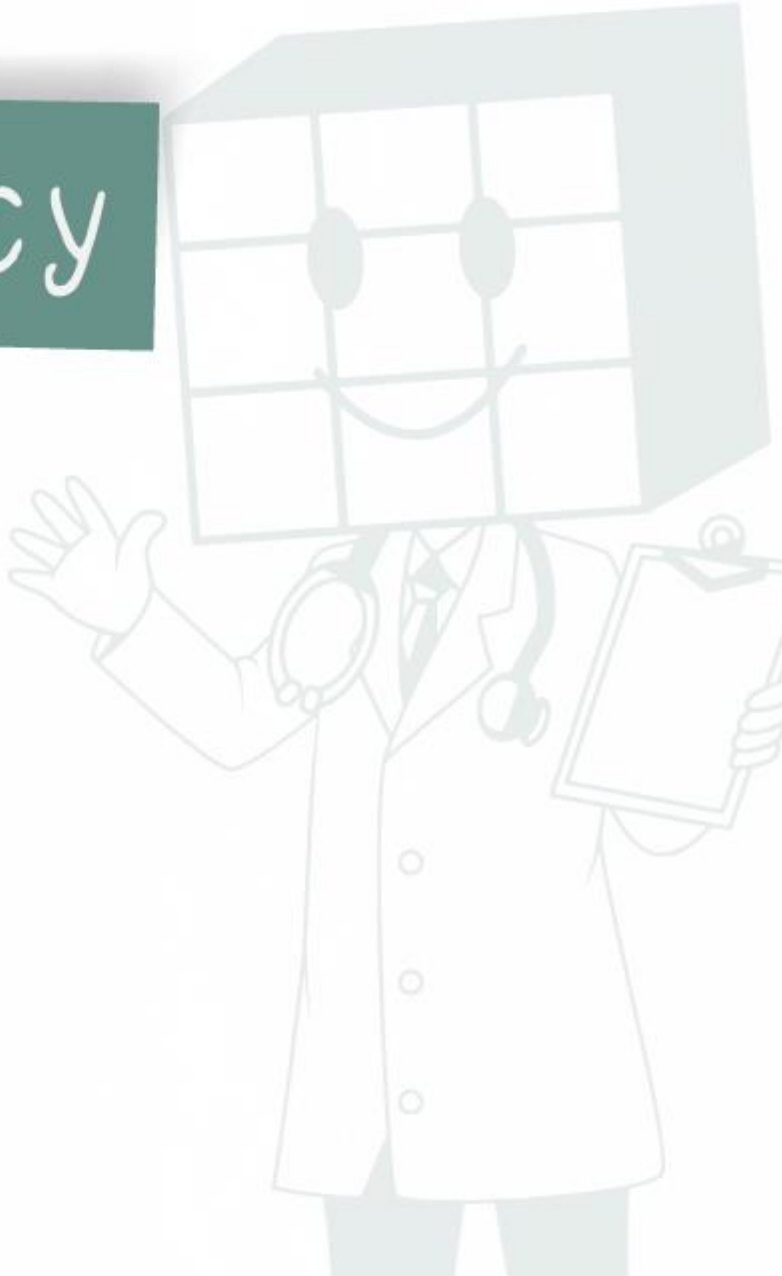
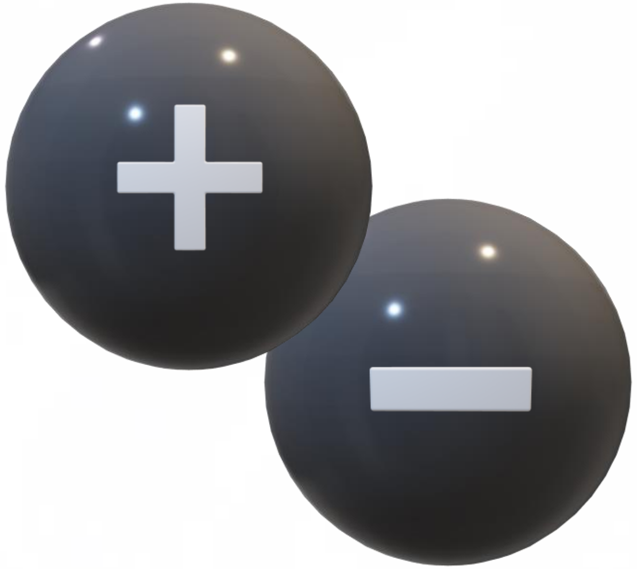
Physical Pharmacy



Ionic Equilibria 2



Contents

In this lecture, you'll learn:

- Understand the concepts of acid-base equilibria
  a. The ionization of weak acids and weak bases.
  b. The Ionization of polyprotic electrolytes
  c. The ionization of water

- Ampholytes

- Proton Balance Equation (PBE)

Equilibrium

- **can be defined as a balance between two opposing forces or actions**

- When a neutral molecule which does not contain ions but when dissolved in water splits to produce ions in the solution, the process is called ionization.

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Equilibrium

Ionic Equilibrium :

- The equilibrium between ions and unionized molecules in a solution of weak electrolytes is called “**ionic equilibrium**”.

- **Note**: ionic equilibrium occurs in solutions of weak electrolytes because the molecules are becoming ionized and the ions are constantly reuniting.

- The ionisation of a weak electrolyte, AB, is represented as :

  $K = \frac{[A^{+}]\,[B^{-}]}{[AB]}$ **K is the ionization constant**

- **$AB(s) + aq \rightleftharpoons A^{+}(aq) + B^{-}(aq)$**

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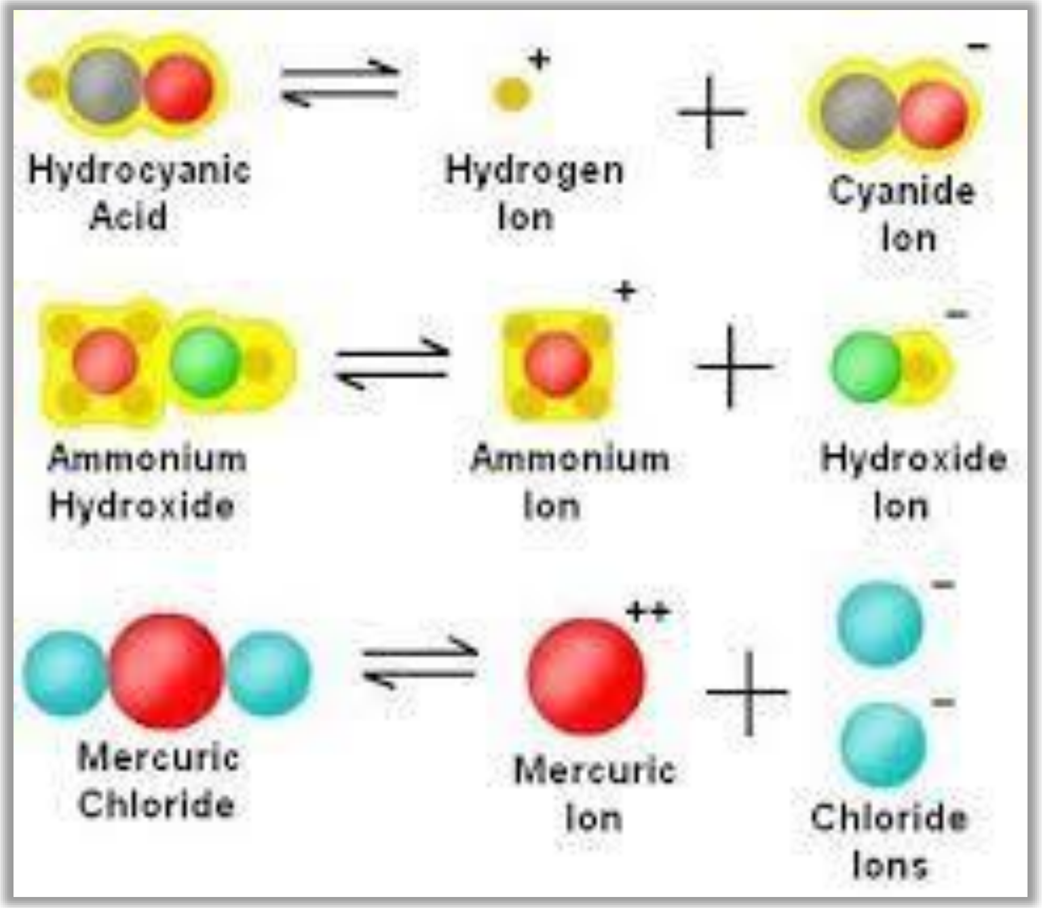
Equilibrium



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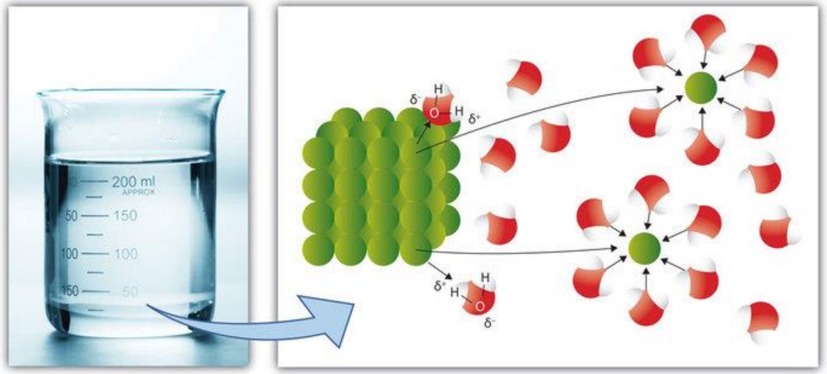
Equilibrium

Ionic Equilibrium : Reactions involving ionic equilibrium may be classified as follows:

1. **Equilibria involving soluble ionic compounds such as weak acids and weak bases.**

2. **Equilibria involving sparingly soluble ionic compounds: Solubility product.**



- When an ionic compound is dissolved in water the ions which are already present in the solid compound separates out.

- The process is called **dissociation**.

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Equilibrium

Ionization of acids and bases:

- Acids that are capable of donating one **proton = monotropic acid**
- Bases capable of accepting one **proton = monotropic base**

- **The ionization of incompletely ionized acids may be considered a reversible reaction of the type**

$$HA \rightleftarrows H^{+} + A^{-}$$

- **where HA is the molecular acid and A– is its anion.**

- **An equilibrium expression based on the law of mass action may be applied to the reaction:**

$$Ka = \frac{[H^{+}][H^{-}]}{[HA]}$$

- **Ionization of bases may be written as:**

$$B + H_2O \quad BH^{+} + OH^{-}$$

- **The equilibrium expression for this reaction is:**

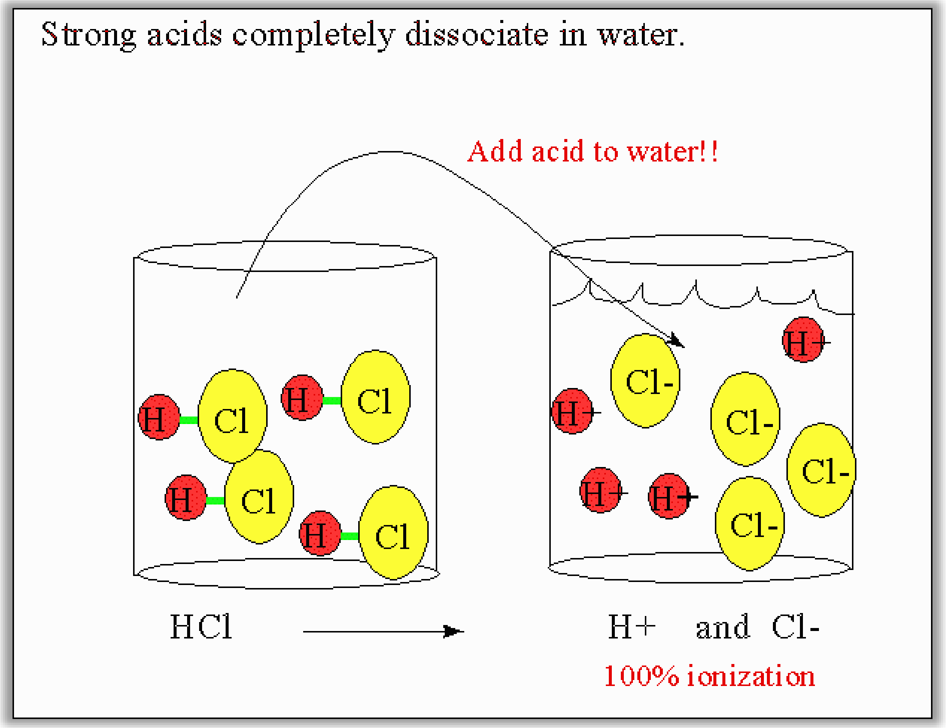
$$Kb = \frac{[BH^{+}][OH^{-}]}{[B]}$$

- **[H2O] is constant and not written**

Equilibrium

Ionization of acids and bases:

- where Ka and Kb are the ionization constants or dissociation constant of acid and base, respectively, and the brackets signify the concentration of each species.



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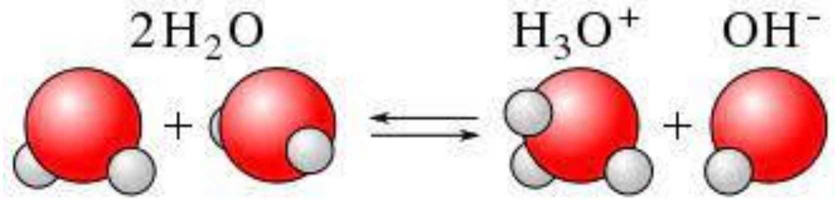
Equilibrium

The Ionization of Water:

- In a manner corresponding to the dissociation of weak acids and bases, water ionizes slightly to yield hydrogen and hydroxyl ions.

- A weak electrolyte requires the presence of water or some other polar solvent for ionization.



- Accordingly, one molecule of water can be thought of as a weak electrolytic solute that reacts with another molecule of water as the solvent.

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Equilibrium

The Ionization of Water:

- This autoprotolytic reaction is represented as:

$$H2O + H2O \rightleftharpoons H3O^{+} + OH^{-}$$

- The law of mass action is then applied to give the equilibrium expression

$$K = \frac{[H3O^{+}]\,[OH^{-}]}{[H2O]^{2}}$$

- $[H2O]^{2}$ is considered as a constant and is combined with k to give a new constant, Kw, known as the dissociation constant, the autoprotolysis constant, or the ion product of water:

$$Kw = k\,x\,[H2O]^{2}$$

- The value of the ion product is approximately $1\,x\,10^{-14}$ at 25°C; it depends strongly on temperature

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Equilibrium

Relationship Between Ka and Kb

- A simple relationship exists between the dissociation constant of a weak acid and that of its conjugate base, or between a weak base and its conjugated acid, when the solvent is amphiprotic.

- **The relationship is:**

$$KaKb = [H3O^{+}][OH^{-}] = Kw$$

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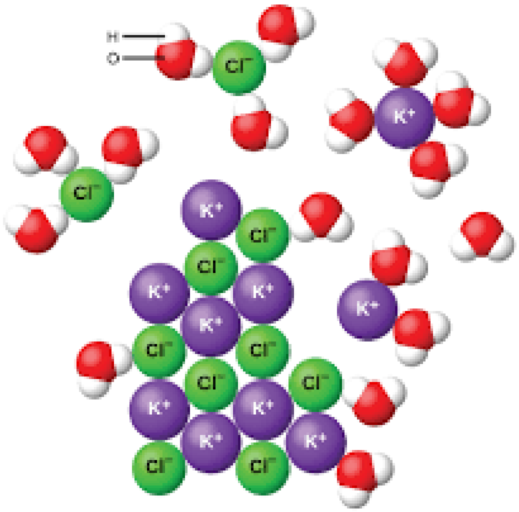
Equilibrium

Ionization of polyprotic electrolytes :

- Acids that are capable of donating more than one proton = polyprotic acid
- Bases capable of accepting more than one proton = polyprotic base

- The ionization of a polyprotic acid occurs in stages, two stages to diprotic (or dibasic) acids, three stages for triprotic acids



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Equilibrium

Ionization of polyprotic electrolytes :

- **Example:ionization of phosphoric acid, a tribasic acid**

$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^- \qquad K_1 = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = 7.5 \times 10^{-3}$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-} \qquad K_2 = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.2 \times 10^{-8}$$

$$HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-} \qquad K_3 = \frac{[H_3O^+][PO_4^{3-}]}{} = 2.1 \times 10^{-13}$$

Note:In any polyprotic electrolyte, the primary protolysis is greatest, and succeeding stages become less complete at any given acid concentration.

- The negative charges on the ion $\mathbf{HPO4^{-2}}$ make it difficult for water to remove the proton from the phosphate ion, as reflected in the small value of **K3**.

- Thus, phosphoric acid is weak in the third stage of ionization, and a solution of this acid contains practically no $\mathbf{PO4^{-3}}$ ions.

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Equilibrium

Ionization of polyprotic electrolytes :

- Each of the species formed by the ionization of a polyprotic acid can also act as a base. Thus, for the phosphoric acid system:

$$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^- \qquad K_{b1} = \frac{[HPO_4^{2-}][OH^-]}{[PO_4^{3-}]} = 4.8 \times 10^{-2}$$

$$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^- \qquad K_{b2} = \frac{[H_2PO_4^-][OH^-]}{[HPO_4^{2-}]} = 1.6 \times 10^{-7}$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^- \qquad K_{b3} = \frac{[H_3PO_4][OH^-]}{[H_2PO_4^-]} = 1.3 \times 10^{-12}$$

Equilibrium

Ionization of polyprotic electrolytes :

- **Notes:**

a. For a polyprotic substance (e.g., HnA), there are n+1 possible species in solution

b. Thus, for the phosphoric acid system, n = 3, so 3+1 =4, it means we have 4 possible species which are: $\boldsymbol{H3PO4}$, $\boldsymbol{H2PO4^{-}}$, $\boldsymbol{HPO4^{-2}}$, $\boldsymbol{PO4^{-3}}$

c. The total concentration of all species must equal the initial concentration of the acid

d. And Kw = K1Kb3 = K2Kb2 = K3Kb1

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Ampholytes

- A species that can function either as an acid or as a base is called an ampholyte and is said to be amphoteric in nature
- Water act both as an acid as well as a base, hence it's called "**amphoteric** " or "**amphiprotic**"
- In general, for a polyprotic acid system, all the species, with the exception of H_nA and A^{-n} are amphoteric
- **For example:** In the phosphoric acid system ($\boldsymbol{H3PO4}$), the species $\boldsymbol{H2PO4}^{-}$ and $\boldsymbol{HPO4}^{-2}$ can function either as an acid or a base

Equilibrium

Amphoytes

- Amino acids and proteins are ampholytes of particular interest in pharmacy.

- **Example**: glycine hydrochloride when dissolved in water, it ionizes as follows (observe the underline parts):

$$^{+}NH_3CH_2COOH + H_2O \rightleftarrows {}^{+}\underline{NH_3CH_2COO^{-}} + H_3O^{-}$$ Can accept a proton: act as a base

$$^{+}\underline{NH_3CH_2COO^{-}} + H_2O \rightleftarrows {}^{+}NH_2CH_2COO^{-} + H_3O^{-}$$ Can lose a proton (from the amine part): act as an acid

Equilibrium

Ampholytes

- The amphoteric species $^{+}$**NH3CH2COO**$^{-}$ is called a **zwitterion** and differs from the amphoteric species formed from phosphoric acid in that it carries both a positive and a negative charge, and the whole molecule is electrically neutral

- The pH at which the zwitterion concentration is a maximum is known as the **isoelectric point.**

- At the isoelectric point the net movement of the solute molecules in an electric field is negligible.

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Equilibrium

Calculation of pH : Proton Balance Equations

- In the Bronsted–Lowry system, the total number of protons released by the acidic species must equal the total number of protons consumed by basic species.

- This results in a very useful relationship known as the proton-balance equation (PBE).

$$\boldsymbol{PH = -\log[H3O^{+}]}$$

- PBE is an equation in which the sum of the concentration terms for species that form by proton consumption is equated to the sum of the concentration terms for species that are formed by the release of protons

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Equilibrium

Calculation of pH : Proton Balance Equations

- Generally, the PBE can be obtained in the following manner:

1. Start with the species added to water.
2. Place all species that can form when protons are released on the right side of the equation.
3. Place all species that can form when protons are consumed on the left side of the equation.
4. Multiply the concentration of each species by the number of protons gained or lost to form that species.
5. Add $[H3O^{+}]$ the left side of the equation and $[OH^{-}]$ to the right side of the equation.

- These result from the interaction of two molecules of water as shown previously during the explanation of ionization of water.

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Equilibrium

Calculation of pH : Proton Balance Equations

- For example:

a. When HCl is added to water, it dissociates completely into $H3O^+$ and Cl^- ions.

$$HCl + H2O \longrightarrow Cl^- + H3O^+$$

b. In the same solution, and actually in all aqueous solutions, $H3O^+$ and OH^- result from the dissociation of two water moleculesaccording to the equation

$$H2O + H2O \rightleftharpoons H3O^+ + OH^-$$

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Equilibrium

Calculation of pH : Proton Balance Equations

- Thus, Cl^-, OH^-, is formed by proton release **So** We write these species on the right side of PBE
- and $H3O^+$ is formed by proton consumption , **So** We write these species on the right side of PBE
- **Note**: Although $H3O^+$ is formed from two reactions (one from hydrolysis of water and the other from hydrolysis of HCl) , it is included only once in the PBE.
- The same would be true for OH^- if it came from more than one source
- Thus, the PBE for this reaction is: $[\boldsymbol{H3O^+}] = [\boldsymbol{HO^-}] + [\boldsymbol{Cl^-}]$

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Equilibrium

Calculation of pH : Proton Balance Equations (Examples)

What is the PBE when H3PO4 is added to water?.

Answer :

$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$$

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{-2}$$

$$HPO_4^{-2} + H_2O \rightleftharpoons H_3O^+ + PO_4^{-3}$$

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Calculation of pH : Proton Balance Equations (Examples)

We thus have :

$$[H_3O^+] = [OH^-] + [H_2PO_4^-] + 2[HPO_4^{-2}] + 3[PO_4^{-3}]$$

The species $H_2PO_4^-$ forms with the release of one proton, fom H_3PO_4.

The species HPO_4^{-2} forms with the release of two protons from H_3PO_4

The species PO_4^{-3} forms with the release of three protons.fom H_3PO_4

Equilibrium

Calculation of pH : Proton Balance Equations (Examples)

What is the PBE when Na_2HPO_4 is added to water? , Answer :

$$Na_2HPO_4 \longrightarrow 2Na + HPO_4^{-2}$$

$$HPO_4^{-2} + H_2O \longleftrightarrow PO_4^{-3} + H_3O^{+}$$

Action as acid (lost proton)

The HPO_4^{-2} is considered the starting species

$$HPO_4^{-2} + H_2O \longleftrightarrow H_2PO_4^{-} + OH^{-}$$

Action as base (consumed proton)

Remember: HPO_4^{-2} is ampholyte, can act as acid or base

$$H_2PO_4^{-} + H_2O \longleftrightarrow H_3PO_4 + OH^{-}$$

$$[H_3O^{+}] + [H_2PO_4^{-}] + 2[H_3PO_4] = [OH^{-}] + [PO_4^{-3}]$$

This is the proton balance equation

Calculation of pH : Proton Balance Equations (Examples)

What is the PBE when sodium acetate is added to water?

Answer :

$$CH_3COONa + H_2O \longrightarrow Na^+ + CH_3COO^-$$

$$CH_3COO^- + H_2O \longleftrightarrow CH_3COOH + OH$$

$$[H_3O^+] + [CH_3COOH] = [OH^-]$$

TheCH_2COO^- is considered to be the starting species.

The CH_3COOH can form whenCH_3COOH^- consumes one proton.

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Thank You !

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