



Ionic Equilibria



PHYSICAL PHARMACY
1ST SEMESTER / 2026-
2027

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Outline

Definitions:

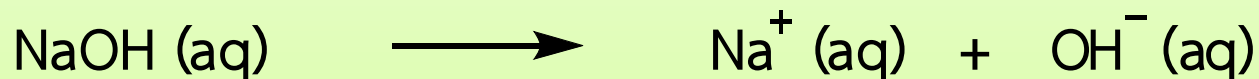
- Arrhenius, Brønsted–Lowry, Lewis
- Solvent classification
- Acid–base equilibrium, K_a , K_b , K_w
- Dissociation constant - K_a
- Ionization of Weak Bases (K_b)
- Autoionization of Water & K_w
- Relation Between K_a and K_b
- SÖRENSEN'S pH
- Proton Balance Equation (PBE)
- Calculation of pH

Arrhenius Definition

Acid: a substance that liberates H^+ upon dissociation.



Base: a substance that supplies OH^- upon dissociation.



Brønsted–Lowry Definition

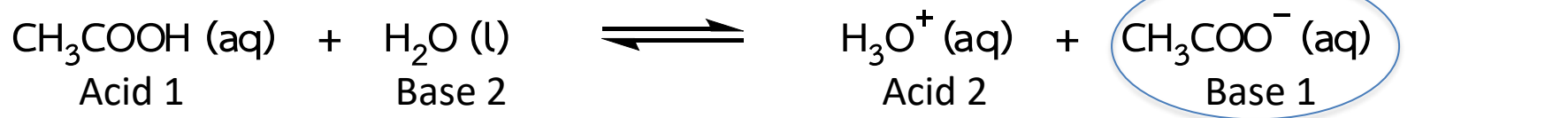


Acid: proton (H^+) donor. Any species that donates an H^+ ion. An acid must contain H in its formula; HNO_3 and H_2PO_4^- are two examples, all Arrhenius acids are Brønsted-Lowry acids.

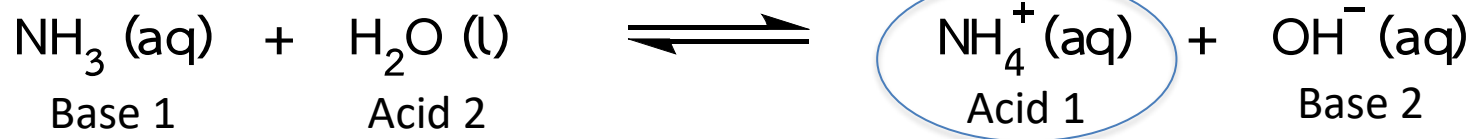
Base: proton (H^+) acceptor. Any species that accepts an H^+ ion. A base must contain lone pair of electrons to bind the H^+ ion; a few examples are NH_3 , CO_3^{2-} , F^- , as well as OH^- .

- In an acid-base reaction, the transfer of protons occurs from an acid to a base.

❖ Conjugate base:



❖ Conjugate acid:



- The relative strengths of acids and bases are measured by the tendencies of these substances to give up and take on protons.
- The strength of an acid **depends not only on** its ability to give up a proton but also on the ability of the solvent to accept the proton from the acid.



This is called the **basic strength of the solvent**.

Lewis Electronic Theory

Lewis acid: electron-pair acceptor (e.g.: BF_3 , AlCl_3 which don't contain H and acts as an acid).

Any substance, such as the H^+ ion, that can accept a pair of nonbonding electrons.

Lewis base: electron-pair donor:

Amines (R-NH_2): Nitrogen has a lone pair of electrons.

Ethers (R-O-R): Oxygen atom has two lone pairs.

Carboxylic acid anhydrides (R-CO-O-CO-R): Oxygen atoms have lone pairs that can interact with electron-deficient species.

(They don't contain OH and they act as a base).

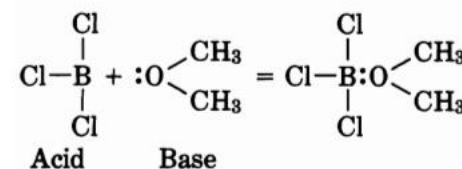
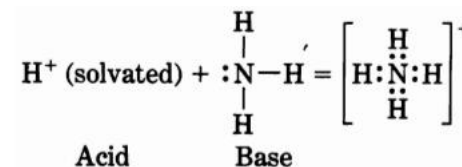
Any substance, such as the OH^- ion, that can donate a pair of nonbonding electrons.



Al has 3 valence electrons, forms 3 bonds with Cl

3 lone pairs (6 electrons)

1 unpaired electron (1 electron available for bonding) because valence is 7

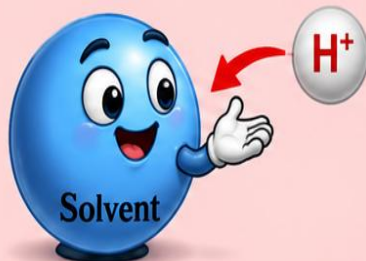


Classification of Solvents

1. **A Protophilic (basic solvent):** is one that is capable of accepting protons from the solute. Such solvents as acetone, ether, and liquid ammonia.
2. **A Protogenic (acidic solvent):** is a proton donating compound and is represented by acids such as formic acid, acetic acid, sulfuric acid, liquid HCl, and liquid HF.
3. **Amphiprotic solvents:** act as both proton acceptors and proton donors, and this includes water and the alcohols.
4. **Aprotic solvents:** these solvents neither accept nor donate protons. such as the hydrocarbons.

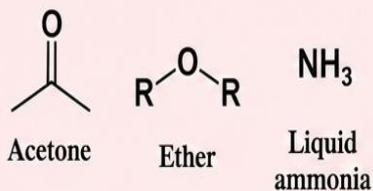
Classification of Solvents Based on Proton Transfer

1. Protophilic (Basic solvent)



Accepts protons (H^+)
from the solute

Examples:

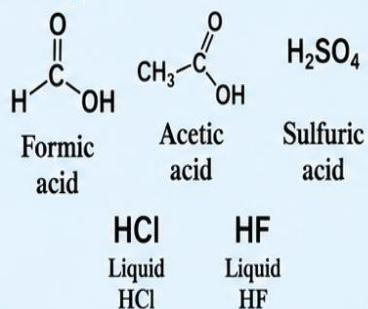


2. Protogenic (Acidic solvent)

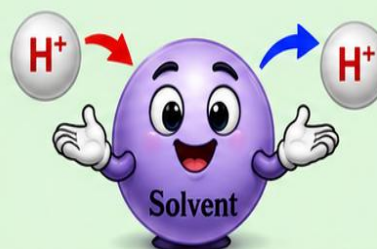


Donates protons (H^+)
to the solute

Examples:

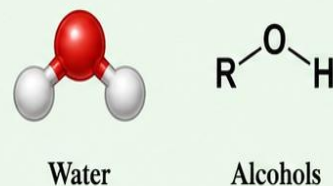


3. Amphiprotic solvents

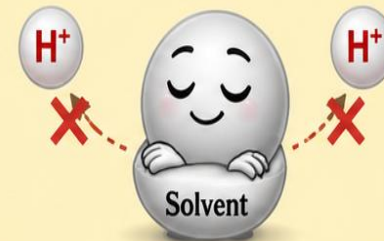


Act as both proton
acceptors and proton donors

Examples:



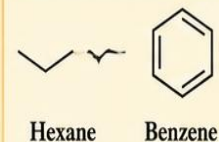
4. Aprotic solvents



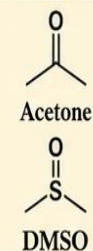
Neither accept nor donate
protons

Examples:

Nonpolar aprotic
(hydrocarbons)

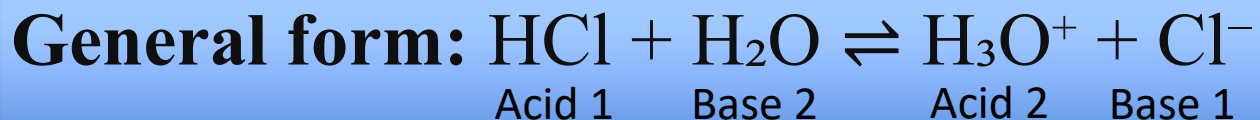


Polar aprotic



Acid–Base Equilibrium

- ▶ Acid–base reactions occur when an acid reacts with a base to form a new acid and a new base.



- ▶ The arrows pointing in the forward and reverse directions indicate that the reaction is proceeding to the right and left simultaneously.

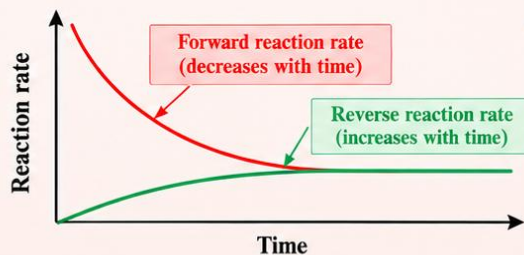
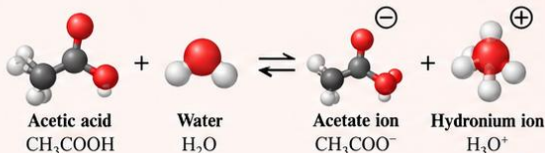
Acid–Base Equilibrium

According to the concept of equilibrium:

The rate of the **forward reaction decreases** with time as acetic acid is depleted, whereas the **rate of the reverse reaction begins at zero and increases** as larger quantities of hydrogen ions and acetate ions are formed. Finally, a **balance is attained when the two rates are equal**.

1. Initial stage

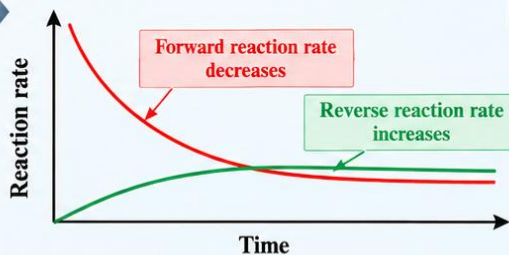
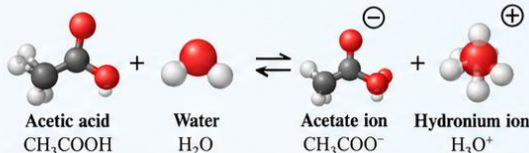
(High concentration of acetic acid)



At the beginning, the concentration of acetic acid is high, so the forward reaction rate is high, while the reverse reaction rate is very low.

2. As the reaction proceeds

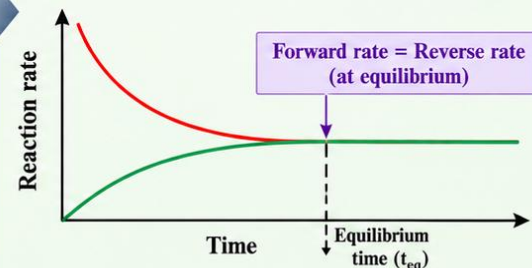
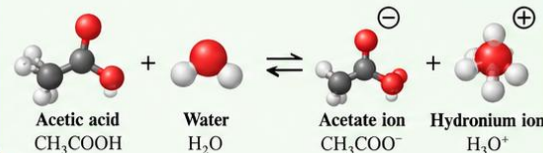
(Acetic acid is consumed and products form)



As acetic acid is depleted, the forward reaction rate decreases, whereas the reverse reaction rate increases due to the formation of H_3O^+ and acetate ions.

3. Dynamic equilibrium

(Rates are equal and concentrations remain constant)



A dynamic equilibrium is established when the forward and reverse reaction rates are equal. The concentrations of all species remain constant after this point.

Acid–Base Equilibrium

Strengths of Conjugate Acid-Base Pairs

ACID STRENGTH (increases upwards)

BASE STRENGTH (increases downwards)

Category	Acid	Conjugate Base
Strong	HCl	Cl ⁻
	H ₂ SO ₄	HSO ₄ ⁻
	HNO ₃	NO ₃ ⁻
	H ₃ O ⁺	H ₂ O
	HSO ₄ ⁻	SO ₄ ²⁻
	H ₂ SO ₃	HSO ₃ ⁻
	H ₃ PO ₄	H ₂ PO ₄ ⁻
	HF	F ⁻
	CH ₃ COOH	CH ₃ COO ⁻
	H ₂ CO ₃	HCO ₃ ⁻
Weak	H ₂ S	HS ⁻
	HSO ₃ ⁻	SO ₃ ²⁻
	H ₂ PO ₄ ⁻	HPO ₄ ²⁻
	NH ₄ ⁺	NH ₃
	HCO ₃ ⁻	CO ₃ ²⁻
	HPO ₄ ²⁻	PO ₄ ³⁻
	H ₂ O	OH ⁻
	HS ⁻	S ²⁻
	OH ⁻	O ²⁻
	Negligible	

Acid–Base Equilibrium (clarification)

Relative Strengths of Common Conjugate Acid–Base Pairs

Acid (HA) (proton donor)		Stronger acid (weaker base)	Conjugate base (A ⁻) (proton acceptor)	
Strong acids (complete dissociation in water)	• HCl (hydrochloric acid) • H₂SO₄ (sulfuric acid) • HNO₃ (nitric acid) • H₃O⁺ (hydronium ion)		• Cl⁻ (chloride) • HSO₄⁻ (hydrogen sulfate) • NO₃⁻ (nitrate) • H₂O (water)	Very weak bases (negligible basicity in water)
	• HSO₄⁻ (hydrogen sulfate) • H₂SO₃ (sulfurous acid) • H₃PO₄ (phosphoric acid) • HF (hydrofluoric acid) • CH₃COOH (acetic acid) • H₂CO₃ (carbonic acid) • H₂S (hydrosulfuric acid) • NH₄⁺ (ammonium ion) • HCO₃⁻ (bicarbonate) • H₂PO₄⁻ (dihydrogen phosphate)		• SO₄²⁻ (sulfate) • HSO₃⁻ (hydrogen sulfite) • H₂PO₄⁻ (dihydrogen phosphate) • F⁻ (fluoride) • CH₃COO⁻ (acetate) • HCO₃⁻ (bicarbonate) • HS⁻ (hydrosulfide) • NH₃ (ammonia) • CO₃²⁻ (carbonate) • PO₄³⁻ (phosphate)	Weak bases (partial proton acceptance in water)
	• H₂O (water) • HS⁻ (hydrosulfide) • OH⁻ (hydroxide)		• OH⁻ (hydroxide) • S²⁻ (sulfide) • O²⁻ (oxide)	Strong bases (strong proton acceptors in water)
Very weak acids (negligible dissociation in water)		Weaker acid (stronger base)		

Dissociation Constant — Ka

Equilibrium constant (Ka) quantifies acid strength (means how much an acid dissociates (ionizes) in water).

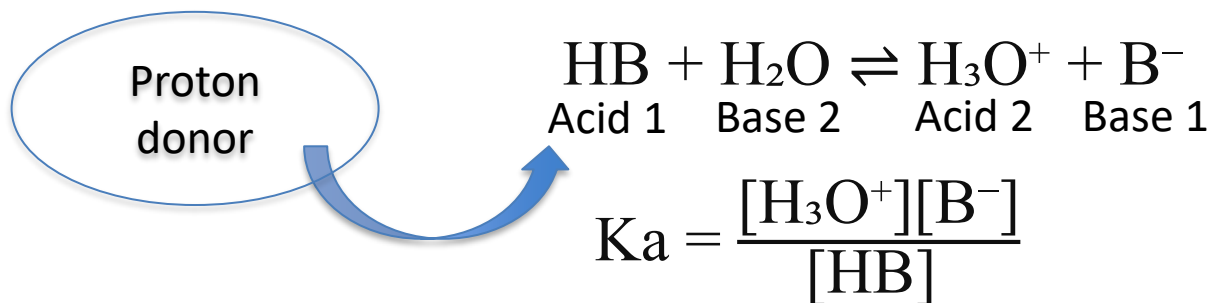


Larger Ka → stronger acid (more ionized) (means that the concentration of H^+ and A^- is high compared to undissociated acid (HA)).

Means equilibrium lies far to the **right** → most acid molecules have given up their protons (H^+).

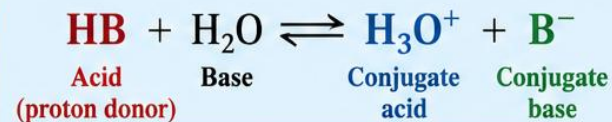
While Small Ka → weak acid (slightly ionized).

In general, the **acidity constant** for an **uncharged weak acid HB** can be expressed by:



Dissociation Constant (K_a)

The **dissociation constant (K_a)** quantifies the **strength** of an acid, i.e. how much it **dissociates (ionizes)** in water.

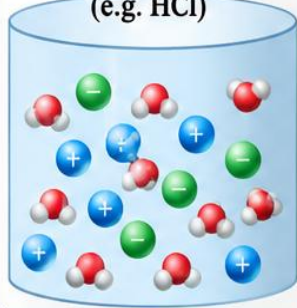


$$K_a = \frac{[\text{H}_3\text{O}^+][\text{B}^-]}{[\text{HB}]}$$

Large $K_a \rightarrow$ Strong acid

(more ionized in water)

Strong acid
(e.g. HCl)



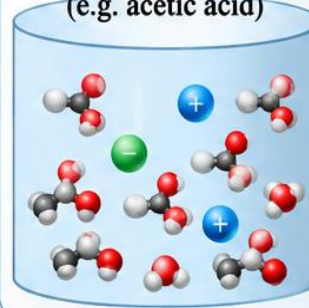
Equilibrium lies far to the right
(most molecules dissociate).

K_a is large
(e.g. HCl, $K_a \approx 10^6$)

Small $K_a \rightarrow$ Weak acid

(slightly ionized in water)

Weak acid
(e.g. acetic acid)



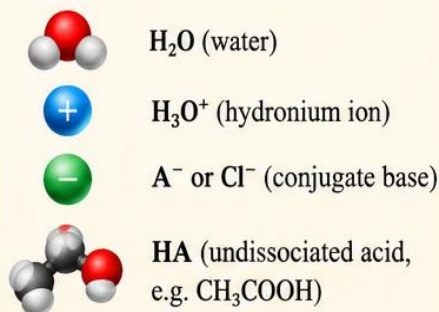
Equilibrium lies to the left
(only a small fraction dissociates).

K_a is small
(e.g. CH_3COOH , $K_a \approx 1.8 \times 10^{-5}$)

Key points

- **Larger $K_a \rightarrow$ stronger acid**
(more H_3O^+ and A^- formed).
- **Smaller $K_a \rightarrow$ weaker acid**
(slightly ionized).
- K_a reflects the position of equilibrium.
- Only applicable to weak (partially ionized) acids (HA or HB).

Symbols in the beaker



Summary

Large $K_a \rightarrow$ Strong acid
(more ionization, equilibrium to the right).

Small $K_a \rightarrow$ Weak acid
(slight ionization, equilibrium to the left).

Dissociation Constant — K_a

Example 7.1:

In a liter of 0.1 M solution, acetic acid was found by conductivity analysis to dissociate into 1.32×10^{-3} g ions (“moles”) each of hydrogen and acetate ion at 25°C. What is the acidity or dissociation constant K_a for acetic acid?

$$K_a = \frac{(1.32 \times 10^{-3})^2 \cancel{\text{mole}}}{0.1 \cancel{\text{mole}}}$$

$$K_a = \frac{1.74 \times 10^{-6}}{1 \times 10^{-1}} = 1.74 \times 10^{-5}$$

Note:

Molarity (M) = $\frac{\text{moles of solute}}{\text{liters of solution}}$

So if:

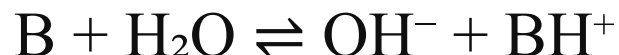
$$M = 0.1 \text{ M}, \quad V = 1 \text{ L}$$

Then:

$$\begin{aligned} \text{Moles of solute} &= M \times V \\ &= 0.1 \times 1 = 0.1 \text{ mol} \end{aligned}$$

Ionization of Weak Bases (K_b)

- weak bases B, exemplified by NH₃, react with water as follows:



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

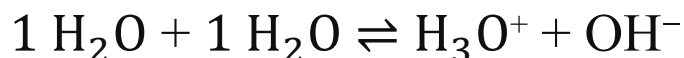
Example:



$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Autoionization of Water & Kw

Relation: $K_a \cdot K_b = K_w$ (for conjugate weak acid and weak base pairs)



$$K_C = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

The ion-product for water, Kw:

$$K_C \times [\text{H}_2\text{O}]^2 = K_W = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ M (at } 25^\circ\text{C)}$$

For pure water the concentration of hydroxyl and hydronium ions must be equal:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} \text{ M (at } 25^\circ\text{C)}$$

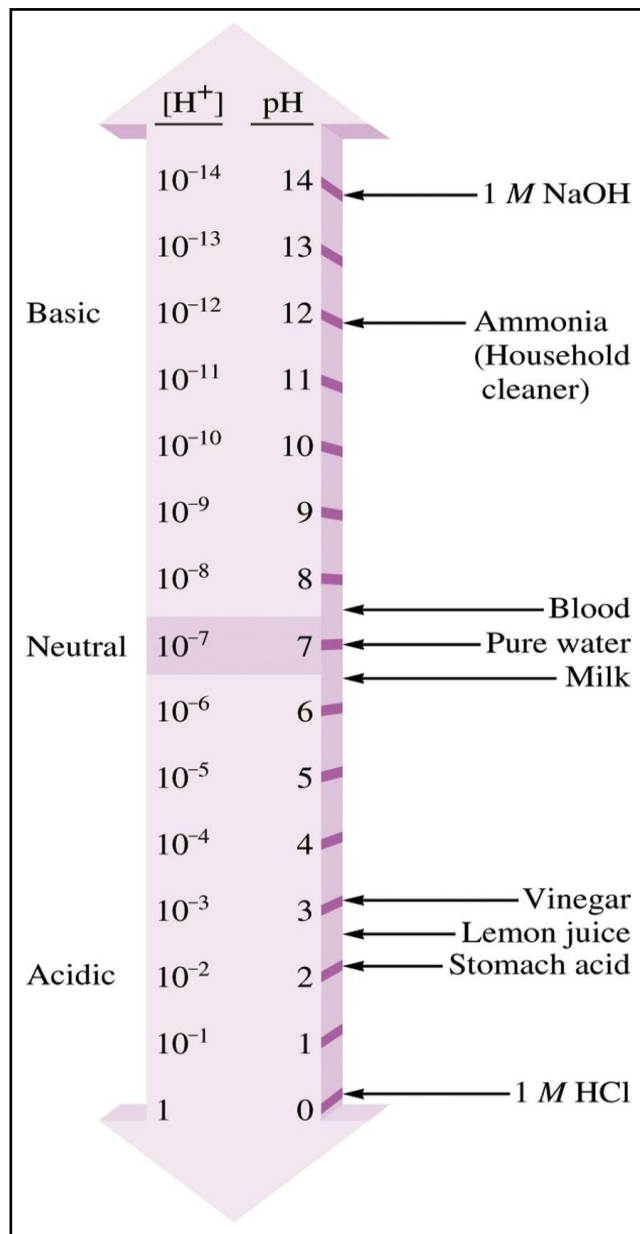
Autoionization of Water & K_w

Example 7.3:

A quantity of HCl ($1.5 \times 10^{-3}\text{M}$) is added to water at 25°C to increase the hydrogen ion concentration from 1×10^{-7} to 1.5×10^{-3} mole/liter. What is the new hydroxyl ion concentration?

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{1.5 \times 10^{-3}} = 6.7 \times 10^{-12} \text{ mole/liter}$$



The pH scale and pH values of some common substances

Relation Between K_a and K_b

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

$$K_a K_b = \frac{[H_3O^+][B^-]}{[HB]} \cdot \frac{[OH^-][HB]}{[B^-]} \\ = [H_3O^+][OH^-] = K_w$$

$$K_b = \frac{K_w}{K_a}$$

$$K_a = \frac{K_w}{K_b}$$

Relation Between K_a and K_b

Example 7.4:

Calculate K_a

Ammonia has a K_b of 1.74×10^{-5} . Calculate K_a for its conjugate acid, NH_4^+ .

$$K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{1.74 \times 10^{-5}} = 5.75 \times 10^{-10}$$

SÖRENSEN'S pH

$$\text{pH} = -\log[\text{H}_3\text{O}^+]; \quad \text{pOH} = -\log[\text{OH}^-]$$

The pH of a solution can be considered in terms of a numeric scale having values from 0 to 14, which expresses in a quantitative way the **degree of acidity (7 to 0)** and **alkalinity (7-14)**.

The **value 7** at which the hydrogen and hydroxyl ion concentrations are about equal at room temperature is referred to as the **neutral point, or neutrality**.

$$\text{pH} + \text{pOH} = \text{pK}_w = 14.00 \text{ (at } 25^\circ\text{C)}.$$

$$\text{pK}_a + \text{pK}_b = \text{pK}_w$$

Calculation of pH

Example 7.5:

The hydronium ion concentration of a 0.05 M solution of HCl is 0.05 M. what is the pH of the solution.

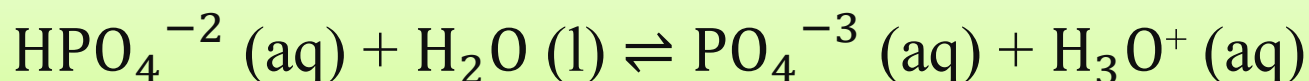
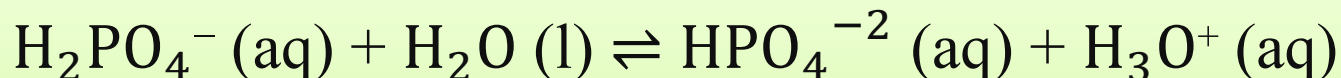
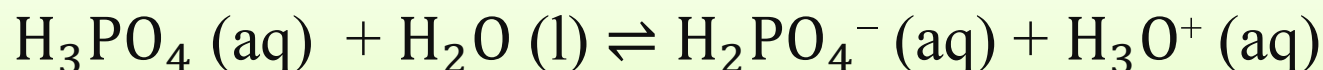
$$\begin{aligned}\text{pH} &= -\log[\text{H}^+] = -\log (5.0 \times 10^{-2}) \\ &= -\log 10^{-2} - \log 5.0 = 2 - 0.7 = 1.3\end{aligned}$$

Proton Balance Equation (PBE)

Stepwise Dissociation of Phosphoric Acid (H_3PO_4)

Phosphoric acid (weak acid), normally only loses 1 proton in solution, but loses all 3 when reacted (strong base with heat).

1. Add water:



2- Left side $[\text{H}_3\text{O}^+]$ + Consume proton x No. of proton gained
= Right side $[\text{OH}^-]$ + Release proton x No. of proton lost

3 - PBE: $[\text{H}_3\text{O}^+] = [\text{OH}^-] + [\text{H}_2\text{PO}_4^-] + 2[\text{HPO}_4^{2-}] + 3[\text{PO}_4^{3-}]$

Calculation of pH

Solutions of Strong Acids and Bases

Strong acids and bases are considered to ionize 100% when placed in water.

$$[\text{H}_3\text{O}^+] \cong C_a$$

C_a : Total acid concentration (1×10^{-6} or more)

A similar treatment for a solution of a strong base such as NaOH gives

$$[\text{OH}^-] \cong C_b$$

C_b : Total base concentration (1×10^{-6} or more)

Calculation of pH

Solutions Containing Only a Weak Acid

$$[\text{H}_3\text{O}^+] = \sqrt{K_a C_a}$$

Example 7.13:

Calculate pH

Calculate the pH of a 1 g/100 ml solution of ephedrine sulfate. The molecular weight of the salt is 428.5, and K_b for ephedrine base is 2.3×10^{-5}

(a) Ephedrine sulfate $(\text{BH}^+)_2\text{SO}_4$ dissociate completely into two BH^+ cations and one SO_4^{2-} anion. Thus, the concentration of the weak acid (ephedrine cation) is twice the concentration, C_s , of the salt added.

$$C_a = 2C_s = \frac{2 \times 10 \text{ g/L}}{428.5 \text{ g/mole}} = 4.67 \times 10^{-2} \text{ M}$$

$$(b) \quad K_a = \frac{1 \times 10^{-14}}{2.3 \times 10^{-5}} = 4.35 \times 10^{-10}$$

$$(c) \quad [\text{H}_3\text{O}^+] = \sqrt{4.35 \times 10^{-10} \times 4.67 \times 10^{-2}} = 4.51 \times 10^{-6} \text{ M}$$

$$\text{pH} = -\log (4.51 \times 10^{-6}) = 5.35$$

$$\text{Molarity (M)} = \frac{\text{Concentration (g/L)}}{\text{Molecular Weight (g/mol)}}$$

Calculation of pH

Solutions Containing Only a Weak Base

$$[\text{OH}^-] = \sqrt{K_b C_b}$$

Example 7.13:

Calculate pH

What is the pH of 0.0033 M solution of cocaine base, which has the basicity constant of 2.6×10^{-6} ?

$$[\text{OH}^-] = \sqrt{(2.6 \times 10^{-6}) \times (3.3 \times 10^{-3})} = 9.26 \times 10^{-5} \text{ M}$$

$$\text{pOH} = -\log (9.26 \times 10^{-5}) = 4.03$$

$$\text{pH} = 14 - 4.03 = 9.97$$

Calculation of pH

Solutions Containing a Single Conjugate Acid–Base Pair

In a solution composed of a weak acid and a salt of that acid (e.g., acetic acid and sodium acetate) or a weak base and a salt of that base (e.g., ephedrine and ephedrine hydrochloride).

$$[\text{H}_3\text{O}^+] = \frac{K_a C_a}{C_b}$$

Example 7.16:

Calculate pH

What is the pH of a solution acetic acid 0.3 M and sodium acetate 0.05 M?

$$[\text{H}_3\text{O}^+] = \frac{(1.75 \times 10^{-5}) \times (0.3)}{5 \times 10^{-2}} = 1.05 \times 10^{-4}$$

$$\text{pH} = -\log (1.05 \times 10^{-4}) = 3.98$$

Calculation of pH

Example 7.17:

Calculate pH

What is the pH of a solution containing ephedrine 0.1 M (**conjugate base**) and ephedrine HCl 0.01 M (**acid**)? Ephedrine has a basicity constant 2.3×10^{-5} ; thus, the acidity constant for its conjugate is 4.35×10^{-10}

$$[\text{H}_3\text{O}^+] = \frac{(4.35 \times 10^{-10}) \times (1 \times 10^{-2})}{1 \times 10^{-1}} = 4.35 \times 10^{-11}$$

$$\text{pH} = -\log (4.35 \times 10^{-11}) = 10.36$$

Calculation of pH

Solutions Containing Two Weak Acids

$$[\text{H}_3\text{O}^+] = \sqrt{K_1 C_{a1} + K_2 C_{a2}}$$

Example 7.16:

Calculate pH

What is the pH of a solution containing acetic acid, 0.01 mole/ L, and formic acid, 0.001 mole/L?

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \sqrt{(1.75 \times 10^{-5})(1.0 \times 10^{-2}) + (1.77 \times 10^{-4})(1.0 \times 10^{-3})} \\ &= 5.93 \times 10^{-4} \text{ M} \end{aligned}$$

$$\text{pH} = -\log (5.93 \times 10^{-4}) = 3.23$$

A solid dark blue horizontal bar at the top of the slide, with a thin gold line just below it.

**Thank
you**