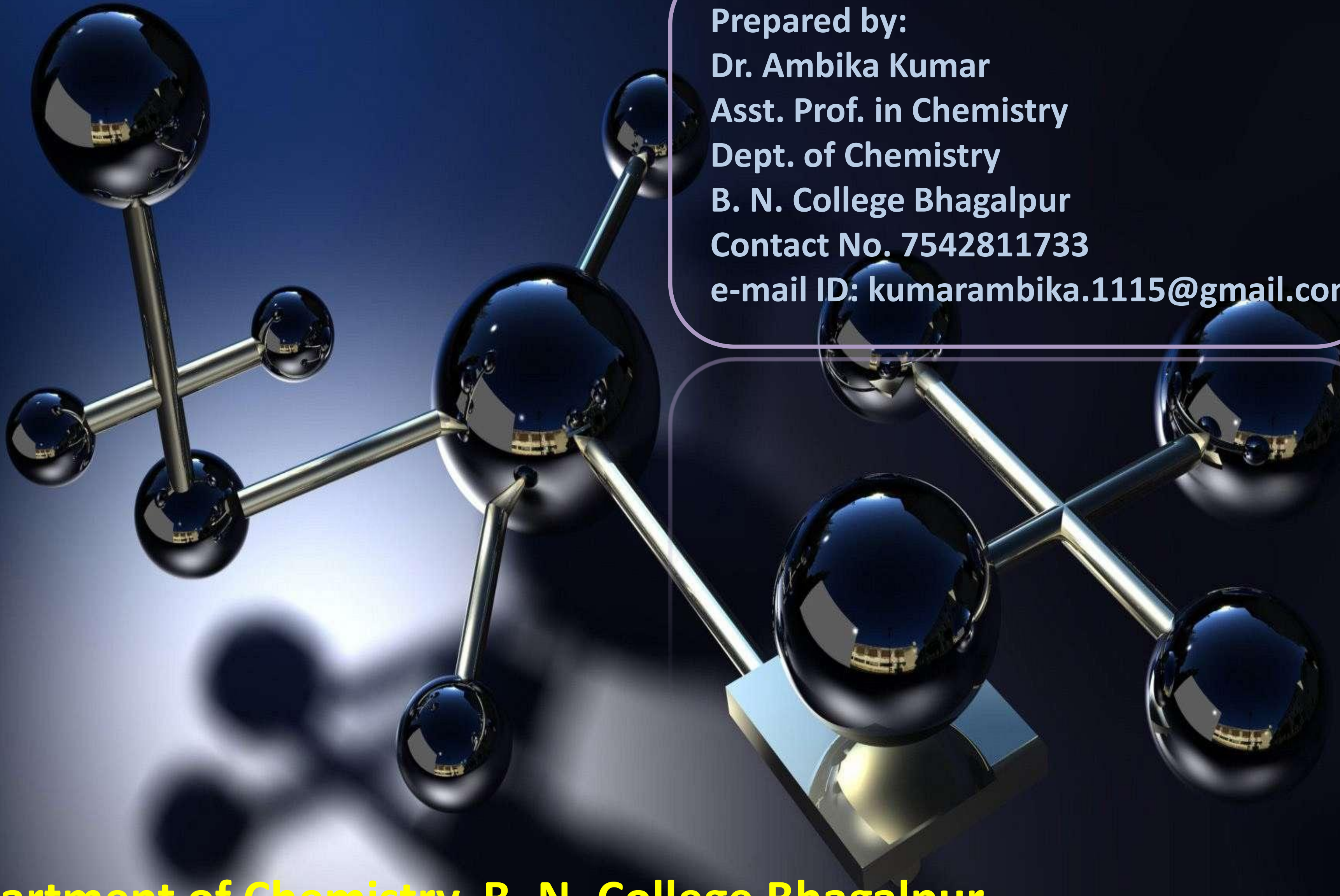

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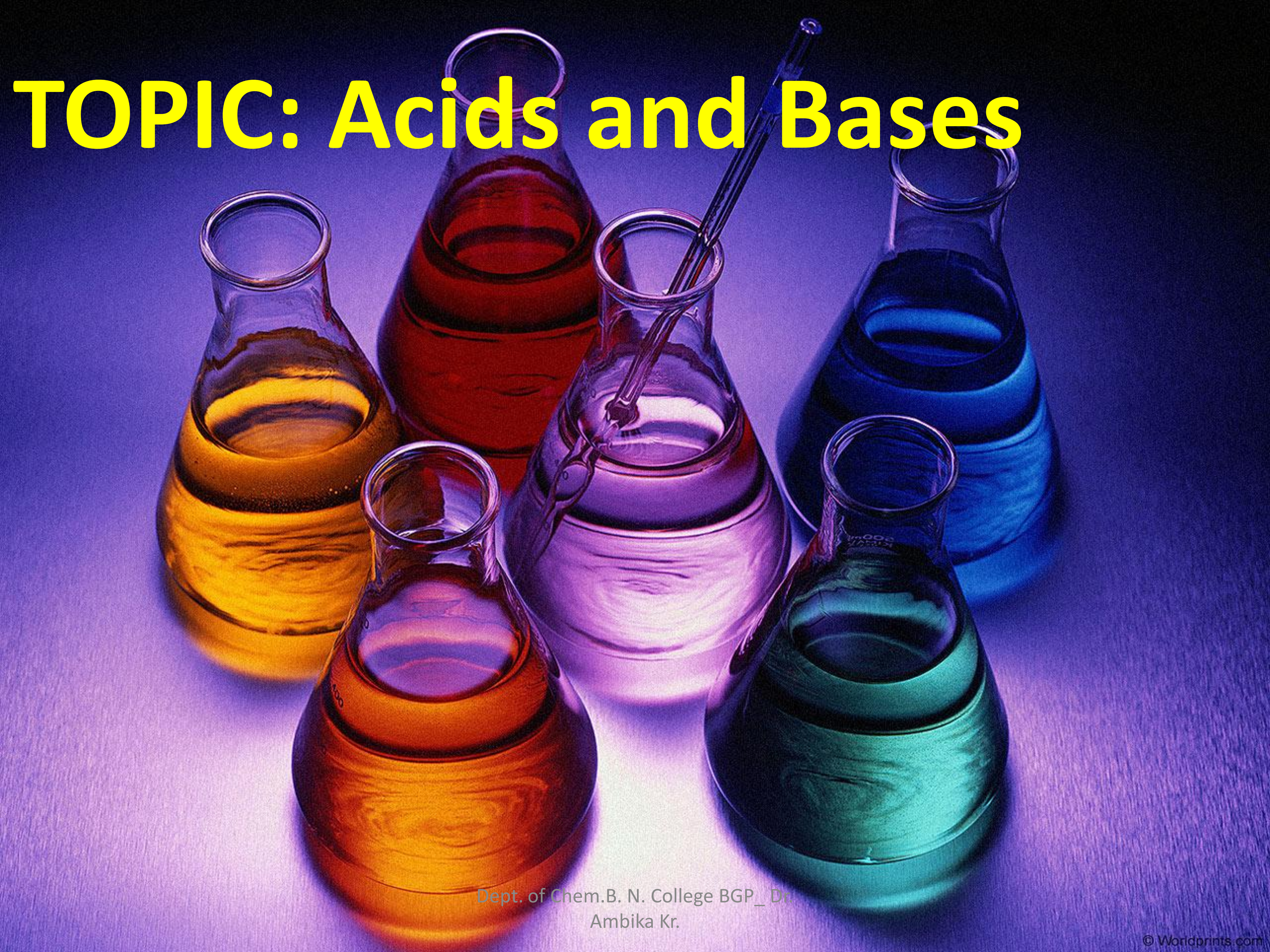
TOPIC: Acids and Bases



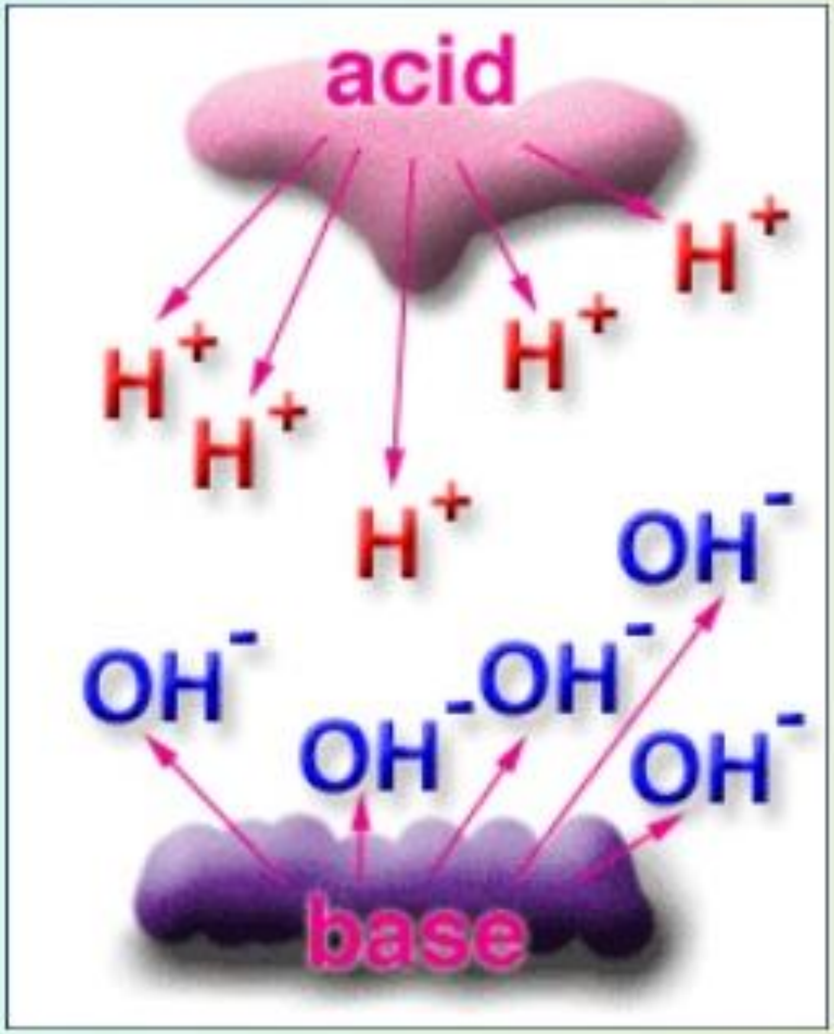
Contents:

- Introduction to Acids and Bases
- Arrhenius Concept
- Bronsted-Lowry Concept
- Lux-Food System
- Lewis Concept
- Solvent effect on acid base

Arrhenius theory of acid

- Arrhenius was a Sweedish chemist
- Put forward a theory of acids in the 1880’s
- Stated that:

  An acid is a substance that dissociates in water to form H^+ ions.



Arrhenius theory of acids

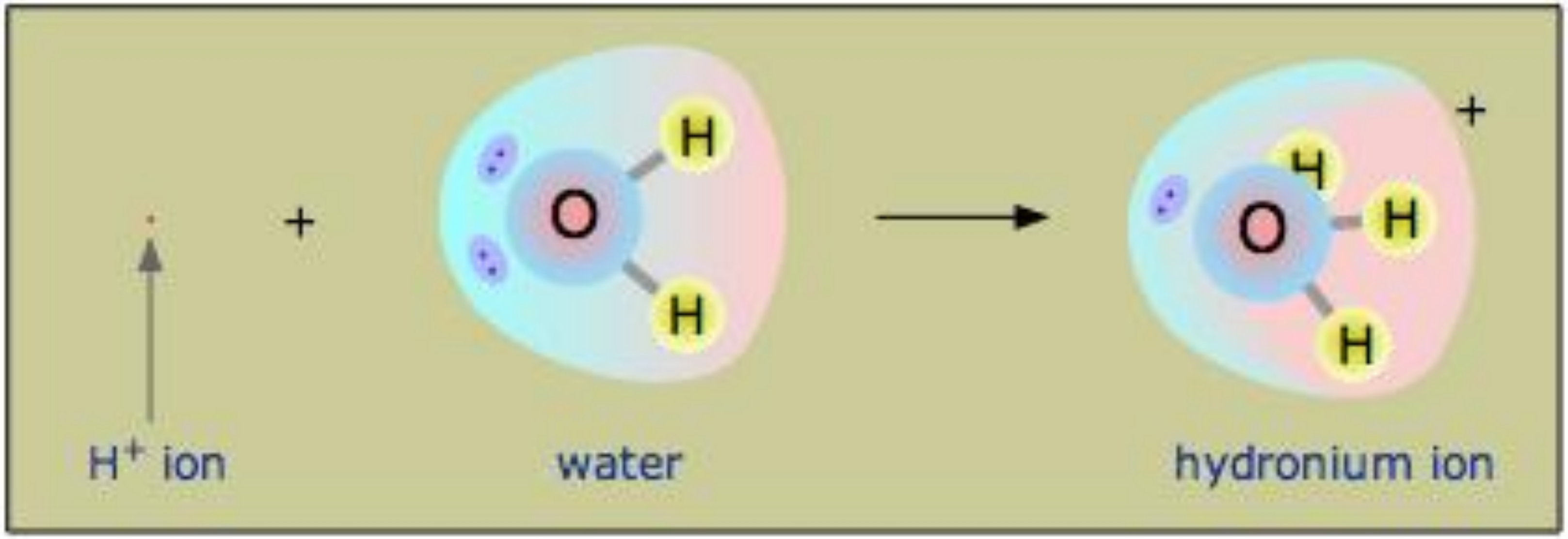
Arrhenius definition of an acid: any compound that contains hydrogen and **produces** H^+ (H_3O^+ when reacts with water) ions when dissolved in water.

A **strong acid** is a water-soluble compound that completely dissociates to give H_3O^+ ions.

A **weak acid** is a water-soluble compound that dissociates only partially, producing few H_3O^+ ions.

NOTE: In Arrhenius concept, solvent must be **WATER**

When an acid dissociates in water, it liberates H^+ ions, which immediately react with water to form H_3O^+



Arrhenius theory of acids

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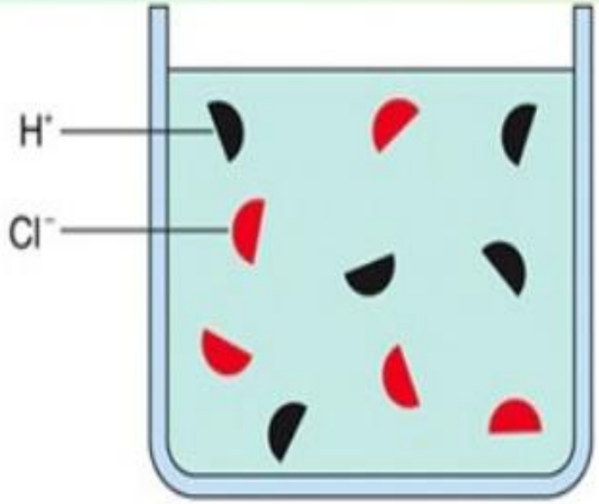
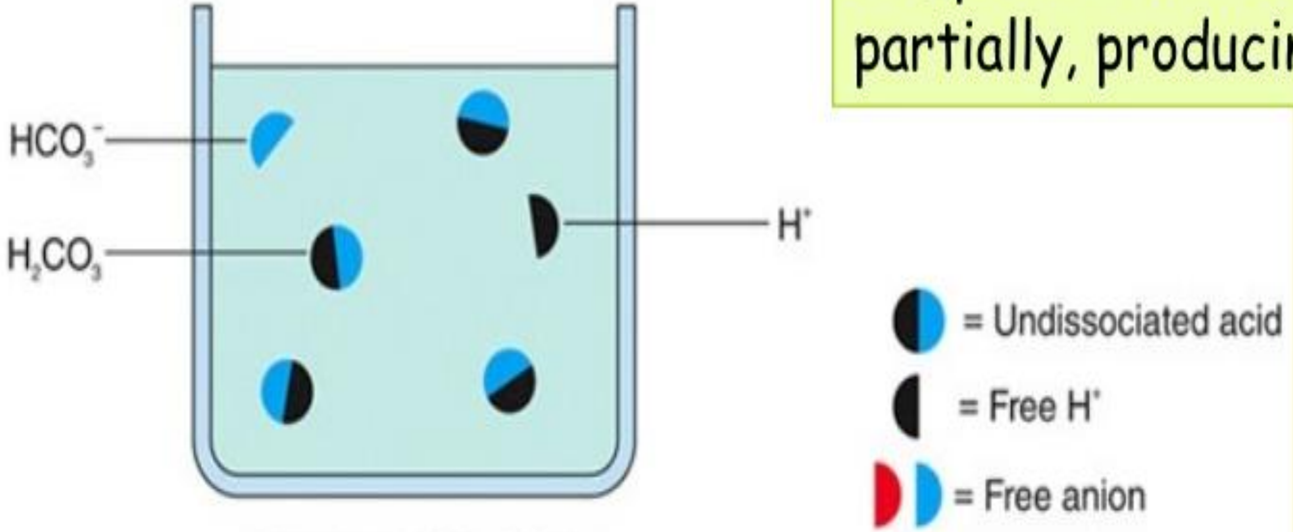
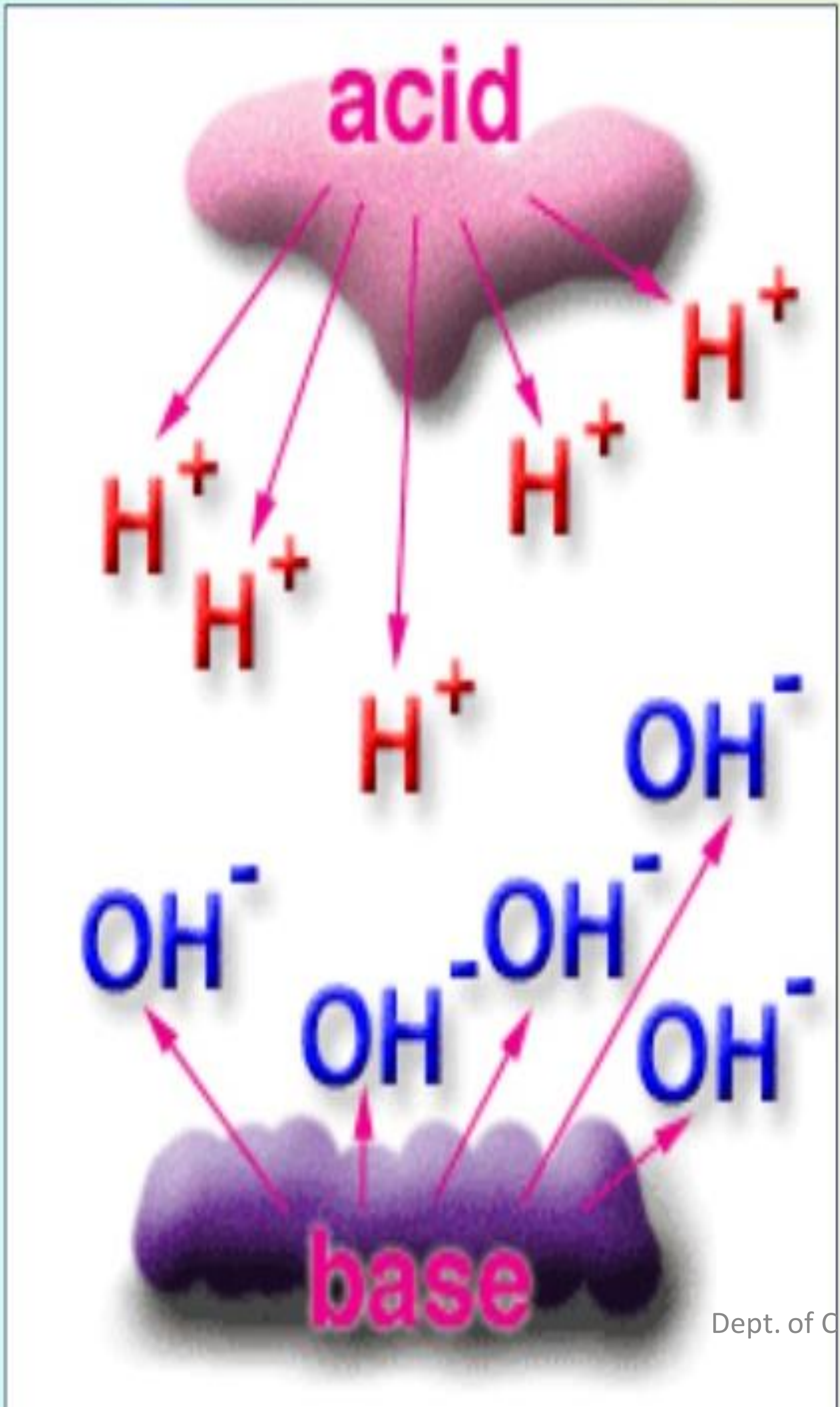


Strong acid (HCl)
(a)



Weak acid (H_2CO_3)
(b)



Arrhenius theory of bases

Arrhenius definition of a base: any compound that contains a metal and hydroxide (OH^-) group **produces OH^-** (hydroxide) ions when dissolved in water.

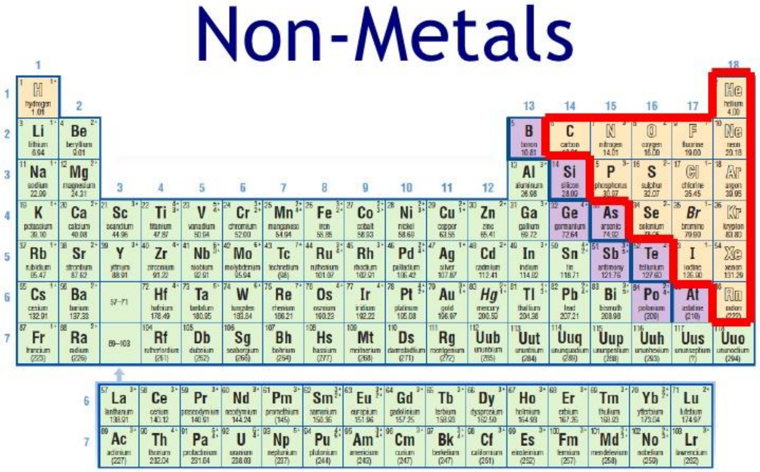
All hydroxides are **strong bases** because their dissociation reaction go essentially to completion.

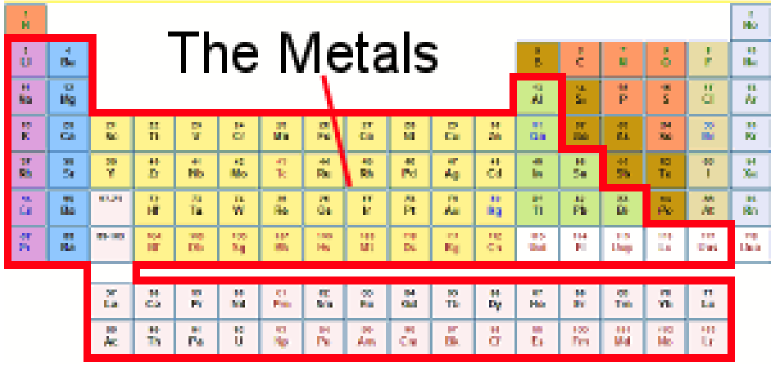
Application of Arrhenius Concept

- Non-metallic oxides (in aqueous medium) are generally acidic in nature

- Metallic oxides (in aqueous medium) are generally basic in nature

- Some non-metallic hydrides (in aqueous medium) are basic in nature, e.g., NH_3

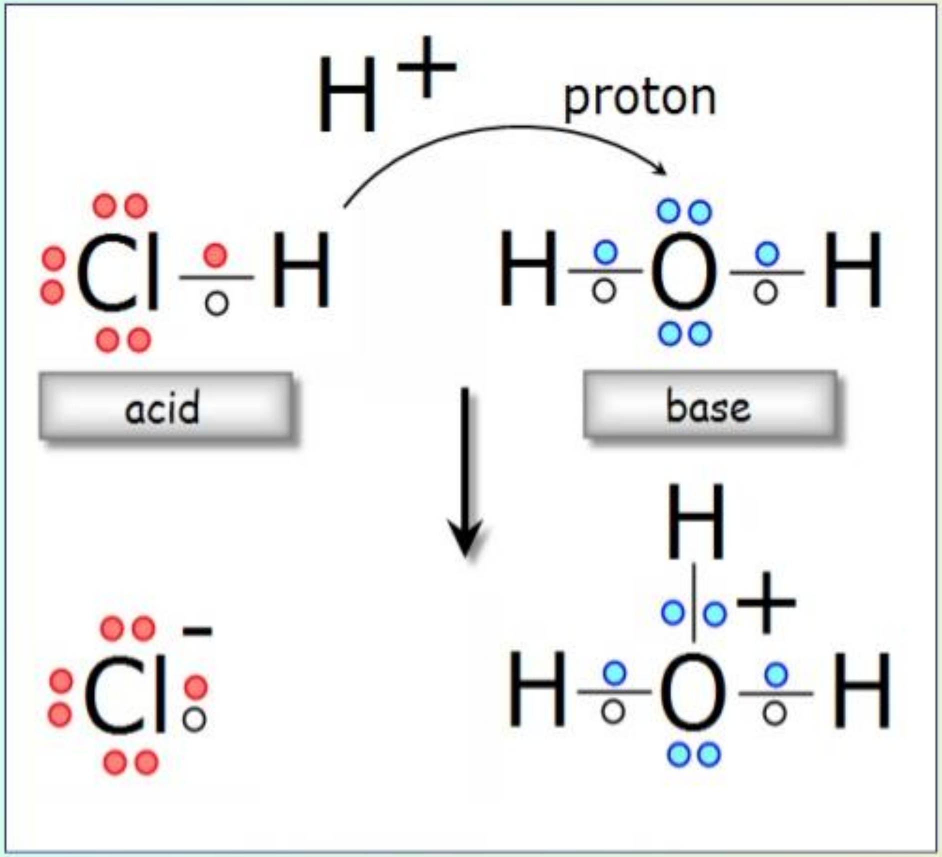




Limitations of Arrhenius Theory

- Hydronium ions exist in solution not H^+ ions as suggested by Arrhenius
- Arrhenius restricted his definitions to aqueous (water based) solutions
- Not all acid-base reactions require water as suggested by Arrhenius e.g. rxn of ammonia gas with hydrogen chloride gas

Bronsted –Lowery Concept:



Bronsted-Lowry theory of acids and bases

They proposed that acids and bases can be defined in terms of their ability to transfer protons.

An acid is a substance (molecule or ion) that can transfer protons to another substance.

A base is a substance than can accept a proton.

Rafa Muñoa
Lizardi Institutua
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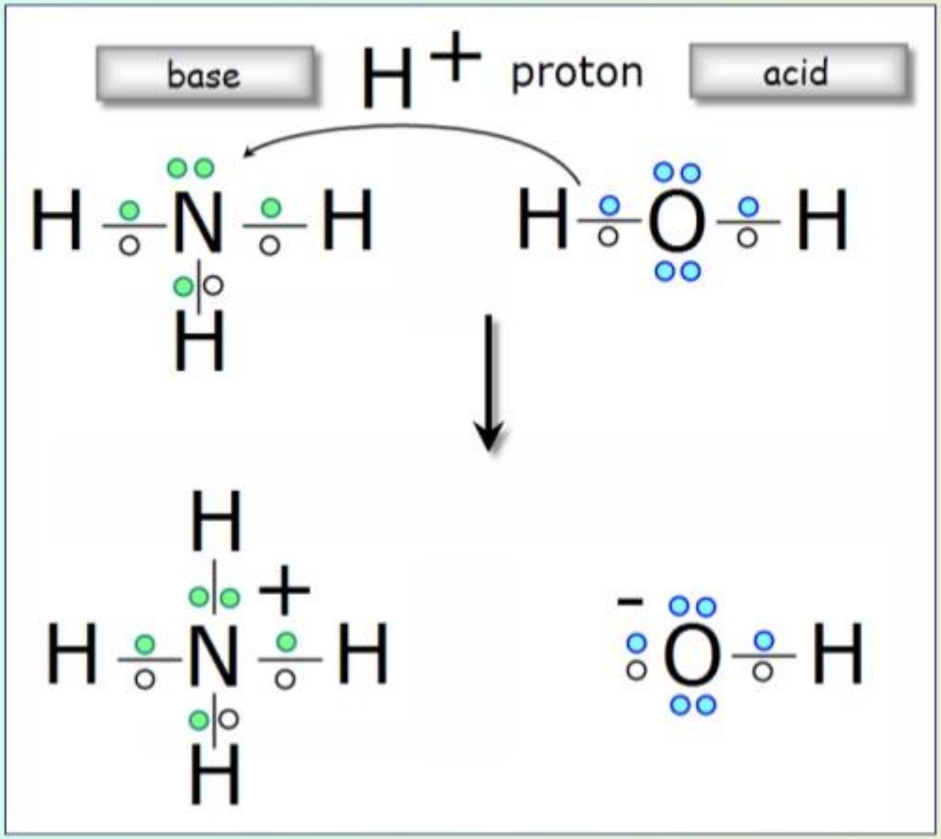
Acids and Bases: Theory

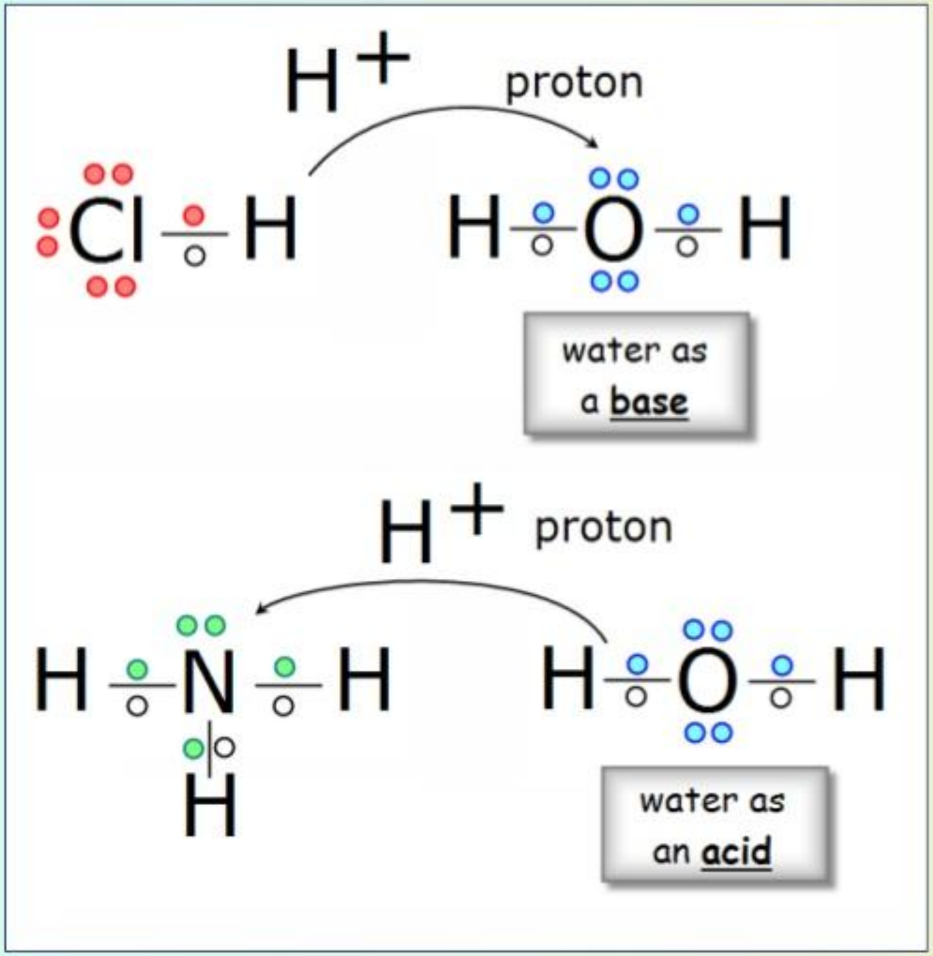


Bronsted-Lowry theory of acids and bases

An acid and a base always work together to transfer a proton.

In other words, a substance can function **as an acid only if another substance simultaneously behaves as a base**.

Acids and Bases: Theory



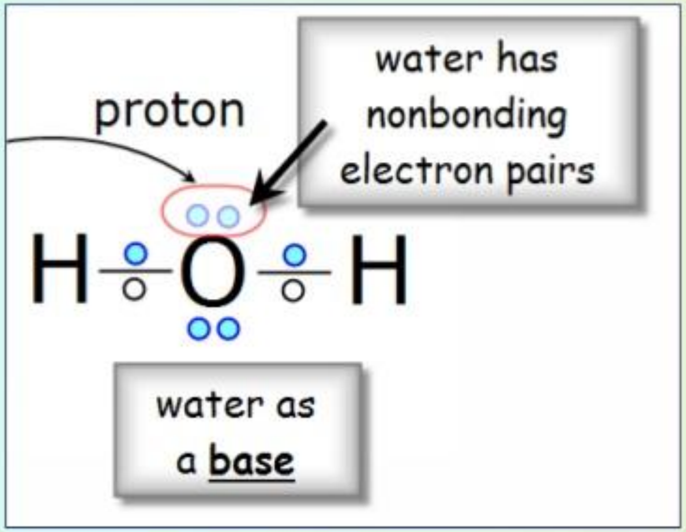
Bronsted-Lowry theory of acids and bases

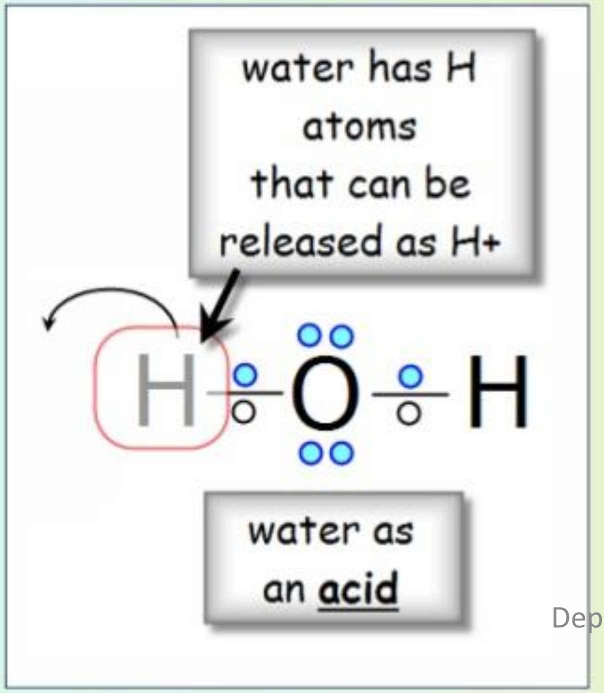
Some substances can act as an **acid in one reaction and as a base in another**.

For example, H_2O is a Bronsted-Lowry base in its reaction with HCl and a Bronsted-Lowry acid in its reaction with NH_3.

Those substances are called amphoteric.

Acids and Bases: Theory





Bronsted-Lowry theory of acids and bases

To be a Bronsted-Lowry **acid**, a molecule or ion must have a **hydrogen atom** that it can lose as H^+ ion.

To be a Bronsted-Lowry **base**, a molecule or ion must have a **nonbonding pair of electrons** that it can use to bind the H^+ ion.

Every Arrhenius acid (H^+ donor) **is** Bronsted acid (H^+ donor)

Example: All protic acids

BUT

Every Arrhenius bases (OH– donor) is **not** Bronsted Base (H^+ accepter)

Example: NaOH is arrhenius base, can donate OH^- but can not accept H+

Again NH_2CONH_2 (urea) is Bronsted base, can accept H^+, but can not donate OH^-

ADVANTAGES OF BRONSTED -LOWRY CONCEPT

I. It is not limited to molecules but includes even the ionic species to act as acids or bases.

II. It does not require aqueous medium to explain acidic or basic nature.

III. It can explain the basic nature of ions or molecules having no OH^- ion. E.g. NH_3, Na_2CO_3 etc.

LIMITATIONS OF BRONSTED -LOWRY CONCEPT

I. It could not explain the acidic and basic nature of compounds having no tendency to lose or gain H^+ ions. E.g. CO_2, NH_3, SO_2, SO_3 etc.

II. It could not explain the basic nature of compounds having OH^- ions. E.g. NaOH, $Ca(OH)_2$, KOH etc.

Acids and Bases: Theory

Conjugate acid-base pairs

In any acid-base equilibrium both the forward reaction (to the right) and reverse reaction (to the left) involve proton transfers.

$$HX\ (aq) + H_2O\ (l) \longleftrightarrow X^-\ (aq) + H_3O^+\ (aq)$$

In the forward reaction HX donates a proton to H2O. Therefore, HX is the Bronsted-Lowry acid, and H2O is the Bronsted-Lowry base.

$$HX\ (aq) + H_2O\ (l) \xrightarrow{\text{Forward reaction}} X^-\ (aq) + H_3O^+\ (aq)$$

acid base

Acids and Bases: Theory

Conjugate acid-base pairs

In the reverse reaction, the H_3O^+ ion donates a proton to the X^- ion; H_3O^+ is the acid and X^- is the base

$$HX\ (aq) + H_2O\ (l) \neg \underline{\text{reverse reaction}}\ \underset{\text{base}}{X^-}\ (aq) + \underset{\text{acid}}{H_3O^+}\ (aq)$$

An acid and a base such as HX and X^- that differ only in one proton are called **conjugated acid-base pair**.

Every acid has a conjugate base, formed by the removal of a proton from the acid.

Acids and Bases: Theory

Conjugate acid-base pairs

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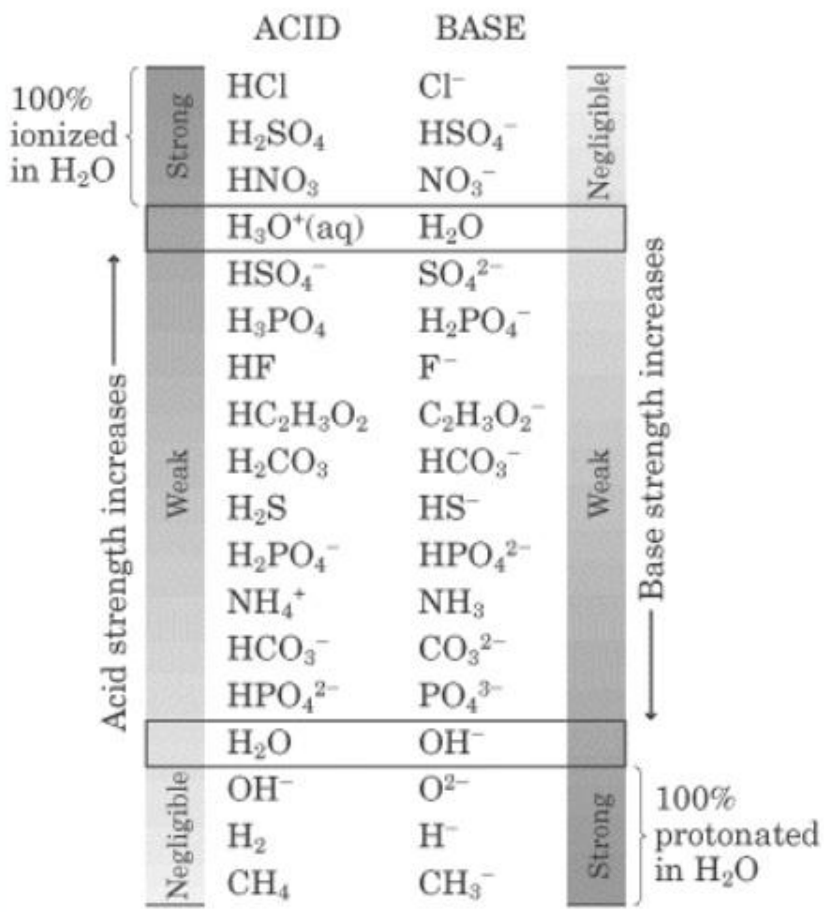
Acids and Bases: Theory



ACID	BASE
HCl	Cl^-
H_2SO_4	HSO_4^-
HNO_3	NO_3^-
$H_3O^+(aq)$	H_2O
HSO_4^-	SO_4^{2-}
H_3PO_4	$H_2PO_4^-$
HF	F^-
$HC_2H_3O_2$	$C_2H_3O_2^-$
H_2CO_3	HCO_3^-
H_2S	HS^-
$H_2PO_4^-$	HPO_4^{2-}
NH_4^+	NH_3
HCO_3^-	CO_3^{2-}
HPO_4^{2-}	PO_4^{3-}
H_2O	OH^-
OH^-	O^{2-}
H_2	H^-
CH_4	CH_3^-

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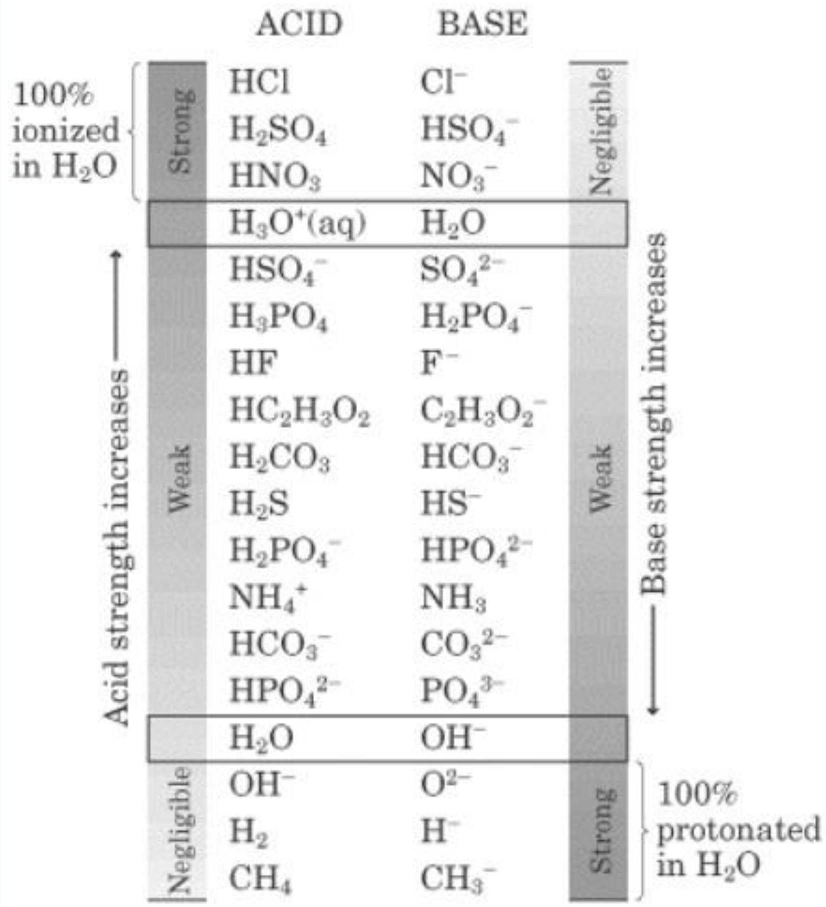
Relative strengths of acids and bases

The relationship between the strengths of acids and their conjugate bases is inverse:

1. the **strong acids** are those that **completely transfer** their protons to water, leaving no undissociated molecules in solution. Their **conjugate bases** have a **negligible tendency** to combine with a proton in aqueous solution.

Acids and Bases: Theory



		ACID	BASE		
100% ionized in H_2O	Strong	HCl	Cl^-	Negligible	
		H_2SO_4	HSO_4^-		
		HNO_3	NO_3^-		
		$H_3O^+(aq)$	H_2O		
	Weak	HSO_4^-	SO_4^{2-}	Weak	
		H_3PO_4	$H_2PO_4^-$		
		HF	F^-		
		$HC_2H_3O_2$	$C_2H_3O_2^-$		
		H_2CO_3	HCO_3^-		
		H_2S	HS^-		
		$H_2PO_4^-$	HPO_4^{2-}		
		NH_4^+	NH_3		
		HCO_3^-	CO_3^{2-}		
		HPO_4^{2-}	PO_4^{3-}		
		H_2O	OH^-		
	Negligible	OH^-	O^{2-}	Strong	100% protonated in H_2O
		H_2	H^-		
		CH_4	CH_3^-		

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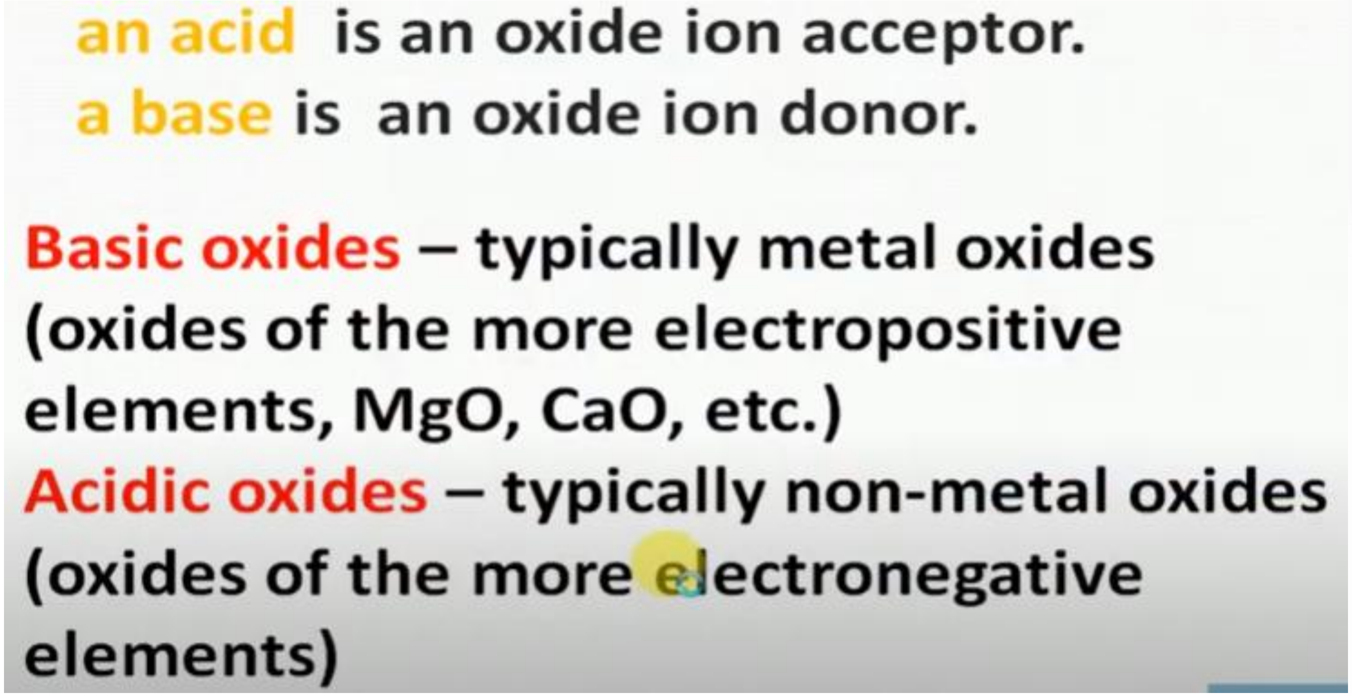
Relative strengths of acids and bases

2. the **weak acids** are those that **only partially dissociate** in aqueous solution and therefore exist in the solution as a mixture of acid molecules and ions. Their **conjugate bases are weak bases**, showing a slight ability to remove protons from water.

Lux-Flood Concept*:



an acid is an oxide ion acceptor.

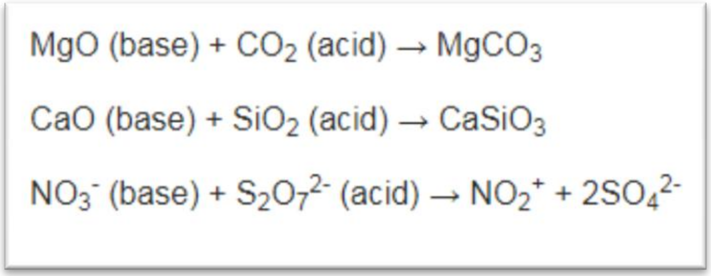
a base is an oxide ion donor.

Basic oxides – typically metal oxides (oxides of the more electropositive elements, MgO, CaO, etc.)

Acidic oxides – typically non-metal oxides (oxides of the more electronegative elements)

Hakon Flood

Hermann Lux



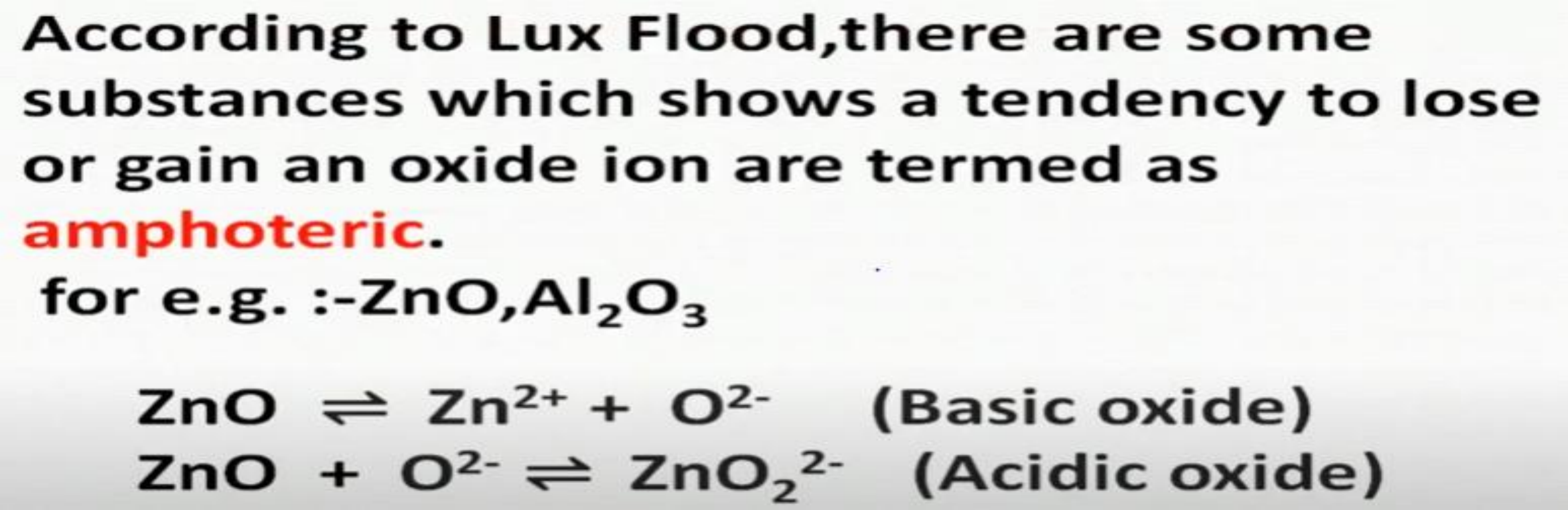
MgO (base) + CO_2 (acid) → $MgCO_3$

CaO (base) + SiO_2 (acid) → $CaSiO_3$

NO_3^- (base) + $S_2O_7^{2-}$ (acid) → $NO_2^+ + 2SO_4^{2-}$

(This acid–base theory was a revival of oxygen theory of acids and bases, proposed by German chemist Hermann Lux in 1939, further improved by Hakon Flood in1947)

* Concept applicable for non-aqueous/non-protic systems

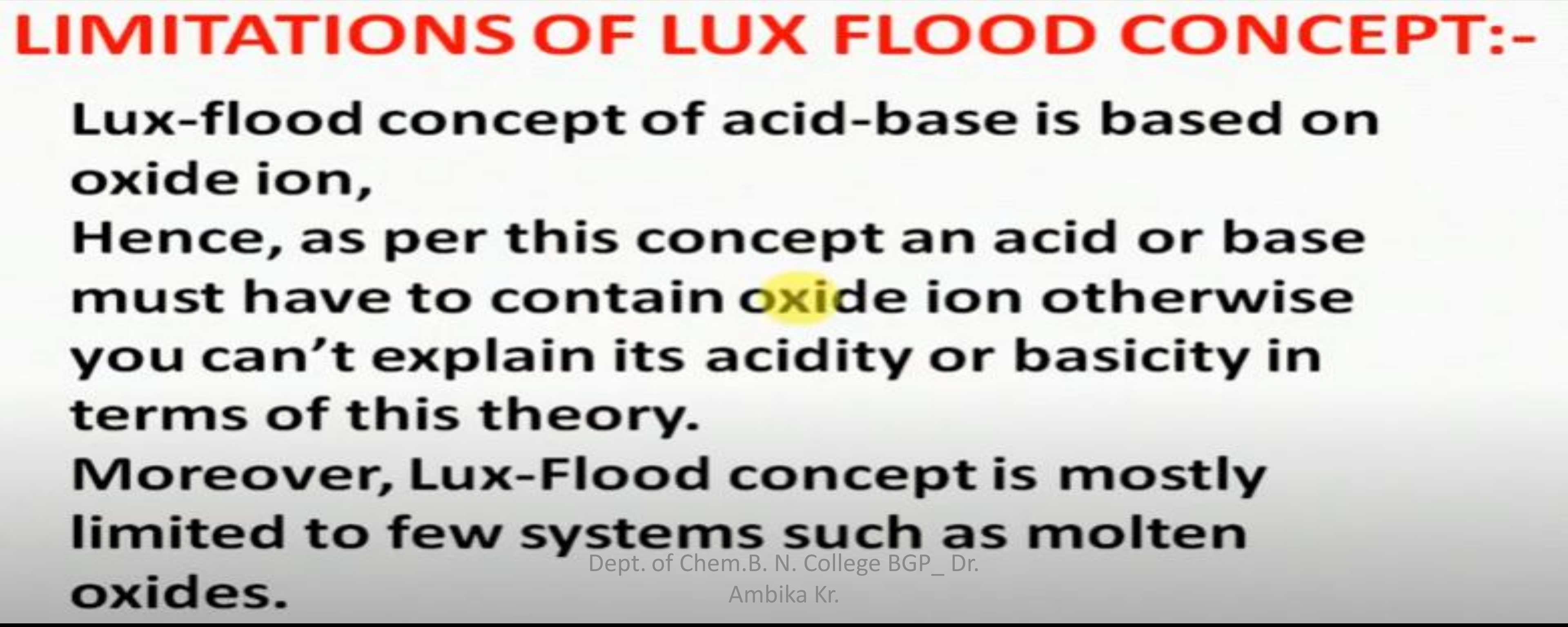


According to Lux Flood,there are some substances which shows a tendency to lose or gain an oxide ion are termed as **amphoteric**.

for e.g. :-ZnO,Al_2O_3

$ZnO \rightleftharpoons Zn^{2+} + O^{2-}$ (Basic oxide)

$ZnO + O^{2-} \rightleftharpoons ZnO_2^{2-}$ (Acidic oxide)

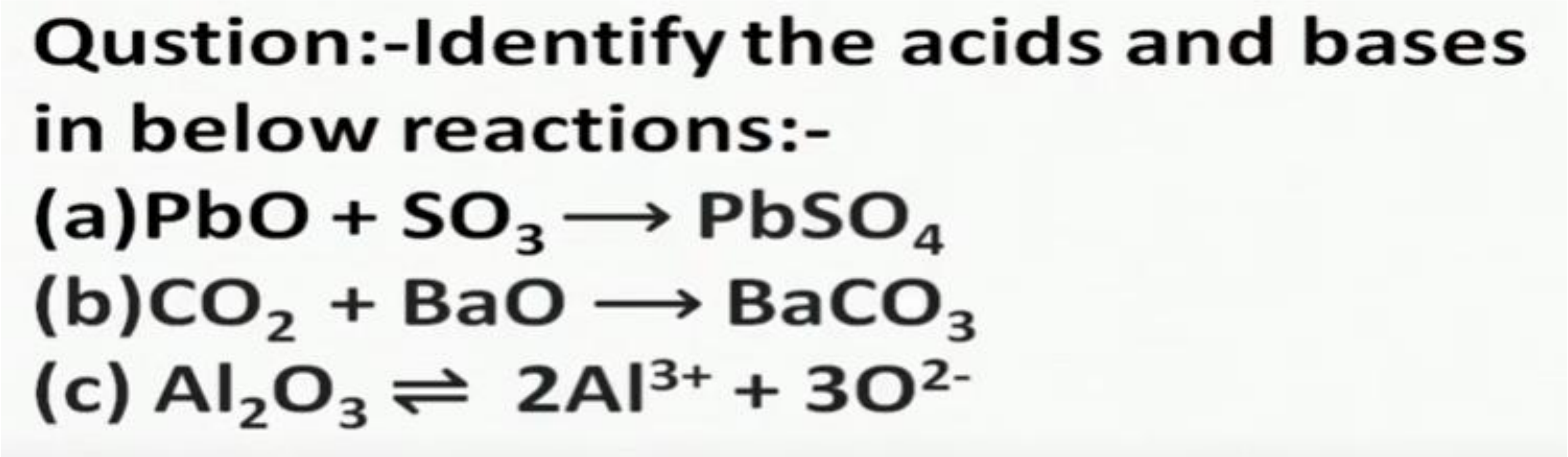


LIMITATIONS OF LUX FLOOD CONCEPT:-

Lux-flood concept of acid-base is based on oxide ion,

Hence, as per this concept an acid or base must have to contain oxide ion otherwise you can't explain its acidity or basicity in terms of this theory.

Moreover, Lux-Flood concept is mostly limited to few systems such as molten oxides.



Qustion:-Identify the acids and bases in below reactions:-

(a)$PbO + SO_3 \longrightarrow PbSO_4$

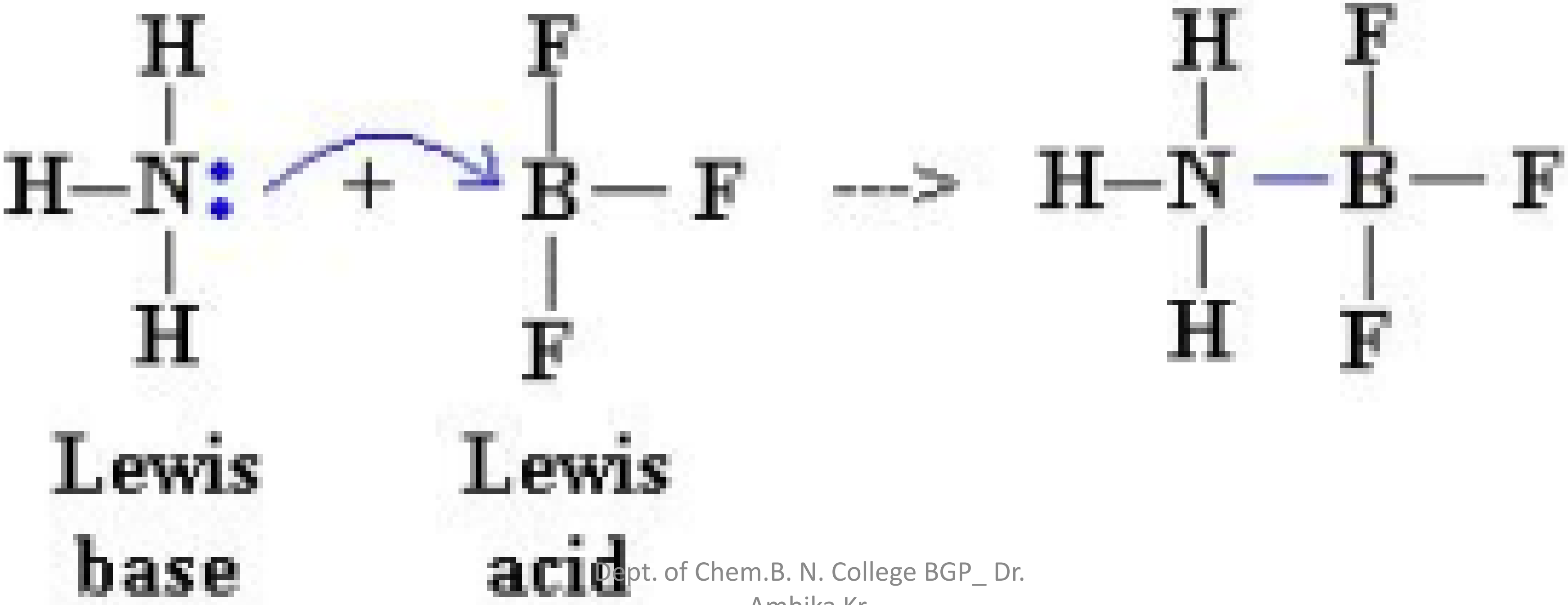
(b)$CO_2 + BaO \longrightarrow BaCO_3$

(c) $Al_2O_3 \rightleftharpoons 2Al^{3+} + 3O^{2-}$

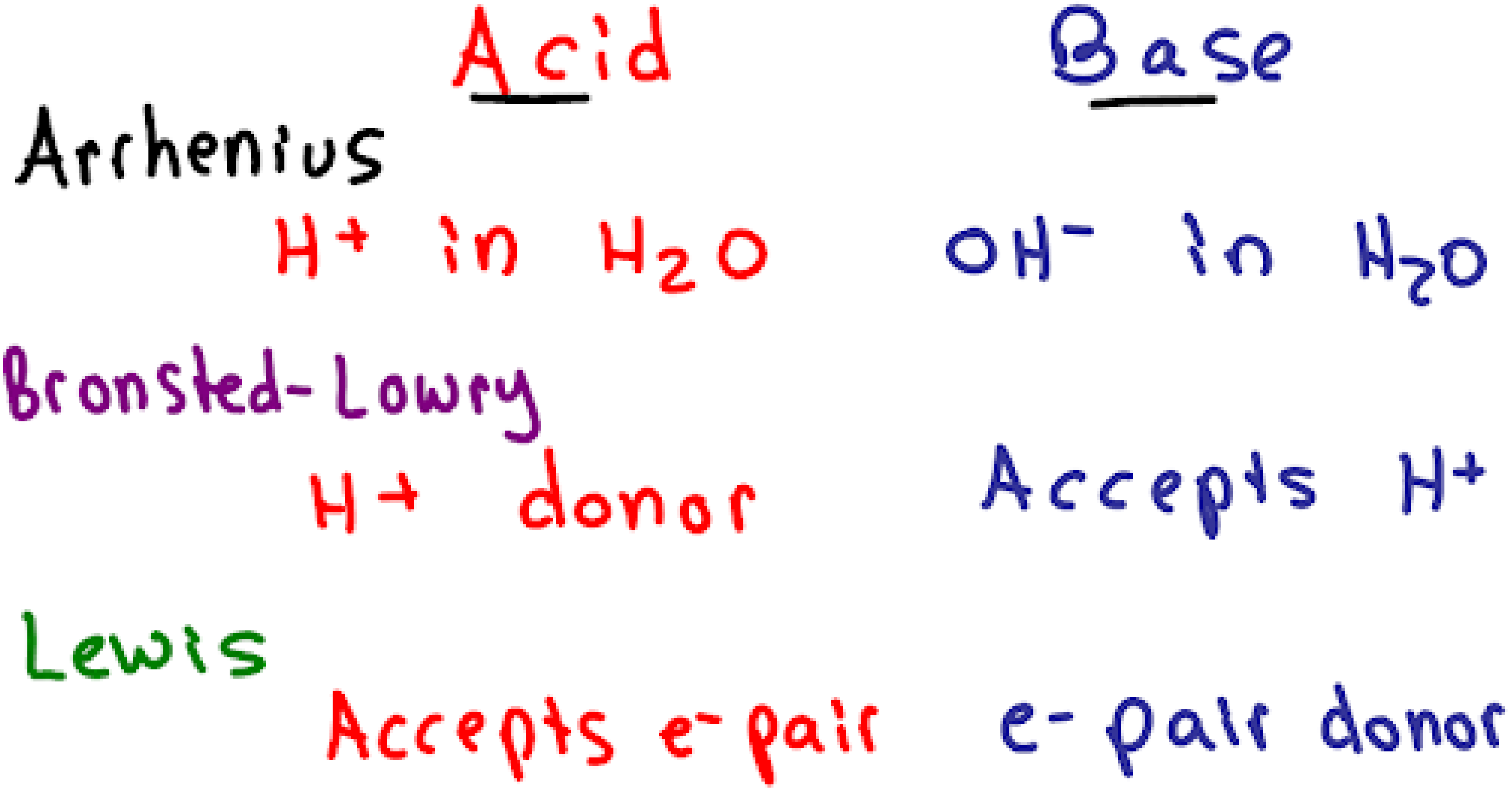
Acids and Bases: Theory

Lewis acids and bases

Lewis proposed a definition of acid and base that emphasizes the shared electron pair. Lewis acid is defined as an electron-pair acceptor, and a Lewis base is an electron-pair donor.



SUMMARY:



	Acid	Base
Arrhenius	H^+ in H_2O	OH^- in H_2O
Bronsted-Lowry	H^+ donor	Accepts H^+
Lewis	Accepts e^- pair	e- pair donor

Solvent Effect on Acidity and Basicity

Leveling effect or solvent leveling refers to the effect of solvent on the properties of acids and bases. The strength of a strong acid is limited ("leveled") by the basicity of the solvent. Similarly the strength of a strong base is leveled by the acidity of the solvent. When a strong acid is dissolved in water, it reacts with it to form hydronium ion (H_3O^+). An example of this would be the following reaction, where "HA" is the strong acid:

Any acid that is stronger than H_3O^+ reacts with H_2O to form H_3O^+. Therefore, no acid stronger than H_3O^+ exists in H_2O. Similarly, when ammonia is the solvent, the strongest acid is amonium (NH_4^+),

Similarly, in water OH^- is the strongest base. Thus, even though sodium amide ($NaNH_2$) is an exceptional base (pK_a of $NH_3 \sim 33$), in water it is only as good as sodium hydroxide. On the other hand, $NaNH_2$ is a far more basic reagent in ammonia than is NaOH.

The pH range allowed by a particular solvent is called the acid-base discrimination window

Leveling and differentiating solvents:

In a differentiating solvent, various acids dissociate to different degrees and thus have different strengths. In a leveling solvent, several acids are completely dissociated and are thus of the same strength. A weakly basic solvent has less tendency than a strongly basic one to accept a proton. Similarly a weak acid has less tendency to donate protons than a strong acid. As a result a strong acid such as perchloric acid exhibits more strongly acidic properties than a weak acid such as acetic acid when dissolved in a weakly basic solvent. On the other hand, all acids tend to become indistinguishable in strength when dissolved in strongly basic solvents owing to the greater affinity of strong bases for protons. This is called the leveling effect. Strong bases are leveling solvents for acids, weak bases are differentiating solvents for acids. Because of the leveling effect of common solvents, studies on super acids are conducted in solvents that are very weakly basic such as sulphur dioxide (liquefied) and SO_2ClF.

Types of solvent on the basis of proton interaction On the basis of proton interaction, solvents are of four types,

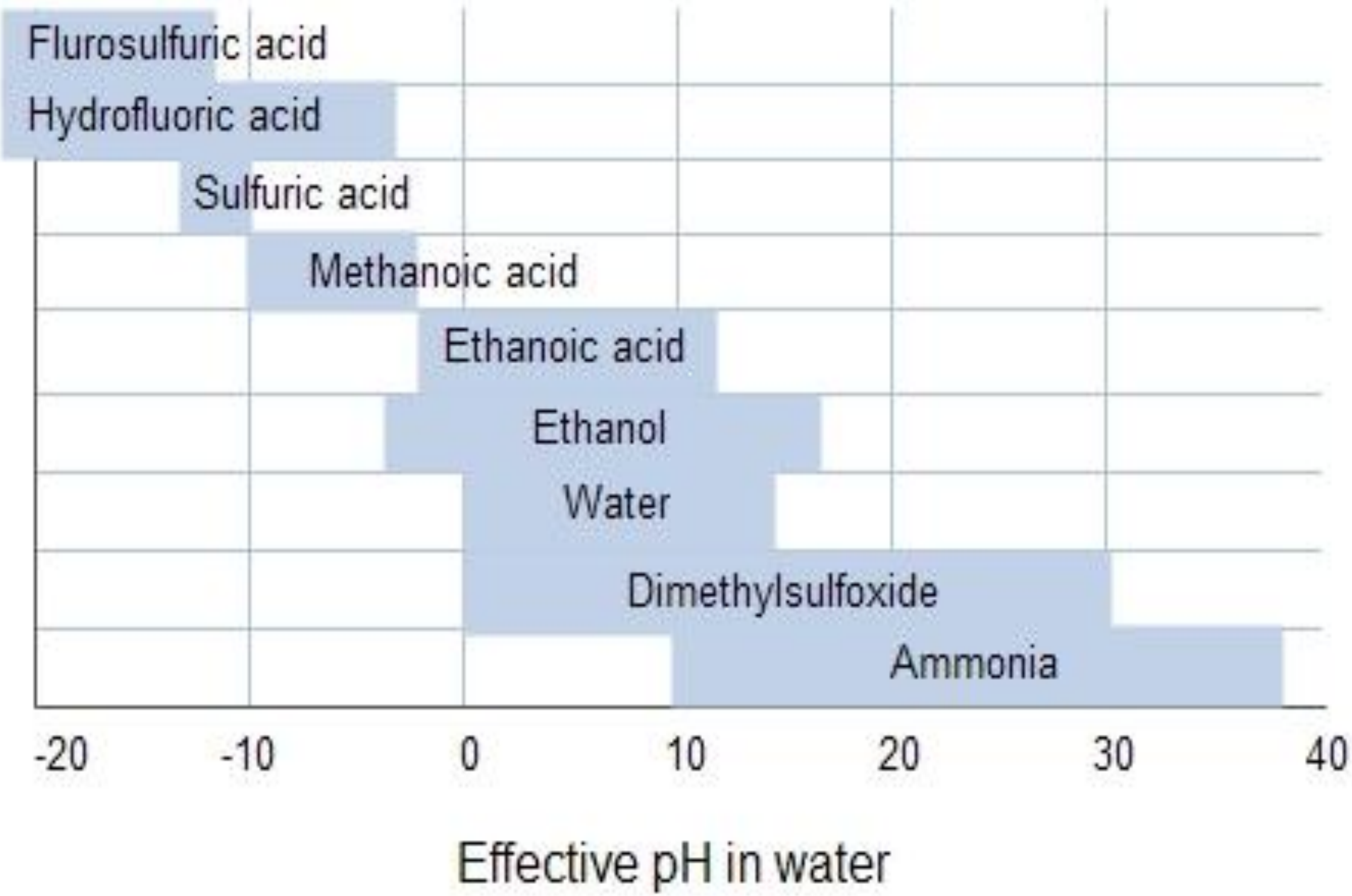
(i) Protophilic solvents: Solvents which have greater tendency to accept protons, i.e., water, alcohol, liquid ammonia, etc.

(ii) Protogenic solvents: Solvents which have the tendency to produce protons, i.e., water, liquid hydrogen chloride, glacial acetic acid, etc.

(iii) Amphiprotic solvents: Solvents which act both as protophilic or protogenic, e.g., water, ammonia, ethyl alcohol, etc.

(iv) Aprotic solvents: Solvents which neither donate nor accept protons, e.g., benzene, carbon tetrachloride, carbon disulphide, etc.

HCl acts as an acid in H_2O, a stronger acid in NH_3, a weak acid in CH_3COOH, neutral in C_6H_6 and a weak base in HF.


Flurosulfuric acid
Hydrofluoric acid
Sulfuric acid
Methanoic acid
Ethanoic acid
Ethanol
Water
Dimethylsulfoxide
Ammonia
-20
-10
0
10
20
30
40
Effective pH in water

Question:

1. Arrange in accordance with strong acidity:

(A) H_3PO_4, H_2SO_4, HNO_3

(B) $HClO_4$ $HClO_3$, $HClO_2$, $HClO$

(C) H_3PO_4, H_3PO_3, H_3PO_2