

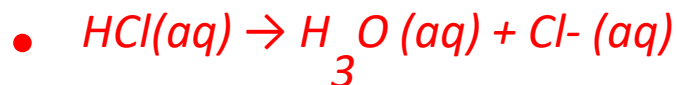
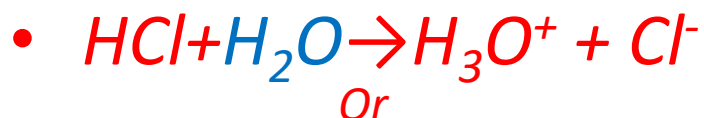
ACID BASE AND SALT

- *CLASSIFICATION BASED ON THEORIES/CONCEPTS*
- 1. ARRHENIUS CONCEPT OF ACID BASE
- 2. BRONSTED LOWRY THEORY
- 3. LEWIS THEORY
- 4. LUX-FLOOD CONCEPT
- 5. SOFT AND HARD ACID BASE THEORY

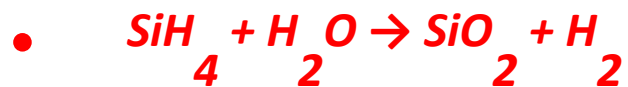
ARRHENIUS CONCEPT

- ACID PRODUCES

HYDROGEN ION IN AQUEOUS SOLUTION



- $HI > HBr > HCl > HF$ (decreasing strength of acidity)



$CH_4 + H_2O \rightarrow$ no reaction

HF, H₂O, NH₃, CH₄ Acidity??

- Base produces

Hydroxyl ion in aqueous solution



$KOH > NaOH > LiOH$ (Fajan's concept)

$Te(OH)_6 > Si(OH)_6 > B(OH)_3$

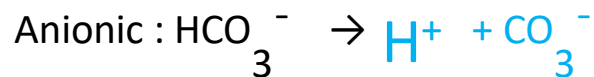
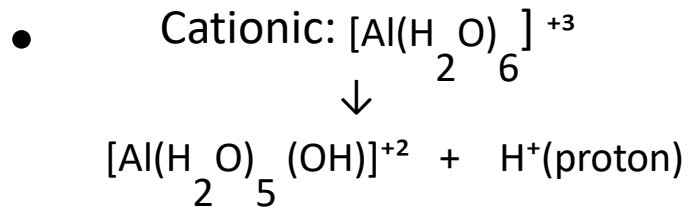
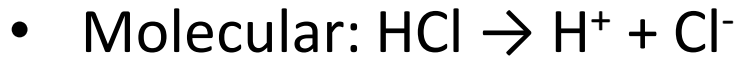
DRAWBACKS

- Unable to explain why NH_3 which contains no OH^- ions, is a base and not an acid
 - Why a solution of FeCl_3 is acidic or why Na_2S is alkaline
 - Limited to aqueous media only. Failed to explain why NaNH_2 is alkaline and NH_4Cl acidic in liquor ammonia
 - Failed to define inherent acid-base character (phenol/picric acid)
- Arrange in order of increasing acidity:
 1. H_3PO_2 , H_3PO_3 , H_3PO_4
 2. HClO_4 , HClO_3 , HClO_2 , HOCl
 3. $[\text{Al}(\text{H}_2\text{O})_6]^{+3}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{+2}$, $[\text{Co}(\text{H}_2\text{O})_6]^{+2}$

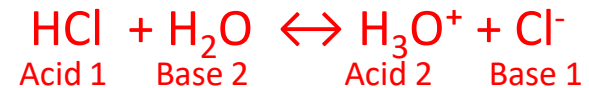
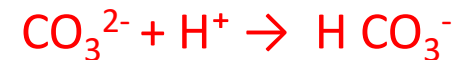
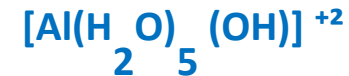
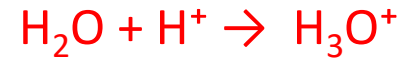
Bronsted-Lowry Theory

The Proton-donor-acceptor system

• Bronsted Acids



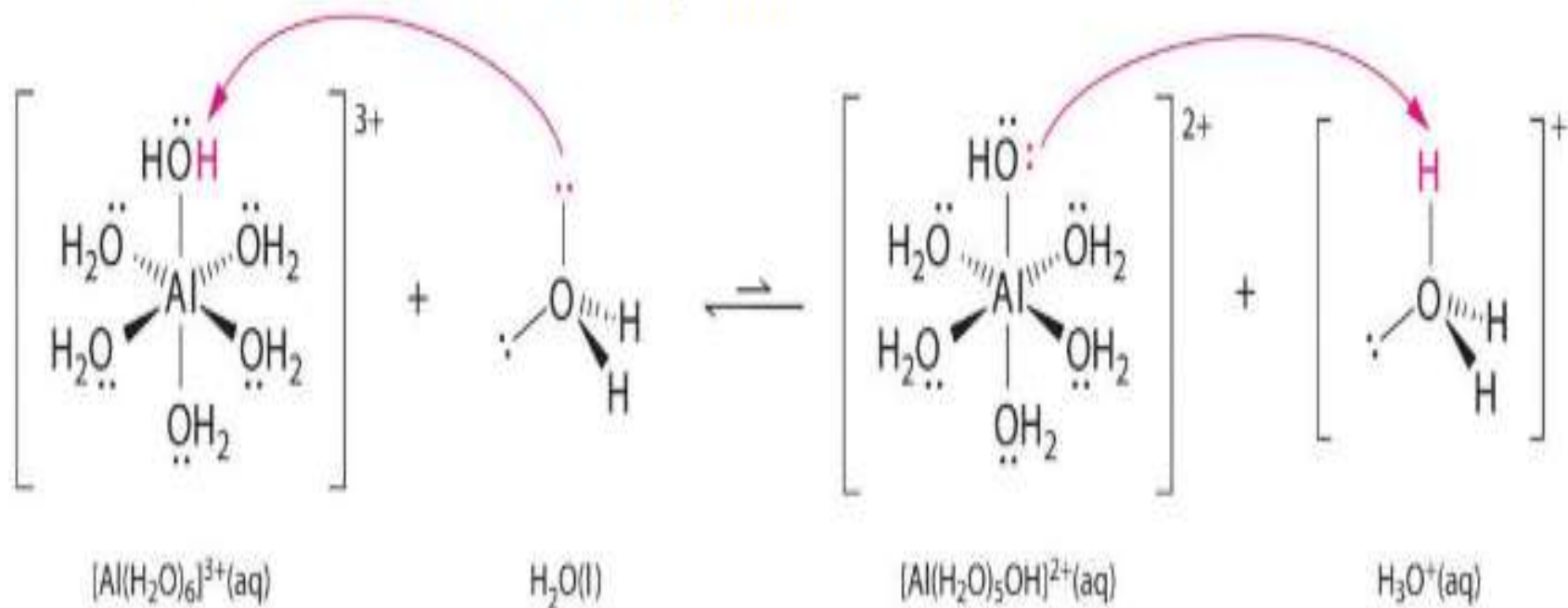
• Bronsted Bases



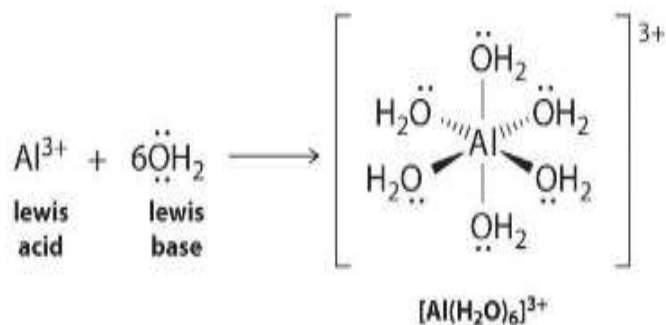
(Conjugate acid-base pair)

Reactions in aqueous media

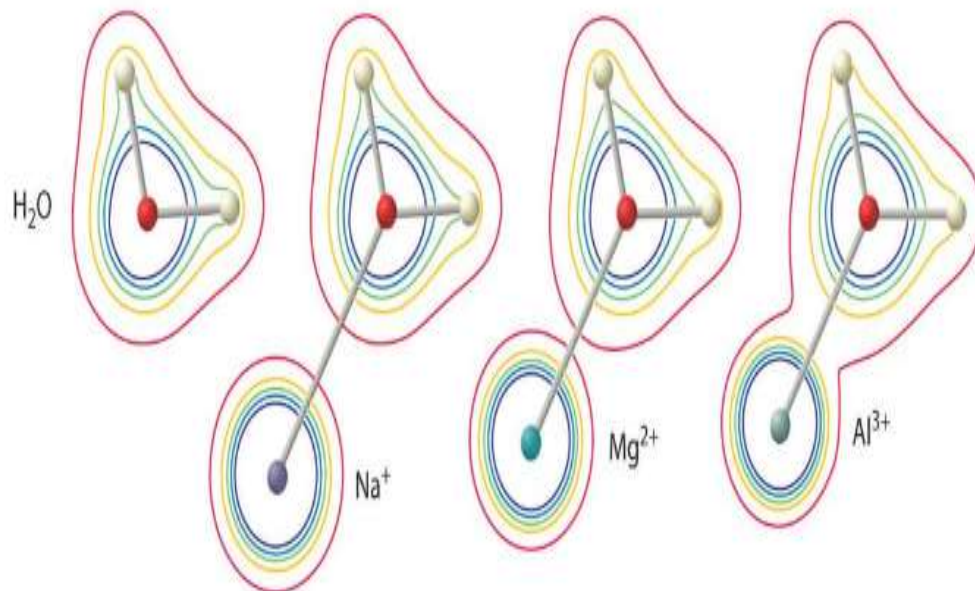
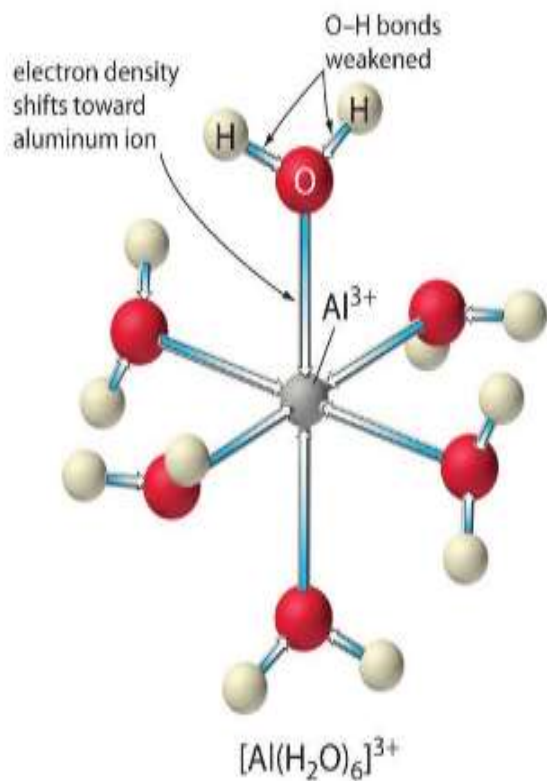
"Reactions in Aqueous Solution". A water molecule coordinated to a metal ion is more acidic than a free water molecule for two reasons. First, repulsive electrostatic interactions between the positively charged metal ion and the partially positively charged hydrogen atoms of the coordinated water molecule make it easier for the coordinated water to lose a proton.



Effect of charge on acidity



(a)



The contours show the electron density on the O atoms and the H atoms in both a free water molecule (left) and water molecules coordinated to Na⁺, Mg²⁺, and Al³⁺ ions. These contour maps demonstrate that the smallest, most highly charged metal ion (Al³⁺) causes the greatest decrease in electron density of the O-H bonds of the water molecule. Due to this effect, the acidity of hydrated metal ions increases as the charge on the metal ion increases and its radius decreases. Thus aqueous solutions of small, highly charged metal ions, such as Al³⁺ and Fe³⁺, are acidic:

Comparison of Hydracids

hydracid	Ka value	BDE(kJ/mol)
HF	7.2×10^{-4}	570
HCl	1×10^6	430
HBr	1×10^9	370
HI	3.3×10^9	300

- The acid strength increases with increase in the size of atoms

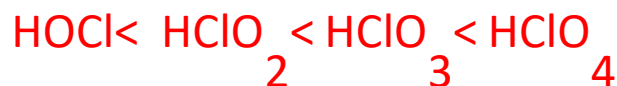


Gas phase acidity increases across a period and down a group in the p-block binary acids

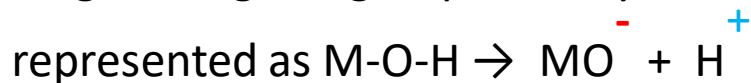
Oxo and Hydroxo acids

- An oxo acid is one in which the acidic proton is on a hydroxyl group with an oxo group attached to the same atom. Usually represented as $M(O)_x(OH)_y$

The acidity of these oxyacids increases significantly as the oxidation state of the central atom becomes larger



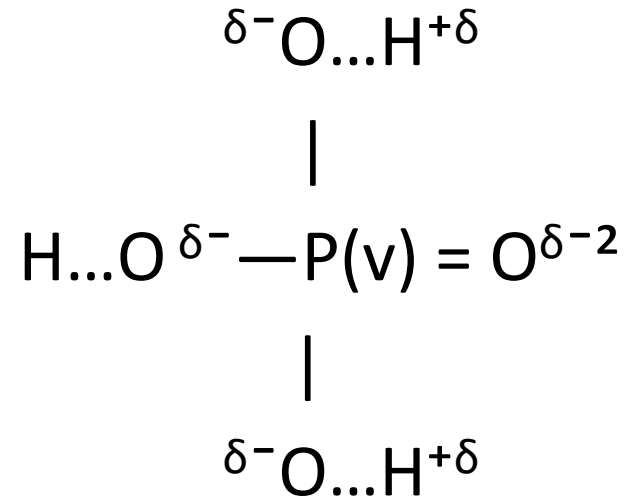
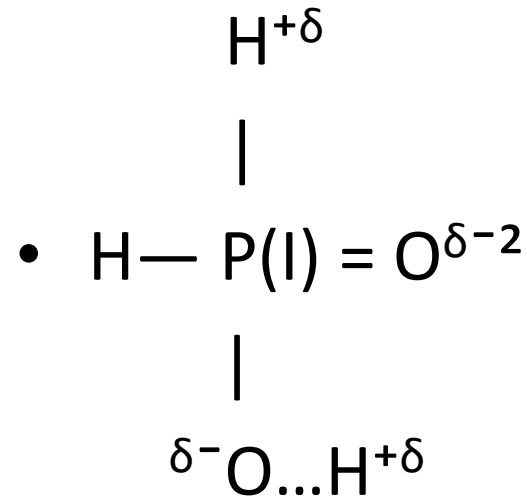
A hydroxo acid is one in which the acidic proton is on a hydroxy group without a neighboring oxo group. Usually



Oxy acid	$M(O)_x(OH)_y$	Value of X	pKa = 8-5x	Ka	pka expt
HOCl	Cl(OH)	0	8- (5 x 0) =8	3×10^{-8}	7.5
HClO ₂	ClO(OH)	1	8- (5x1) =3	1×10^{-2}	2.0
HClO ₃	Cl(O) ₂ (OH)	2	8- (5x2) = -2	5×10^2	-1.3
HClO ₄	Cl(O) ₃ (OH)	3	8- (5x3) = -7	1×10^3	-10

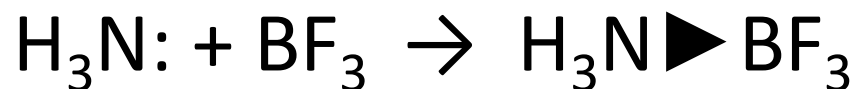
Oxo acids of Phosphorus

- H_3PO_2 (Monobasic with one hydroxyl and one oxo group)
- H_3PO_3 (Dibasic with two hydroxyl and one oxo group)
- H_3PO_4 (Tribasic, Three hydroxyl and one oxo group)
- $\text{H}_3\text{PO}_2 > \text{H}_3\text{PO}_3 > \text{H}_3\text{PO}_4$
Strong acid
weak acid



Lewis concept of Acid and bases

- Lewis acid: A chemical species that contains an empty orbital to accept a pair of electrons and form a coordinate covalent bond
- Lewis base: A substance that has a filled orbital containing non-bonding electron pair which it can donate to form a dative bond with a Lewis acid.

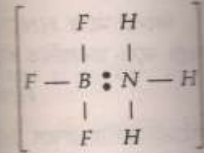


Lewis base L. acid acid-base adduct



-----Lewis acid st increases →

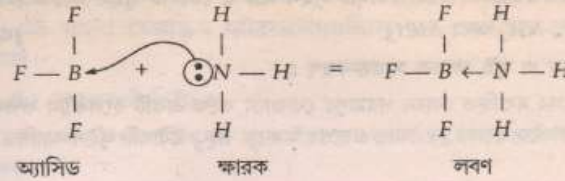
সিড ও ক্ষারকের সংজ্ঞা
তা হল অ্যাসিড আর যে
গুলি অ্যাসিড, কারণ এরা
OH⁻ ইত্যাদি যৌগ
।



জোড়া ইলেকট্রন গ্রহণ করে।
নাইট্রোজেন পরমাণুটি তার
ক্ষারক।
যৌগটির মধ্যস্থ কোন একটি
(l.p.) থাকা প্রয়োজন। যেমন
সিড।

গোলে যৌগটির মধ্যস্থ কোন
ইলেকট্রন জোড়া (lone-pair of
electron) পরমাণুর যোজ্যতা কক্ষকে

কক্ষকে স্থান পাওয়ার মাধ্যমে
সৃষ্টি হওয়ার ঘটনাকে বলে
ন জোড়া দাতার ভূমিকা এবং
মন, NH₃ ও BF₃-এর মধ্যে



Q. 13. দেখাও যে জল লুইস অ্যাসিড এবং লুইস বেস উভয় হিসাবেই কাজ করতে পারে।

[V.U. '99]

অথবা

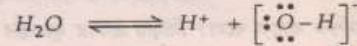
দেখাও যে জল লুইসের অম্ল ও ক্ষারক হিসাবে কাজ করে।

[C.U. '94]

Ans. ► জল একটি লুইস অম্ল ও লুইস ক্ষারক হওয়ার কারণ :

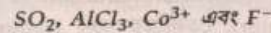
জলের অণুতে (H₂O) অক্সিজেন পরমাণুর দুটি নিঃসঙ্গ ইলেকট্রন জোড়া আছে। সুতরাং, এই পদার্থটি উপযুক্ত গ্রহীতাকে ইলেকট্রন জোড়া দান করার মাধ্যমে অসমযোজী বন্ধন সৃষ্টি করতে পারে। তাই জল একটি লুইস ক্ষারক।

আবার, জল একটি মৃদু তড়িৎ বিশ্লেষ্য পদার্থ। এটি স্বল্প পরিমাণে আয়নিত হয়ে H⁺ ও OH⁻ আয়ন উৎপাদন করে।



H⁺ আয়নের যোজ্যতা কক্ষের 1s কক্ষকটি ইলেকট্রন-শূন্য আছে। তাই H⁺ আয়নটি উক্ত কক্ষকে ইলেকট্রন জোড়া গ্রহণ করতে পারে। ফলে H⁺ আয়ন তথা H₂O একটি লুইস অ্যাসিড।

Q. 14. নিম্নলিখিত আয়ন ও যৌগগুলির মধ্যে কোনগুলি লুইস অম্ল ও কোনগুলি লুইস ক্ষারক নির্দেশ কর :



[C.U. '96]

Ans. ► লুইস অম্ল ও লুইস ক্ষারক সনাক্তকরণ :

(i) SO₂ যৌগের মধ্যস্থিত S পরমাণুর যোজ্যতা কক্ষে ইলেকট্রন কক্ষক খালি অবস্থায় আছে। এ কক্ষকে ইলেকট্রন জোড়া গ্রহণের মাধ্যমে SO₂ লুইস অ্যাসিড হিসাবে কাজ করে।

(ii) AlCl₃ যৌগের মধ্যস্থিত Al পরমাণুর যোজ্যতা কক্ষে ইলেকট্রন কক্ষক খালি অবস্থায় আছে। এ কক্ষকে ইলেকট্রন জোড়া গ্রহণের মাধ্যমে AlCl₃ লুইস অ্যাসিড হিসাবে কাজ করতে পারে।

(iii) F⁻ আয়নের যোজ্যতা কক্ষে নিঃসঙ্গ ইলেকট্রন জোড়া বর্তমান আছে। এই ইলেকট্রন জোড়া উপযুক্ত গ্রহীতাকে দান করার মাধ্যমে F⁻ আয়ন লুইস বেস (লুইস ক্ষারক) হিসাবে কাজ করতে পারে।

(iv) Co³⁺ একটি উচ্চ কক্ষক আধানবিশিষ্ট আয়ন এবং এর বহিস্থ কক্ষে ইলেকট্রন কক্ষক খালি অবস্থায় আছে। এ কক্ষকে উপযুক্ত গ্রহীতাকে ইলেকট্রন জোড়া গ্রহণের মাধ্যমে Co³⁺ আয়নটি লুইস অ্যাসিড হিসাবে কাজ করতে পারে।

Group Characteristics of Lewis acids



Correlates with the decrease in electron withdrawing power of the halogen from F to I



Super acid

Oxides of Group 16 family like Sulfur dioxide can act as Lewis acid by accepting an electron pair at S-atom, and can also act as a base by donating its lone pair either from sulfur or from oxygen

Bromine and Iodine molecules of Group 17 family act as mild Lewis acids

Boric acid behaves as strong acid in presence of diols

- Boric acid (H_3BO_3) is a weak acid which does not act as a proton donor but acts as a Lewis acid, accepting a pair of electrons from hydroxyl ion.

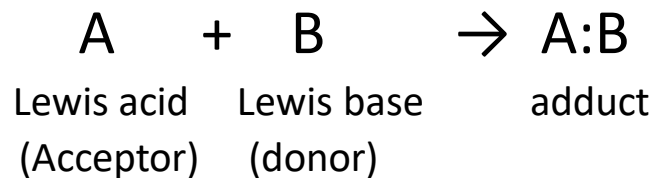


The proton can now be treated against strong alkali using phenolphthalein indicator

- 1. Arrange the bases HS^- , F^- , I^- , NH_2^- in order of increasing proton affinity
- 2. Thermally most stable: PH_4Cl , PH_4Br , PH_4I
- 3. Most acidic oxide: Ag_2O , V_2O_5 , CO

Soft and Hard Acid Base Principle

- Ralph G. Pearson (1963) proposed the principle, abbreviated as SHAB. The complex A:B is most stable when A and B are either both soft or both hard. The complex is least stable when one of the reactants is very hard and the other is very soft.



Hard base: hard to oxidise

Characteristics: High electronegativity/ low polarisability/presence of filled orbitals

Hard acids: Difficult or hard to polarise.

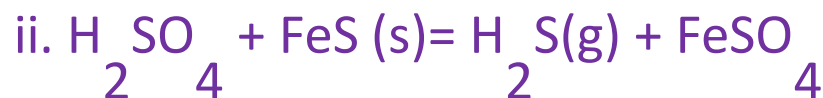
Characteristics: high oxidation state/a small size/a noble gas electronic configuration

Methyl mercury cation CH_3Hg^+ is proton like and monopositive soft Lewis acid



if $K < 1$, B is hard

Indicate with reason the direction of the following reaction:



Lux Flood Concept

- The definition covers things which would become acids or bases if dissolved in water



CO_2 is considered an anhydride of carbonic acid and CaO as base since it would give Ca(OH)_2 in water

An acid is an oxide ion acceptor and a base is an oxide ion donor

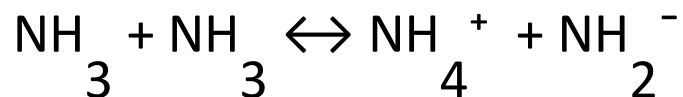
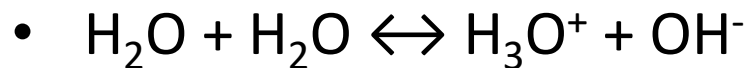
The concept is generally used in high temperature anhydrous systems and in molten state Chemistry



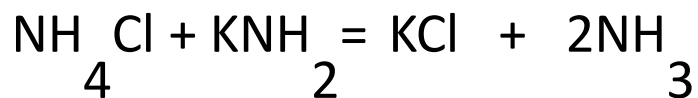
Base acid

Other solvent system

Ammonia as solvent

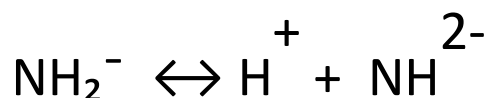


NH_4Cl (ammonium chloride) reacts with KNH_2 (potassium amide) to give salt and solvent

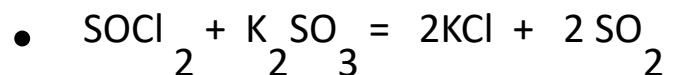


Acid Base Salt Solvent

$\text{BiI}_3 + \text{KNH}_2 \rightarrow \text{product?}$



Sulphur dioxide as solvent



Acid Base salt solvent

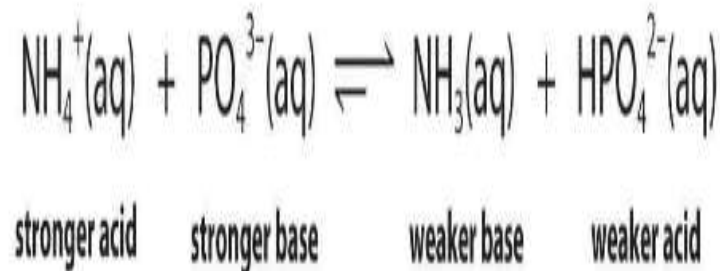


Conjugate acid base pair

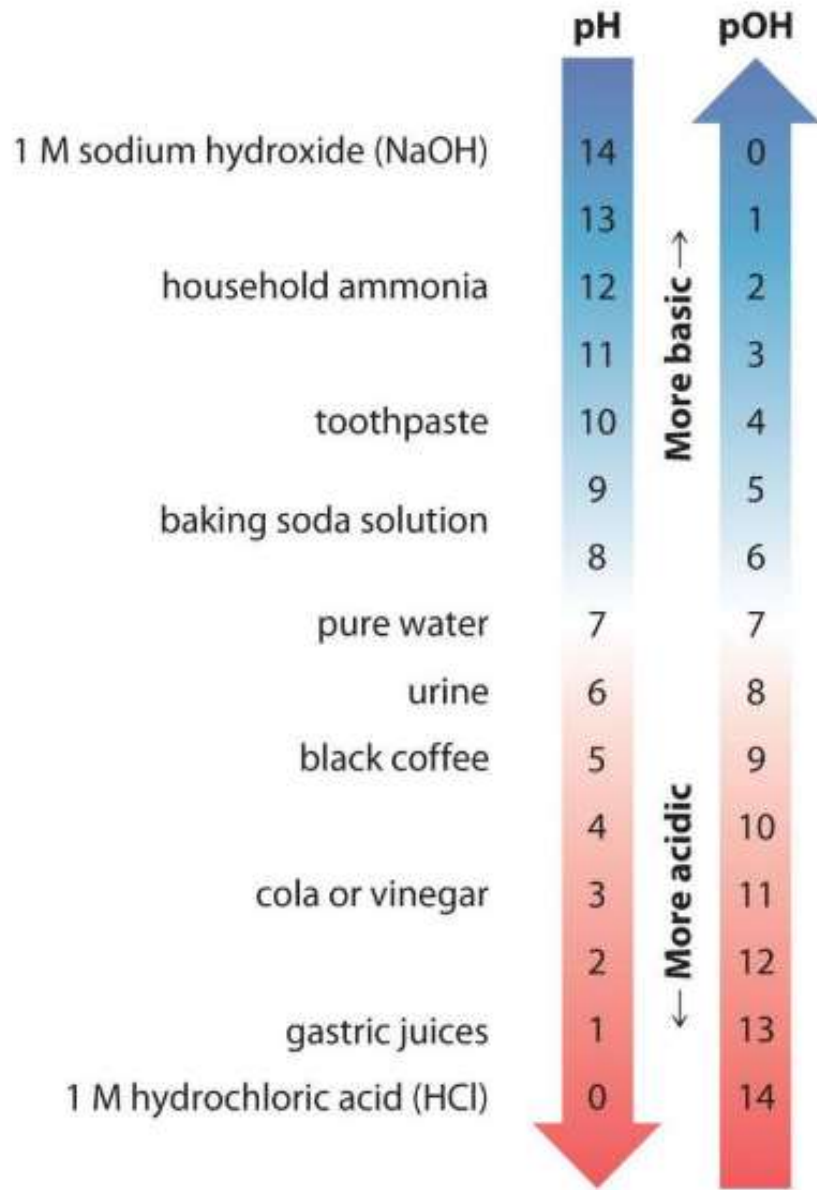
	ACID		BASE	
negligible	OH^-		O^{2-}	strong
	HS^-		S^{2-}	
weak	H_2O		OH^-	weak
	HPO_4^{2-}		PO_4^{3-}	
	HCO_3^-		CO_3^{2-}	
	NH_4^+		NH_3	
	HCN		CN^-	
	H_2PO_4^-		HPO_4^{2-}	
	HSO_3^-		SO_3^{2-}	
	H_2S		HS^-	
	H_2CO_3		HCO_3^-	
	$\text{C}_5\text{H}_5\text{NH}^+$		$\text{C}_5\text{H}_5\text{N}$	
	$\text{CH}_3\text{CO}_2\text{H}$		CH_3CO_2^-	
	HF		F^-	
	H_3PO_4		H_2PO_4^-	
	H_2SO_3		HSO_3^-	
	HSO_4^-		SO_4^{2-}	
strong	H_3O^+		H_2O	
	HNO_3		NO_3^-	

a. The conjugate acid–base pairs are $\text{NH}_4^+/\text{NH}_3$ and $\text{HPO}_4^{2-}/\text{PO}_4^{3-}$. According to Table 16.2 "Values of K_a " and Table 16.3 "Values of K_b ", NH_4^+ is a stronger acid ($\text{p}K_a = 9.25$) than HPO_4^{2-} ($\text{p}K_a = 12.32$), and PO_4^{3-} is a stronger base ($\text{p}K_b = 1.68$) than NH_3 ($\text{p}K_b = 4.75$). The equilibrium will therefore lie to the right, favoring

the formation of the weaker acid–base pair:



pH of a solution = $-\log_{10}[\text{H}^+]$



- $\text{pH} + \text{pOH} = 14$

The K_w for water at 100°C is 4.99×10^{-13} . Calculate $\text{p}K_w$ for water at this temperature and the pH and the pOH for a neutral aqueous solution at 100°C . Report pH and pOH values to two decimal places.

Given: K_w

Asked for: $\text{p}K_w$, pH, and pOH

Strategy:

A Calculate $\text{p}K_w$ by taking the negative logarithm of K_w .

B For a neutral aqueous solution, $[\text{H}_3\text{O}^+] = [\text{OH}^-]$. Use this relationship and Equation 16.7 to calculate $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$. Then determine the pH and the pOH for the solution.

Solution:

A Because $\text{p}K_w$ is the negative logarithm of K_w , we can write

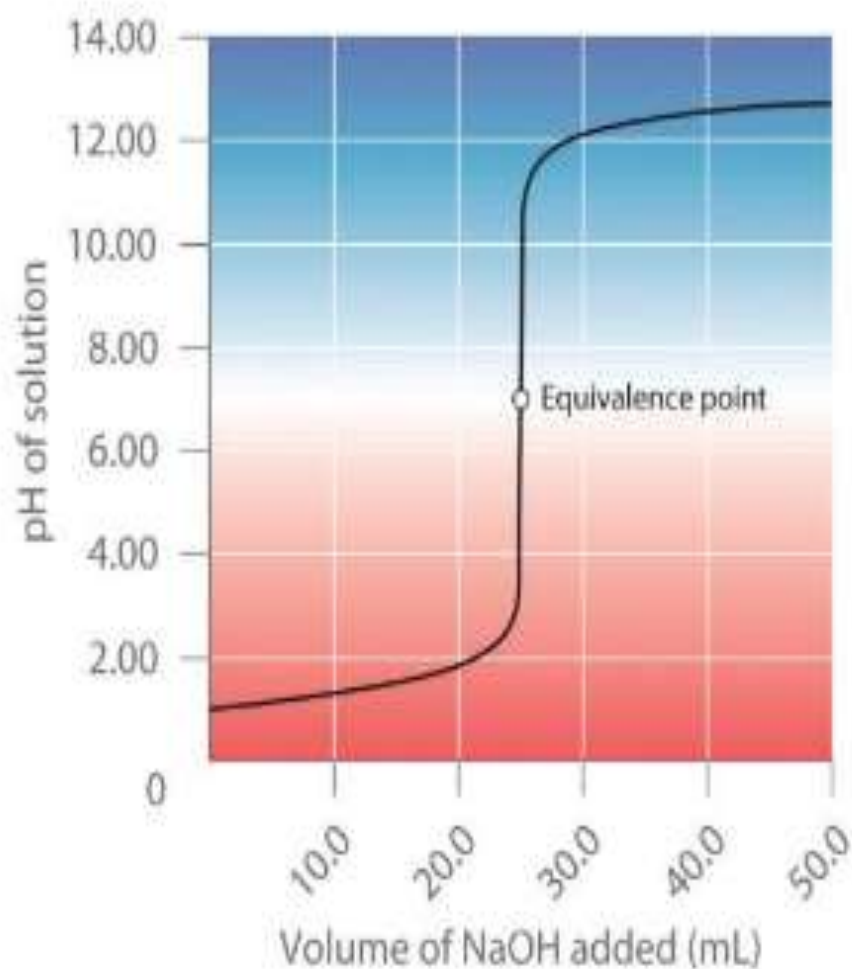
$$\text{p}K_w = -\log K_w = -\log(4.99 \times 10^{-13}) = 12.302$$

For a neutral solution, $\text{pH} = \text{pOH}$

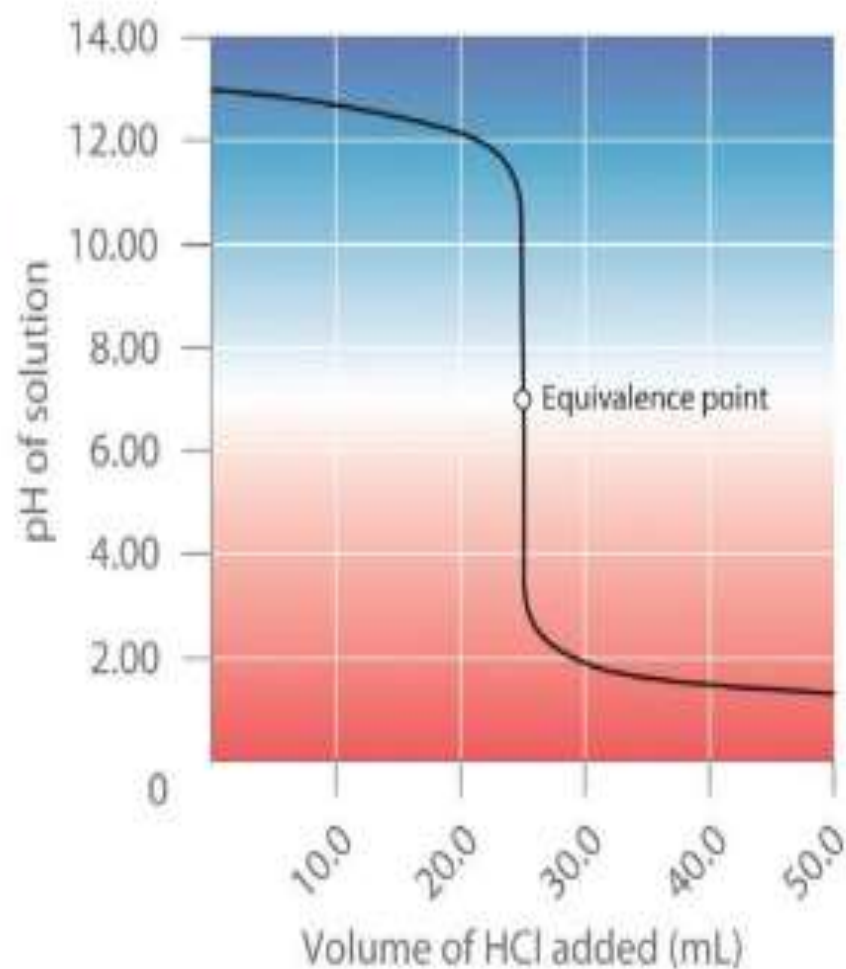
And $\text{pH} + \text{pOH} = \text{p}K_w$

Therefore $2\text{pH} = 12.30$, or $\text{pH} = 6.15$

Strong Acid

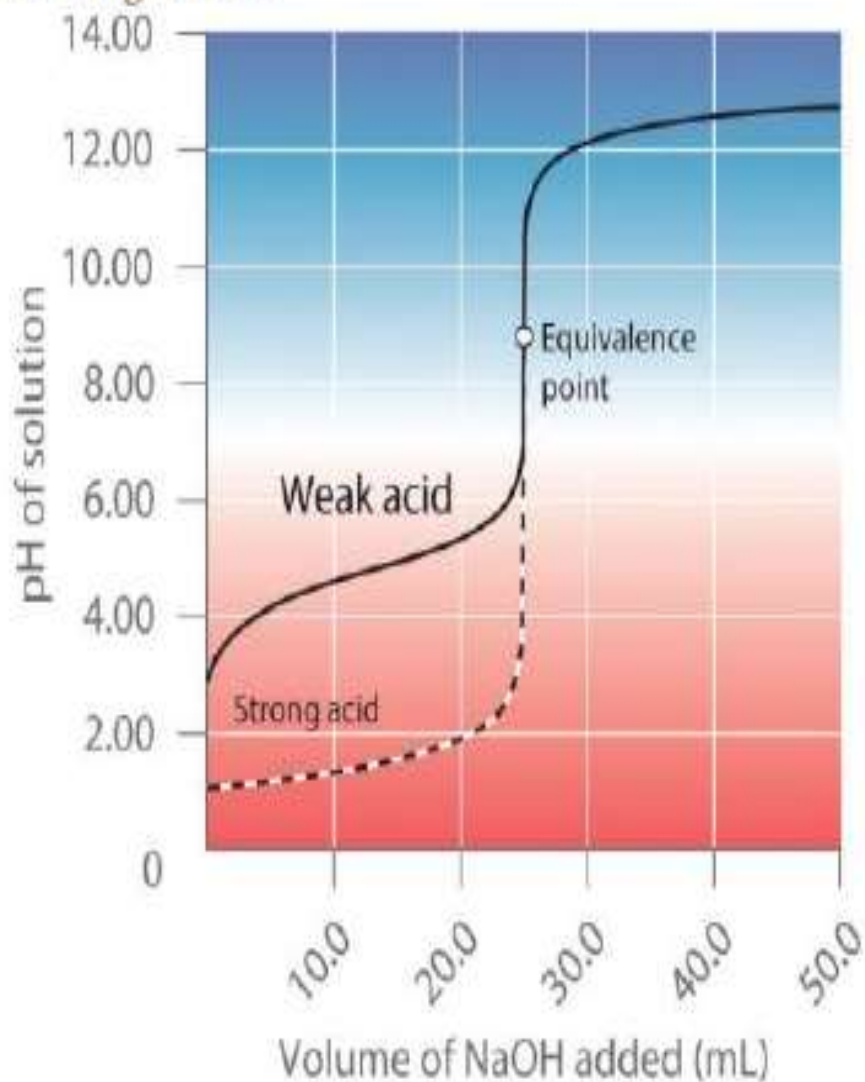


(a) Strong acid titrated with strong base

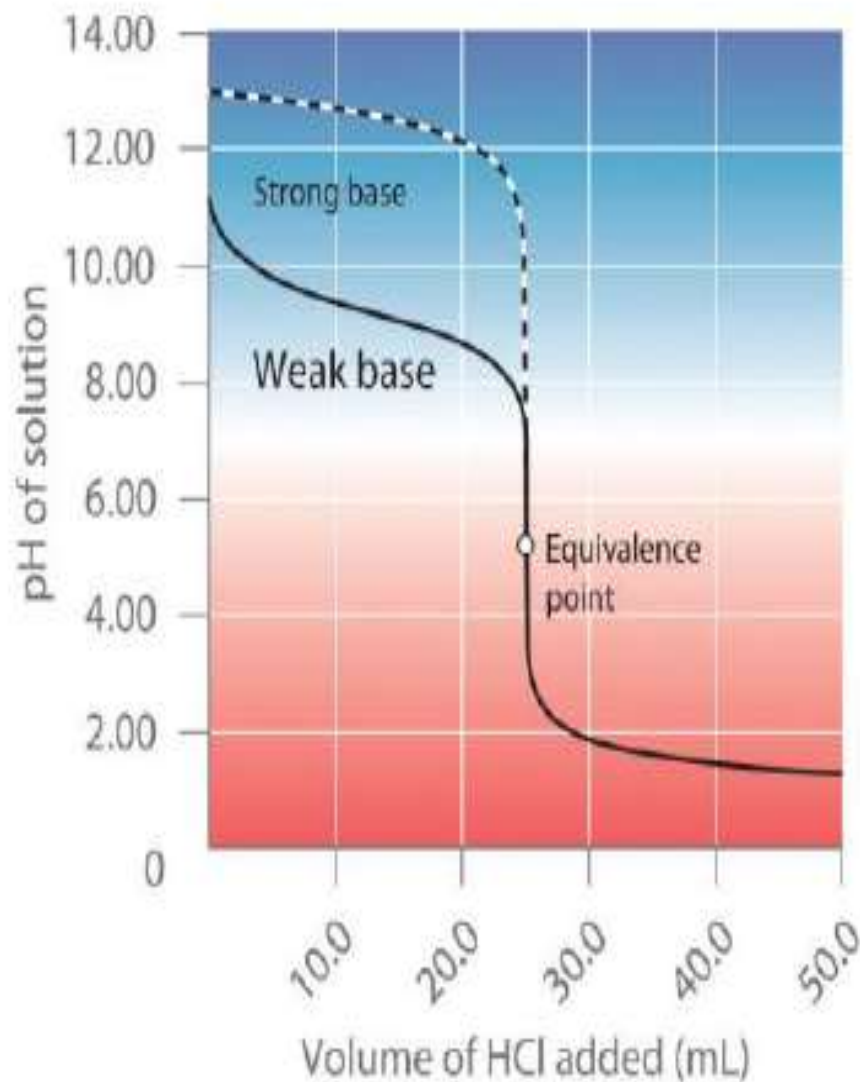


(b) Strong base titrated with strong acid

Strong Acid



(a) Weak acid titrated with strong base



(b) Weak base titrated with strong acid