End Lecture 8

Start Lecture 9
Acid Base Reactions
Lewis Acid Base
Acid-Base Properties of Salts

Syllabus Learning Outcomes : 6, 7

If only the salt's cation affects pH, the solution is acidic

Is NH_4Cl acidic or basic in water?

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Is NH_4Cl acidic or basic in water?

$NH_4Cl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$

Answer: (a) React anion, Cl^-, with H_2O

Cl^-	+	H_2O	$\rightarrow$	HCl	+	OH^-
base		acid		acid		base

Because Cl^- is the conjugate base of a very strong acid (HCl), Cl^- does not affect pH.

Cl^- gives a neutral solution, no effect on pH

If only the salt's cation affects pH, the solution is acidic

$NH_4Cl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$

Answer: (b) React cation, NH_4^+, with H_2O

NH_4^+	+	H_2O	$\rightarrow$	NH_3	+	H_3O^+
acid		base		base		acid

NH_4^+ is a weak acid, and NH_3 is a weak base.

NH_4^+ gives an acidic solution

or $Ka(NH_4^+) > Kb(Cl^-)$ so solution is acidic

If only the salt's anion affects pH, the solution is basic

Calculate the pH of 0.10 M Na_2CO_3, K_b=2.1 x 10^{-4}.

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Answer: (a) Cation: $Na^+ + H_2O \rightarrow$ neutral

(b) Anion: $CO_3^{2-} + H_2O \rightarrow$ weak base

CO_3^{2-}	+	H_2O	$\leftrightarrow$	HCO_3^-	+	OH^-
base		acid		acid		base

Step 1. Set up ICE table for weak base

	$[CO_3^{2-}]$	$[HCO_3^-]$	$[OH^-]$
initial			
change			
equilib			

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If only the salt's anion affects pH, the solution is basic

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(b) Anion: $CO_3^{2-} + H_2O \rightarrow$ weak base

CO_3^{2-} +	H_2O ↔	HCO_3^- +	OH^-
base	acid	acid	base

Step 1. Set up ICE table for weak base

	$[CO_3^{2-}]$	$[HCO_3^-]$	$[OH^-]$
initial	0.10	0	0
change	-x	+x	+x
equilib	0.10 - x	x	x

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If only the salt's anion affects pH, the solution is basic

Calculate the pH of 0.10 M Na_2CO_3, K_b=2.1 x 10^{-4}.

Step 2. Solve equilibrium expression

$$Kb = 2.1\times10^{-4} = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = \frac{x^2}{0.10-x}$$

100*Kb<0.1, so 0.10-x ≈ 0.10, giving

x= $[HCO_3^-]$= $[OH^-]$= 0.00458M

pOH= 2.33, and pH= 11.66

0.1M Na_2CO_3 is a basic solution.

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If neither the salt's cation nor anion affects pH, the solution is neutral, pH=7

Is 0.1M NaCl acidic or basic in water?

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If neither the salt's cation nor anion affects pH, the solution is neutral, pH=7

Is 0.1M NaCl acidic or basic in water?

Answer: (a) We did Na^+ and Cl^-, before.

Neither Na^+ nor Cl^- affect pH (Na^+ from NaOH and Cl^- from HCl).

0.1M NaCl is neutral in water.

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If both the salt's cation and anion affect pH, the larger of Ka and Kb determine pH

Is 0.1M NH_4Bz acidic or basic in water?

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If both the salt's cation and anion affect pH, the larger of Ka and Kb determine pH

Is 0.1M NH_4Bz acidic or basic in water?

Answer: Look up Ka(NH_4^+) and Kb(Bz^-)

(a) Ka for NH_4^+ = 5.6x10^{-10}

(b) Kb for Bz^- = 1.6x10^{-10}

Ka(NH_4^+) > Kb(Bz^-)

NH_4Bz makes weakly acidic aqueous solutions.

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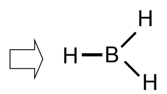
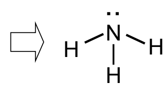
Define Lewis acid & Lewis base

Lewis acid: a substance that accepts an electron pair



Lewis base: a substance that donates an electron pair



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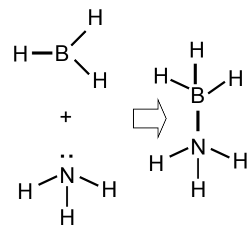
Lewis acids and bases react



- New bond (Coordinate covalent bond) forms using electron pair from the Lewis base.
- Geometry changes after reaction (VSEPR model).

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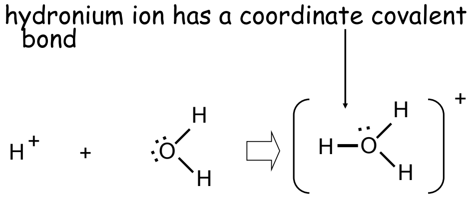
Lewis acids & bases react

hydronium ion has a coordinate covalent bond



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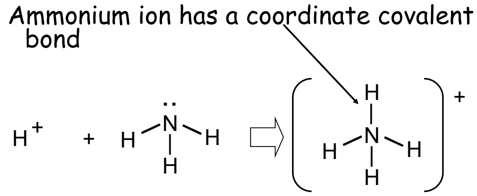
Lewis acids & bases react

Ammonium ion has a coordinate covalent bond



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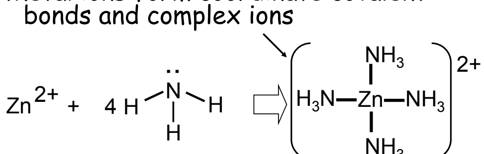
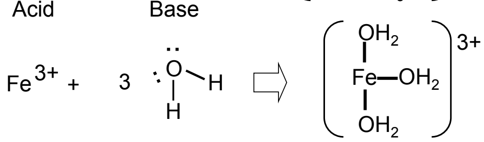
Lewis acids & bases react

Metal ions form coordinate covalent bonds and complex ions



Acid Base



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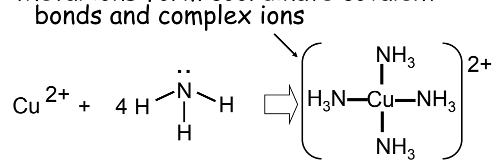
Lewis acids & bases react

Metal ions form coordinate covalent bonds and complex ions



As a result, copper ion (a Lewis acid) can react with ammonia (a Lewis base).

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Lewis acids & bases react in biology

- The heme group in hemoglobin interacts with O_2 and CO.
- The Fe ion in hemoglobin is a Lewis acid
- O_2 and CO can act as Lewis bases
- CO has a strong (irreversible) binding constant with hemoglobin, whereas O_2 binds more weakly and reversibly.

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Many water-containing complex ions hydrolyze

(undergo hydrolysis) to give acidic solutions.

$$[Cu(H_2O)_4]^{2+} + H_2O \rightarrow [Cu(H_2O)_3(OH)]^{+} + H_3O^{+}$$

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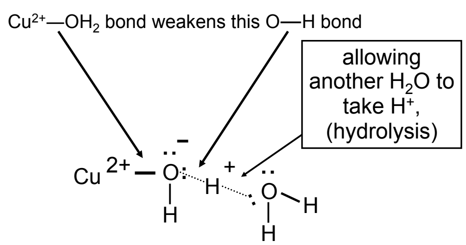
Hydrolysis makes solutions of Fe^{3+}, Al^{3+}, Cu^{2+}, and Pb^{2+} acidic.



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Brønsted and Lewis theories explain amphoteric nature of some metal hydroxides.

$Al(OH)_3(s) + 3\ H^+ \rightarrow Al^{3+} + 3\ H_2O$

Here $Al(OH)_3$ is a Brønsted base.

$Al(OH)_3(s) + OH^- \rightarrow Al(OH)_4^-$

Here $Al(OH)_3$ is a Lewis acid. $Al^{3+} \leftarrow :OH^-$

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Complex ion formation can dissolve a precipitate

$AgCl(s) \leftrightarrow Ag^+ + Cl^-$ $K_{sp} = 1.8 \times 10^{-10}$

$Ag^+ + 2NH_3 \leftrightarrow Ag(NH_3)_2^+$ $K_{form} = 1.6 \times 10^7$

——————————————————

$AgCl(s) + 2NH_3 \leftrightarrow Ag(NH_3)_2^+ + Cl^-$ $K_{net}=$

$K_{net} = K_{sp} * K_{form} = 2.9\times10^{-3}$, so some precipitate dissolves

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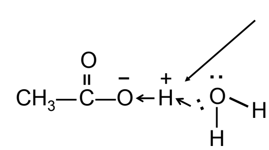
CH_3CO_2H is an Acid

1. Electronegativity of O atoms takes e^-, weakening O—H bond.
2. H atom in O—H can be taken by H_2O to form H_3O^+.



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CH_3CO_2H | CCl_3CO_2H
Acetic acid | Trichloroacetic acid
$K_a = 1.8 \times 10^{-5}$ | $K_a = 0.3$

- Trichloroacetic acid is stronger than acetic acid because electronegative Cl in $-CCl_3$ stabilizes $—O^-$ anion more than the H in $-CH_3$.

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Basisity oxoanions ↑as – charge↑

NO_3^-	CO_3^{2-}	PO_4^{3-}
Least basic		Most basic

As charge↑, water interaction↑, basicity ↑

These are both Bronsted and Lewis bases

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Basisity oxoanions ↑ as #O↓

Least basic | Most basic

$ClO_3^- < ClO_2^- < ClO^-$

As # oxygens ↑ , strength of acid ↑, basicity conjugate base ↓. Recall that $HClO_4$ is a strong acid.