CHEM 206 section 01

LECTURE #21 Wed. March 26, 2008

LECTURE TOPICS:

TODAY'S CLASS: continue Ch.17

NEXT CLASS: continue Ch.17

So: to understand acids,
we must learn to analyze base strength.
= basicity

17.10 Molecular structure, bonding & Brønsted acid-base behaviour

- Why are some compounds acids?
  - → they contain a δ^+ H atom
    - *i.e.,* a polar covalent bond to H
- Why are some compounds bases?
  - → they contain a *reactive* lone pair
  - → can use it to form a new bond to H^+
- Why do acids & bases vary in strength?
- Can we predict variations in acidity & basicity?

To address this properly:
- **Must learn more about the interaction between lone pairs & H^+**
- **Start by learning GENERAL ideas of this type…**

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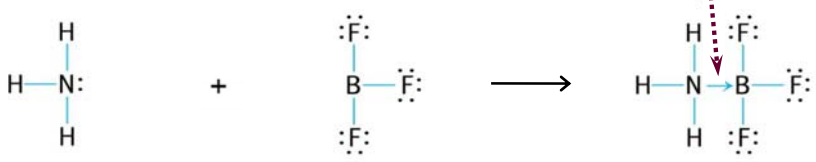
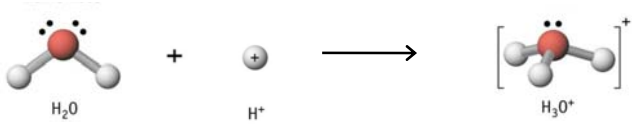
17.9 Lewis acid-base theory: a general view

- **Mechanistic view: δ^+ & δ^- interact → orbital overlap → e^-sharing…**
- **Explains many types of rxns, including H^+ transfer rxns**

LEWIS BASES	LEWIS ACIDS	ADDUCTS: B:→A
= Lone pair donors *(have pair, will share)*	= e- pair acceptors *(need two from you)*	"coordinate bonding" = covalent bonding where both e^-s supplied by one atom *(arrow shows e^-s being donated to Lewis acid)*
• water, alcohols • ammonia, amines • ***anything with a lone pair…***	• H^+: empty 1s orbital • Be, B, Al: open valence… • metal cations: + charge • ***anything e^--deficient…***	



Don't usually refer to Brønsted base-to-H^+ bonds as coordinate bonds…
…but they are:



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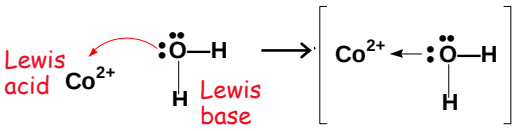
Solutions of highly-charged metal cations are acidic due to Lewis acid-base interactions of M^{n+} & H_2O (Fig. 17.6)



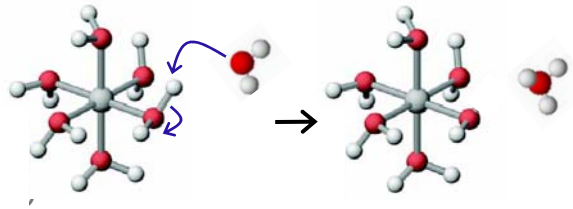
Commonly have 4 or 6 waters coordinated to a metal cation in solution

- M^{n+} pulls on O's lone pair via coordinate bond
- makes O pull harder on O-H bonding pair ⇨ bond more polar
- H is more δ^+ ∴more attractive to incoming bases

⇨ **Coordinated water molecules (pK_a ~ 3-7) are more acidic than free water molecules (pK_a = 14)**

- HYDROLYSIS occurs: solvent-H_2O deprotonates a coordinated-H_2O

$[Co(H_2O)_6]^{2+} + H_2O \rightarrow [Co(H_2O)_5(OH)]^{+} + H_3O^{+}$



- True for: highly charged cations transition metal ions (Al^{3+}, Fe^{3+}, Cu^{2+}, Pb^{2+}…)
- NOT alkali metal ions or alkali earth ions

Thinking about acid strength…

HOW ATTRACTIVE IS THIS δ^+H TO A LEWIS BASE?

- H-X bond MORE POLAR
  ⇨ more attracted to base's lone pair

HOW STABLE IS THE ACID'S CONJUGATE BASE?

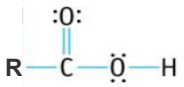
- If anion is very stable
  ⇨no great need to bond
  ⇨ **not** a very reactive base
  ⇨ its conj. acid easily loses H^+

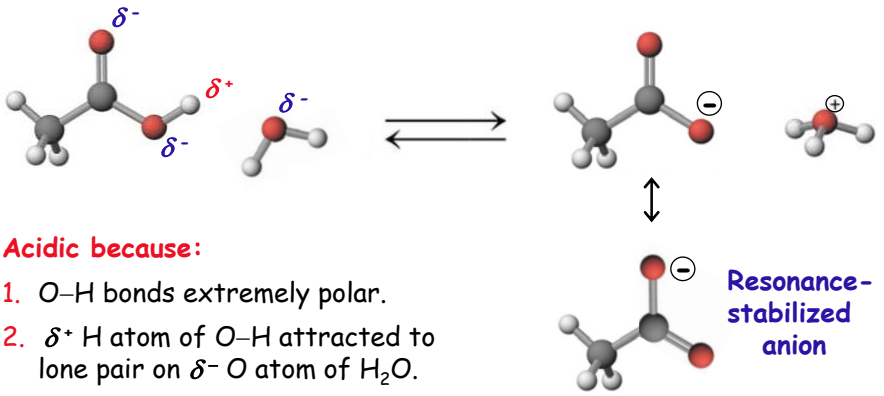
THE PLAN = Understand acid's strength by analyzing its conj.base:

Will the conj.base's $2e^-$s easily act as a pair & attack the H^+ again?

- **How delocalized is the lone pair?** (more stable anion ⇨ less basic)
  - by resonance OR because of large atom size
    OR by other atoms "pulling"
- **If the lone pair is localized on 1 atom, how "exposed" is it?**
  - on a small, not-so-electronegative atom ⇨ reactive, highly basic
  - on a highly electronegative atom ⇨ not very reactive, less basic

Why are carboxylic acids weak acids?





Acidic because:

1. O–H bonds extremely polar.
2. δ^+ H atom of O–H attracted to lone pair on δ^- O atom of H_2O.

Resonance-stabilized anion

Relatively strong "weak acid" because: conjugate base = weak base
lone pair causing -ve charge is on highly electronegative atom
AND
it is delocalized by resonance: oxygen has average $-\,^1/_2$ charge

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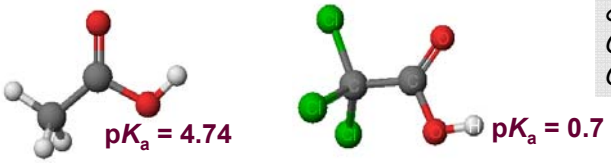
Comparing two carboxylic acids: why such different acidities?



$pK_a = 4.74$ — **Acetic acid**

$pK_a = 0.7$ — **Trichloroacetic acid**

& compare to…
$CH_2ClCOOH$: $pK_a = 2.85$
$CHCl_2COOH$: $pK_a = 1.59$

both conjugate bases have 2 resonance forms…

New idea: "INDUCTIVE EFFECTS" of "e^--withdrawing groups"
= neighbouring electronegative atoms in molecule pull on e^-s

- **CCl_3COO^- has stronger inductive effects than CH_3COO^-**
  - ⇨ e^- density pulled from rest of molecule towards Cls
  - ⇨ makes O pull harder on the extra lone pair
  - ⇨ lone pair held tightly by atom, therefore is less reactive
  - ⇨ weaker base, therefore cannot compete as well for the H^+
- If the conjugate base is too weak to get the H^+ back often
  - ⇨ eqm favours deprotonation ⇨ acid is *relatively strong*

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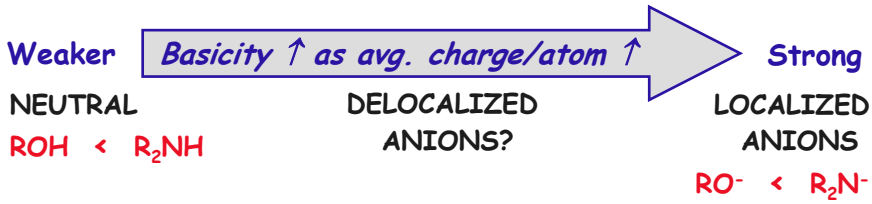
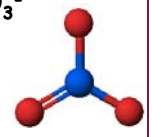
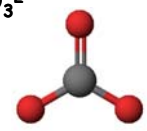
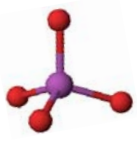
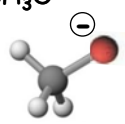
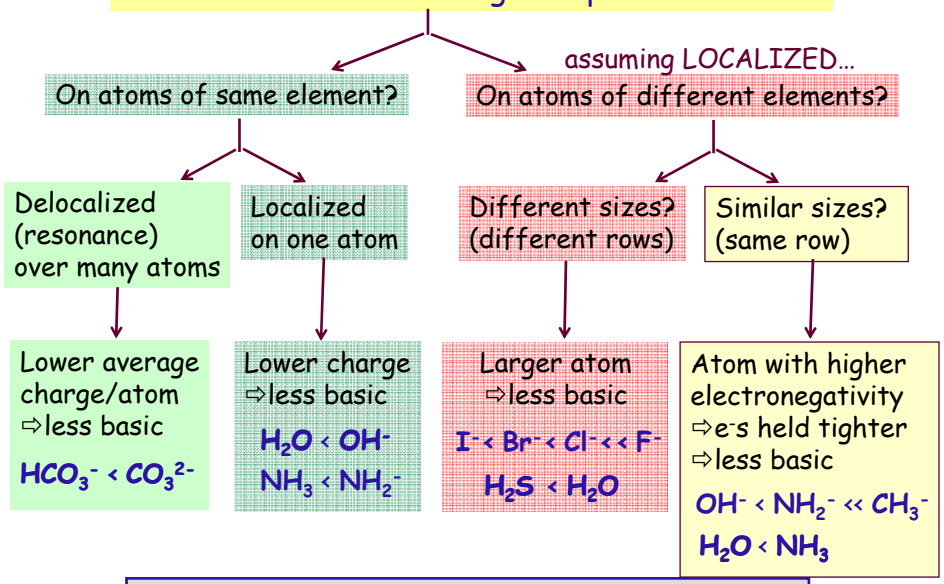
Common bases: have lone pair on O or N



Basicity of oxoanions varies with # resonance structures & charge

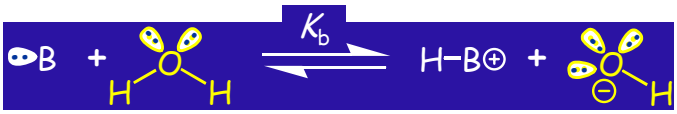
Ion	NO_3^-	CO_3^{2-}	PO_4^{3-}	CH_3O^-
				
Charge/O				
pK_b	huge	3.68	1.55	< 0
Basicity	**Extremely weak base**	**Moderate weak base**	**Relatively strong weak base**	**STRONG base**
CA's pK_a	< 0	10.32	12.45	Huge (> 14)

To compare strengths of two bases, ask: Where is the attacking lone pair located?



GENERAL RULE: More stable e⁻ pair = less basic

BASES: react with water to yield OH^-...



PROPERTY	STRONG base	WEAK base
K_b value	very large	small
pK_b value	very small	large
Equilibrium position	right	left
$[OH^-]$ compared to $[B:]_0$	$[OH^-] \approx [B:]_0$	$[OH^-] \ll [B:]_0$
Strength of B: compared to OH^-	B: >> OH^-	B: << OH^-

ASSIGNED READINGS:

BEFORE NEXT CLASS:

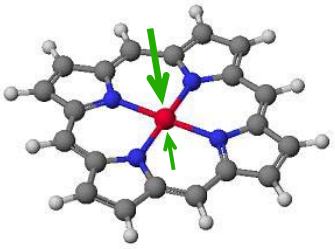
Read: Ch.17 up to section 17.4 (to 6th Ed. p.809),
& 17.7 (to 6th Ed. p.824)
& 17.10

+ WORK ON Problems from Ch.16 & Ch.17
including finding the pH of weak acid solutions
***e.g.*, section 17.7 problems, #47-50**

Extra example:
why it is so interesting to know something about Lewis acids & bases…

Aside: biological relevance of Lewis acid-base interactions…

***e.g.*, heme groups in hemoglobin…**



***A Heme* group:**
- a planar ring of C,N,H
  4 N atoms = Lewis bases
  each has 3 bonds & 1 lone pair
- **an Fe(II) cation** = Lewis acid
  coordinated by these N atoms & held in centre of ring

- Heme Fe^{II} is "open" on top/bottom
  - One side bound to protein (*e.g.*, bottom)
  - Other side can accept another lone pair
- THUS: can interact with Lewis bases
  O_2 = desirable…but binds weakly
  CO = undesirable…and binds strongly

TASK: draw Lewis structures (+ formal charges) to rationalize differing abilities to coordinate…

Some molecules are Lewis acids

…which leads to their solutions being acidic (*i.e.*, low pH…)

Recall: CO_2, SO_2, NO_2
…nonmetal oxides yield acidic solutions in water

WHY do they react with water?
WHY does the soln become acidic?