

Acid-Base Concepts -- Chapter 15

1. Arrhenius Acid-Base Concept (last semester)

Acid: H⁺ supplier

Base: OH⁻ supplier

2. Brønsted-Lowry Acid-Base Concept (more general)

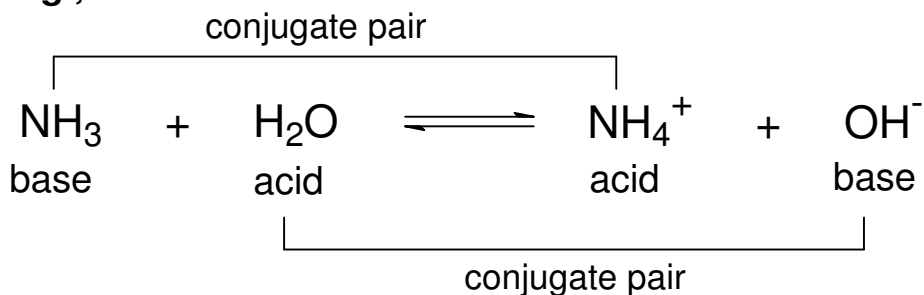
(a) Definition (H⁺ transfer)

Acid: H⁺ donor

Base: H⁺ acceptor



e.g.,

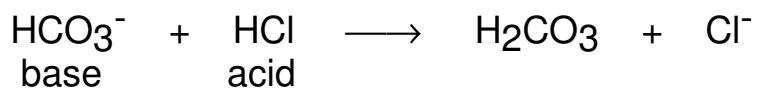
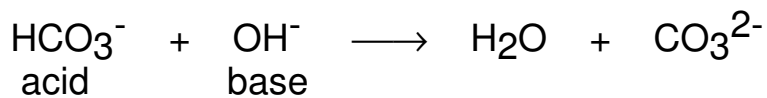


more examples:

conjugate acids \rightarrow		
NH ₂ ⁻	NH ₃	NH ₄ ⁺
OH ⁻	H ₂ O	H ₃ O ⁺
O ²⁻	OH ⁻	H ₂ O
HSO ₄ ⁻	H ₂ SO ₄	H ₃ SO ₄ ⁺
CH ₃ ⁻	CH ₄	" CH ₅ ⁺ "
\leftarrow conjugate bases		

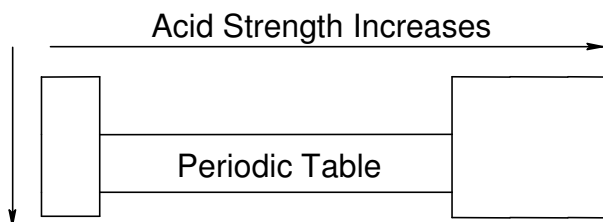
(b) Amphoteric Substances -- molecules or ions that can function as both acids and bases (e.g., H₂O itself !)

e.g., the bicarbonate ion, HCO₃⁻



(c) Relative Strengths of Brønsted Acids

Binary Acids e.g., HCl, HBr, H₂S, etc.

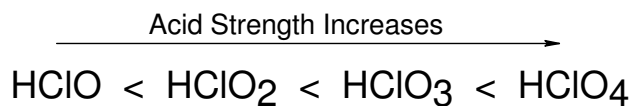


e.g., relative acidity: HCl > H₂S (across a period)

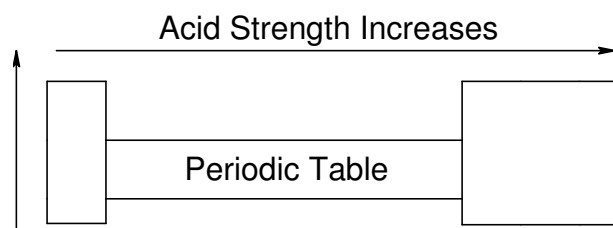
HI > HBr > HCl > HF (up in a group)

Oxo acids e.g., HNO₃, H₂SO₄, H₃PO₄, etc.

1. for same central element,
acid strength increases with # of oxygens



2. for different central element, but same # oxygens,
acid strength increases with electronegativity



(d) Relative strengths of conjugate acid-base pairs

For example,



In this case, the equilibrium lies mainly on reactant side.
Therefore, " HF is a weaker acid than H₃O⁺ "

In general, weak Brønsted acids have
strong conjugate bases. (*vice versa*)

3. Lewis Acid-Base Concept (most general)

(a) Definition (electron pair transfer)

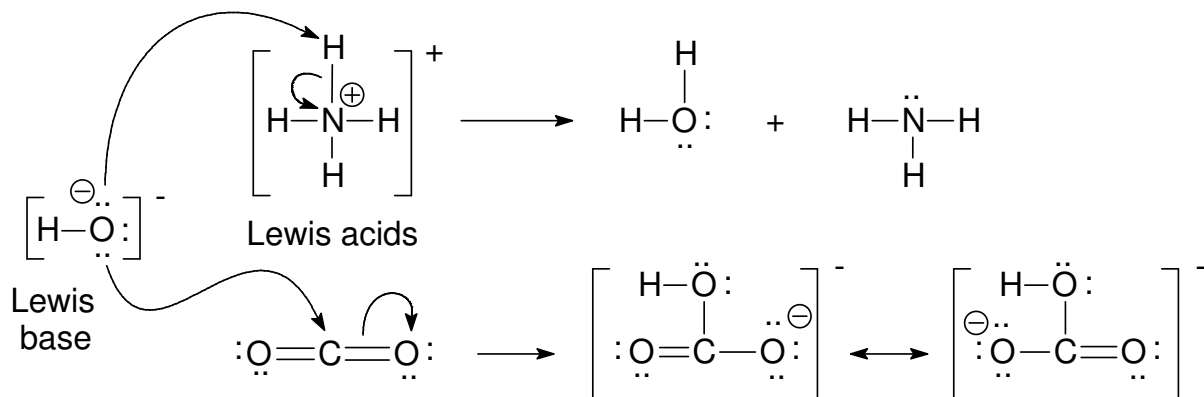
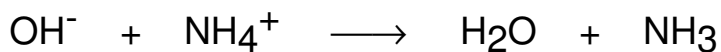
Acid: e^- pair acceptor

Base: e^- pair donor

Lewis acids -- electron deficient molecules or *cations*.

Lewis bases -- electron rich molecules or *anions*.
(have one or more unshared e^- pairs)

(b) Lewis acid-base reactions (i.e., all non-redox reactions!)



4. Auto-ionization of Water and the pH Scale

(a) water undergoes self-ionization to slight extent:



H_3O^+ = hydronium ion

OH^- = hydroxide ion

or, in simplified form:



equilibrium constant:

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

but, $[\text{H}_2\text{O}] \sim \text{constant} \sim 55.6 \text{ mole/L}$ at 25°C

so, instead, use the "ion product" for water = K_W

$$K_W = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14} \quad (\text{at } 25^\circ\text{C})$$

in pure water: $[\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$

(b) the pH scale: **$\text{pH} = -\log [\text{H}^+]$**

in general: $\text{pX} = -\log X$

e.g., $\text{pOH} = -\log [\text{OH}^-]$

and, in reverse: $[\text{H}^+] = 10^{-\text{pH}} \text{ mole/L}$

$[\text{OH}^-] = 10^{-\text{pOH}} \text{ mole/L}$

since $K_W = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$

$$\text{p}K_W = \text{pH} + \text{pOH} = 14.00$$

(c) relative acidity of solutions:

neutral solution

$$[\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$$

$$\text{pH} = \text{pOH} = 7.00$$

acidic solution

$$[\text{H}^+] > 10^{-7} \text{ (i.e., greater than in pure water)}$$

$$\text{so, pH} < 7.00$$

$$[\text{OH}^-] < 10^{-7} \quad \text{and} \quad \text{pOH} > 7.00$$

$$\text{e.g., if } [\text{H}^+] = 1.00 \times 10^{-3} \text{ M} \\ \text{then pH} = 3.00 \text{ and pOH} = 11.00$$

basic solution

$$[\text{H}^+] < 10^{-7} \text{ (i.e., less than in pure water)}$$

$$\text{so, pH} > 7.00$$

$$[\text{OH}^-] > 10^{-7} \quad \text{and} \quad \text{pOH} < 7.00$$

$$\text{e.g., if } [\text{OH}^-] = 1.00 \times 10^{-3} \text{ M} \\ \text{then pOH} = 3.00 \text{ and pH} = 11.00$$

Problem

The water in a soil sample was found to have $[\text{OH}^-]$ equal to 1.47×10^{-9} mole/L. Determine $[\text{H}^+]$, pH, and pOH

$$[\text{H}^+] = K_w / [\text{OH}^-] = (1.00 \times 10^{-14}) / (1.47 \times 10^{-9}) \\ = 6.80 \times 10^{-6}$$

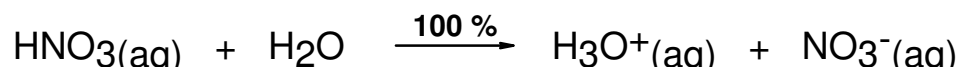
$$\text{pH} = -\log [\text{H}^+] = -\log (6.80 \times 10^{-6}) = 5.17 \quad (\text{acidic !})$$

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 5.17 = 8.83$$

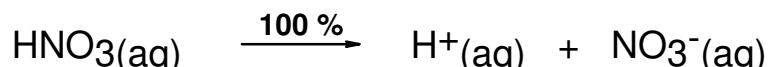
$$\{ \text{or, pOH} = -\log [\text{OH}^-] = -\log (1.47 \times 10^{-9}) = 8.83 \}$$

5. Strong acids and Bases

(a) **Strong Acids (e.g., HCl, HNO₃, etc.) -- 100 % ionized**



or, in simplified form:

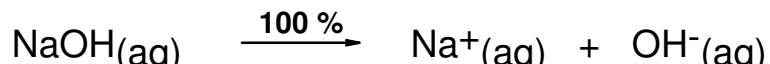


$$[\text{H}^+] = \text{initial M of HNO}_3$$

e.g., in a 0.050 M HNO₃ solution:

$$[\text{H}^+] = 0.050 \quad \text{and} \quad \text{pH} = -\log(0.050) = 1.30$$

(b) **Strong Bases (metal hydroxides) -- 100 % ionized**

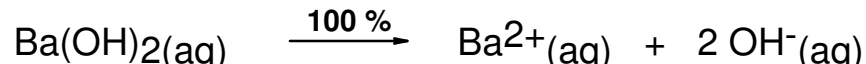


$$[\text{OH}^-] = \text{initial M of NaOH}$$

Problem

What mass of Ba(OH)₂ (171.34 g/mole) is required to prepare 250 mL of a solution with a pH of 12.50?

First: What is the solution process ?



so, $[\text{OH}^-] = 2 \times \text{M of Ba}(\text{OH})_2 \text{ solution}$ (2:1 ratio)

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 12.50 = 1.50$$

$$[\text{OH}^-] = 10^{-1.50} = 0.0316 \text{ M}$$

Next: How much Ba(OH)₂ is needed for that much OH⁻ ?

$$250 \text{ mL} \times (0.0316 \text{ mol OH}^- / 1000 \text{ mL}) = 0.00790 \text{ mol OH}^-$$

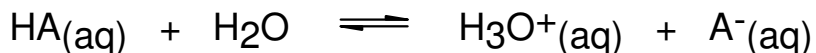
$$0.00790 \text{ mol OH}^- \times [1 \text{ mol Ba}(\text{OH})_2 / 2 \text{ mol OH}^-]$$

$$\times [171.34 \text{ g / mol Ba}(\text{OH})_2] = 0.677 \text{ g}$$

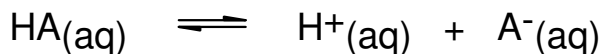
6. Weak Acids and Bases

(a) Weak Acids -- less than 100% ionized (equilibrium !)

in general: HA is a weak acid, A⁻ is its conjugate base



or, in simplified form:



Acid Dissociation Constant: K_a

$$K_a = [\text{H}^+][\text{A}^-] / [\text{HA}]$$

relative acid strength:

weak acid: $K_a < \sim 10^{-3}$

moderate acid: $K_a \sim 1 \text{ to } 10^{-3}$

strong acid: $K_a \gg 1$

Problem

Hypochlorous acid, HOCl, has a pK_a of 7.52. What is the pH of 0.25 M solution of HOCl? What is the percent ionization?

$$pK_a = -\log K_a$$

$$K_a = 10^{-pK_a} = 10^{-7.52} = 3.02 \times 10^{-8}$$

	HOCl(aq)	\rightleftharpoons	H ⁺	+	OCl ⁻ (aq)
Initial	0.25		0		0
Change	- x		+ x		+ x
Equil	0.25 - x		x		x

now, substitute the appropriate equilibrium concentrations:

$$K_a = [H^+] [OCl^-] / [HOCl] = 3.02 \times 10^{-8}$$

$$(x) (x) / (0.25 - x) = x^2 / (0.25 - x) = 3.02 \times 10^{-8}$$

since K_a is very small, assume $x \ll 0.25$

$$x^2 / (0.25) \approx 3.02 \times 10^{-8} \Rightarrow x \approx 8.69 \times 10^{-5}$$

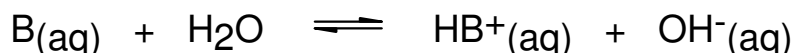
(assumption is OK)

$$pH = -\log (8.69 \times 10^{-5}) = 4.06 \text{ (solution is acidic!)}$$

$$\begin{aligned} \% \text{ ionization} &= (\text{amount HA ionized}) / (\text{initial}) \times 100\% \\ &= 100\% \times (8.69 \times 10^{-5}) / (0.25) = 0.035 \% \end{aligned}$$

(b) Weak Bases

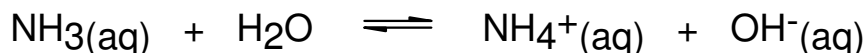
in general: B is a weak base, HB^+ is its conjugate acid



Base Dissociation Constant: K_b

$$K_b = [HB^+] [OH^-] / [B]$$

e.g., NH_3 is a weak base:



$$K_b = [NH_4^+] [OH^-] / [NH_3] = 1.8 \times 10^{-5}$$

$$pK_b = -\log K_b = 4.74$$

Note: Since OH^- rather than H^+ appears here, first find $[OH^-]$ or pOH , and then convert to pH

sample problem: 0.25 M solution of NH_3

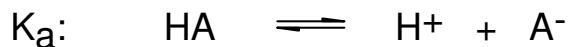
set up conc table as usual, solve for $x = [OH^-]$

$$[OH^-] = 2.12 \times 10^{-3}$$

$$pOH = 2.67 \qquad pH = 11.33 \text{ (basic !)}$$

7. Salts of Weak Acids and Bases

(a) Conjugate Acid - Base Pairs (HA and A⁻)



for any conjugate acid-base pair:

$$K_a K_b = K_w \quad \text{and} \quad \text{p}K_a + \text{p}K_b = 14.00$$

(b) Salt of a Weak Acid (e.g., NaCN) -- *Basic Solution*

Anion acts as a weak base:



$$K_b = K_w / K_a = [\text{OH}^-] [\text{HCN}] / [\text{CN}^-]$$

e.g., K_a for HCN is 6.2×10^{-10}
what is pH of a 0.50 M NaCN solution ?

$$\begin{aligned} K_b &= K_w / K_a = (1 \times 10^{-14}) / (6.2 \times 10^{-10}) \\ &= 1.6 \times 10^{-5} \end{aligned}$$

use a concentration table based on K_b reaction above:

$$x = [\text{OH}^-] = [\text{HCN}]$$

$$[\text{CN}^-] = 0.50 - x \approx 0.50 \quad (\text{since } K_b \text{ is small})$$

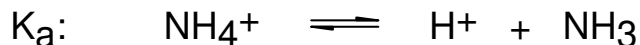
$$K_b = [\text{OH}^-] [\text{HCN}] / [\text{CN}^-] \approx x^2 / 0.50 \approx 1.6 \times 10^{-5}$$

$$x = [\text{OH}^-] \approx 2.8 \times 10^{-3}$$

$$\text{pOH} = 2.55 \quad \text{and} \quad \text{pH} = 11.45 \quad (\text{basic !})$$

(c) Salt of a Weak Base (e.g., NH₄Cl) -- *Acidic Solution*

Cation acts as a weak acid:



$$K_a = K_w / K_b = [\text{H}^+] [\text{NH}_3] / [\text{NH}_4^+]$$

e.g., K_b for NH₃ is 1.8×10^{-5}
what is pH of a 0.50 M NH₄Cl solution?

$$\begin{aligned} K_a &= K_w / K_b = (1 \times 10^{-14}) / (1.8 \times 10^{-5}) \\ &= 5.56 \times 10^{-10} \end{aligned}$$

use a concentration table based on K_a reaction above:

$$x = [\text{H}^+] = [\text{NH}_3]$$

$$[\text{NH}_4^+] = 0.50 - x \approx 0.50 \quad (\text{since } K_a \text{ is small})$$

$$K_a = [\text{H}^+] [\text{NH}_3] / [\text{NH}_4^+] \approx x^2 / 0.50 \approx 5.56 \times 10^{-10}$$

$$x = [\text{H}^+] \approx 1.67 \times 10^{-5}$$

$$\text{pH} = 4.78 \quad (\text{acidic !})$$

Problem

The $\text{p}K_a$ value for HCN is 9.21. What molar concentration of NaCN is required to make a solution with a pH of 11.75?
[answer: 2.0 M NaCN]

8. Polyprotic Acids

e.g., diprotic acids, H_2A , undergo stepwise dissociation:



usually, $K_{a1} \gg K_{a2}$ so that:

the 1st equilibrium produces most of the H^+

but, the 2nd equilibrium determines $[A^{2-}]$

Problem

Ascorbic acid (vitamin C), $H_2C_6H_2O_6$, is an example of a diprotic acid with $K_{a1} = 7.9 \times 10^{-5}$ and $K_{a2} = 1.6 \times 10^{-12}$. For a 0.10 M solution of ascorbic acid, determine the pH and the concentrations of the mono anion, $HC_6H_2O_6^-$, and the dianion, $C_6H_2O_6^{2-}$.

based on the first equilibrium:

$$x = [H^+] \approx [HA^-] \quad \text{and} \quad [H_2A] = 0.10 - x \approx 0.10$$

$$K_{a1} = 7.9 \times 10^{-5} \approx x^2 / (0.10)$$

$$\therefore x \approx 2.8 \times 10^{-3} \quad \text{so,} \quad \text{pH} = 2.55$$

must use the 2nd equilibrium to find $[A^{2-}]$:

$$K_{a2} = [A^{2-}][H^+] / [HA^-] \quad \text{but, from above } [H^+] \approx [HA^-]$$

$$\therefore K_{a2} \approx [A^{2-}] \quad (\text{a general result for } H_2A !)$$

$$[A^{2-}] \approx 1.6 \times 10^{-12}$$