

Acid-Base Reactions

Acid-Base Theories

Arrhenius

acid - delivers $H^+(aq)$ ions to solution upon dissolution in water

base - delivers $OH^-(aq)$ ions to solution upon dissolution in water

problem -

Modified Arrhenius

acid - increases concentration of hydrogen ion in water

base - increases concentration of hydroxide ion in water

still a problem -

Brønsted-Lowry - focus on hydrogen ion

acid - substance that can **donate** a hydrogen ion

base - substance that can **accept** a hydrogen ion

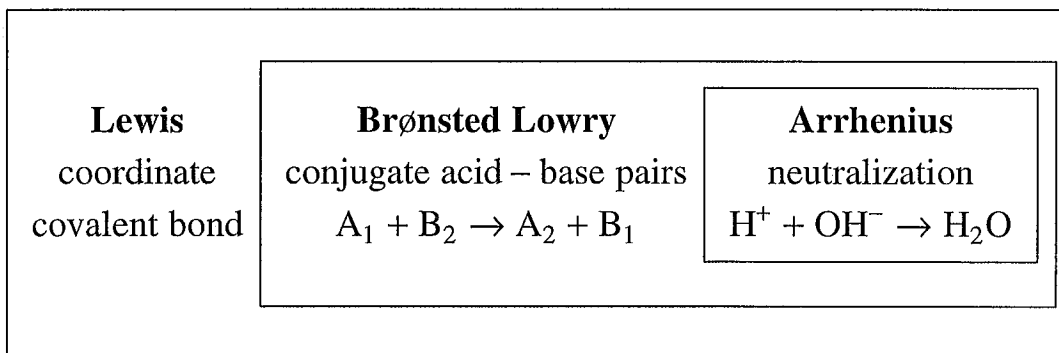
little problem -

Lewis (section 8-8) - focus on electron pair

acid - species that accepts a lone pair of electrons

base - species that donates a lone pair of electrons

advantage -



Brønsted-Lowry Acid-Base Theory

acids - proton donors => forms a species [acid - H⁺] called **conjugate base**

bases - proton acceptors => forms a species [base + H⁺] called **conjugate acid**

EX 1. For each of the following acids write the formula of its conjugate base and for each of the bases write the formula of its conjugate acid.

ACIDS - conjugate base

HCl

H₂O

NH₄⁺

CH₃COOH

SH⁻

BASES - conjugate acid

NH₃

NaOH

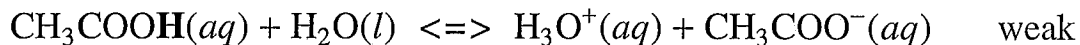
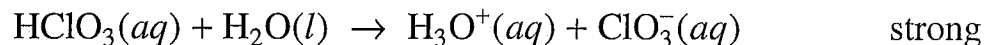
H₂S

O²⁻

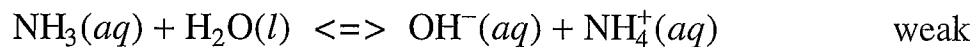
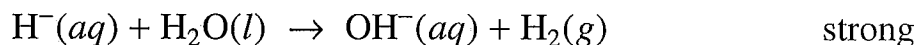
CN⁻

Conjugate Acid-Base Pairs: $A_1 + B_2 \rightarrow A_2 + B_1$

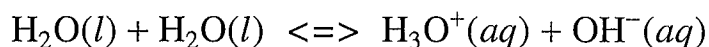
acid - proton donor



base - proton acceptor



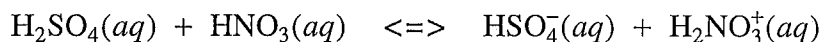
autoionization of water



amphoteric nature of water

EX 2. Show how the reaction of aqueous potassium hydroxide with aqueous ammonium sulfate can be viewed as a Brønsted-Lowry acid-base reaction.

EX 3. From the Brønsted-Lowry point of view which is the stronger acid in the following reaction



Water and the pH Scale

autoionization of water (at 25°C):



Temperature Dependence of K_w	
Temp (°C)	K_w
0	0.114×10^{-14}
10	0.292×10^{-14}
20	0.681×10^{-14}
25	1.01×10^{-14}
30	1.47×10^{-14}
40	2.92×10^{-14}
50	5.47×10^{-14}
60	9.61×10^{-14}

EX 4. $K_w = 2.4 \times 10^{-14}$ at body temperature (98.6°F = 37.0°C).

a) What is the hydrogen ion concentration?

b) What is the pH?

pH scale:

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$$

$$\text{pOH} = -\log_{10}[\text{OH}^-]$$

$$\text{p}K_w = -\log_{10}K_w$$

condition	concentration	only at 25°C
acidic	$[\text{H}_3\text{O}^+] > [\text{OH}^-]$	pH < 7
neutral	$[\text{H}_3\text{O}^+] = [\text{OH}^-]$	pH = 7
basic	$[\text{H}_3\text{O}^+] < [\text{OH}^-]$	pH > 7

EX 5. Answer each of the following

a) $[\text{H}_3\text{O}^+] = 2.5 \times 10^{-14}$, pH?

b) pH = 9.3, $[\text{H}_3\text{O}^+]?$

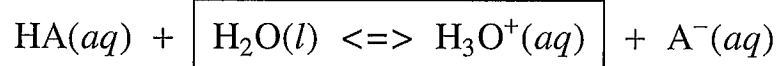
c) 0.40 moles of $\text{Ba}(\text{OH})_2$ is dissolved in a liter of water, pOH?

d) pH = 9.3, $[\text{OH}^-]?$

Acid and Base Strength

strong/weak electrolytes

acid strength - determined by extent of reaction of acid with water to form $\text{H}_3\text{O}^+(\text{aq})$ - then for any acid HA



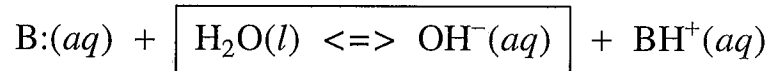
equilibrium constant

leveling effect of water

Various Ways to Describe the Strength of an Acid, HA

property	strong acid	weak acid
value of K_a	K_a large	K_a small
position of the ionization (dissociation) equilibrium	far to right	far to left
equilibrium concentration of H^+ compared with initial concentration of HA	$[\text{H}^+] \sim [\text{HA}]_0$	$[\text{H}^+] \ll [\text{HA}]_0$
strength of conjugate base compared with that of water	A^- much weaker base than water	A^- much stronger base than water

base strength - (aside from Group I and Group II hydroxides) determined by extent of reaction of base with water to form $\text{OH}^-(aq)$ - then for any base B:



equilibrium constant

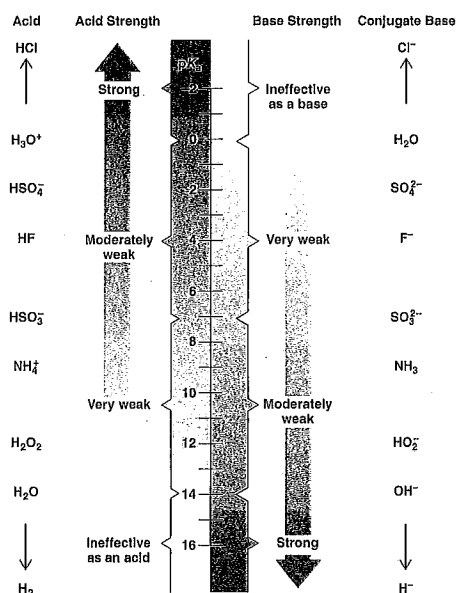
Various Ways to Describe the Strength of a Base, B:

property	strong base	weak base
value of K_b	completely, either	K_b small
position of the ionization (dissociation) equilibrium	1) dissociates to give $[\text{OH}^-]$ ions to the solution or 2) reacts with water	far to the left
equilibrium concentration of OH^- compared with initial concentration of B:	in either case:	$[\text{OH}^-] \ll [\text{B}]_0$
strength of conjugate acid compared with that of water	$[\text{OH}^-] = [\text{BOH}]_0$	BH^+ much stronger acid than water

conjugate acid-base pairs

the stronger the acid
the weaker is its conjugate base
the stronger the base
the weaker is its conjugate acid

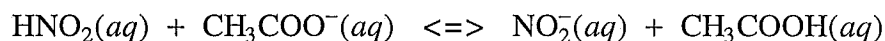
FIG I. Relative Strengths of HA and A⁻



EX 6. K_a for hydrosulfuric acid is 9.1×10^{-10} at 25°C .

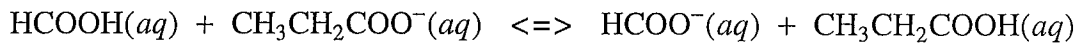
- What is its conjugate base?
- What is the basicity constant (K_b) for its conjugate base?
- To which reaction does K_b correspond?

EX 7. For the reaction



- From the Brønsted-Lowry point of view, identify each acid and its conjugate base and each base and its conjugate acid.
- If $K_a(\text{HNO}_2) = 4.6 \times 10^{-4}$ and $K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$ what is K for the reaction?
- Identify the stronger acid and stronger base in part a)

EX 8. If $K_a(\text{HCOOH}) = 1.8 \times 10^{-4}$ and $K_a(\text{CH}_3\text{CH}_2\text{COOH}) = 1.3 \times 10^{-5}$ will the following reaction go as written?



indicators - generally a weak organic acid whose conjugate base is a different color

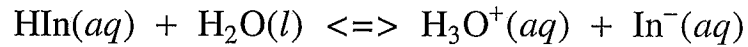
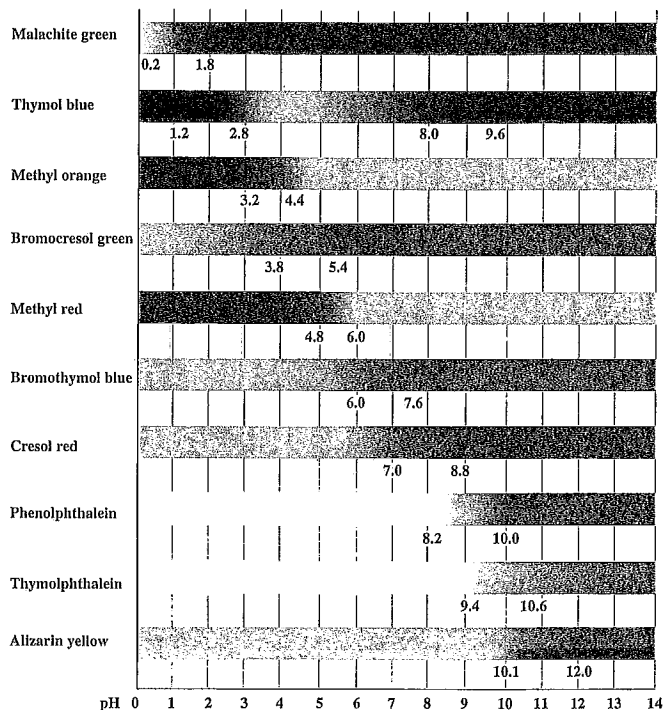


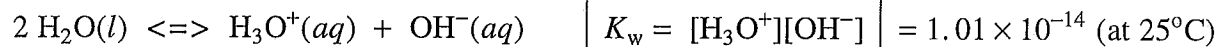
FIG II. Typical Indicators



Equilibria Involving Weak Acids and Bases

determined by properties of the solvent, generally water

autoionization of water - water ionization constant, K_w

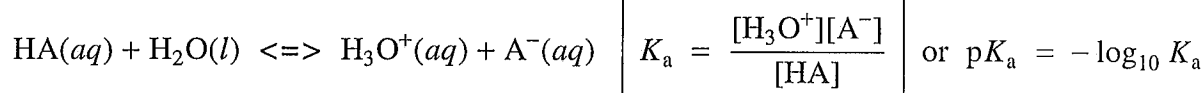


pH scale

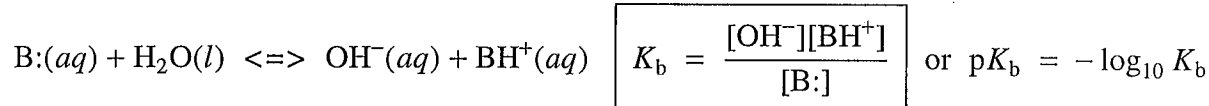
$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] \Rightarrow [\text{H}_3\text{O}^+] = 10^{-\text{pH}} \quad \text{pOH} = -\log_{10}[\text{OH}^-] \Rightarrow [\text{OH}^-] = 10^{-\text{pOH}}$$

$$\text{p}K_w = -\log_{10} K_w \Rightarrow \text{p}K_w = \text{pH} + \text{pOH} = 14 \text{ (at } 25^\circ\text{C)}$$

acid (HA) ionization



base (B:) ionization



conjugate acid/base pair

$$K_a \times K_b = K_w \quad \text{or} \quad \text{p}K_w = \text{p}K_a + \text{p}K_b$$

Weak Acids

EX 9. What is the pH of 1.0 M HF? ($K_a = 6.6 \times 10^{-4}$)

EX 10. $K_a = 1.76 \times 10^{-5}$ for acetic acid, CH_3COOH . Determine $[\text{H}_3\text{O}^+]$, pH, and % ionization for 1.00 M and 0.00100 M acetic acid.

Dilution of Weak Acid

effect on equilibrium

effect on $[\text{H}_3\text{O}^+]$

effect on pH

effect on ionization

Approximations in Equilibrium Calculations (pp. 362-365)

5% rule: $[\text{HA}]_0 - x \approx [\text{HA}]_0$ if $x \leq 5\% [\text{HA}]_0$

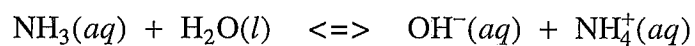
Weak Bases

FIG III. Some Conjugate Acid-Base Pairs

Acid	K_a	Base	K_b
HNO ₃	(Strong acid)	NO ₃ ⁻	(Negligible basicity)
HF	6.8×10^{-4}	F ⁻	1.5×10^{-11}
HC ₂ H ₃ O ₂	1.8×10^{-5}	C ₂ H ₃ O ₂ ⁻	5.6×10^{-10}
H ₂ CO ₃	4.3×10^{-7}	HCO ₃ ⁻	2.3×10^{-8}
NH ₄ ⁺	5.6×10^{-10}	NH ₃	1.8×10^{-5}
HCO ₃ ⁻	5.6×10^{-11}	CO ₃ ²⁻	1.8×10^{-4}
OH ⁻	(Negligible acidity)	O ²⁻	(Strong base)

EX 11. $K_b = 1.8 \times 10^{-5}$ for NH₃.

a) What is the pH of a 0.25 M solution of ammonia in water?



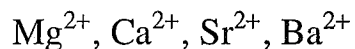
b) What is the pH of a 0.025 M solution of ammonia in water?

Hydrolysis: Acid/Base Properties of Salt Solutions

Salt

cation*	anion**	example	pH of solution
from strong base	from strong acid (conjugate base of)	MgI ₂ , KHSO ₄	neutral
from strong base	from weak acid (conjugate base of)	NaF, Ag(CN) ₂	basic
from weak base (conjugate acid of)	from strong acid (conjugate base of)	NH ₄ Br	acidic
from weak base (conjugate acid of)	from weak acid (conjugate base of)	NH ₄ NO ₂	acidic if $K_a > K_b$ basic if $K_b > K_a$ neutral if $K_a = K_b$
highly charged metal ion (hydrated in water)	from strong acid (conjugate base of)	Al(NO ₃) ₃ , FeCl ₃	acidic

*cation from strong base (group I and II hydroxides, excluding Be) and silver:



**anion from strong acids: conjugate base of seven common strong acids:

