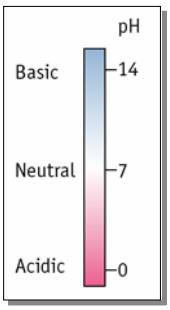
How can we define the strengths of acids and bases?



Higher the pH → the stronger the base

Strong BASE $[OH^-] = [BASE]$

Weak BASE $[OH^-] << [BASE]$

Weak ACID $[H_3O^+] << [ACID]$

Strong ACID $[H_3O^+] = [ACID]$

Lower the pH → the stronger the acid

17.4

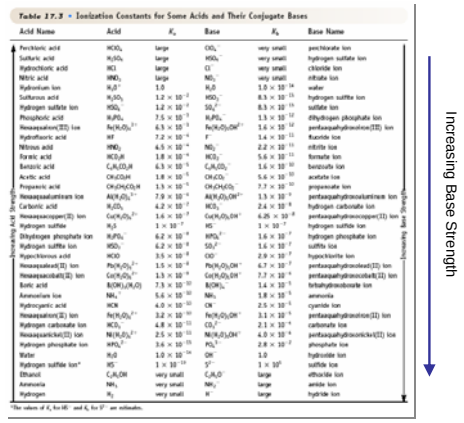


Table 17.3 • Ionization Constants for Some Acids and Their Conjugate Bases

Acid Name	Acid	K_a	Base	K_b	Base Name
Perchloric acid	$HClO_4$	large	ClO_4^-	very small	perchlorate ion
Sulfuric acid	H_2SO_4	large	HSO_4^-	very small	hydrogen sulfate ion
Hydrochloric acid	HCl	large	Cl^-	very small	chloride ion
Nitric acid	HNO_3	large	NO_3^-	very small	nitrate ion
Hydronium ion	H_3O^+	1.0	H_2O	1.0×10^{-14}	water
Sulfurous acid	H_2SO_3	1.2×10^{-2}	HSO_3^-	8.3×10^{-13}	hydrogen sulfite ion
Hydrogen sulfate ion	HSO_4^-	1.2×10^{-2}	SO_4^{2-}	8.3×10^{-13}	sulfate ion
Phosphoric acid	H_3PO_4	7.5×10^{-3}	$H_2PO_4^-$	1.3×10^{-12}	dihydrogen phosphate ion
Hexaaquairon(III) ion	$Fe(H_2O)_6^{3+}$	6.3×10^{-3}	$Fe(H_2O)_5OH^{2+}$	1.6×10^{-12}	pentaaquahydroxoiron(III) ion
Hydrofluoric acid	HF	7.2×10^{-4}	F^-	1.4×10^{-11}	fluoride ion
Nitrous acid	HNO_2	4.5×10^{-4}	NO_2^-	2.2×10^{-11}	nitrite ion
Formic acid	HCO_2H	1.8×10^{-4}	HCO_2^-	5.6×10^{-11}	formate ion
Benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	$C_6H_5CO_2^-$	1.6×10^{-10}	benzoate ion
Acetic acid	CH_3CO_2H	1.8×10^{-5}	$CH_3CO_2^-$	5.6×10^{-10}	acetate ion
Propanoic acid	$CH_3CH_2CO_2H$	1.3×10^{-5}	$CH_3CH_2CO_2^-$	7.7×10^{-10}	propanoate ion
Hexaaquaaluminum ion	$Al(H_2O)_6^{3+}$	7.9×10^{-6}	$Al(H_2O)_5OH^{2+}$	1.3×10^{-9}	pentaaquahydroxoaluminum ion
Carbonic acid	H_2CO_3	4.2×10^{-7}	HCO_3^-	2.4×10^{-8}	hydrogen carbonate ion
Hexaaquacopper(II) ion	$Cu(H_2O)_6^{2+}$	1.6×10^{-7}	$Cu(H_2O)_5OH^+$	6.25×10^{-8}	pentaaquahydroxocopper(II) ion
Hydrogen sulfide	H_2S	1×10^{-7}	HS^-	1×10^{-7}	hydrogen sulfide ion
Dihydrogen phosphate ion	$H_2PO_4^-$	6.2×10^{-8}	HPO_4^{2-}	1.6×10^{-7}	hydrogen phosphate ion
Hydrogen sulfite ion	HSO_3^-	6.2×10^{-8}	SO_3^{2-}	1.6×10^{-7}	sulfite ion
Hypochlorous acid	$HClO$	3.5×10^{-8}	ClO^-	2.9×10^{-7}	hypochlorite ion
Hexaaquairon(II) ion	$Fe(H_2O)_6^{2+}$	1.5×10^{-9}	$Fe(H_2O)_5OH^+$	6.7×10^{-6}	pentaaquahydroxoiron(II) ion
Hexaaquacobalt(II) ion	$Co(H_2O)_6^{2+}$	1.3×10^{-9}	$Co(H_2O)_5OH^+$	7.7×10^{-6}	pentaaquahydroxocobalt(II) ion
Boric acid	$B(OH)_3(H_2O)$	7.3×10^{-10}	$B(OH)_4^-$	1.4×10^{-5}	tetrahydroxoborate ion
Ammonium ion	NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}	ammonia
Hydrocyanic acid	HCN	4.0×10^{-10}	CN^-	2.5×10^{-5}	cyanide ion
Hexaaquairon(II) ion	$Fe(H_2O)_6^{2+}$	3.2×10^{-10}	$Fe(H_2O)_5OH^+$	3.1×10^{-5}	pentaaquahydroxoiron(II) ion
Hydrogen carbonate ion	HCO_3^-	4.8×10^{-11}	CO_3^{2-}	2.1×10^{-4}	carbonate ion
Hexaaquanickel(II) ion	$Ni(H_2O)_6^{2+}$	2.5×10^{-11}	$Ni(H_2O)_5OH^+$	4.0×10^{-4}	pentaaquahydroxonickel(II) ion
Hydrogen phosphate ion	HPO_4^{2-}	3.6×10^{-13}	PO_4^{3-}	2.8×10^{-2}	phosphate ion
Water	H_2O	1.0×10^{-14}	OH^-	1.0	hydroxide ion
Hydrogen sulfide ion*	HS^-	1×10^{-19}	S^{2-}	1×10^{5}	sulfide ion
Ethanol	C_2H_5OH	very small	$C_2H_5O^-$	large	ethoxide ion
Ammonia	NH_3	very small	NH_2^-	large	amide ion
Hydrogen	H_2	very small	H^-	large	hydride ion

Increasing Acid Strength

Increasing Base Strength

*The values of K_a for HS^- and K_b for S^{2-} are estimates.

Remember

- $K_w = [H_3O^+]\,[OH^-]$

pX = -logX

- $pK_w = pH + pOH = 14$ (at 25 °C)
- $K_w = K_a\,K_b$ (for a conjugate pair only!)
- $pK_w = pK_a + pK_b = 14$ (at 25 °C)

Aqueous solutions of salts: the pH after dissolution of the salt

Salt in water → Cation + Anion

Cation from:	Anion from:	pH	
Strong base	Strong acid	=7	NaCl
Strong base	Weak acid	>7	NaF
Weak base	Strong acid	<7	NH_4Cl
Weak base	Weak acid depends on the K_a and K_b		NH_4HCO_3

if $K_a > K_b$ → <7

if $K_a < K_b$ → >7

The strongest rule

Salt from Polyprotic Acids: Acid or Basic Solutions?

Na_2HPO_4 (aq) ⇆ $2Na^+$ (aq) + HPO_4^{2-} (aq)

$HPO_4^{2-} + H_2O$ (l) ⇆ $PO_4^{3-} + H_3O^+$ $K_a = 3.6\ 10^{-13}$

$HPO_4^{2-} + H_2O$ (l) ⇆ $H_2PO_4^{3-} + HO^-$ $K_b = 1.6\ 10^{-7}$

$K_b > K_a$ → pH increase (Basic solution)

Today

Talk about:

1. Types of Acid-Base Reactions
2. The carbonic acid equilibrium.
3. Alternative definitions of acids and bases: Arrhenius, Brønsted-Lowry, Lewis

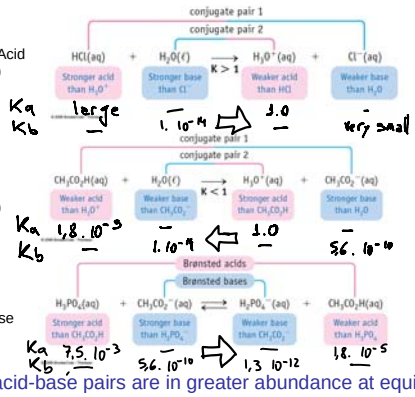
Predicting Reaction Extents

17.5

HCl: Strong Acid (Weak Base)

Acetic Acid: Weak Acid (Weak Base)

Mixture of an Acid and a Base



The weak acid-base pairs are in greater abundance at equilibrium

Types of Acid-Base Reactions

		pH
Strong base NaOH	Strong acid HCl	=7
Strong base NaOH	Weak acid CH_3CO_2H	>7
Weak base NH_3	Strong acid HCl	<7
Weak base NH_3	Weak acid CH_3CO_2H	depends if $K_a > K_b$ <7 $K_a < K_b$ >7 $K_a = K_b$ 7

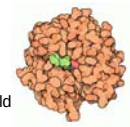
17.6

What Did We See?

(1) CO_2 (g) ⇆ CO_2 (aq)

(2) CO_2 (aq) ⇆ H_2CO_3 (aq)

(In the body, this reaction is catalyzed by an enzyme, Carbonic Anhydrase, which can increase the rate 10^6-fold



(3) H_2CO_3 (aq) + H_2O (l) ⇆ HCO_3^- + H_3O^+

(4?) HCO_3^- + H_2O (l) ⇆ CO_3^{2-} + H_3O^+

The dissolved CO_2 lowers pH

The pH of (unbuffered) water drops as a result of the absorption of CO_2 from air and the dissociation of H_2CO_3

H_2CO_3 ⇆ HCO_3^- + H_3O^+ $K_{A1} = 4.2 \times 10^{-7}$ *M*

HCO_3^- ⇆ CO_3^{2-} + H_3O^+ $K_{A2} = 4.8 \times 10^{-11}$ *M*

Q: Suppose that the pH = 5.

Calculate: $[H_2CO_3]$, $[HCO_3^-]$ and $[CO_3^{2-}]$

First: Calculate the $[H_2CO_3]$

NIE:	H_2CO_3 + H_2O	⇆	HCO_3^- +	H_3O^+
Eq.	*X*		10^{-5}	10^{-5}

$$K_{A1} = \frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]} = \frac{(10^{-5})^2}{X} \rightarrow X = \frac{(10^{-5})^2}{K_{A1}} = \frac{10^{-10}}{4.2 \cdot 10^{-7}} = 2.38 \cdot 10^{-4} M$$

$[H_2CO_3] = 2.38 \times 10^{-4}$ M at pH = 5

Note that the concentration of HCO_3^- is equal to the H_3O^+ concentration, and that both are well above the concentration of H_3O^+ generated by the auto-ionization of water.

Second: Calculate the $[CO_3^{2-}]$

HCO_3^- is an even weaker acid than H_2CO_3

NIE:	HCO_3^- + H_2O	⇆	CO_3^{2-} +	H_3O^+
Eq.	10^{-5} M - y		y	10^{-5} M + y

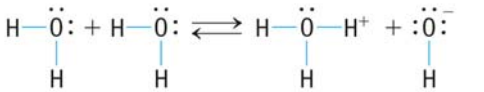
$K_{a2} = [CO_3^{2-}]\,[H3O^+]/[HCO_3^-] = 5.6\ 10^{-11}$

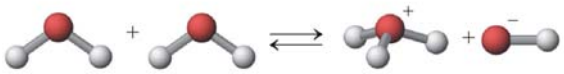
$y << 10^{-5}$ → $[CO_3^{2-}] = 5.6\ 10^{-11}$

Conclusion: Further dissociation of bicarbonate to carbonate contributes little to the pH drop.

Auto Ionization of Water

$$2\ H_2O(\ell) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$





NH_4^+ and NH_3 - a conjugate acid-base pair

$$NH_3(aq) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Base

Weak base

$K_B = 1.8 \times 10^{-5}$

$$NH_4^+(aq) + H_2O(\ell) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

Acid

Weak acid

$K_A = 5.6 \times 10^{-10}$

For any conjugate acid/base pair

(such as NH_3/NH_4^+):

$K_W = K_A K_B$

Therefore: $K_A = K_W/K_B$ and $K_B = K_W/K_A$

$\log K_W = \log K_A + \log K_B \rightarrow pK_W = pK_A + pK_B$