Topic 6C - Weak Acids and Bases

Weak Acids and Bases

Acids:

$$HA\ (aq) + H_2O\ (l) \rightleftarrows H_3O^+\ (aq) + A^-\ (aq)$$

$$K_a = \frac{a_{H_3O^+}\, a_{A^-}}{a_{HA}} \approx \frac{[H_3O^+][A^-]}{[HA]}$$

$$pK_a = -\log K_a$$

Strong:	$[HA] << [H_3O^+]$	$K_a >> 1$
Weak:	$[HA] >> [H_3O^+]$	$K_a << 1$

Bases:

$$B\ (aq) + H_2O\ (l) \rightleftarrows HB^+\ (aq) + OH^-\ (aq)$$

$$K_b = \frac{a_{HB^+}\, a_{OH^-}}{a_B} \approx \frac{[HB^+][OH^-]}{[B]}$$

$$pK_b = -\log K_b$$

Strong:	$[B] << [HB^+]$	$K_b >> 1$
Weak:	$[B] >> [HB^+]$	$K_b << 1$

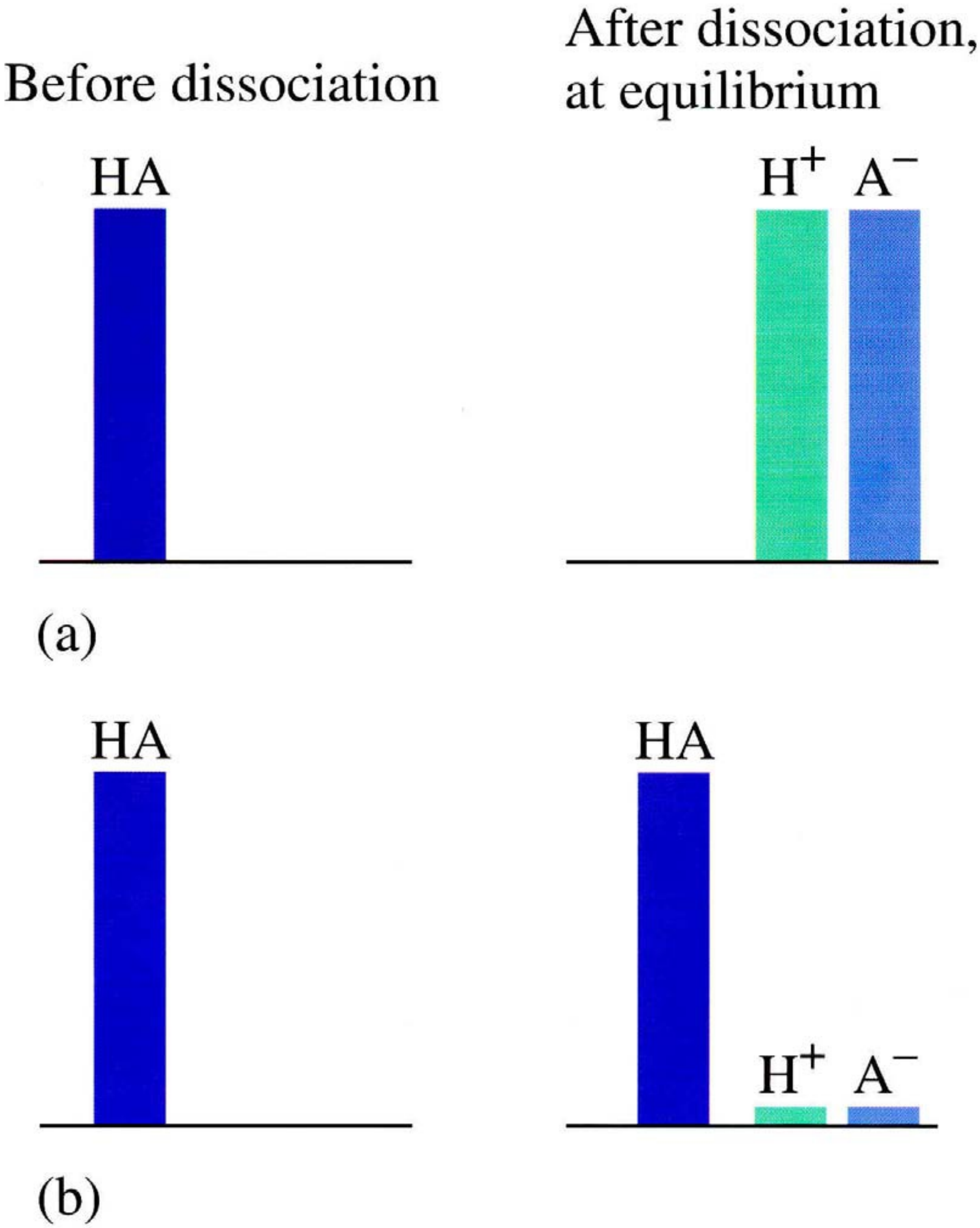


Figure 14.1
Graphical representations of strong and weak acid equilibria

Table 12.1: Acid Ionization Constants

TABLE 12.1

Acid ionization constants K_a for selected monoprotic acids in aqueous solution

Acid name	Formula	K_a	pK_a
Hydrofluoric	HF	7.0×10^{-4}	3.15
Hydrochloric	HCl	$\sim 1. \times 10^{7}$	−7.
Hydrobromic	HBr	$\sim 1. \times 10^{9}$	−9.
Hydroiodic	HI	$\sim 1. \times 10^{11}$	−11.
Hypochlorous	$HClO$	3.0×10^{-8}	7.52
Chlorous	$HClO_2$	1.1×10^{-2}	1.96
Chloric	$HClO_3$	$\sim 1. \times 10^{3}$	−3.
Perchloric	$HClO_4$	$\sim 1. \times 10^{7}$	−7.
Hypobromous	$HBrO$	2.1×10^{-9}	8.68
Bromic	$HBrO_3$	$>1.$	$<0.$
Hypoiodous	HIO	$\sim 1. \times 10^{-11}$	11.
Iodic	HIO_3	1.6×10^{-1}	0.80
Periodic	H_5IO_6	5.1×10^{-4}	3.29
Nitrous	HNO_2	4.6×10^{-4}	3.34
Nitric	HNO_3	$2. \times 10^{1}$	−1.3
Hypophosphorous	H_3PO_2	$1. \times 10^{-2}$	2.0
Hydrocyanic	HCN	4.9×10^{-10}	9.31
Formic	$HCOOH$	1.77×10^{-4}	3.75
Acetic	CH_3COOH	1.76×10^{-5}	4.75
Propionic	CH_3CH_2COOH	1.34×10^{-5}	4.87
Butyric	$CH_3(CH_2)_2COOH$	1.54×10^{-5}	4.81
Chloroacetic	$CH_2ClCOOH$	1.40×10^{-3}	2.85
Dichloroacetic	$CHCl_2COOH$	3.32×10^{-2}	1.48
Trichloroacetic	CCl_3COOH	$2. \times 10^{-1}$	0.70
Benzoic	C_6H_5COOH	6.46×10^{-5}	4.19
Glycine	H_2NCH_2COOH	1.67×10^{-10}	9.78

Table 6-2 Ionization Constants of Acids at 25°C

Acid	HA	A^-	K_a	pK_a
Hydriodic	HI	I^-	$\sim 10^{11}$	~ -11
Hydrobromic	HBr	Br^-	$\sim 10^{9}$	~ -9
Perchloric	$HClO_4$	ClO_4^-	$\sim 10^{7}$	~ -7
Hydrochloric	HCl	Cl^-	$\sim 10^{7}$	~ -7
Chloric	$HClO_3$	ClO_3^-	$\sim 10^{3}$	~ -3
Sulfuric (1)	H_2SO_4	HSO_4^-	$\sim 10^{2}$	~ -2
Nitric	HNO_3	NO_3^-	~ 20	~ -1.3
Hydronium ion	H_3O^+	H_2O	1	0.0
Iodic	HIO_3	IO_3^-	1.6×10^{-1}	0.80
Oxalic (1)	$H_2C_2O_4$	$HC_2O_4^-$	5.9×10^{-2}	1.23
Sulfurous (1)	H_2SO_3	HSO_3^-	1.54×10^{-2}	1.81
Sulfuric (2)	HSO_4^-	SO_4^{2-}	1.2×10^{-2}	1.92
Chlorous	$HClO_2$	ClO_2^-	1.1×10^{-2}	1.96
Phosphoric (1)	H_3PO_4	$H_2PO_4^-$	7.52×10^{-3}	2.12
Arsenic (1)	H_3AsO_4	$H_2AsO_4^-$	5.0×10^{-3}	2.30
Chloroacetic	$CH_2ClCOOH$	CH_2ClCOO^-	1.4×10^{-3}	2.85
Hydrofluoric	HF	F^-	6.6×10^{-4}	3.18
Nitrous	HNO_2	NO_2^-	4.6×10^{-4}	3.34
Formic	$HCOOH$	$HCOO^-$	1.77×10^{-4}	3.75
Benzoic	C_6H_5COOH	$C_6H_5COO^-$	6.46×10^{-5}	4.19
Oxalic (2)	$HC_2O_4^-$	$C_2O_4^{2-}$	6.4×10^{-5}	4.19
Hydrazoic	HN_3	N_3^-	1.9×10^{-5}	4.72
Acetic	CH_3COOH	CH_3COO^-	1.76×10^{-5}	4.75
Propionic	CH_3CH_2COOH	$CH_3CH_2COO^-$	1.34×10^{-5}	4.87
Pyridinium ion	$HC_5H_5N^+$	C_5H_5N	5.6×10^{-6}	5.25
Carbonic (1)	H_2CO_3	HCO_3^-	4.3×10^{-7}	6.37
Sulfurous (2)	HSO_3^-	SO_3^{2-}	1.02×10^{-7}	6.91
Arsenic (2)	$H_2AsO_4^-$	$HAsO_4^{2-}$	9.3×10^{-8}	7.03
Hydrosulfuric	H_2S	HS^-	9.1×10^{-8}	7.04
Phosphoric (2)	$H_2PO_4^-$	HPO_4^{2-}	6.23×10^{-8}	7.21
Hypochlorous	$HClO$	ClO^-	3.0×10^{-8}	7.53
Hydrocyanic	HCN	CN^-	6.17×10^{-10}	9.21
Ammonium ion	NH_4^+	NH_3	5.6×10^{-10}	9.25
Carbonic (2)	HCO_3^-	CO_3^{2-}	4.8×10^{-11}	10.32
Arsenic (3)	$HAsO_4^{2-}$	AsO_4^{3-}	3.0×10^{-12}	11.53
Hydrogen peroxide	H_2O_2	HO_2^-	2.4×10^{-12}	11.62
Phosphoric (3)	HPO_4^{2-}	PO_4^{3-}	2.2×10^{-13}	12.67
Water	H_2O	OH^-	1.0×10^{-14}	14.00

TABLE 12.2

Weak base ionization constants K_b for selected monobasic nitrogen bases in aqueous solution

Base name	Formula	K_b	pK_b
Ammonia	NH_3	1.79×10^{-5}	4.75
Methylamine	CH_3NH_2	4.4×10^{-4}	3.36
Ethylamine	$CH_3CH_2NH_2$	4.7×10^{-4}	3.33
Propylamine	$CH_3(CH_2)_2NH_2$	3.8×10^{-4}	3.42
Butylamine	$CH_3(CH_2)_3NH_2$	4.1×10^{-4}	3.39
Dimethylamine	$(CH_3)_2NH$	5.1×10^{-4}	3.29
Trimethylamine	$(CH_3)_3N$	0.6×10^{-4}	4.22
Glycine	$HOOCCH_2NH_2$	2.2×10^{-12}	11.66
Aniline	$C_6H_5NH_2$	4.2×10^{-10}	9.38
Pyridine	C_5H_5N	2.3×10^{-9}	8.64

Conjugate Acids and Bases

$$HA\,(aq) + H_2O\,(l) \rightleftarrows H_3O^+\,(aq) + A^-\,(aq)$$

acid — base — conjugate acid — conjugate base

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$A^-\,(aq) + H_2O\,(l) \rightleftarrows HA\,(aq) + OH^-\,(aq)$$

base — acid — conjugate acid — conjugate base

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

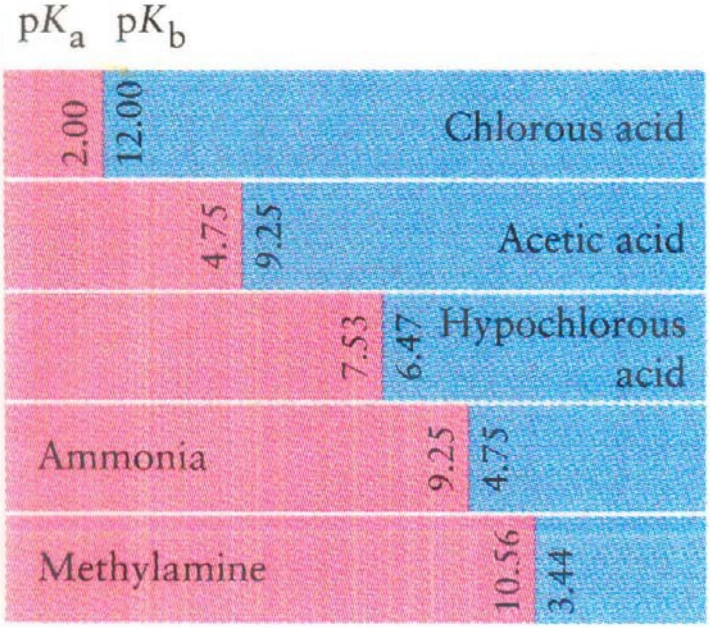
Strong acid → Weak conjugate base (weak H^+ acceptor)

Weak acid → Strong conjugate base (strong H^+ acceptor)

$$K_a \times K_b = \frac{[H_3O^+][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]} = [H_3O^+][OH^-] = K_w$$

Thus,

$$pK_a + pK_b = pK_w = 14 \text{ (at 25°C)}$$



Acid → Conjugate Base

$HClO_2$ → ClO_2^-

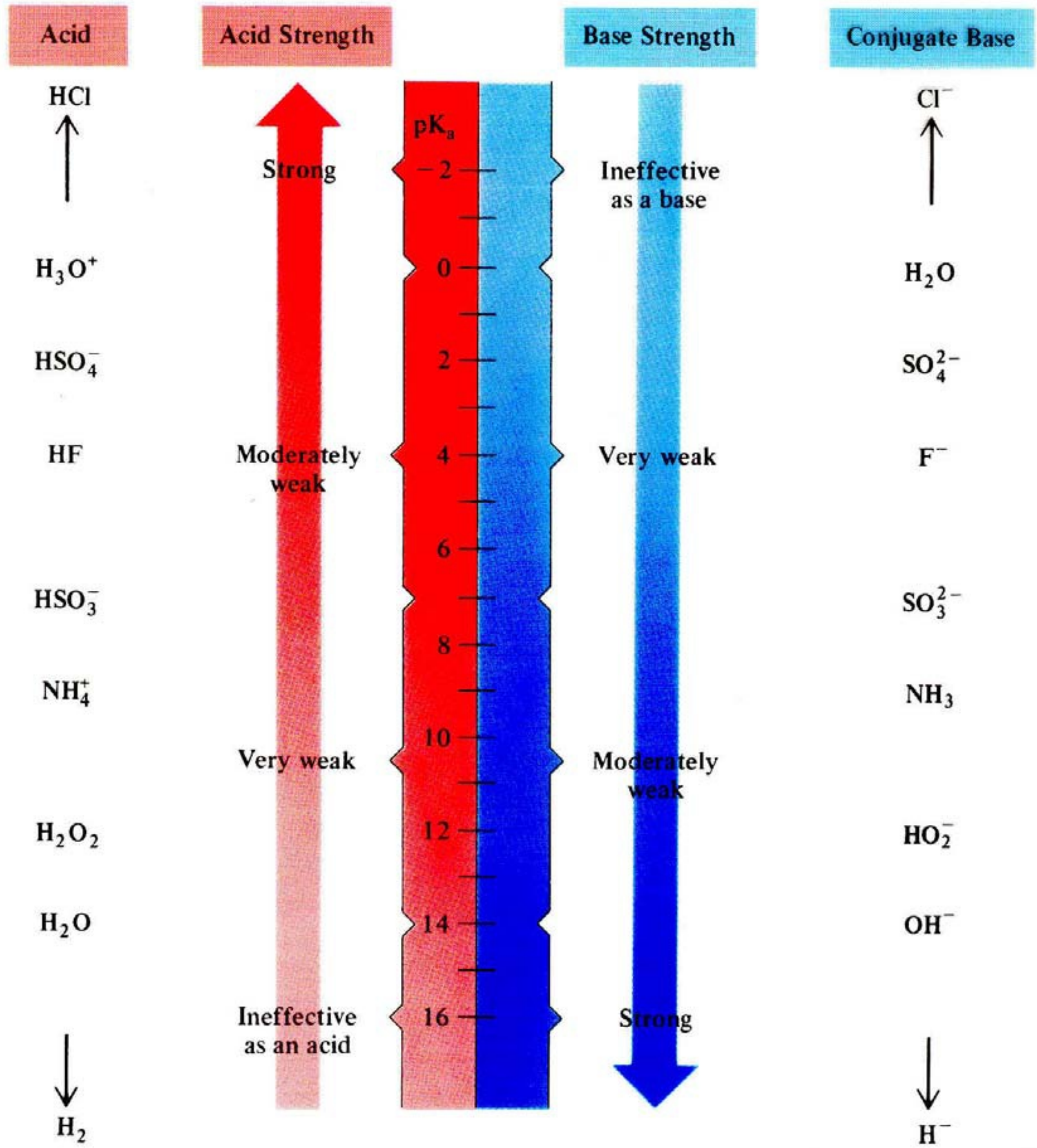
CH_3COOH → CH_3COO^-

$HClO$ → ClO^-

NH_4^+ → NH_3

$CH_3NH_3^+$ → CH_3NH_2

FIGURE 11.17 As shown here for five conjugate acid–base pairs, the sum of the pK_a of an acid (pink) and the pK_b of its conjugate base (blue) is constant and equal to pK_w, which is 14.00 at 25°C.



Acid
Acid Strength
Base Strength
Conjugate Base
HCl
Cl⁻
pKa
Strong
−2
Ineffective as a base
H_3O^+
0
H_2O
HSO_4^-
2
SO_4^{2-}
HF
Moderately weak
4
Very weak
F^-
6
HSO_3^-
SO_3^{2-}
8
NH_4^+
NH_3
10
Very weak
Moderately weak
H_2O_2
12
HO_2^-
H_2O
14
OH^-
Ineffective as an acid
16
Strong
H_2
H^-

Table of Acids with Ka and pKa Values* CLAS

Acid	HA	A⁻	Ka	pKa	Acid Strength	Conjugate Base Strength
Hydroiodic	HI	I^-				
Hydrobromic	HBr	Br^-				
Perchloric	$HClO_4$	ClO_4^-	Strong acids completely dissociate in aq solution			
Hydrochloric	HCl	Cl^-	(Ka > 1, pKa < 1).			
Chloric	$HClO_3$	ClO_3^-	Conjugate bases of strong acids are ineffective bases.			
Sulfuric (1)	H_2SO_4	HSO_4^-				
Nitric	HNO_3	NO_3^-				
Hydronium ion	H_3O^+	H_2O	1	0.0	↑	↓
Iodic	HIO_3	IO_3^-	1.6×10^{-1}	0.80		
Oxalic (1)	$H_2C_2O_4$	$HC_2O_4^-$	5.9×10^{-2}	1.23		
Sulfurous (1)	H_2SO_3	HSO_3^-	1.54×10^{-2}	1.81		
Sulfuric (2)	HSO_4^-	SO_4^{2-}	1.2×10^{-2}	1.92		
Chlorous	$HClO_2$	ClO_2^-	1.1×10^{-2}	1.96		
Phosphoric (1)	H_3PO_4	$H_2PO_4^-$	7.52×10^{-3}	2.12		
Arsenic (1)	H_3AsO_4	$H_2AsO_4^-$	5.0×10^{-3}	2.30		
Chloroacetic	$CH_2ClCOOH$	CH_2ClCOO^-	1.4×10^{-3}	2.85		
Citric (1)	$H_3C_6H_5O_7$	$H_2C_6H_5O_7^-$	8.4×10^{-4}	3.08		
Hydrofluoric	HF	F^-	7.2×10^{-4}	3.14		
Nitrous	HNO_2	NO_2^-	4.0×10^{-4}	3.39		
Formic	HCOOH	$HCOO^-$	1.77×10^{-4}	3.75		
Lactic	$HCH_3H_5O_3$	$CH_3H_5O_3^-$	1.38×10^{-4}	3.86		
Ascorbic (1)	$H_2C_6H_6O_6$	$HC_6H_6O_6^-$	7.9×10^{-5}	4.10		
Benzoic	C_6H_5COOH	$C_6H_5COO^-$	6.46×10^{-5}	4.19		
Oxalic (2)	$HC_2O_4^-$	$C_2O_4^{2-}$	6.4×10^{-5}	4.19		
Hydrazoic	HN_3	N_3^-	1.9×10^{-5}	4.72		
Citric (2)	$H_2C_6H_5O_7^-$	$HC_6H_5O_7^{2-}$	1.8×10^{-5}	4.74		
Acetic	CH_3COOH	CH_3COO^-	1.76×10^{-5}	4.75		
Propionic	CH_3CH_2COOH	$CH_3CH_2COO^-$	1.34×10^{-5}	4.87		
Pyridinium ion	$C_5H_4NH^+$	C_5H_4N	5.6×10^{-6}	5.25		
Citric (3)	$HC_6H_5O_7^{2-}$	$C_6H_5O_7^{3-}$	4.0×10^{-6}	5.40		
Carbonic (1)	H_2CO_3	HCO_3^-	4.3×10^{-7}	6.37		
Sulfurous (2)	HSO_4^-	SO_4^{2-}	1.02×10^{-7}	6.91		
Arsenic (2)	$H_2AsO_4^-$	$HAsO_4^{2-}$	$8/9.3 \times 10^{-8}$	7.10/7.03		
Hydrosulfuric	H_2S	HS^-	$1.0 \times 10^{-7}/9.1 \times 10^{-8}$	7/7.04		
Phosphoric (2)	$H_2PO_4^-$	HPO_4^{2-}	6.23×10^{-8}	7.21		
Hypochlorous	HClO	ClO^-	$3.5/3.0 \times 10^{-8}$	7.46/7.53		
Hypobromous	HBrO	BrO^-	2×10^{-9}	8.70		
Hydrocyanic	HCN	CN^-	6.17×10^{-10}	9.21		
Boric (1)	H_3BO_3	$H_2BO_3^-$	5.8×10^{-10}	9.23		
Ammonium ion	NH_4^+	NH_3	5.6×10^{-10}	9.25		
Phenol	C_6H_5OH	$C_6H_5O^-$	1.6×10^{-10}	9.80		
Carbonic (2)	HCO_3^-	CO_3^{2-}	4.8×10^{-11}	10.32		
Hypoiodous	HIO	IO^-	2×10^{-11}	10.70		
Arsenic (3)	$HAsO_4^{2-}$	AsO_4^{3-}	$6.0 \times 10^{-10}/3.0 \times 10^{-12}$	9.22/11.53		
Hydrogen peroxide	H_2O_2	HO_2^-	2.4×10^{-12}	11.62		
Ascorbic (2)	$HC_6H_6O_6^-$	$C_6H_6O_6^{2-}$	1.6×10^{-12}	11.80		
Phosphoric (3)	HPO_4^{2-}	PO_4^{3-}	$4.8/2.2 \times 10^{-13}$	12.32/12.66		
Water	H_2O	OH^-	1.0×10^{-14}	14.0		
Group I metal hydroxides (LiOH, NaOH, etc.)			Strong bases completely dissociate in aq solution			
Group II metal hydroxides ($Mg(OH)_2$, $Ba(OH)_2$, etc.)			(Kb > 1, pKb < 1). Conjugate acids (cations) of strong bases are ineffective bases.			

* Compiled from Appendix 5 Chem 1A, B, C Lab Manual and Zumdahl 6th Ed. The pKa values for organic acids can be found in Appendix II of Bruice 5th Ed.

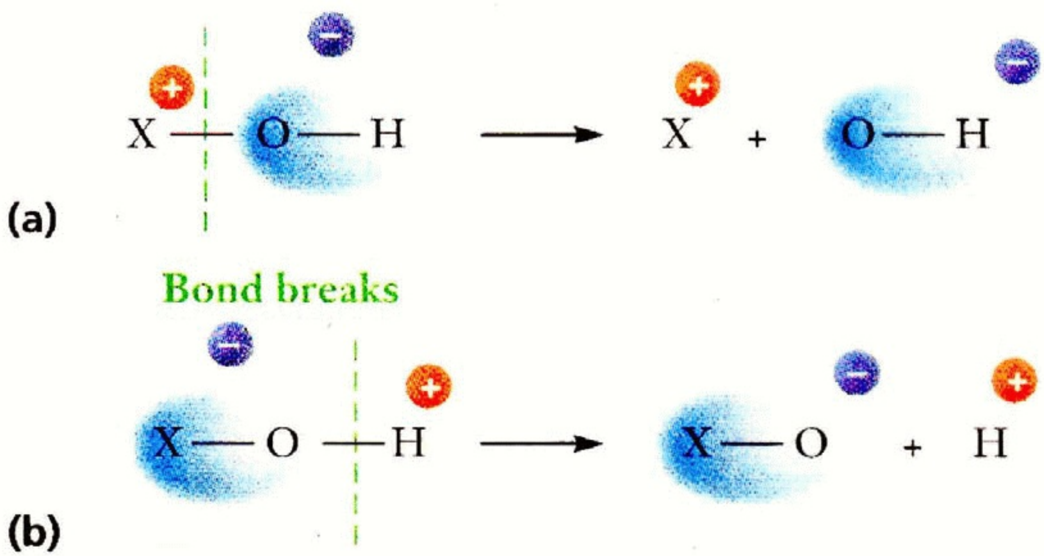


FIGURE 10.6 In part a, the atom X is electropositive, so extra electron density (blue areas) accumulates on the OH group. The X—O bond then breaks easily, making the compound a base. In part b, X is electronegative, so electron density is drawn from the H atom to the X—O bond. Now it is the O—H bond that breaks easily, and the compound is an acid.

See This Article on Relative Strengths of Acids and Bases

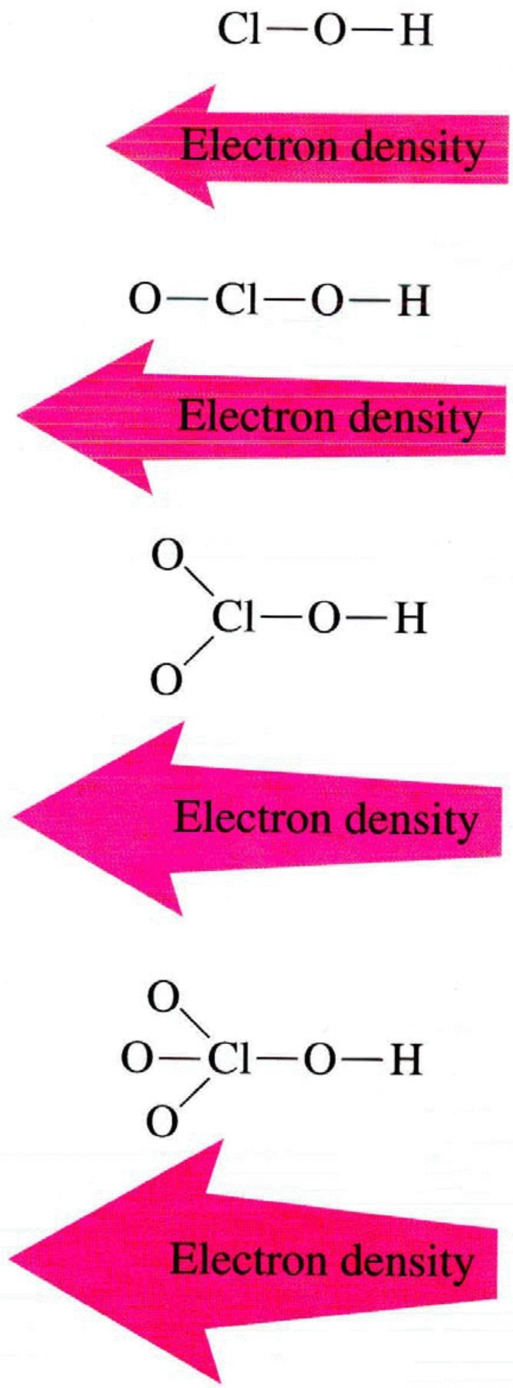


Figure 14.6
Electron withdrawing power of oxygen atoms in oxy chloro acids

TABLE 10.3

ACID IONIZATION CONSTANTS FOR OXOACIDS OF THE NONMETALS

$X(OH)_m$ Very Weak	K_a	$XO(OH)_m$ Weak	K_a	$XO_2(OH)_m$ Strong	K_a	$XO_3(OH)_m$ Very Strong	K_a
$Cl(OH)$	3×10^{-8}	$H_2PO(OH)$	8×10^{-2}	$SeO_2(OH)_2$	10^3	$ClO_3(OH)$	2×10^7
$Te(OH)_6$	2×10^{-8}	$IO(OH)_5$	2×10^{-2}	$ClO_2(OH)$	5×10^2		
$Br(OH)$	2×10^{-9}	$SO(OH)_2$	2×10^{-2}	$SO_2(OH)_2$	1×10^2		
$As(OH)_3$	6×10^{-10}	$ClO(OH)$	1×10^{-2}	$NO_2(OH)$	2×10^1		
$B(OH)_3$	6×10^{-10}	$HPO(OH)_2$	1×10^{-2}	$IO_2(OH)$	1.6×10^1		
$Ge(OH)_4$	4×10^{-10}	$PO(OH)_3$	8×10^{-3}				
$Si(OH)_4$	2×10^{-10}	$AsO(OH)_3$	5×10^{-3}				
$I(OH)$	4×10^{-11}	$SeO(OH)_2$	3×10^{-3}				
		$TeO(OH)_2$	3×10^{-3}				
		$NO(OH)$	5×10^{-4}				

TABLE 17.1 Acidity Constants of Some Alcohols and Phenols

Alcohol or phenol	pK_a		
$(CH_3)_3COH$	18.00		Weaker acid
CH_3CH_2OH	16.00		↓
HOH (water)	(15.74)	(K_w /55.5)	
CH_3OH	15.54		
CF_3CH_2OH	12.43		
p-Aminophenol	10.46		
p-Methoxyphenol	10.21		
p-Methylphenol	10.17		
Phenol	9.89		
p-Chlorophenol	9.38		
p-Bromophenol	9.35		
p-Nitrophenol	7.15		
2,4,6-Trinitrophenol	0.60		Stronger acid

Alcohol: R-OH

Phenol: