Acids

Gerber - Jabir ibn Hayyan
(721-815)

Andreas Libau (Libavius)
(1540-1616)

Gerber – prepared HNO_3, HCl and *aqua regia* (from H_2SO_4 and salts, isolated citric, acetic, and tartaric acids
Libavius - prepared HCl and *aqua regia* (dissolves Au)

The world highest tonnage per annum chemical commodity:

H_2SO_4

Acids

R. Boyle (1627 - 1691): changes of color of litmus

L. Lavoisier (1743-1794) : Oxygenium = acid forming

Oxides of nonmetals reacts with water to acids

H. Davy (1779-1829)
J. Liebig (1803-1873)

Hydrogen is released during reactions of acids with metals = H governs acidic properties

Arrhenius Theory of Acids and Bases

Svante Arrhenius
(1859-1927)

Acids:

Taste acidic

Release H^+ in aqueous soln.

Reacts with base metals with release of H_2

K, Ca, Na, Mg, Al, Zn, Fe, Ni, Sn, Pb

Color litmus red (R. Boyle)

Neutralize bases

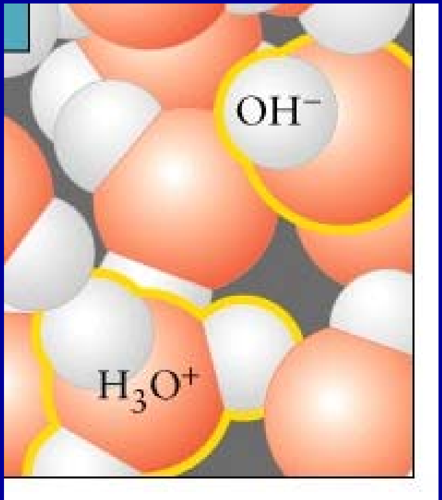
Bases:

Taste bitter

Release OH^- in aqueous soln.

Color litmus blue

Neutralize acids



Strong and Weak Arrhenius Acids

Strong Acids : **completely** ionized in water

(100% dissociated)

$HNO_3 \quad \rightarrow \quad H^+_{(aq)} + NO_3^-{}_{(aq)}$

$HCl, HNO_3, H_2SO_4, HClO_4, HI, HBr, HClO_3, HBrO_3, ...$

Weak Acids : **partially** ionized in water

(0% < dissoc. degree <100%)

$CH_3CO_2H \leftrightarrows H^+_{(aq)} + CH_3CO_2^-{}_{(aq)}$

Organic acids, $H_2CO_3, H_3BO_3, H_3PO_4, H_2S, H_2SO_3, ...$

Strong Arrhenius Bases

Strong Bases : **completely** ionized in water

(100% dissociated)

$KOH_{(s)} \rightarrow K^{+}_{(aq)} + OH^{-}_{(aq)}$

Alkali metal hydroxides, alkaline earth metal hydroxides, soluble hydroxides

No weak bases in Arrhenius theory

Brønsted–Lowry Acids and Bases

Wider definition, not limited to aqueous solutions

Acid = proton donor = Arrhenius acid

Base = proton acceptor

$H_3SO_4^+$	H_3O^+
H_2SO_4	H_2O
HSO_4^-	HO^-
SO_4^{2-}	O^{2-}

Proton H^+

H^+ hydronium H_3O^+ oxonium

Grotthus mechanism
– extremely fast H^+ movement

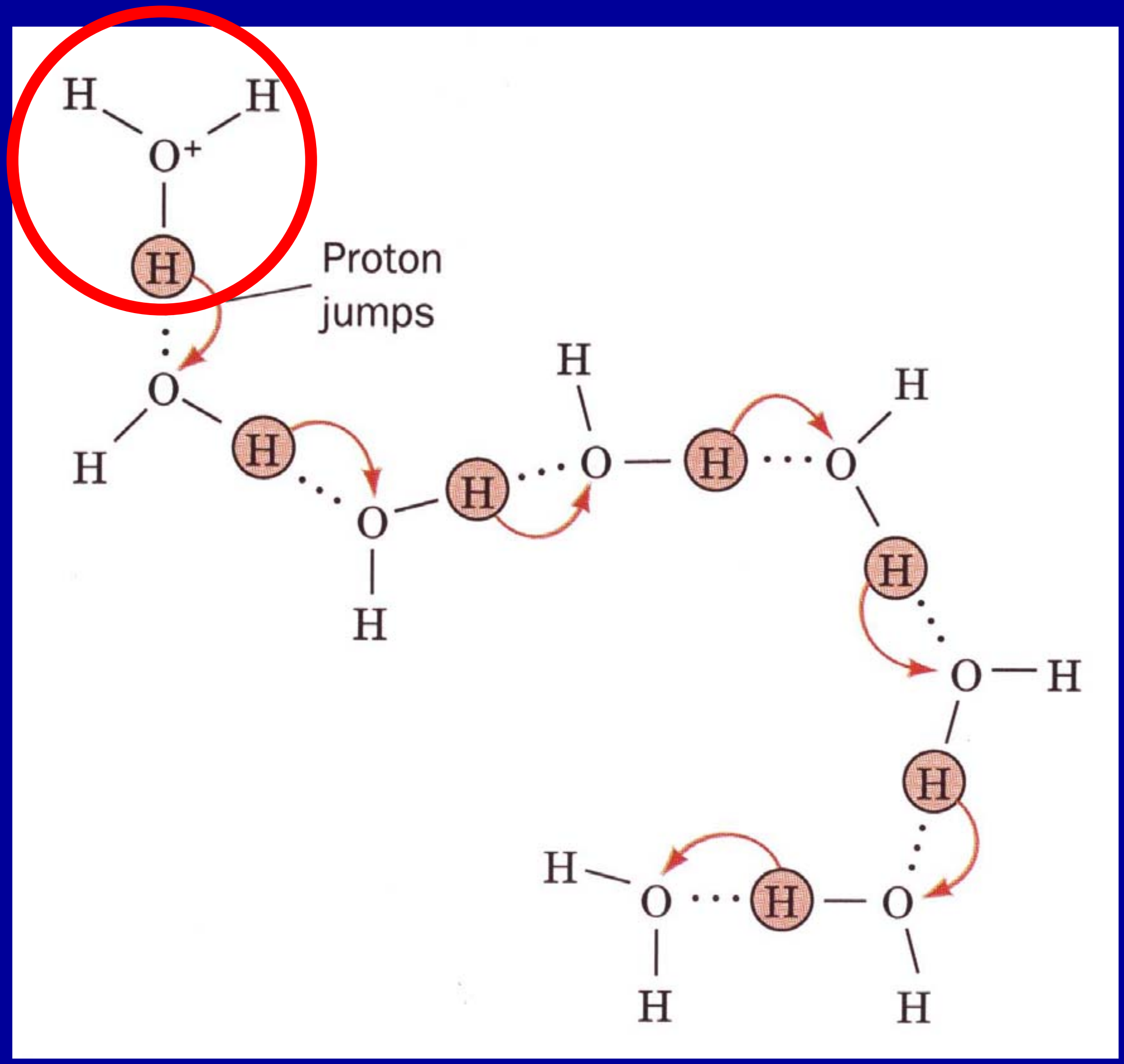
$H_9O_4^+ = [H_3O(H_2O)_3]^+$ M. Eigen
lifetime H_3O^+ 1 - 4 ps

$[H_3O(H_2O)_{20}]^+$

Protonation of solvent (S) is exothermic
$H^+ + n\,S \rightarrow H(S)_n^+ \qquad \Delta H < 0$

High Proton H^+ Mobility

$[H_3O]^+$



Brønsted–Lowry Strong and Weak Acids

$HSO_4^-(aq) + H_2O \leftrightarrows H_3O^+(aq) + SO_4^{2-}(aq)$

Equilibrium constant of proton dissociation
= ionization constant of acid
= acid dissociation constant

Water is a reagent and solvent

$K_C = [H_3O^+]\,[SO_4^{2-}] / [HSO_4^-]\,[H_2O]$

$[H_2O] \sim 55.6$ M

$K_a = [H_3O^+]\,[SO_4^{2-}] / [HSO_4^-]$

$$pK_a = -\log K_a$$

$$K_a = \frac{\left[H_3O^+\right]\cdot\left[SO_4^{\ 2-}\right]}{\left[HSO_4^{\ -}\right]}$$

Acid Strength

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

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

Acid Strength increases

Acid	pK_a
NH_3	35
ROH	15 – 18
H_2O	15.57
CF_3CH_2OH	12.4
PhOH	10.0
NH_4^+	9.2
HCN	9.1
CH_3COOH	4.75
HF	3.2
H_3O^+	–1.75
HCl	–7
$HClO_4$	–10

NH_3 + H_2O $\leftrightarrows$ H_3O^+(aq) + NH_2^-(aq)

Weak acids
pK_a positive

$pK_a = -\log K_a$

Strong acids
pK_a negative

Acid Strength and ΔG

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

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

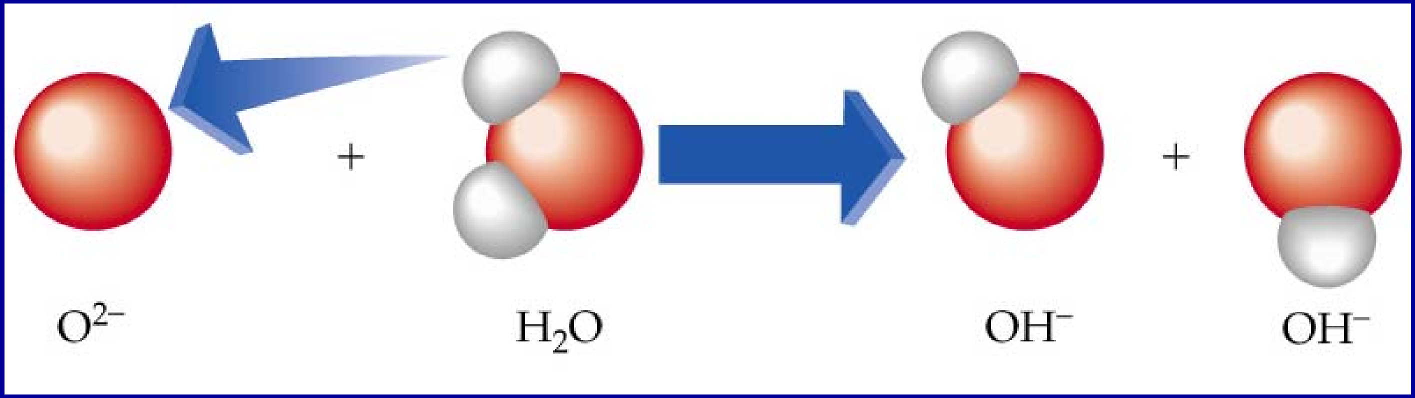
$K_a = [H_3O^+]\ [A^-]\ /\ [HA]$

$pK_a = -\log K_a$

$$\Delta G = -RT \ln K_a = 2.3\ RT\ pK_a$$

	K_a	pK_a	ΔG
Weak acids	< 1	> 0	> 0
Strong acids	> 1	< 0	< 0

Brønsted–Lowry Strong Bases



$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$\mathbf{NH_3 + H_2O \;\leftrightarrows\; H_3O^+ + NH_2^-}$$

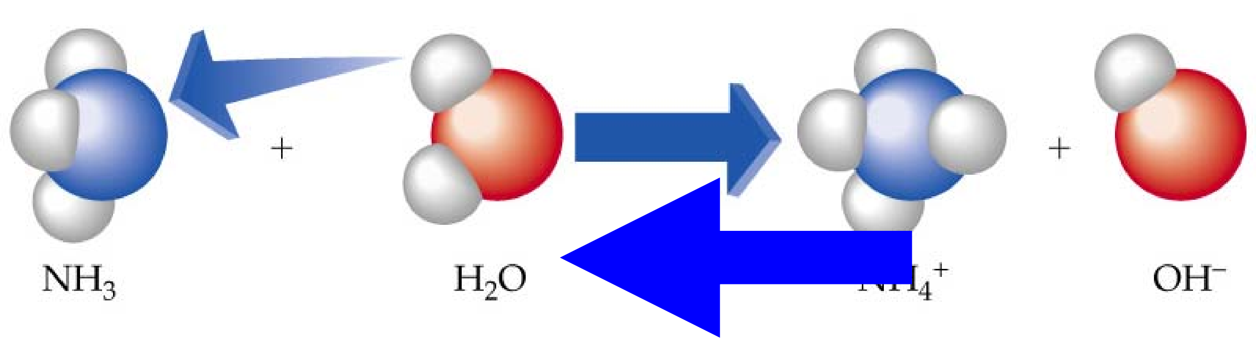
$$\longleftarrow$$

$$pK_a\,(NH_3) > pK_a(H_2O)$$

Brønsted–Lowry Weak Bases

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

Equilibrium constant of base protonation by water
= ionization constant of base
= base dissociation constant



$K = [NH_4^+] [OH^-] / [NH_3] [H_2O]$

$K_b = [NH_4^+] [OH^-] / [NH_3]$ base dissociation constant

$pK_b = -\log K_b$

Brønsted–Lowry Weak Bases

Methylamin

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$$

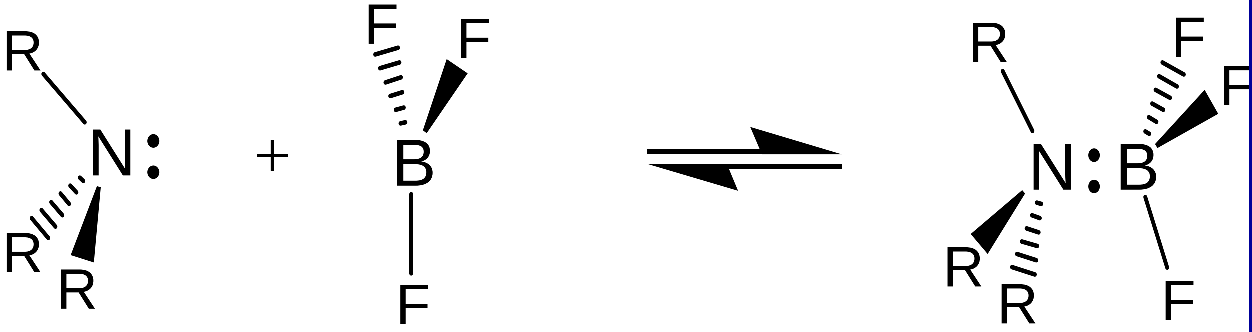
$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} = 4.4x10^{-4}$$

$$pK_b = -\log K_b$$

Lewis Acids and Bases

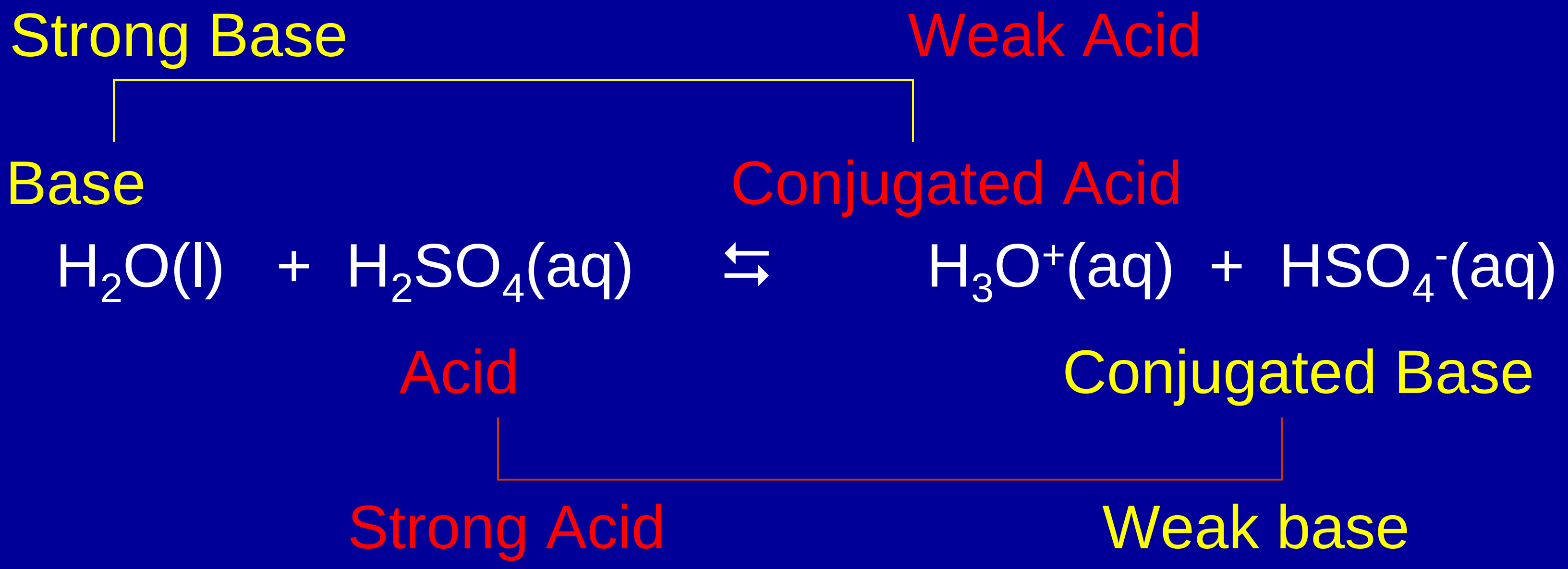
Lewis Acids – acceptors of electron pair

Lewis Bases – donors of electron pair



Lewis Base **Lewis Acid**

Conjugated Pairs of Acids and Bases



Strong Base

Weak Acid

Base

Conjugated Acid

$$H_2O(l) + H_2SO_4(aq) \rightleftarrows H_3O^+(aq) + HSO_4^-(aq)$$

Acid

Conjugated Base

Strong Acid

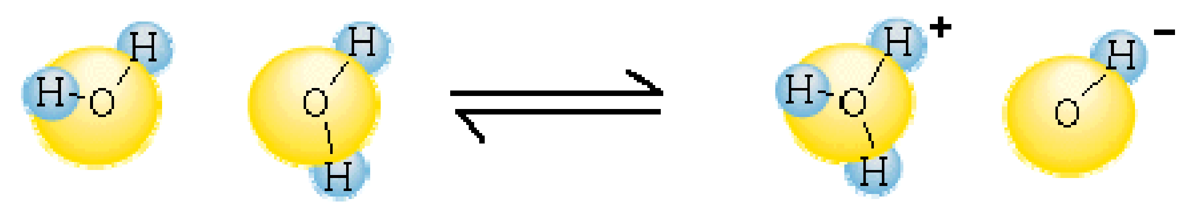
Weak base

Conjugated pairs of acids and bases are connected by proton exchange

Acid-Base Properties of Water

Autoionization $H_2O(l) \leftrightarrows H^+(aq) + OH^-(aq)$

Water is a very weak electrolyte



$2\ H_2O(l) \leftrightarrows H_3O^+(aq) + OH^-(aq)$

$K_C = [H^+][OH^-] / [H_2O]^2$

Water is amphoteric – behaves as an acid and a base

$K_w = [H^+][OH^-]$ K_w = ion product of water

$K_w = 1\ 10^{-14}\ M^2$ $[H^+] = [OH^-] = 1\ 10^{-7}\ M$

$pK_w = 14$ in pure water at 25 °C and 101.325 kPa

pH and pOH Scales

$$pH = -\log [H^+]$$

1909
S. P. L. Sørensen
Beer brewing

in pure water

$[H^+] = 1\ 10^{-7}$ M
$pH = -\log [1\ 10^{-7}]$
$pH = 7$

$[OH^-] = 1\ 10^{-7}$ M
$pOH = -\log [1\ 10^{-7}]$
$pOH = 7$

$[H^+][OH^-] = K_w$
$pH + pOH = pK_W = 14.00$

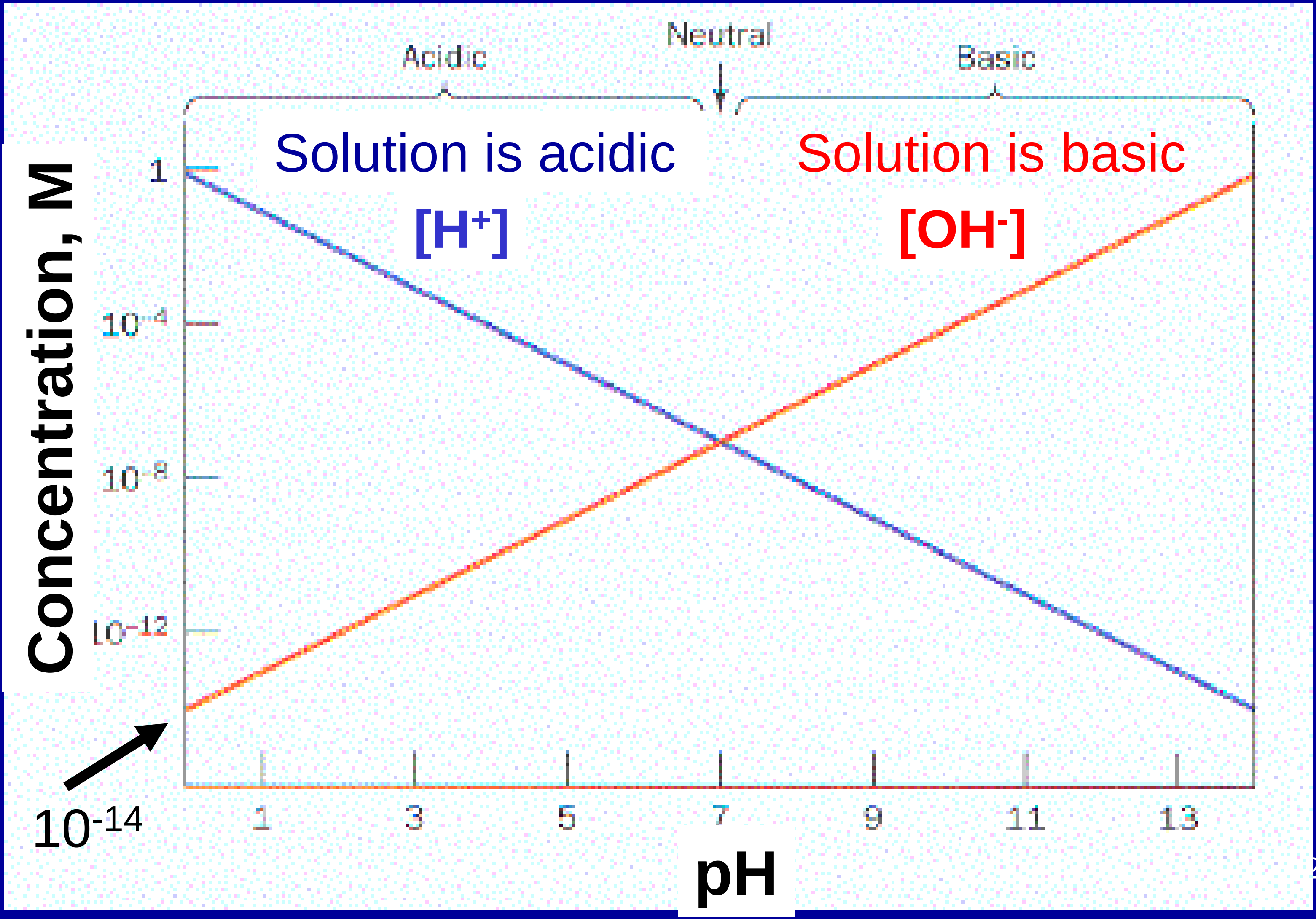
Constant inaqueous solutions (ionic product of water)

$pH < 7$	Solution is acidic
$pH = 7$	Solution is neutral
$pH > 7$	Solution is basic

pH and pOH Scales

pH	pOH	$[H^+]$ M	$[OH^-]$ M
0	14	1.0	10^{-14}
2	12	0.01	10^{-12}
4	10	0.0001	10^{-10}
6	8	10^{-6}	10^{-8}
8	6	10^{-8}	10^{-6}
10	4	10^{-10}	0.0001
12	2	10^{-12}	0.01
14	0	10^{-14}	1.0

pH and pOH Scales



Neutralization

$H_3O^+(aq) + OH^-(aq) \rightarrow 2\ H_2O(l) \qquad k = 1.4\ 10^{11}$

$2\ H_2O(l) \rightarrow H_3O^+(aq) + OH^-(aq) \qquad k = 2.5\ 10^{-5}$

$H^+ + OH^- \rightarrow H_2O \qquad \Delta H = -\ 56.9\ \text{kJ mol}^{-1}$

$H_2SO_4 + 2\ KOH \rightarrow 2\ H_2O + K_2SO_4$

$H_3PO_4 + 3\ NaOH \rightarrow 3\ H_2O + Na_3PO_4$

$2\ HCl + Mg(OH)_2 \rightarrow 2\ H_2O + MgCl_2$

$HCl + NaHCO_3 \rightarrow H_2O + NaCl + CO_2$

K_a and K_b of Conjugated Pairs

$$\mathbf{NH_4^+}(aq) + H_2O \leftrightarrows H_3O^+(aq) + \mathbf{NH_3}(aq)$$

$K_a = [H_3O^+]\,[NH_3] / [NH_4^+]$ acidity constant of NH_4^+

$$\mathbf{NH_3}(aq) + H_2O \leftrightarrows \mathbf{NH_4^+}(aq) + OH^-(aq)$$

$K_b = [NH_4^+]\,[OH^-] / [NH_3]$ basicity constant of NH_3

$K_w = [H^+][OH^-]$ ion product of water

$$K_a \times K_b = [H_3O^+]\,[NH_3] / [NH_4^+] \times [NH_4^+]\,[OH^-] / [NH_3] = K_w$$

$$\mathbf{K_a \times K_b = K_w}$$

K_a and K_b of Conjugated Pairs

K_a and K_b relationship

$$CH_3NH_3^+ \rightleftharpoons CH_3NH_2 + H^+$$

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$K_a = \frac{[H^+][CH_3NH_2]}{[CH_3NH_3^+]}$$

$$K_b = \frac{[CH_3NH_3^{\ +}][OH^-]}{[CH_3NH_2]}$$

$$K_w = [OH^-][H^+]$$

$$K_a \times K_b = K_w$$

$$pK_a + pK_b = 14$$

K_a and K_w of Water

Autoionization $2\ H_2O(l) \leftrightarrows H_3O^+(aq) + OH^-(aq)$

$K_C = [H_3O^+]\ [OH^-]\ /\ [H_2O]^2$

$K_w = [H_3O^+]\ [OH^-]$ ionic product

$pK_w = 14$

$K_a = [H_3O^+]\ [OH^-]\ /\ [H_2O] = K_w\ /\ [H_2O]$ acidity constant

$[H_2O] = 55.6\ \text{mol}\ l^{-1}$

$pK_a = 15.74$

Water is a weak acid

K_a of Oxonium Cation $H_3O^+(aq)$

$H_3O^+(aq) + H_2O(l) \leftrightarrows H_2O(l) + H_3O^+(aq)$

$K_C = [H_3O^+]\,[H_2O] / [H_3O^+]\,[H_2O]$

$K_a = [H_3O^+]\,[H_2O] / [H_3O^+] = [H_2O] = 55.6 \text{ mol l}^{-1}$

$pK_a = -1.75$

Oxonium cation is a strong acid

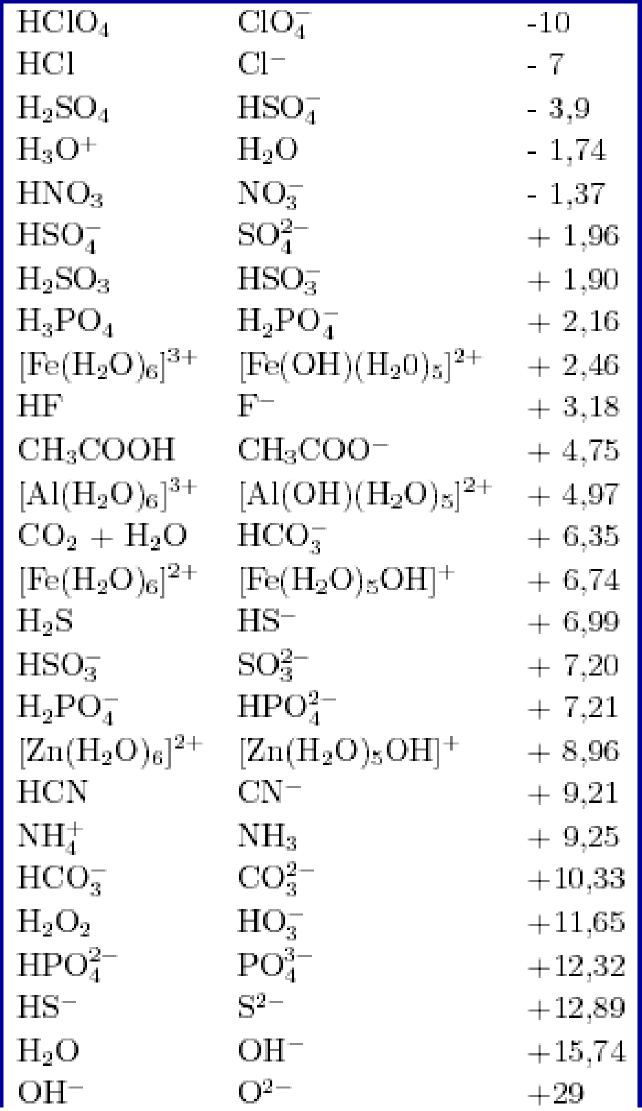
pK_a of Acids

$HA(aq) \leftrightarrows H^+(aq) + A^-(aq)$

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

$pK_a = -\log K_a$

Acid strength incr.



		pK_a
$HClO_4$	ClO_4^-	-10
HCl	Cl^-	- 7
H_2SO_4	HSO_4^-	- 3,9
H_3O^+	H_2O	- 1,74
HNO_3	NO_3^-	- 1,37
HSO_4^-	SO_4^{2-}	+ 1,96
H_2SO_3	HSO_3^-	+ 1,90
H_3PO_4	$H_2PO_4^-$	+ 2,16
$[Fe(H_2O)_6]^{3+}$	$[Fe(OH)(H_2O)_5]^{2+}$	+ 2,46
HF	F^-	+ 3,18
CH_3COOH	CH_3COO^-	+ 4,75
$[Al(H_2O)_6]^{3+}$	$[Al(OH)(H_2O)_5]^{2+}$	+ 4,97
$CO_2 + H_2O$	HCO_3^-	+ 6,35
$[Fe(H_2O)_6]^{2+}$	$[Fe(H_2O)_5OH]^+$	+ 6,74
H_2S	HS^-	+ 6,99
HSO_3^-	SO_3^{2-}	+ 7,20
$H_2PO_4^-$	HPO_4^{2-}	+ 7,21
$[Zn(H_2O)_6]^{2+}$	$[Zn(H_2O)_5OH]^+$	+ 8,96
HCN	CN^-	+ 9,21
NH_4^+	NH_3	+ 9,25
HCO_3^-	CO_3^{2-}	+10,33
H_2O_2	HO_2^-	+11,65
HPO_4^{2-}	PO_4^{3-}	+12,32
HS^-	S^{2-}	+12,89
H_2O	OH^-	+15,74
OH^-	O^{2-}	+29

$$K_a \times K_b = K_w \qquad pK_a + pK_b = 14$$

Acid strength incr.

Acid	Conjug. base	pK_a
$HClO_4$	ClO_4^-	–10
HCl	Cl^-	–7
H_3O^+	H_2O	–1.75
HF	F^-	3.2
CH_3COOH	CH_3COO^-	4.75
HCN	CN^-	9.1
NH_4^+	NH_3	9.2
PhOH	PhO⁻	10.0
CF_3CH_2OH	$CF_3CH_2O^-$	12.4
H_2O	HO^-	15.57
ROH	RO^-	15 – 18
NH_3	NH_2^-	35

Conjug. base strength incr.

Reaction Equilibrium

Reactions are shifted to weak acids and weak bases

Strong acids expel weak acids
Strong bases expel weak bases

PhOH	+	F^-	$\leftrightarrows$	PhO^-	+	HF
Weak acid.		Weak base		Strong base		Strong acid

$\longleftarrow$

Equilibrium shifted to left

$$CH_3COOH + NH_3 \leftrightarrows CH_3COO^- + NH_4^+$$

$\longrightarrow$

Equilibrium shifted to right

Nivelization Effect of Water

Acid	Conjug. base	pK_a
$HClO_4$	ClO_4^-	–10
HCl	Cl^-	–7
H_3O^+	H_2O	–1.75
HF	F^-	3.2
CH_3COOH	CH_3COO^-	4.75
HCN	CN^-	9.1
NH_4^+	NH_3	9.2
PhOH	PhO^-	10.0
CF_3CH_2OH	$CF_3CH_2O^-$	12.4
H_2O	HO^-	15.57
ROH	RO^-	15 – 18
NH_3	NH_2^-	35

Acids stronger than H_3O^+ are completely dissociated in water

Basea stronger than HO^- are completely protonated in water

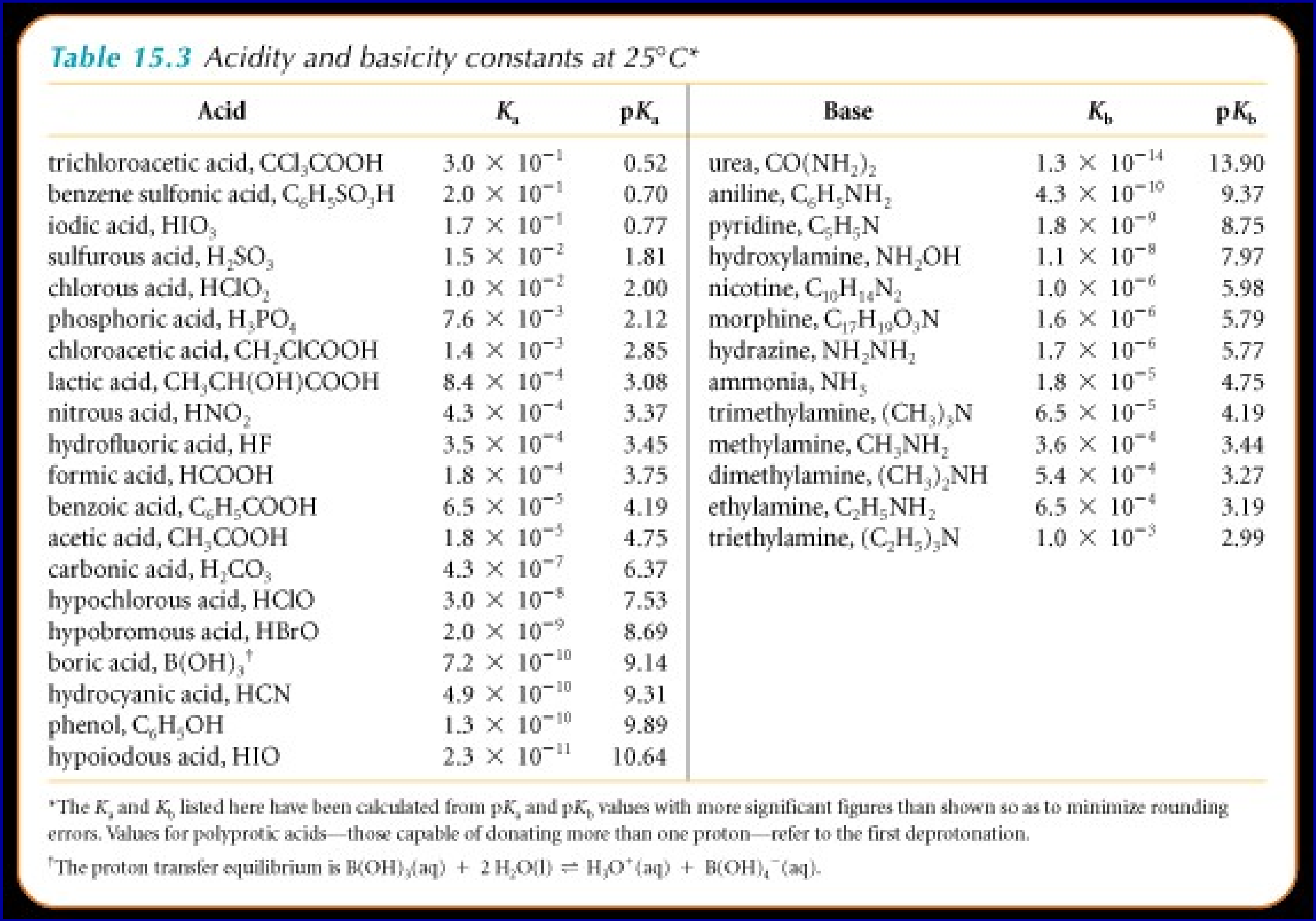


Table 15.3 *Acidity and basicity constants at 25°C**

Acid	K_a	pK_a	Base	K_b	pK_b
trichloroacetic acid, CCl_3COOH	3.0×10^{-1}	0.52	urea, $CO(NH_2)_2$	1.3×10^{-14}	13.90
benzene sulfonic acid, $C_6H_5SO_3H$	2.0×10^{-1}	0.70	aniline, $C_6H_5NH_2$	4.3×10^{-10}	9.37
iodic acid, HIO_3	1.7×10^{-1}	0.77	pyridine, C_5H_5N	1.8×10^{-9}	8.75
sulfurous acid, H_2SO_3	1.5×10^{-2}	1.81	hydroxylamine, NH_2OH	1.1×10^{-8}	7.97
chlorous acid, $HClO_2$	1.0×10^{-2}	2.00	nicotine, $C_{10}H_{14}N_2$	1.0×10^{-6}	5.98
phosphoric acid, H_3PO_4	7.6×10^{-3}	2.12	morphine, $C_{17}H_{19}O_3N$	1.6×10^{-6}	5.79
chloroacetic acid, $CH_2ClCOOH$	1.4×10^{-3}	2.85	hydrazine, NH_2NH_2	1.7×10^{-6}	5.77
lactic acid, $CH_3CH(OH)COOH$	8.4×10^{-4}	3.08	ammonia, NH_3	1.8×10^{-5}	4.75
nitrous acid, HNO_2	4.3×10^{-4}	3.37	trimethylamine, $(CH_3)_3N$	6.5×10^{-5}	4.19
hydrofluoric acid, HF	3.5×10^{-4}	3.45	methylamine, CH_3NH_2	3.6×10^{-4}	3.44
formic acid, HCOOH	1.8×10^{-4}	3.75	dimethylamine, $(CH_3)_2NH$	5.4×10^{-4}	3.27
benzoic acid, C_6H_5COOH	6.5×10^{-5}	4.19	ethylamine, $C_2H_5NH_2$	6.5×10^{-4}	3.19
acetic acid, CH_3COOH	1.8×10^{-5}	4.75	triethylamine, $(C_2H_5)_3N$	1.0×10^{-3}	2.99
carbonic acid, H_2CO_3	4.3×10^{-7}	6.37			
hypochlorous acid, HClO	3.0×10^{-8}	7.53			
hypobromous acid, HBrO	2.0×10^{-9}	8.69			
boric acid, $B(OH)_3$[†]	7.2×10^{-10}	9.14			
hydrocyanic acid, HCN	4.9×10^{-10}	9.31			
phenol, C_6H_5OH	1.3×10^{-10}	9.89			
hypoiodous acid, HIO	2.3×10^{-11}	10.64			

[*] The K_a and K_b listed here have been calculated from pK_a and pK_b values with more significant figures than shown so as to minimize rounding errors. Values for polyprotic acids—those capable of donating more than one proton—refer to the first deprotonation.

[†] The proton transfer equilibrium is $B(OH)_3(aq) + 2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + B(OH)_4^-(aq)$.

pH of Strong Acids and Bases

0.001 M $HNO_3 \rightarrow H^+ + NO_3^-$

$[H^+] = 0.001$ $pH = – \log[0.001] = 3$

0.1 M $KOH \rightarrow K^+ + OH^-$

$[OH^-] = 0.1$ $pOH = – \log[0.1] = 1$ $pH = 14 – pOH = 13$

$1\ 10^{-9}$ M $HCl \rightarrow H^+ + Cl^-$

~~$[H^+] = 1x10^{-9}$ $pH = -\log(1x10^{-9}) = 9$~~

$H_2O \rightarrow H^+ + OH^-$ $[H^+] = 1\ 10^{-7}$

HA ⇆ H^+ + A^-

pH of Weak Acids

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad pK_a = -\log(K_a)$$

$$[H^+] = [A^-]$$

$$[HA] = [HA]_0 - [H^+] \approx [HA]_0 = c_{HA}$$

$$K_a = \frac{[H^+]^2}{[HA]_0}$$

$$[H^+] = \sqrt{K_a[HA]_0}$$

$[H^+]$ is very small in weak acids,
then $[HA] = [HA]_0$

Starting acid concentration

pH = ½ pK_a – ½ log c_{HA}

$HA \leftrightarrows H^+ + A^-$

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad pK_a = -\log(K_a)$$

Solution of 0.1 M HCOOH, $K_a = 1.74\ 10^{-4}$. pH = ?

$HCOOH \leftrightarrows H^+ + HCOO^-$

	HCOOH	H^+	$HCOO^-$
Initial	0.1	0	0
Change	– x	x	x
Equilibrium	0.1 – x	x	x
	0.1	$4.12\ 10^{-3}$	$4.12\ 10^{-3}$

$$K_a = \frac{[x][x]}{[0.1-x]} = 1.7\,x10^{-4} \qquad [0.1-x] \approx 0.1$$

$$x^2 = 1.7x10^{-5}$$

$$x = 4.12x10^{-3}$$

x very small,
then $[HA] = [HA]_0$

pH = – log($4.12\ 10^{-3}$) = 2.39

pH = ½ pK_a – ½ log c_{HA}

Solution of 0.1 M HCOOH

	HCOOH	H^+	$HCOO^-$
Initial	0.01	0	0
Change	– x	x	x
Equilibrium	0.01 – x	x	x
	0.01	$1.22\ 10^{-3}$	$1.22\ 10^{-3}$

$$K_a = \frac{[x][x]}{[0.01 - x]} = 1.7\,x10^{-4}$$

$$x^2 + 1.7x10^{-4}\,x - 1.76x10^{-6}$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-1.7x10^{-4} \pm \sqrt{1.7x10^{-4} - 4(-1.76x10^{-6})}}{2}$$

$$x = 1.22x10^{-3}$$

When x comparable to c_{HA}
Then quadratic equation

pH = – log($1.22\ 10^{-3}$) = 2.9

Factors Influencing Acid Strength

$HA + H_2O \leftrightarrows H^+ (aq) + A^- (aq) \qquad \Delta H_r$

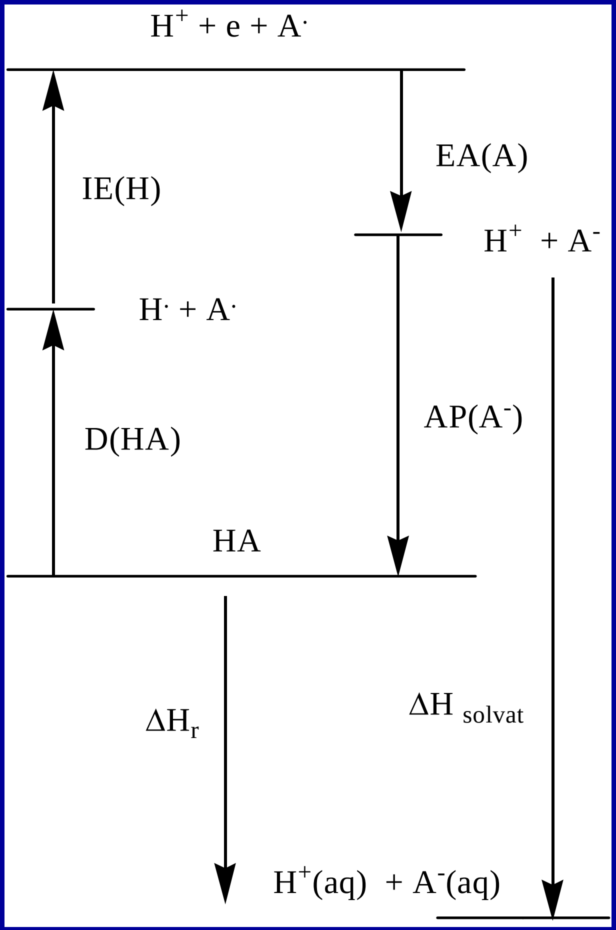
Bond dissociation energy, D(HA)
$H\text{-}A \rightarrow H\cdot + \cdot A$

Ionization energy of H, IE(H)
$H\cdot \rightarrow H^+ + e^-$

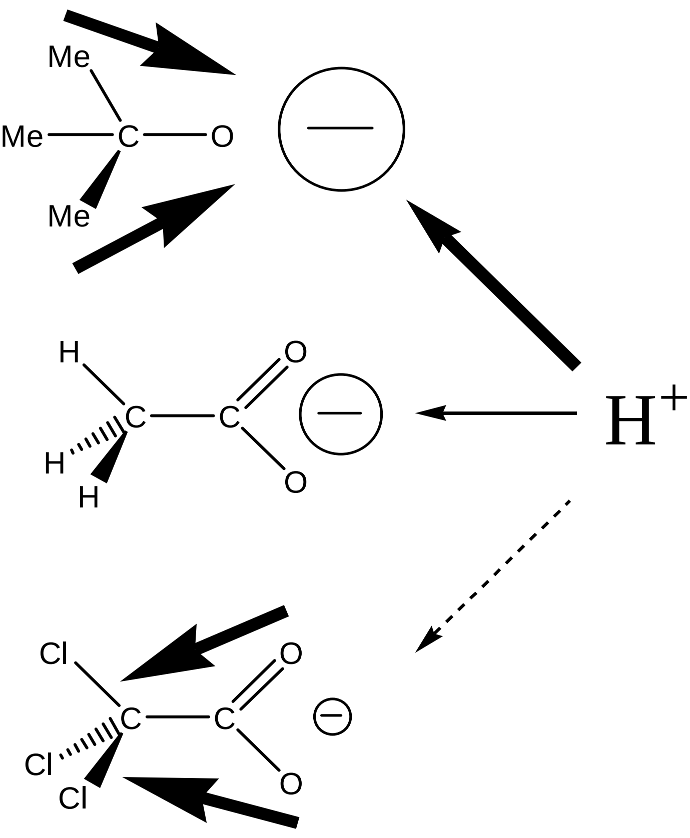
Electron affinity A, EA(A)
$\cdot A + e^- \rightarrow A^-$

Proton affinity A⁻ AP(A)
$H^+ + A^- \rightarrow HA$

Hydratation (solvation) enthalpy
$H^+ + n\,H_2O \rightarrow H^+ (aq)$
$A^- + n\,H_2O \rightarrow A^- (aq)$



Factors Influencing Acid Strength



^{t}BuOH pKa = 16

Weak acid

Negative charge on O

= attracts H^+

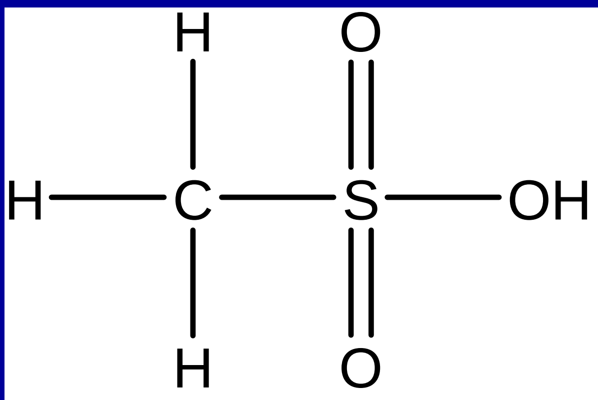
CH_3COOH pKa = 4.75

CCl_3COOH pKa = 0.52

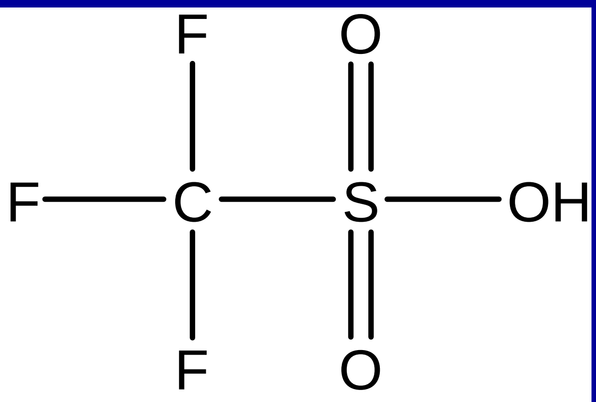
Strong acid

= low attraction to H^+

Factors Influencing Acid Strength


$H_3C-S(=O)_2-OH$

pKa = - 2.5


$F_3C-S(=O)_2-OH$

pKa = - 12

Acidity along Periods Increases

Hydrides = compounds of H with elements
The higher the electronegativity, the higher the acidity,
the better stabilization of negative charge

Hydride	$H\text{-}CH_3$	$H\text{-}NH_2$	H-OH	H-F
pK_a	55	35	15.7	3.2

→ Acidity Increases

NaH = basic hydride:

$$Na^+ (aq) + H^- (aq) + H_2O (l) \rightarrow H_2 (g) + Na^+ (aq) + OH^- (aq)$$

HCl = acidic hydride:

$$H^+ (aq) + Cl^- (aq) + H_2O (l) \rightarrow H_3O^+ (aq) + Cl^- (aq)$$

Acidity along Groups Increases

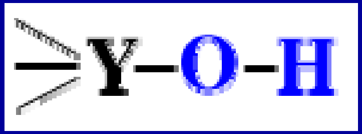
Bond strength incr

HX	pK_a	HX	pK_a
HF	3.2	ROH	15-16
HCl	–7	RSH	10
HBr	–9	RSeH	-
HI	–9.5	RTeH	7

Acidity Increases

Oxyacids

Oxyacids = OH groups bound to an electronegative central atom



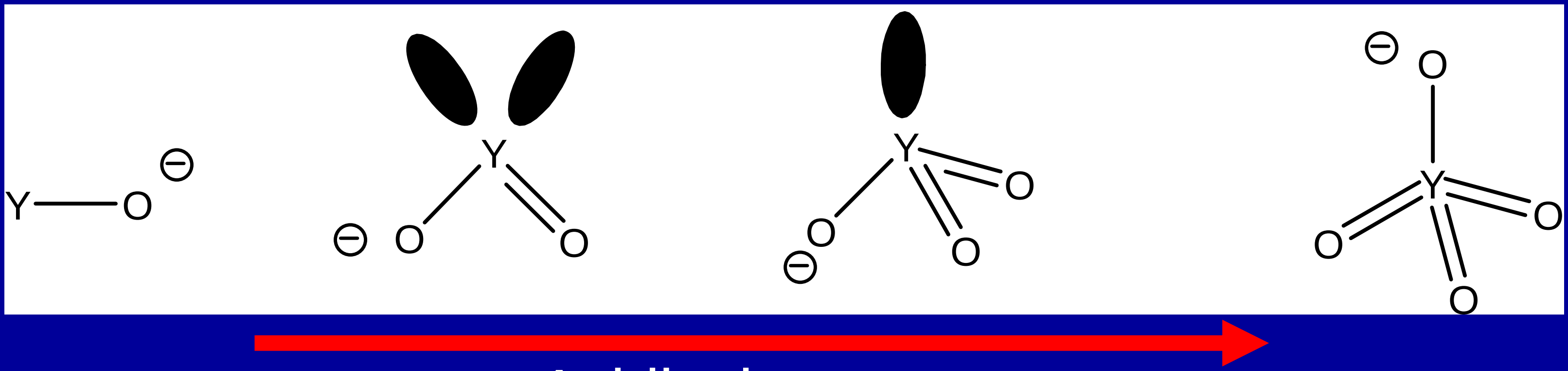
$(O)_n\,Y\,(OH)_m$

Acidity incr

n	pK_a	Strength
0	7	Very weak
1	2	Weak
2	–3	Strong
3	–8	Very strong

$(O)_n Y (OH)_m$

Oxyacids



Acidity incr

- Stabilization of anions by mezomeric effekt (rezonance)
- Increasing charge on Y

  oxidation number of central atom
- Lowering of charge density on O

  electronegativity of central atom
- Removal of e. density by other O atoms (-I)

Facilitate dissociation of H^+ = incr acid strength

Oxidation Number of Central Atom

Acid	Formula	Ox.no.	pK_a
Perchloric	O_3Cl-O-H	7	–10
Chloric	O_2Cl-O-H	5	–3
Chlorous	O Cl-O-H	3	2.00
Hypochloric	Cl-O-H	1	7.53

Electronegativity of Central Atom

Acid	**E-O-H**	**Elneg**	**pK_a**
Hypochloric	Cl-O-H	3.2	7.53
Hypobromic	Br-O-H	3.0	8.69
Hypoiodic	I-O-H	2.7	10.64

Oxyacids

$NaOH\ Mg(OH)_2\ Al(OH)_3\ Si(OH)_4\ OP(OH)_3\ O_2S(OH)_2\ O_3ClOH$

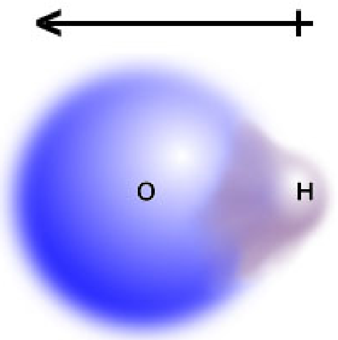
Acidity increases

$$\boxed{M^{n+} - O^{2-} - H}$$

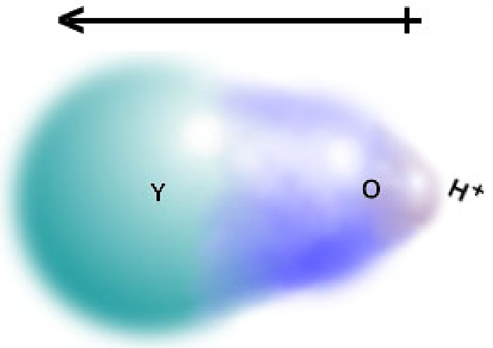
M-O ionic bond
= weak acids (= hydroxides)

M-O covalent = strong acids

Oxyacids



The electrons are unevenly shared between the O and H atoms, forming a polar covalent bond.



Electron density is shifted towards the highly electronegative element, Y, facilitating the release of the H^+ ion.

Factors Influencing Acid Strength

- oxidation number of central atom
- electronegativity of central atom

pK$_a$ of Bound Water in Metal Complexes

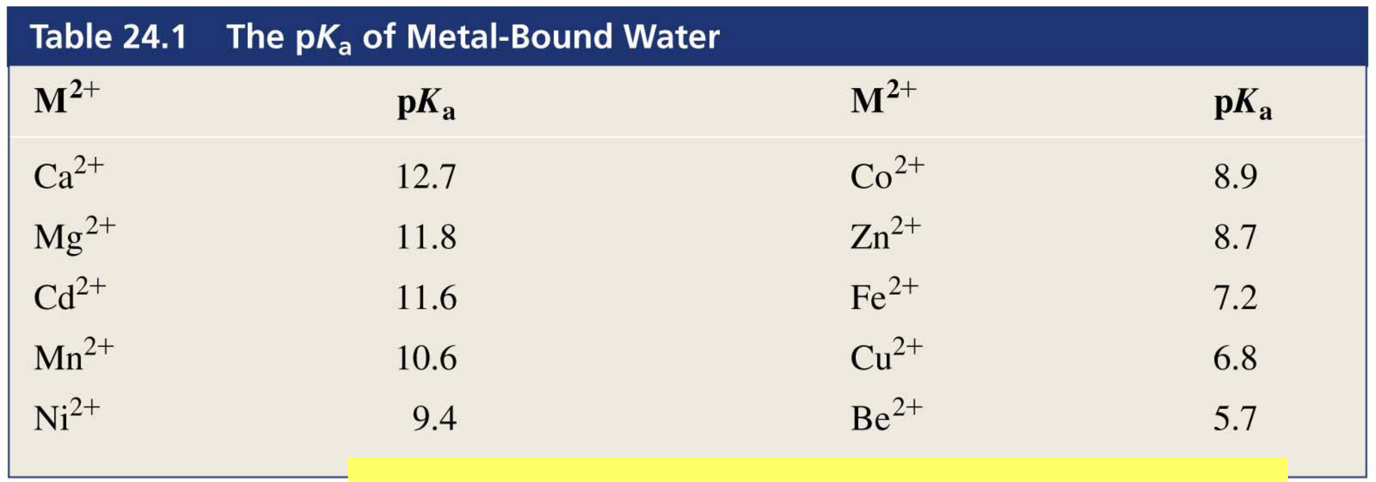
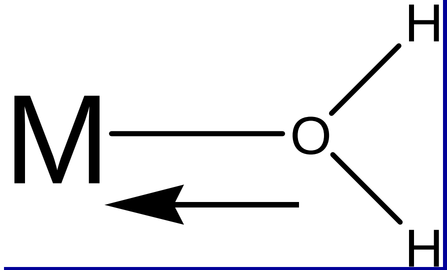
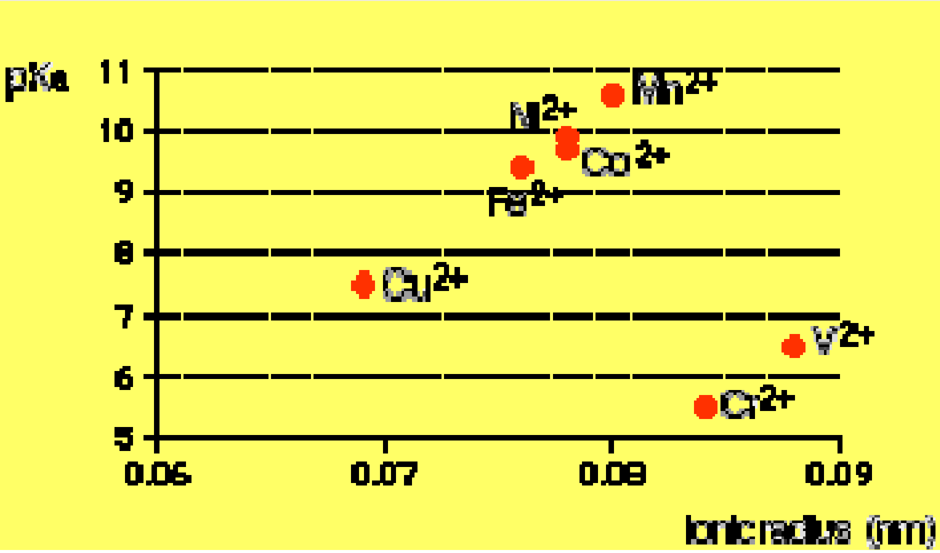


Table 24.1 The pK_a of Metal-Bound Water

M^{2+}	pK_a	M^{2+}	pK_a
Ca^{2+}	12.7	Co^{2+}	8.9
Mg^{2+}	11.8	Zn^{2+}	8.7
Cd^{2+}	11.6	Fe^{2+}	7.2
Mn^{2+}	10.6	Cu^{2+}	6.8
Ni^{2+}	9.4	Be^{2+}	5.7

Acidity incr





Decreasing ion radius

Acidity of Hydrated Cations

Cation	M-O, Å	pK_a
$[Al(H_2O)_6]^{3+}$	1.89	4.9
$[Ga(H_2O)_6]^{3+}$	1.90	2.6
$[In(H_2O)_6]^{3+}$	2.16	3.9
$[Tl(H_2O)_6]^{3+}$	2.23	0.6

Solutions of Salts

Salts of strong acid – strong base

$$HCl + KOH \leftrightarrows H_2O + KCl$$

$$H^+ + Cl^- + K^+ + OH^- \leftrightarrows H_2O + K^+ + Cl^-$$

No effect on pH
Neutral

Salts of strong acid – weak base - hydrolysis

$$HNO_3 + NH_3 \leftrightarrows NH_4^+ + NO_3^-$$

$$NH_4^+ + H_2O \leftrightarrows NH_3 + H^+$$

Acidic soln

$$\boxed{pH = 7 - \tfrac{1}{2}\, pK_b - \tfrac{1}{2} \log c}$$

Solutions of Salts

Salts of weak acid – strong base - hydrolysis

$NaOH + HF \leftrightarrows H_2O + Na^+ + F^-$

$F^- + H_2O \leftrightarrows HF + OH^-$

Basic soln

$$\boxed{pH = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log c}$$

Salts of weak acid – weak base - hydrolysis

$NH_4^+ + H_2O + F^- + H_2O \leftrightarrows HF + OH^- + NH_3 + H^+$

$$pH = 7 + \frac{1}{2} (pK_a - pK_b)$$

Buffers

1 M acetic acid (HAc) and 1 M sodium acetate (NaAc) in 1 l of solution. NaAc decreases acidity of HAc.

$$\mathrm{HAc} + \mathrm{H_2O} \leftrightarrows \mathrm{Ac^-} + \mathrm{H_3O^+}$$

$$\mathrm{Ac^-} + \mathrm{H_2O} \leftrightarrows \mathrm{HAc} + \mathrm{HO^-}$$

Buffer function = keep constant pH

1. Addition of H^+ forms new molecules of HAc
2. Addition of OH^- forms new molecules of Ac^-
3. pH is constant

Buffers

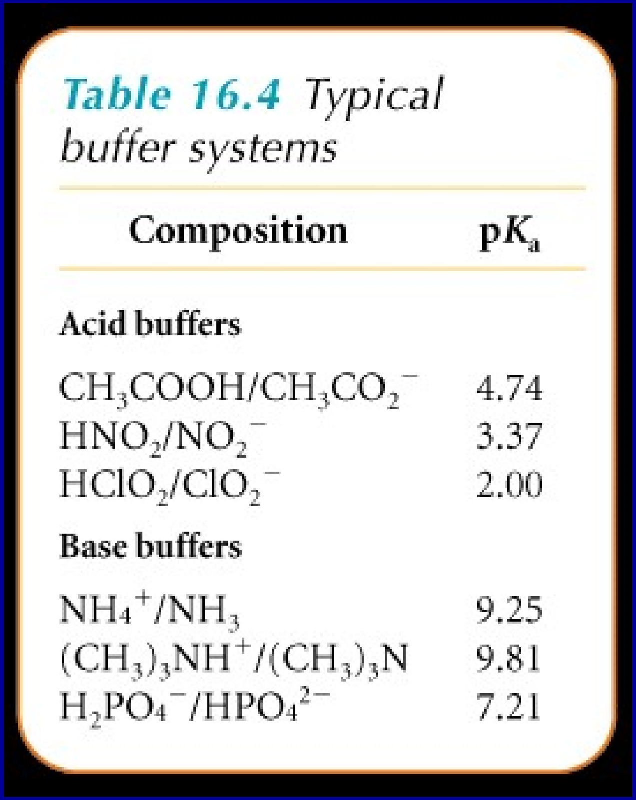


Table 16.4 Typical buffer systems

Composition	pK_a
Acid buffers	
$CH_3COOH/CH_3CO_2^-$	4.74
HNO_2/NO_2^-	3.37
$HClO_2/ClO_2^-$	2.00
Base buffers	
NH_4^+/NH_3	9.25
$(CH_3)_3NH^+/(CH_3)_3N$	9.81
$H_2PO_4^-/HPO_4^{2-}$	7.21

Henderson-Hasselbalch eq

Weak acid and its salt

$$pH = pK_a + \log([A^-] / [HA])$$

Weak base and its salt

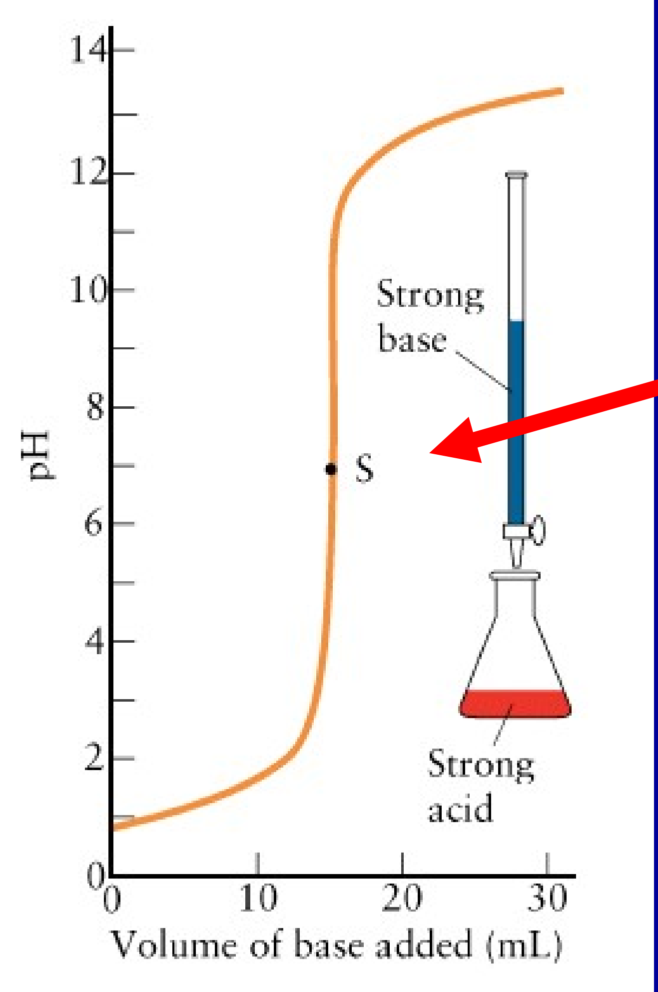
$$pH = pK_a + \log([B] / [BH^+])$$

$$= 14 - pK_b + \log([B] / [BH^+])$$

Acid-Base Equilibria

1. Ion product of water $K_w = [H^+][OH^-]$
2. Dissociation constant $K_a = [H_3O^+]\ [A^-]\ /\ [HA]$
3. Electroneutrality $[H_3O^+] = [A^-] + [OH^-]$
4. Mass balance $[HA]_0 = [A^-] + [HA]$

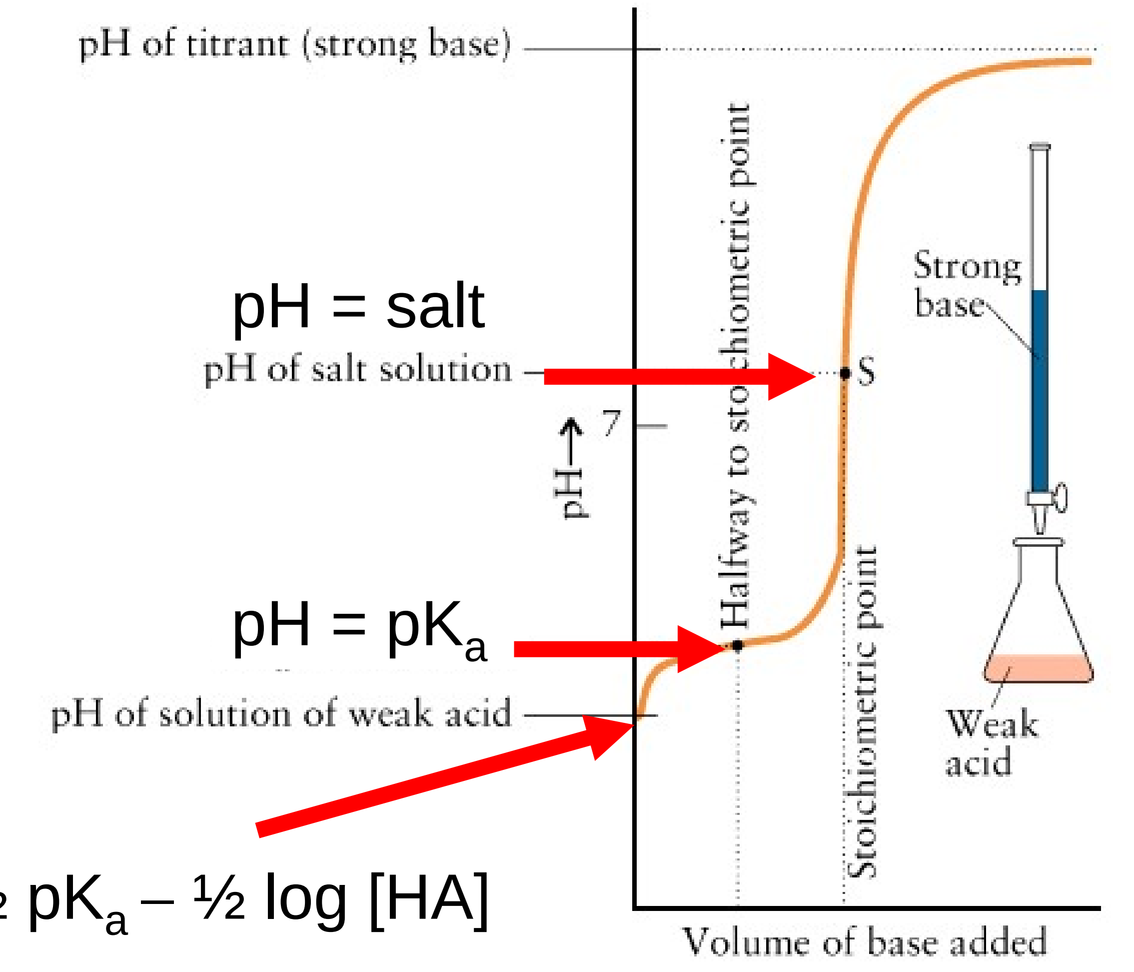
Titration – Controlled Acid-Base Reaction



Titration of strong acid (HCl)
By strong base (KOH)

Equivalence point
= stoichiometric reaction

Titration of Weak Acid by Strong Base



pH = salt

pH = pK_a

pH = ½ pK_a – ½ log [HA]

Titration of Weak Acid by Strong Base

$HAc + OH^- \leftrightarrows Ac^- + H_2O$

Start of titration : $pH = \frac{1}{2} pK_a - \frac{1}{2} \log [HA]$

Half-way
at $[A^-] = [HA]$, tj. 50% neutralized (weak acid. + salt):
$pH = pK_a + \log ([A^-] / [HA])$
$pH = pK_a$

At equivalence, $[A^-] = 100\,[HA]$
NEVER $[HA] = 0$

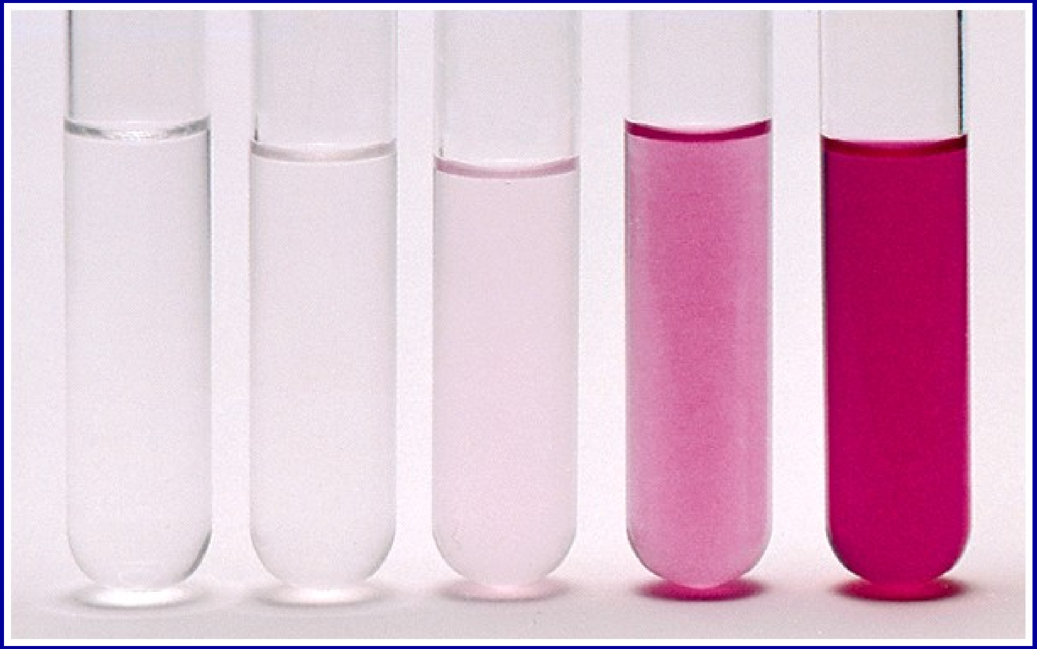
$pH = pK_a + \log (100 / 1) = pK_a + 2$

Indicators

Acid and its conjugated base have different color

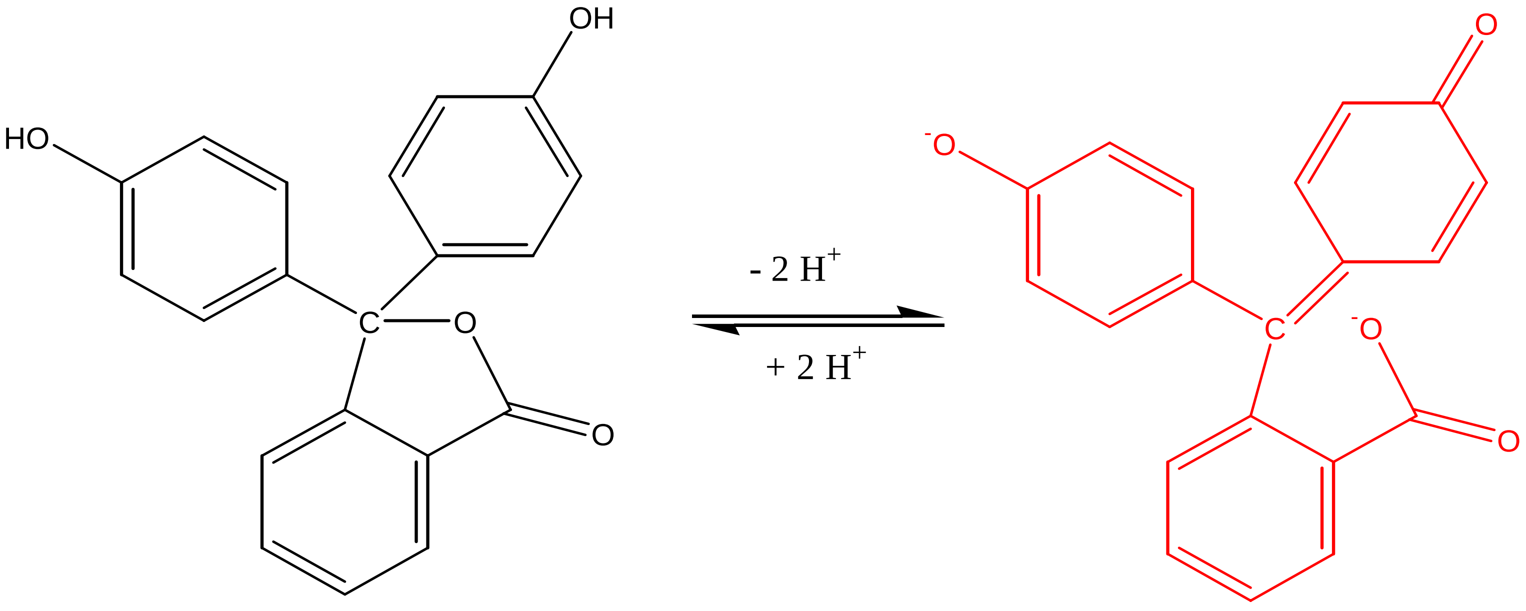
$HIn + H_2O \leftrightarrows H_3O^+ + In^-$

Phenolphtalein



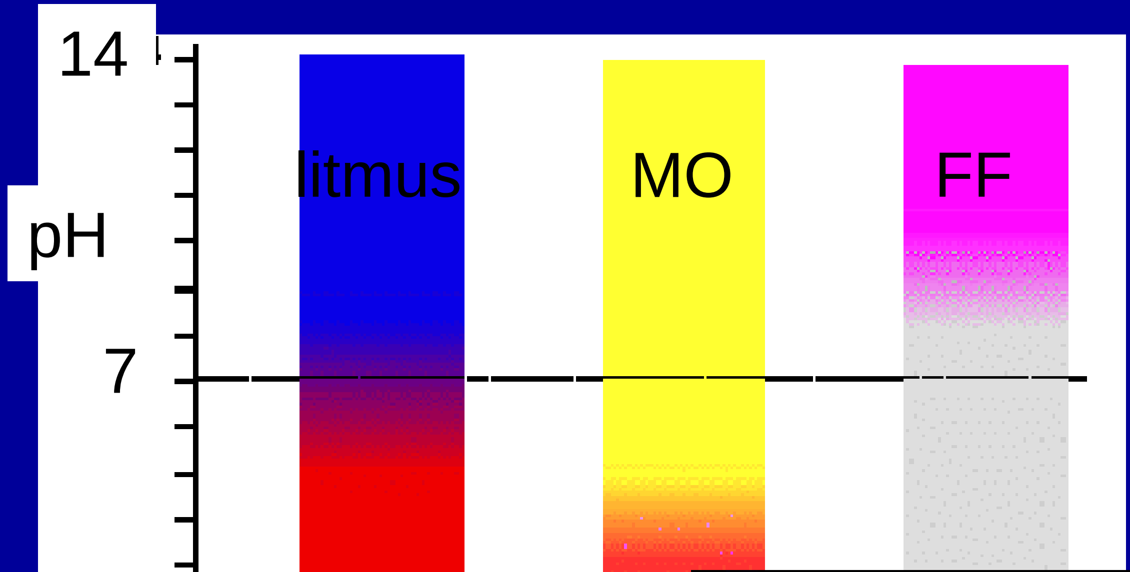
pH = 7.0 8.5 9.4 9.8 12.0

Phenolphtalein



Colorless

Red



Color change
$pH = pK_{IN} \pm 1$

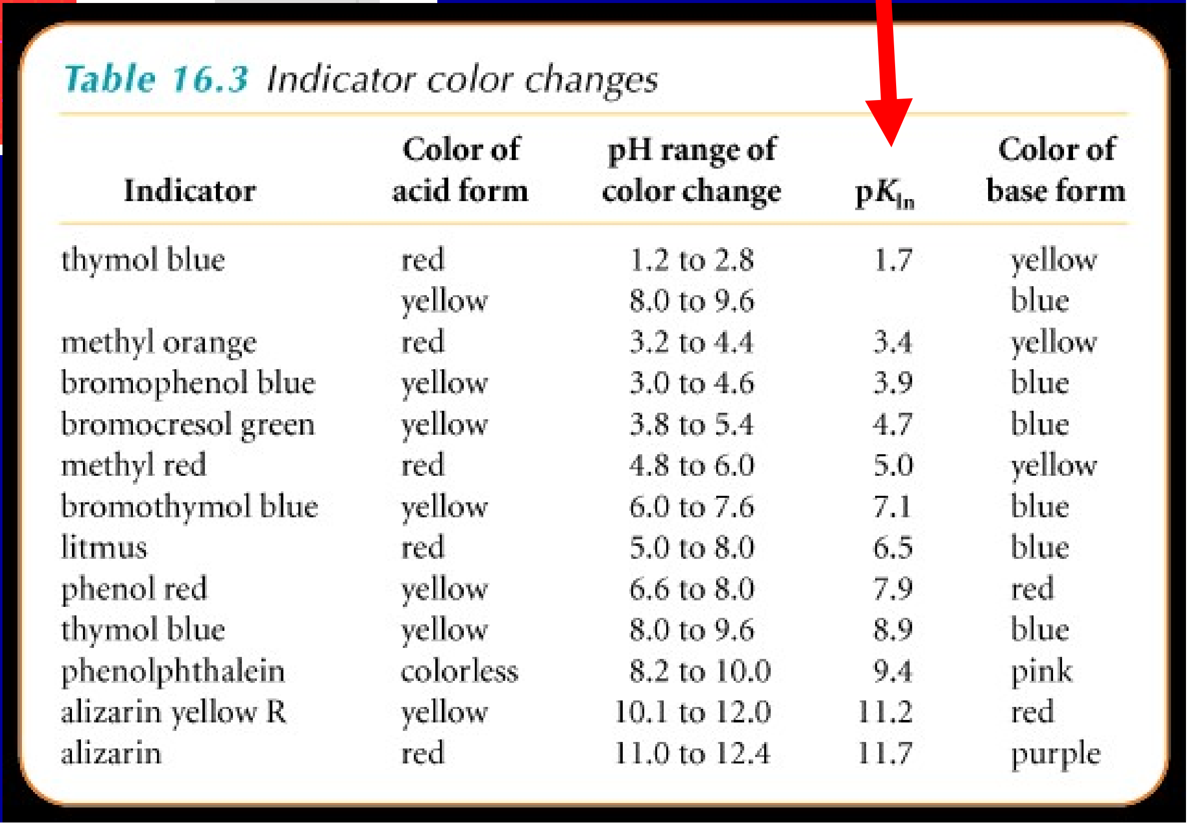


Table 16.3 *Indicator color changes*

Indicator	Color of acid form	pH range of color change	pK_{In}	Color of base form
thymol blue	red	1.2 to 2.8	1.7	yellow
	yellow	8.0 to 9.6		blue
methyl orange	red	3.2 to 4.4	3.4	yellow
bromophenol blue	yellow	3.0 to 4.6	3.9	blue
bromocresol green	yellow	3.8 to 5.4	4.7	blue
methyl red	red	4.8 to 6.0	5.0	yellow
bromothymol blue	yellow	6.0 to 7.6	7.1	blue
litmus	red	5.0 to 8.0	6.5	blue
phenol red	yellow	6.6 to 8.0	7.9	red
thymol blue	yellow	8.0 to 9.6	8.9	blue
phenolphthalein	colorless	8.2 to 10.0	9.4	pink
alizarin yellow R	yellow	10.1 to 12.0	11.2	red
alizarin	red	11.0 to 12.4	11.7	purple

Indicators

$HIn + H_2O \quad \leftrightarrows \quad H_3O^+ + In^-$

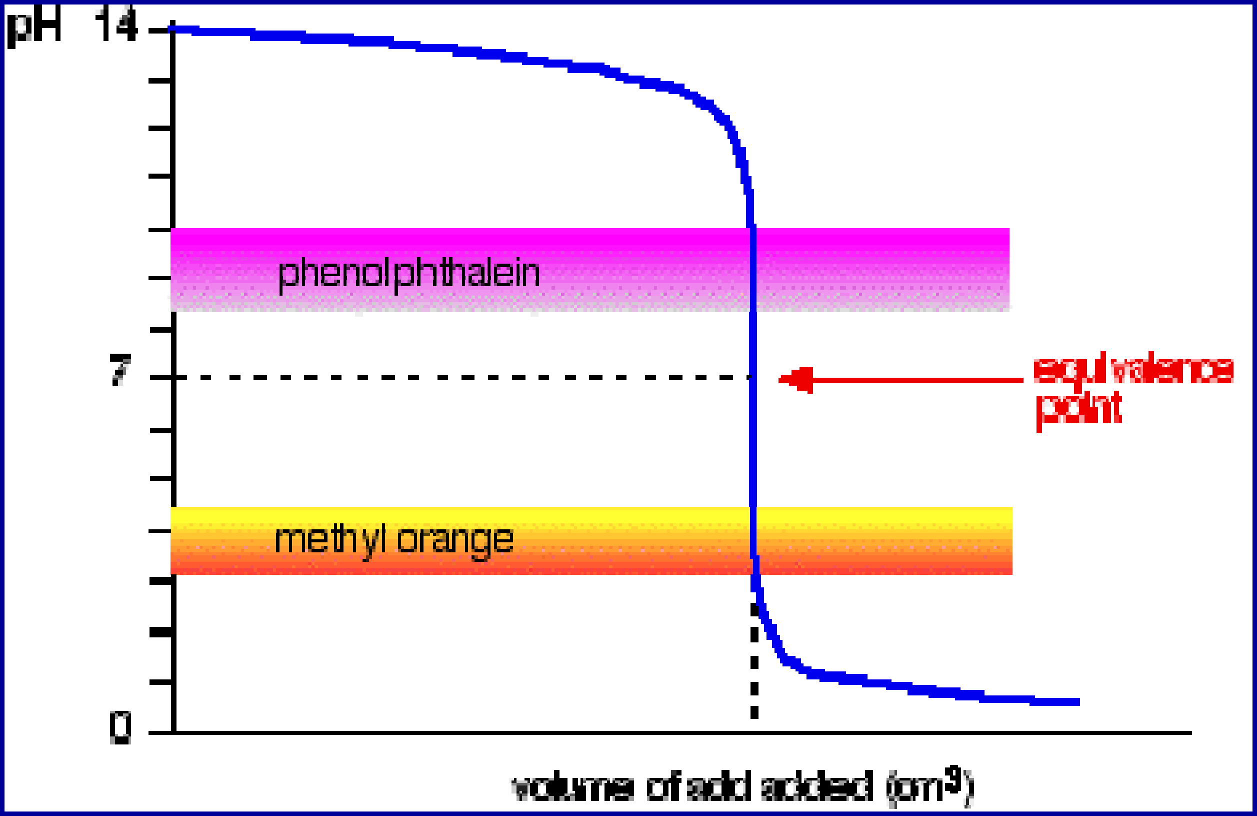
$K_{IN} = [H_3O^+] [In^–] / [HIn]$

A color change is recognizable if the other form is present in at least 10% amount

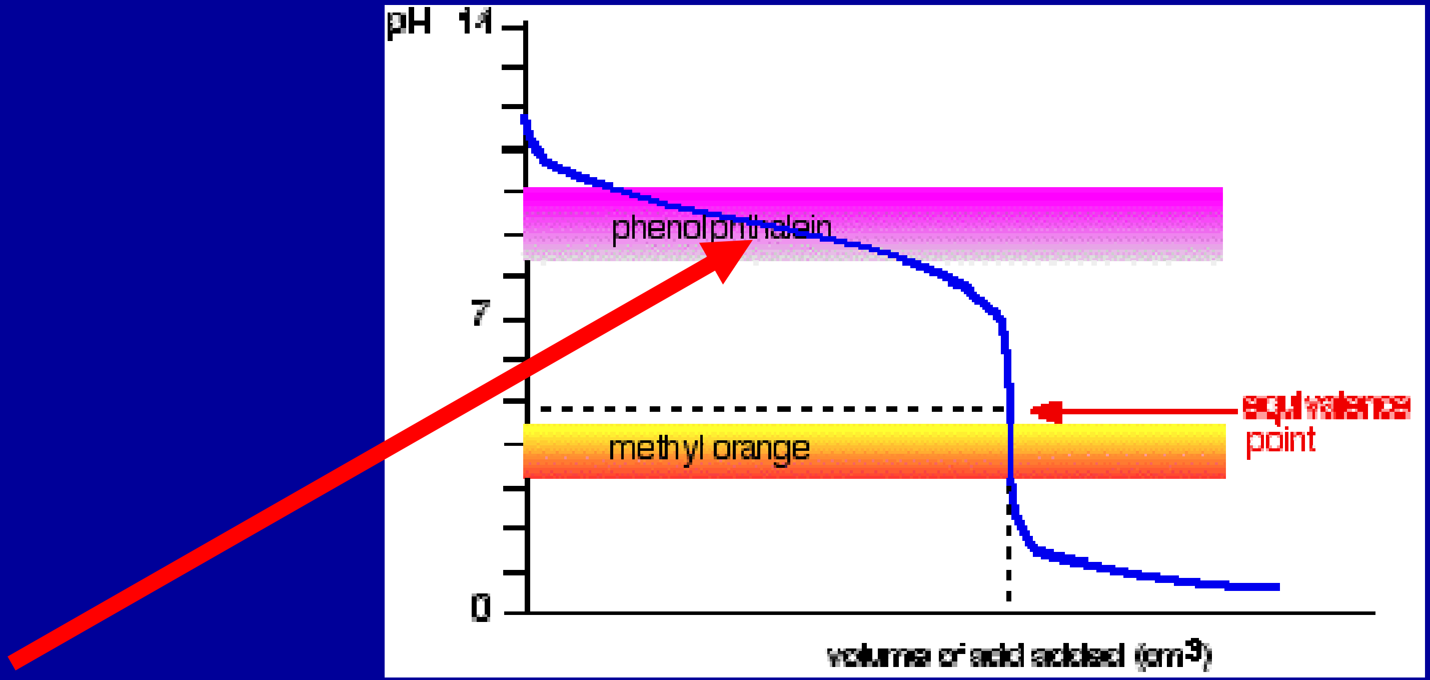
$[H_3O^+] = K_{IN} ([HIn] / [In^–])$ from 10:1 to 1:10

$pH = pK_{IN} \pm 1$

Titration of Strong Base by Strong Acid

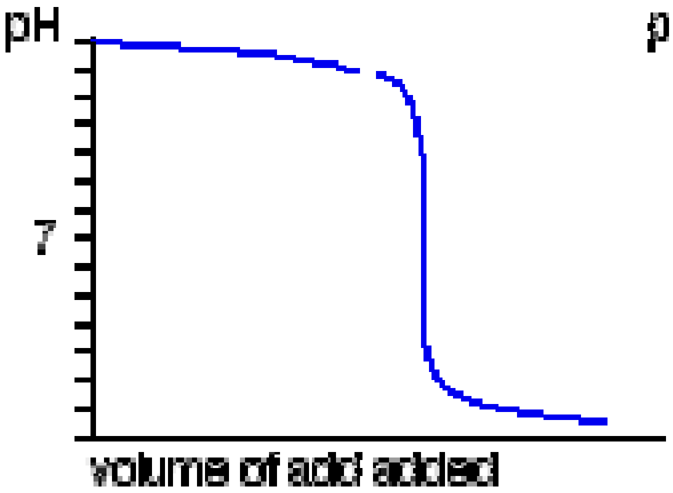


Titration of Weak Base by Strong Acid

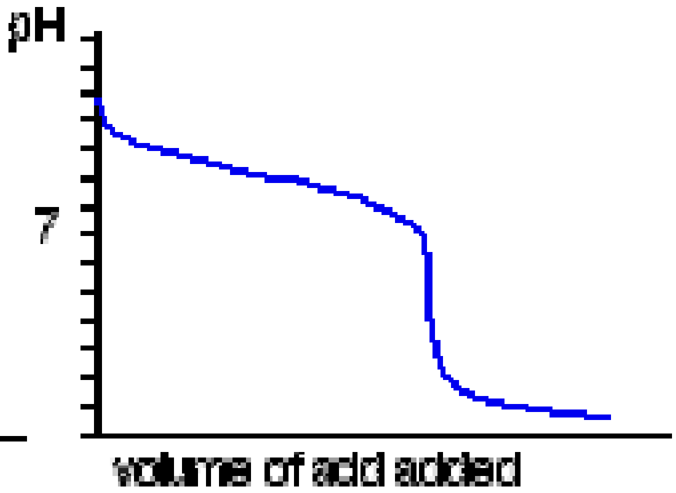


$[B] = [BH^+]$ $\quad pH = pK_a + \log([B] / [BH^+])$
$= 14 - pK_b + \log([B] / [BH^+]) = 14 - pK_b$

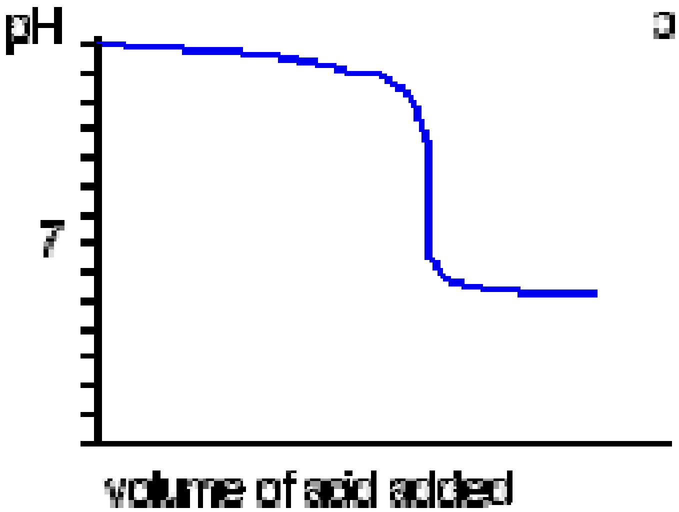
Equivalence $pH = 14 - pK_b + \log([1] / [100]) = 14 - pK_b - 2$



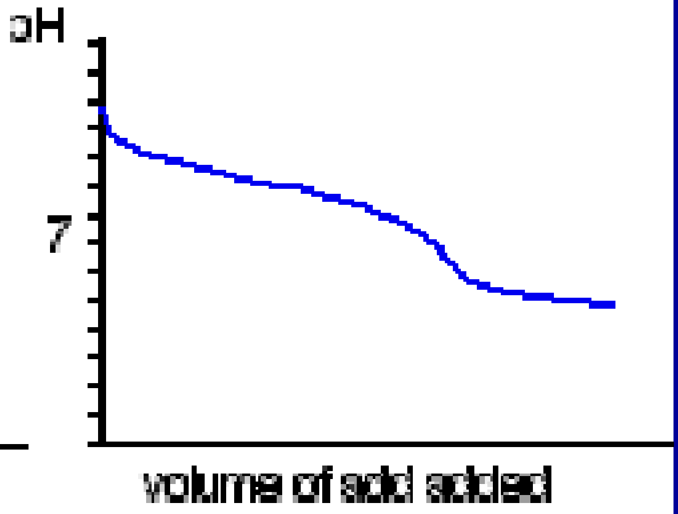
strong acid - strong base



strong acid - weak base



weak acid - strong base



weak acid - weak base

HSAB = Hard and Soft Acids and Bases

Hard Acids

Ti^{4+}, Cr^{3+}, Fe^{3+}, Co^{3+} , H^{+}

Hard Bases

NH_3, NH_2R, N_2H_4, H_2O, OH^-, O^{2-}, ROH, RO^-, OR_2, CO_3^{2-}, SO_4^{2-}, $OClO_3^-$, Cl^-, F^-, NO_3^-, PO_4^{3-}, OCOMe

Soft Acids

Cu^{+}, Ag^{+}, Hg^{+}, Hg^{2+}, Pd^{2+}, Pt^{2+}

Soft Bases

H^-, R^-, C_2H_2, C_6H_6, CN^-, CO, SCN^-, PR_3, $P(OR)_3$, AsR_3, SR_2, SHR, SR^-, I^-

$$SO_3^{2-} + HF \rightleftharpoons HSO_3^{-} + F^{-}$$