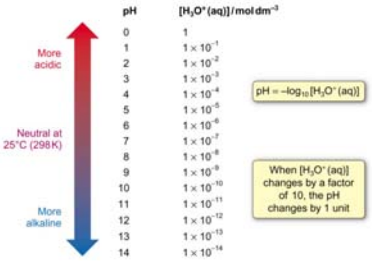
Lecture 14

Acid/base equilibria.

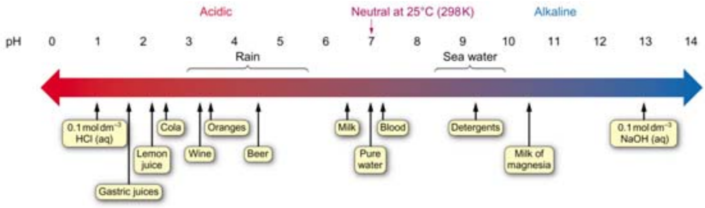
pK_a and pH



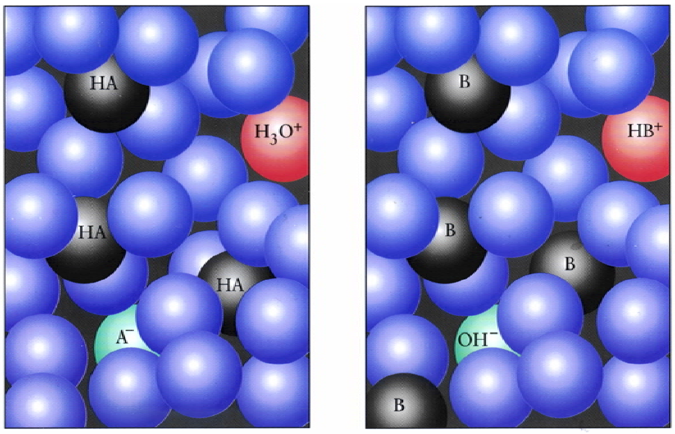
pH	$[H_3O^+(aq)]$ / mol dm^{-3}
0	1
1	1×10^{-1}
2	1×10^{-2}
3	1×10^{-3}
4	1×10^{-4}
5	1×10^{-5}
6	1×10^{-6}
7	1×10^{-7}
8	1×10^{-8}
9	1×10^{-9}
10	1×10^{-10}
11	1×10^{-11}
12	1×10^{-12}
13	1×10^{-13}
14	1×10^{-14}

$pH = -\log_{10}[H_3O^+(aq)]$

When $[H_3O^+(aq)]$ changes by a factor of 10, the pH changes by 1 unit



Acid/base equilibria.



Figures 3 and 4.14, page 520
Atkins/Jones: *Chemistry: Molecules, Matter, and Change*, **3e**
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Acid strength : the acid dissociation constant K_A.

Chemistry^3 Section 6.2. pp.268-270.

Acid dissociation equilibrium

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

$$K_C = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

$$K_A = K_C[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

Acid dissociation constant

- It is easy to quantify the strength of strong acids since they fully dissociate to ions in solution.
- The situation with respect to weak acids is more complex since they only dissociate to a small degree in solution.
- The question is how small is small?
- We quantify the idea of incomplete dissociation of a weak acid HA by noting that the dissociation reaction is an equilibrium process and introducing the acid dissociation constant K_A.

K_A is a measure of the acid strength.
When K_A is large there is considerable Dissociation and the acid is strong.
When K_A is small there is a small degree of dissociation, and the acid is weak.

K_A values vary over a wide range so it is best to use a log scale.

$$pK_A = -\log_{10} K_A$$

The Meaning of K_A , the Acid Dissociation Constant

For the ionization of an acid, HA:

$$HA_{(aq)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + A^-_{(aq)}$$

$$K_c = \frac{[H_3O^+]\,[A^-]}{[HA]\,[H_2O]}$$

Since the concentration of water is high, and does not change significantly during the reaction, it's value is absorbed into the constant.

Therefore:

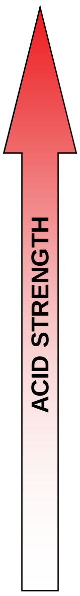
$$K_c = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

The stronger the acid, the higher the $[H_3O^+]$ at equilibrium, and the larger the K_a:

Stronger acid → higher $[H_3O^+]$ → larger K_a

For a weak acid with a relative high K_a (~10^{-2}), a 1 *M* solution has ~10% of the HA molecules dissociated.
For a weak acid with a moderate K_a (~10^{-5}), a 1 *M* solution has ~ 0.3% of the HA molecules dissociated.
For a weak acid with a relatively low K_a (~10^{-10}), a 1 *M* solution has ~ 0.001% of the HA molecules dissociated.

Acid strengths and K_a value.



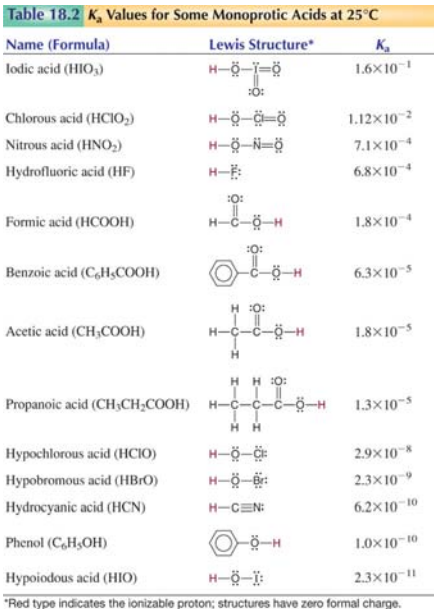


Table 18.2 K_a Values for Some Monoprotic Acids at 25°C

Name (Formula)	Lewis Structure*	K_a
Iodic acid (HIO_3)	H—Ö—Ï=Ö ‖ :O:	1.6×10^{-1}
Chlorous acid ($HClO_2$)	H—Ö—C̈l=Ö	1.12×10^{-2}
Nitrous acid (HNO_2)	H—Ö—N̈=Ö	7.1×10^{-4}
Hydrofluoric acid (HF)	H—F̈:	6.8×10^{-4}
Formic acid (HCOOH)	:O: ‖ H—C—Ö—H	1.8×10^{-4}
Benzoic acid (C_6H_5COOH)	:O: ‖ ⌬—C—Ö—H	6.3×10^{-5}
Acetic acid (CH_3COOH)	H :O: | ‖ H—C—C—Ö—H | H	1.8×10^{-5}
Propanoic acid (CH_3CH_2COOH)	H H :O: | | ‖ H—C—C—C—Ö—H | | H H	1.3×10^{-5}
Hypochlorous acid (HClO)	H—Ö—C̈l:	2.9×10^{-8}
Hypobromous acid (HBrO)	H—Ö—B̈r:	2.3×10^{-9}
Hydrocyanic acid (HCN)	H—C≡N:	6.2×10^{-10}
Phenol (C_6H_5OH)	⌬—Ö—H	1.0×10^{-10}
Hypoiodous acid (HIO)	H—Ö—Ï:	2.3×10^{-11}

*Red type indicates the ionizable proton; structures have zero formal charge.

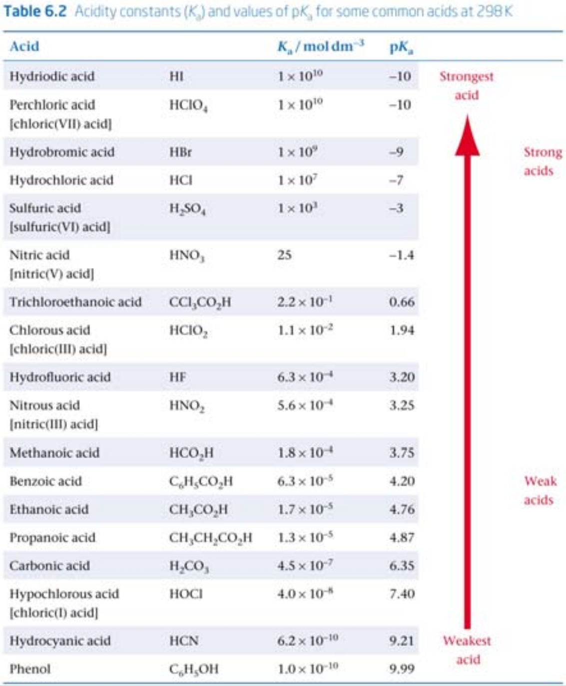


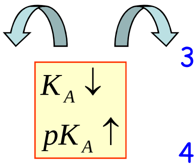
Table 6.2 Acidity constants (K_a) and values of pK_a for some common acids at 298 K

Acid		K_a / mol dm^{-3}	pK_a
Hydriodic acid	HI	1×10^{10}	−10
Perchloric acid [chloric(VII) acid]	$HClO_4$	1×10^{10}	−10
Hydrobromic acid	HBr	1×10^{9}	−9
Hydrochloric acid	HCl	1×10^{7}	−7
Sulfuric acid [sulfuric(VI) acid]	H_2SO_4	1×10^{3}	−3
Nitric acid [nitric(V) acid]	HNO_3	25	−1.4
Trichloroethanoic acid	CCl_3CO_2H	2.2×10^{-1}	0.66
Chlorous acid [chloric(III) acid]	$HClO_2$	1.1×10^{-2}	1.94
Hydrofluoric acid	HF	6.3×10^{-4}	3.20
Nitrous acid [nitric(III) acid]	HNO_2	5.6×10^{-4}	3.25
Methanoic acid	HCO_2H	1.8×10^{-4}	3.75
Benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	4.20
Ethanoic acid	CH_3CO_2H	1.7×10^{-5}	4.76
Propanoic acid	$CH_3CH_2CO_2H$	1.3×10^{-5}	4.87
Carbonic acid	H_2CO_3	4.5×10^{-7}	6.35
Hypochlorous acid [chloric(I) acid]	HOCl	4.0×10^{-8}	7.40
Hydrocyanic acid	HCN	6.2×10^{-10}	9.21
Phenol	C_6H_5OH	1.0×10^{-10}	9.99

The Relationship Between K_a and pK_a

$$\boxed{pK_A = -\log_{10} K_A}$$

Acid Name (Formula)	K_A at 298 K	pK_A
Hydrogen sulfate ion (HSO_4^-)	1.02 x 10^{-2}	1.991
Nitrous acid (HNO_2)	7.1 x 10^{-4}	3.15
Acetic acid (CH_3COOH)	1.8 x 10^{-5}	4.74
Hypobromous acid (HBrO)	2.3 x 10^{-9}	8.64
Phenol (C_6H_5OH)	1.0 x 10^{-10}	10.00



$K_A \downarrow$

$pK_A \uparrow$

When K_A is small pK_A is large and the acid does not dissociate in solution to a large extent. A change in 1 pK_A unit implies a 10 fold change in K_A value and hence acid strength.

K_a and pK_a

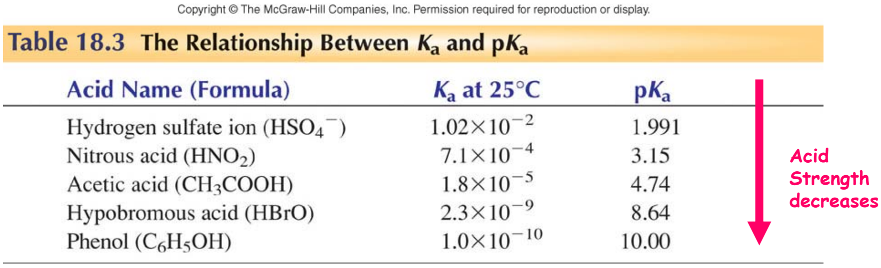


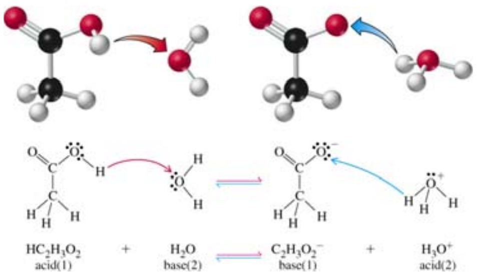
Table 18.3 The Relationship Between K_a and pK_a

Acid Name (Formula)	K_a at 25°C	pK_a
Hydrogen sulfate ion (HSO_4^-)	1.02×10^{-2}	1.991
Nitrous acid (HNO_2)	7.1×10^{-4}	3.15
Acetic acid (CH_3COOH)	1.8×10^{-5}	4.74
Hypobromous acid (HBrO)	2.3×10^{-9}	8.64
Phenol (C_6H_5OH)	1.0×10^{-10}	10.00

Acid Strength decreases

$$\boxed{pK_A = -\log_{10} K_A}$$

pK_a calculation



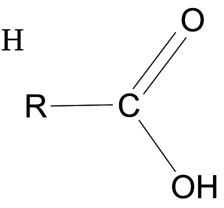
$$K_a = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]} = 1.8x10^{-5}$$

$$pK_a = -\log(1.8x10^{-5}) = 4.74$$

Weak acids

lactic acid $CH_3CH(OH)CO_2H$

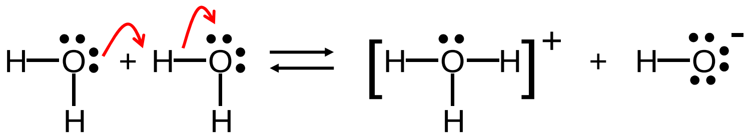
glycine $H_2NCH_2CO_2H$



Acid-Base Properties of Water

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

autoionization of water



base

conjugate acid

$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

acid

conjugate base

15.2

Autoionization of Water

$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+ + OH^-$

$$K_c = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

The ion-product for water, K_w:

$K_c[H_2O]^2 = K_w = [H_3O^+][OH^-] = 1.0 \underline{\text{ x } 10^{-14}}$ (at 298K)

For pure water the concentration of hydroxyl and hydronium ions must be equal:

$[H_3O^+] = [OH^-] = \sqrt{1.0 \text{ x } 10^{-14}}\ \underline{= 1.0 \text{ x } 10^{-7}}\ M$ (at 25°C)

The molarity of pure water is: $\dfrac{1000 g/L}{18.02\ g/mol} = 55.5\ M$

The Ion Product of Water

$$H_2O\ (l) \rightleftharpoons H^+\ (aq) + OH^-\ (aq) \qquad K_c = \frac{[H^+][OH^-]}{[H_2O]} \qquad [H_2O] = \text{constant}$$

$$K_c[H_2O] = K_w = [H^+][OH^-]$$

The ***ion-product constant*** (***K_w***) is the product of the molar concentrations of H^+ and OH^- ions **at a particular temperature.**

$$\boxed{\begin{array}{c}\text{At } 25^0\text{C} \\ K_w = [H^+][OH^-] = 1.0 \times 10^{-14}\end{array}}$$

	Solution Is
$[H^+] = [OH^-]$	neutral
$[H^+] > [OH^-]$	acidic
$[H^+] < [OH^-]$	basic

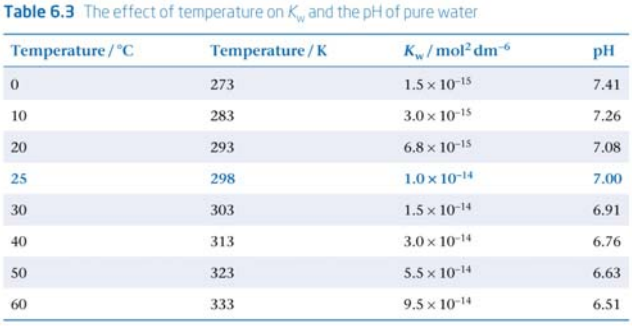


Table 6.3 The effect of temperature on K_w and the pH of pure water

Temperature / °C	Temperature / K	K_w / mol² dm⁻⁶	pH
0	273	1.5×10^{-15}	7.41
10	283	3.0×10^{-15}	7.26
20	293	6.8×10^{-15}	7.08
25	298	1.0×10^{-14}	7.00
30	303	1.5×10^{-14}	6.91
40	313	3.0×10^{-14}	6.76
50	323	5.5×10^{-14}	6.63
60	333	9.5×10^{-14}	6.51

Weak Bases and Base Ionization Constants

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

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

K_b ↑ weak base strength ↑

K_b = base ionization constant

Basicity Constant K_b.

$$B(aq) + H_2O\ (l) \rightleftharpoons BH^+\ (aq) + OH^-\ (aq)$$

- The proton accepting strength of a base is quantified in terms of the basicity constant K_b.
- The larger the value of K_b, the stronger the base.
- If K_b is large then pK_b will be small, and the stronger will be the base.
- Solve weak base problems like weak acids ***except*** solve for $[OH^-]$ instead of $[H^+]$.

$$K_C = \frac{[BH^+][OH^-]}{[B][H_2O]}$$

$$K_b = K_C[H_2O] = \frac{[BH^+][OH^-]}{[B]}$$

$$pK_b = -\log_{10} K_b$$

$$K_a K_b = K_W$$

$$pK_a + pK_b = pK_W$$

Ionization Constants of Conjugate Acid-Base Pairs

$$\cancel{H}A\ (aq) \rightleftharpoons H^+\ (aq) + \cancel{A}^-\ (aq) \qquad K_a$$

$$\underline{\cancel{A}^-\ (aq) + H_2O\ (l) \rightleftharpoons OH^-\ (aq) + \cancel{H}A\ (aq)} \qquad K_b$$

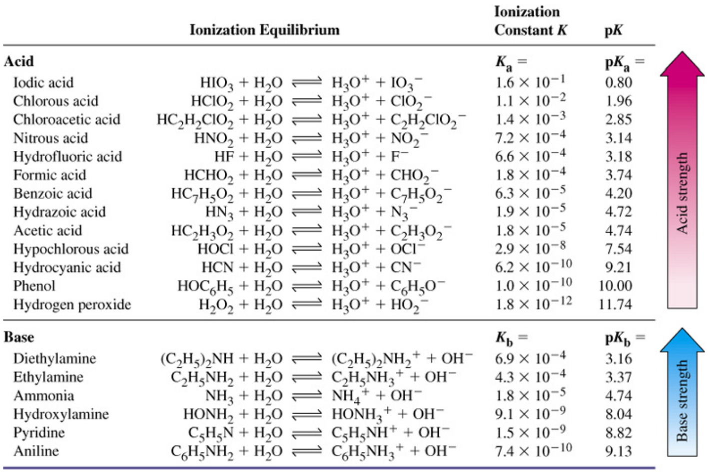
$$H_2O\ (l) \rightleftharpoons H^+\ (aq) + OH^-\ (aq) \qquad K_w$$

$$\boxed{K_aK_b = K_w}$$

Weak Acid and Its Conjugate Base

$$K_a = \frac{K_w}{K_b} \qquad K_b = \frac{K_w}{K_a}$$

Acid and base dissociation constants



	Ionization Equilibrium	Ionization Constant K	pK
Acid		K_a =	pK_a =
Iodic acid	$HIO_3 + H_2O \rightleftharpoons H_3O^+ + IO_3^-$	1.6×10^{-1}	0.80
Chlorous acid	$HClO_2 + H_2O \rightleftharpoons H_3O^+ + ClO_2^-$	1.1×10^{-2}	1.96
Chloroacetic acid	$HC_2H_2ClO_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_2ClO_2^-$	1.4×10^{-3}	2.85
Nitrous acid	$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$	7.2×10^{-4}	3.14
Hydrofluoric acid	$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	6.6×10^{-4}	3.18
Formic acid	$HCHO_2 + H_2O \rightleftharpoons H_3O^+ + CHO_2^-$	1.8×10^{-4}	3.74
Benzoic acid	$HC_7H_5O_2 + H_2O \rightleftharpoons H_3O^+ + C_7H_5O_2^-$	6.3×10^{-5}	4.20
Hydrazoic acid	$HN_3 + H_2O \rightleftharpoons H_3O^+ + N_3^-$	1.9×10^{-5}	4.72
Acetic acid	$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$	1.8×10^{-5}	4.74
Hypochlorous acid	$HOCl + H_2O \rightleftharpoons H_3O^+ + OCl^-$	2.9×10^{-8}	7.54
Hydrocyanic acid	$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	6.2×10^{-10}	9.21
Phenol	$HOC_6H_5 + H_2O \rightleftharpoons H_3O^+ + C_6H_5O^-$	1.0×10^{-10}	10.00
Hydrogen peroxide	$H_2O_2 + H_2O \rightleftharpoons H_3O^+ + HO_2^-$	1.8×10^{-12}	11.74
Base		K_b =	pK_b =
Diethylamine	$(C_2H_5)_2NH + H_2O \rightleftharpoons (C_2H_5)_2NH_2^+ + OH^-$	6.9×10^{-4}	3.16
Ethylamine	$C_2H_5NH_2 + H_2O \rightleftharpoons C_2H_5NH_3^+ + OH^-$	4.3×10^{-4}	3.37
Ammonia	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}	4.74
Hydroxylamine	$HONH_2 + H_2O \rightleftharpoons HONH_3^+ + OH^-$	9.1×10^{-9}	8.04
Pyridine	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.5×10^{-9}	8.82
Aniline	$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$	7.4×10^{-10}	9.13

Determining a Value of K_A from the pH of a Solution of a Weak Acid.

Butyric acid, $HC_4H_7O_2$ (or $CH_3CH_2CH_2CO_2H$) is used to make compounds employed in artificial flavorings and syrups. A 0.250 M aqueous solution of $HC_4H_7O_2$ is found to have a pH of 2.72. Determine K_A for butyric acid.

$HC_4H_7O_2 + H_2O \rightleftarrows C_4H_7O_2 + H_3O^+$ $\quad Ka = ?$

For $HC_4H_7O_2$ K_A is likely to be much larger than K_W.

Therefore assume self-ionization of water is unimportant.

$HC_4H_7O_2 + H_2O \rightleftarrows C_4H_7O_2 + H_3O^+$

Initial conc.	0.250 M	0	0
Changes	$-x$ M	$+x$ M	$+x$ M
Equilbrm. conc.	$(0.250-x)$ M	x M	x M

$\text{Log}[H_3O^+] = -\text{pH} = -2.72$

$[H_3O^+] = 10^{-2.72} = 1.9\text{x}10^{-3} = x$

$$K_a = \frac{[H_3O^+]\,[C_4H_7O_2^-]}{[HC_4H_7O_2]} = \frac{1.9\text{x}10^{-3} \cdot 1.9\text{x}10^{-3}}{(0.250 - 1.9\text{x}10^{-3})}$$

$K_a = 1.5\text{x}10^{-5}$ *Check assumption:* $K_a >> K_W$.

SAMPLE PROBLEM 18.7: Determining Concentrations from K_a and Initial [HA]

PROBLEM: Propanoic acid (CH_3CH_2COOH, which we simplify and HPr) is an organic acid whose salts are used to retard mold growth in foods. What is the $[H_3O^+]$ of 0.10M HPr ($K_a = 1.3\text{x}10^{-5}$)?

PLAN: Write out the dissociation equation and expression; make whatever assumptions about concentration which are necessary; substitute.

Assumptions: For $HPr(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Pr^-(aq)$

$x = [HPr]_{diss} = [H_3O^+]_{from\ HPr} = [Pr^-]$

$$K_a = \frac{[H_3O^+][Pr^-]}{[HPr]}$$

SOLUTION:

Concentration(M)	**$HPr(aq)$**	**$+ H_2O(l)$**	**$\rightleftharpoons H_3O^+(aq)$**	**$+ Pr^-(aq)$**
Initial	0.10	-	0	0
Change	$-x$	-	$+x$	$+x$
Equilibrium	$0.10-x$	-	x	x

Since K_a is small, we will assume that $x << 0.10$

SAMPLE PROBLEM 18.7: Determining Concentrations from K_a and Initial [HA]

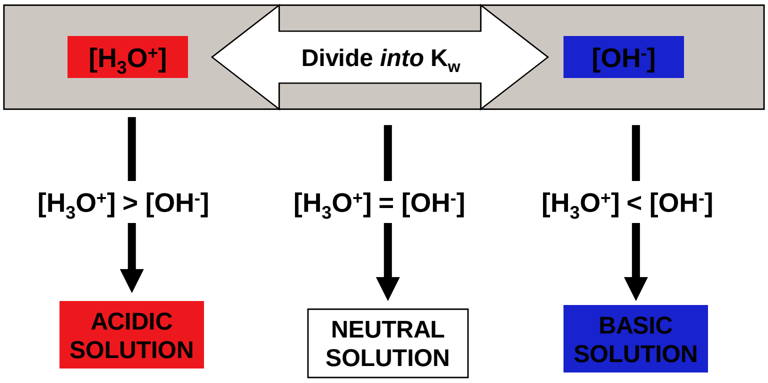
continued

$$1.3\text{x}10^{-5} = \frac{[H_3O^+][Pr^-]}{[HPr]} = \frac{(x)(x)}{0.10}$$

$$x = \sqrt{(0.10)(1.3\text{x}10^{-5})} = 1.1\text{x}10^{-3}\text{M} = [H_3O^+]$$

Check: $[HPr]_{diss} = 1.1\text{x}10^{-3}\text{M}/0.10\text{M} \text{ x } 100 = 1.1\%$

The relationship between $[H_3O^+]$ and $[OH^-]$ and the relative acidity of solutions.



$[H_3O^+]$

Divide *into* K_w

$[OH^-]$

$[H_3O^+] > [OH^-]$

$[H_3O^+] = [OH^-]$

$[H_3O^+] < [OH^-]$

ACIDIC SOLUTION

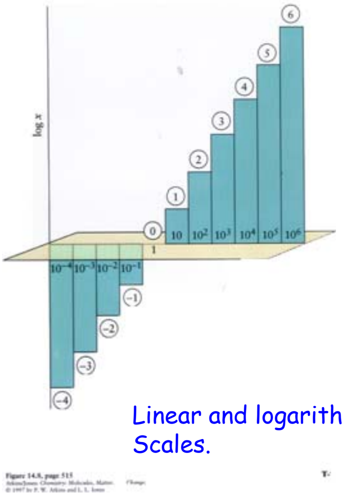
NEUTRAL SOLUTION

BASIC SOLUTION

The pH concept.

- The best quantitative measure of acidity or alkalinity rests in the determination of the concentration of hydrated protons $[H_3O^+]$ present in a solution.
- The $[H_3O^+]$ varies in magnitude over quite a large range in aqueous solution, typically from 1 M to 10^{-14} M.
- Hence to make the numbers meaningful $[H_3O^+]$ is expressed in terms of a logarithmic scale called the pH scale.
- The higher the $[H_3O^+]$, the more acidic the solution and the lower is the solution pH.

$$pH = -\log_{10}\left[H_3O^+\right]$$
$$\left[H_3O^+\right] = 10^{-pH}$$



Linear and logarithmic Scales.

Strong acids and bases

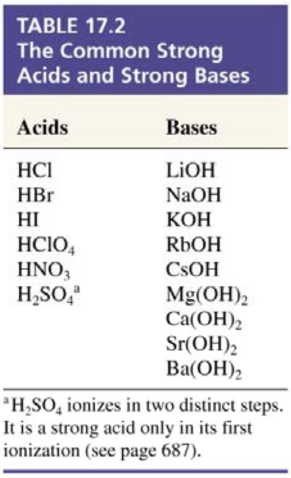


TABLE 17.2
The Common Strong Acids and Strong Bases

Acids	Bases
HCl	LiOH
HBr	NaOH
HI	KOH
$HClO_4$	RbOH
HNO_3	CsOH
H_2SO_4[a]	$Mg(OH)_2$
	$Ca(OH)_2$
	$Sr(OH)_2$
	$Ba(OH)_2$

[a] H_2SO_4 ionizes in two distinct steps. It is a strong acid only in its first ionization (see page 687).

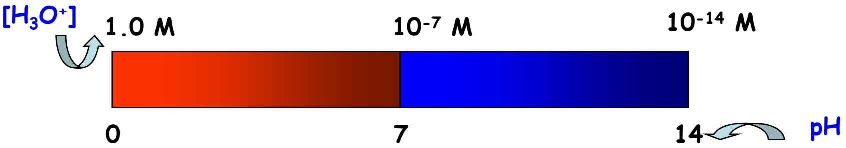
HCl CH_3CO_2H

Thymol Blue Indicator

pH < 1.2 < pH < 2.8 < pH

The pH Scale.

- pH is expressed on a numerical scale from 0 to 14.
- When $[H_3O^+] = 1.0$ M (i.e. 10^0M), pH = 0.
- When $[H_3O^+] = 10^{-14}$ M, pH = 14.
- pH value < 7 implies an acidic solution.
- pH value > 7 implies an alkaline solution.
- pH value = 7 implies that the solution is neutral.
- The definition of pH involves logarithms. Hence a change in one pH unit represents a change in concentration of H_3O^+ ions by a factor of 10.



The pH Values of Some Familiar Aqueous Solutions

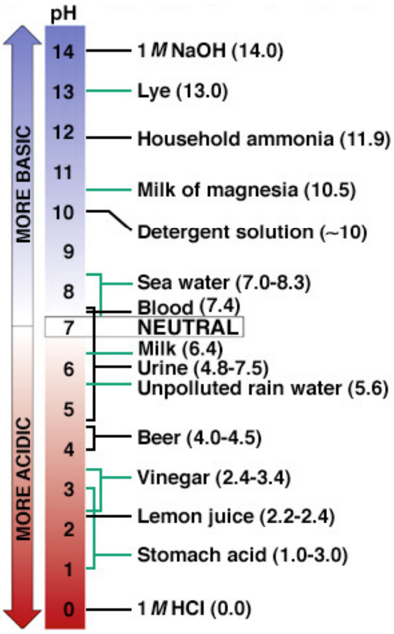
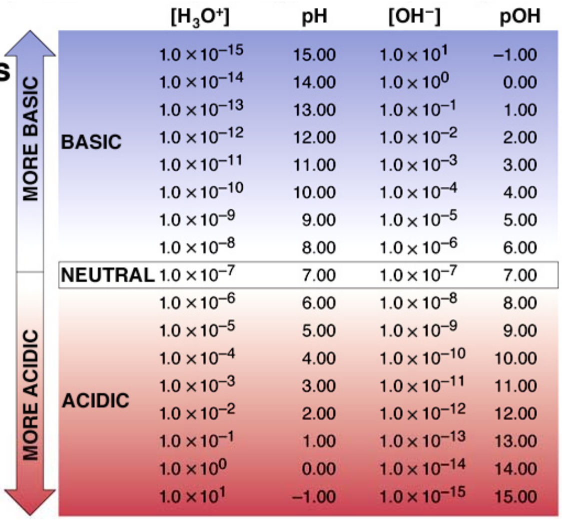


Fig. 18.5

The Relations Among $[H_3O^+]$, pH, $[OH^-]$, and pOH



	$[H_3O^+]$	pH	$[OH^-]$	pOH
BASIC	1.0×10^{-15}	15.00	1.0×10^{1}	−1.00
	1.0×10^{-14}	14.00	1.0×10^{0}	0.00
	1.0×10^{-13}	13.00	1.0×10^{-1}	1.00
	1.0×10^{-12}	12.00	1.0×10^{-2}	2.00
	1.0×10^{-11}	11.00	1.0×10^{-3}	3.00
	1.0×10^{-10}	10.00	1.0×10^{-4}	4.00
	1.0×10^{-9}	9.00	1.0×10^{-5}	5.00
	1.0×10^{-8}	8.00	1.0×10^{-6}	6.00
NEUTRAL	1.0×10^{-7}	7.00	1.0×10^{-7}	7.00
ACIDIC	1.0×10^{-6}	6.00	1.0×10^{-8}	8.00
	1.0×10^{-5}	5.00	1.0×10^{-9}	9.00
	1.0×10^{-4}	4.00	1.0×10^{-10}	10.00
	1.0×10^{-3}	3.00	1.0×10^{-11}	11.00
	1.0×10^{-2}	2.00	1.0×10^{-12}	12.00
	1.0×10^{-1}	1.00	1.0×10^{-13}	13.00
	1.0×10^{0}	0.00	1.0×10^{-14}	14.00
	1.0×10^{1}	−1.00	1.0×10^{-15}	15.00

$$pH = -\log_{10}\left[H_3O^+\right]$$
$$pOH = -\log_{10}\left[OH^-\right]$$

pH – A Measure of Acidity

$$\boxed{pH = -\log [H^+]}$$

Solution Is		At 25°C	
neutral	$[H^+] = [OH^-]$	$[H^+] = 1 \times 10^{-7}$	pH = 7
acidic	$[H^+] > [OH^-]$	$[H^+] > 1 \times 10^{-7}$	pH < 7
basic	$[H^+] < [OH^-]$	$[H^+] < 1 \times 10^{-7}$	pH > 7

pH ↑ $[H^+]$ ↓

Calculating $[H_3O^+]$, pH, $[OH^-]$, and pOH

PROBLEM: In a restoration project, a conservator prepares copper-plate etching solutions by diluting concentrated HNO_3 to 2.0M, 0.30M, and 0.0063M HNO_3. Calculate $[H_3O^+]$, pH, $[OH^-]$, and pOH of the three solutions at 25⁰C.

PLAN: HNO_3 is a strong acid so $[H_3O^+] = [HNO_3]$. Use K_w to find the $[OH^-]$ and then convert to pH and pOH.

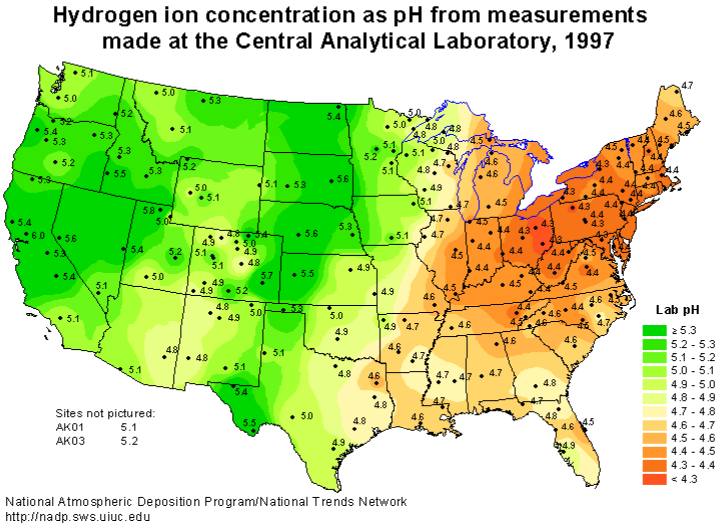
SOLUTION: For 2.0M HNO_3, $[H_3O^+] = 2.0M$ and $-\log [H_3O^+] = -0.30 = pH$
$[OH^-] = K_w/ [H_3O^+] = 1.0\text{x}10^{-14}/2.0 = 5.0\text{x}10^{-15}M$; pOH = 14.30

For 0.3M HNO_3, $[H_3O^+] = 0.30M$ and $-\log [H_3O^+] = 0.52 = pH$

$[OH^-] = K_w/ [H_3O^+] = 1.0\text{x}10^{-14}/0.30 = 3.3\text{x}10^{-14}M$; pOH = 13.48

For 0.0063M HNO_3, $[H_3O^+] = 0.0063M$ and $-\log [H_3O^+] = 2.20 = pH$

$[OH^-] = K_w/ [H_3O^+] = 1.0\text{x}10^{-14}/6.3\text{x}10^{-3} = 1.6\text{x}10^{-12}M$; pOH = 11.80

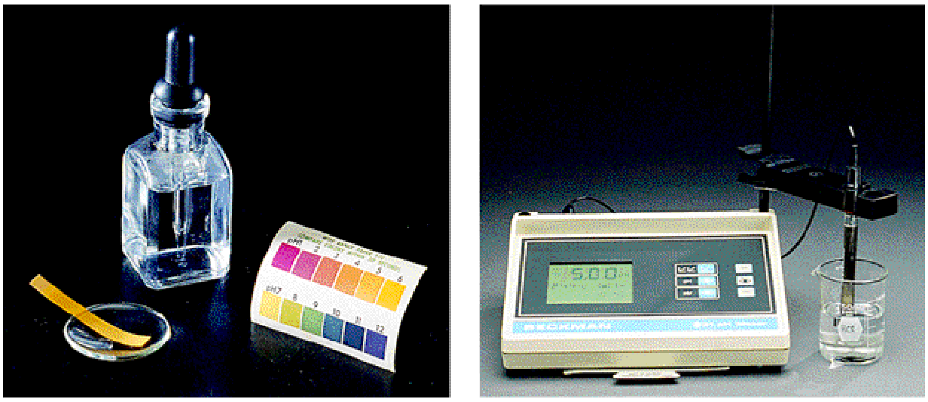


Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 1997

National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

The problem of acid rain.

Methods for Measuring the pH of an Aqueous Solution



(a) pH paper

(b) Electrodes of a pH meter

pH Measurement.

- Approximate pH of a solution determined by use of acid/base indicators.
  - Indicators are substances (weak acids) which change colour over a specific pH range when they donate protons.
  - We add a few drops of indicator (which changes colour over the required pH range) to the test solution and record the colour change produced.
  - This procedure is utilized in acid/base titrations. Universal indicator (mixture of pH indicators) often used for making approximate pH measurements in range 3-10.
  - As solution pH increases, the indicator changes colour from red to orange to yellow to green to blue, and finally to purple.

$$HIn(aq) + H_2O \rightarrow H_3O^+(aq) + In^-$$

- More accurate pH values determined using an electronic instrument called a pH meter.
  - The device (consisting of a probe electrode made of glass and associated electronics) measures the electrical potential generated across a glass membrane (which separates an internal solution of known $[H_3O^+]$ from the external test solution of unknown $[H_3O^+]$) located at the electrode tip.
  - This membrane potential is proportional to the pH of the test solution.
  - A digital readout of solution pH is obtained.
  - The pH meter is essentially a voltmeter connected to a chemical sensor probe which is sensitive to the concentration of hydrated protons.
  - The pH meter is an example of a potentiometric chemical sensor system. In a potentiometric chemical sensor, the measured voltage is proportional to the logarithm of the analyte concentration.

pH calculation : strong and weak acids.

- If acid is **strong** have **complete dissociation** then $[H^+]$ can be directly evaluated from stoichiometry of ionization reaction. Hence pH can be evaluated via its defining equation.
- For **weak** acids have incomplete ionization . To evaluate $[H^+]$ and hence pH we need to evaluate **degree of ionization** α and we also require a knowledge of K_a .

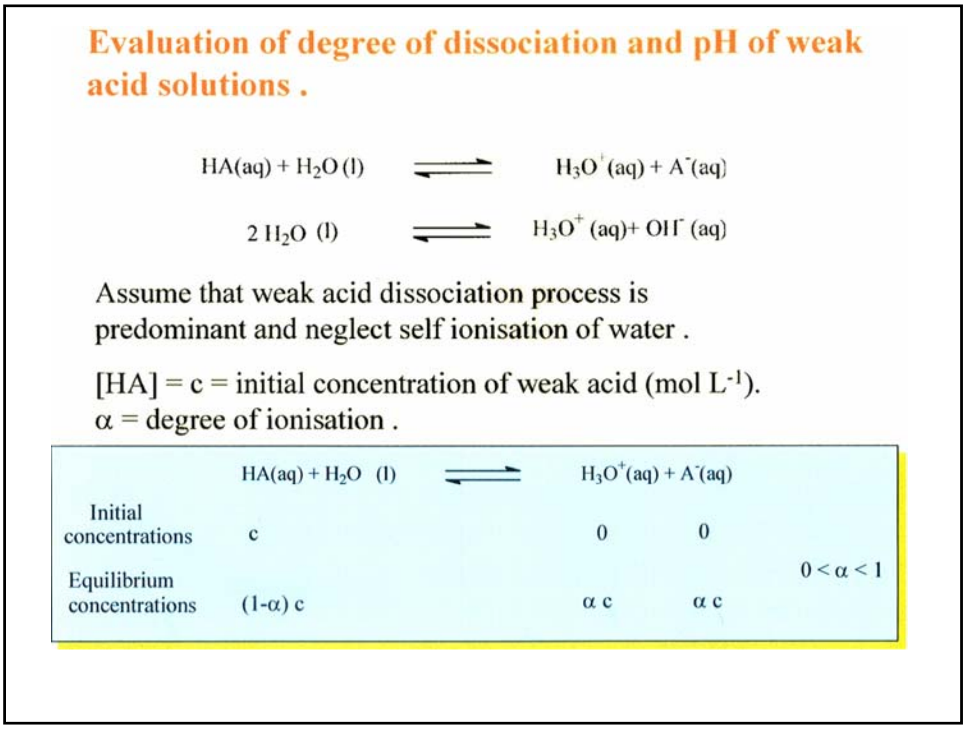
Weak acid case

$$\alpha = \sqrt{\frac{K_a}{c}}$$

$$\left[H_3O^+\right] = \sqrt{cK_a}$$

$$c = [HA]$$

$$pH = \log_{10}\left[H_3O^+\right] = \log_{10}\left\{\sqrt{cK_a}\right\}$$



Evaluation of degree of dissociation and pH of weak acid solutions .

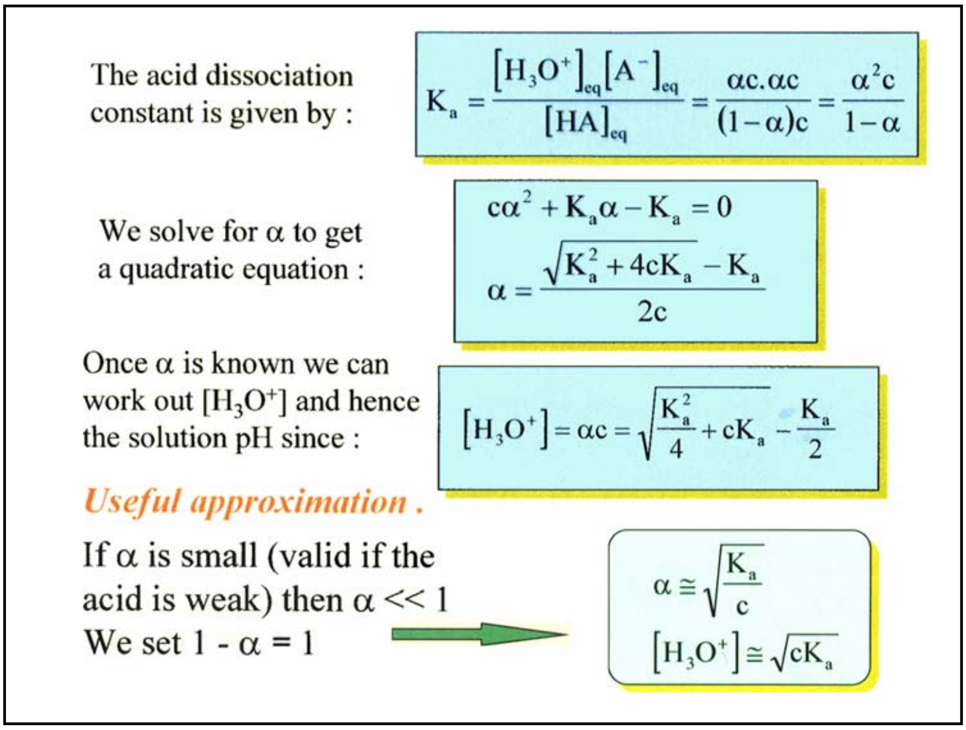
$$HA(aq) + H_2O\,(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

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

Assume that weak acid dissociation process is predominant and neglect self ionisation of water .

$[HA] = c$ = initial concentration of weak acid (mol L^{-1}).
α = degree of ionisation .

	$HA(aq) + H_2O\,(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	$+ A^-(aq)$	
Initial concentrations	c		0	0	
Equilibrium concentrations	$(1-\alpha)\,c$		$\alpha\,c$	$\alpha\,c$	$0 < \alpha < 1$



The acid dissociation constant is given by :

$$K_a = \frac{[H_3O^+]_{eq}[A^-]_{eq}}{[HA]_{eq}} = \frac{\alpha c.\alpha c}{(1-\alpha)c} = \frac{\alpha^2 c}{1-\alpha}$$

We solve for α to get a quadratic equation :

$$c\alpha^2 + K_a\alpha - K_a = 0$$

$$\alpha = \frac{\sqrt{K_a^2 + 4cK_a} - K_a}{2c}$$

Once α is known we can work out $[H_3O^+]$ and hence the solution pH since :

$$[H_3O^+] = \alpha c = \sqrt{\frac{K_a^2}{4} + cK_a} - \frac{K_a}{2}$$

Useful approximation .

If α is small (valid if the acid is weak) then $\alpha << 1$
We set $1 - \alpha = 1$ →

$$\alpha \cong \sqrt{\frac{K_a}{c}}$$

$$[H_3O^+] \cong \sqrt{cK_a}$$