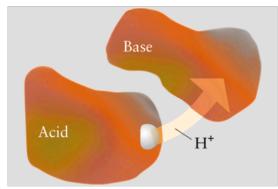
Acid-Base Reactions/ The pH concept. Dr Richard Doyle School of Chemistry Trinity College Dublin. rdoyle5@tcd.ie





Chemistry Preliminary Course 2012

Lecture Outline.

- 2 lectures dealing with some core chemistry :
 - acid/base reactions
 - the pH concept.
- These concepts will be studied in more detail during the main lecture course.
- Topics to be addressed:
 - What are acids and bases?
 - Can we provide a general definition of acid and base?
 How can we quantify acidity and basicity?
 Can we classify acid and base strength?

 - pH concept and pH scale.
 - 'Acid/bas'e react'ions: neutralization
 - How can we monitor an acid/base reaction in real time?
 - Acid/base titrations

Required Reading Material.

- Silberberg, Chemistry, 4th edition.
 - Chapter 18.
 - Acid/base equilibria. pp.766-813.
 - Chapter 19.
 - Ionic equilibria in aqueous systems. pp.814-862.
- Kotz, Treichel and Weaver, 7th edition.
 Chapter 17&18, pp.760-859.
- Burrows et al. Chemistry³ (OUP), 2009.Ch.6, pp.263-300.
- Lecture notes available after course on School of Chemistry website located at: <u>http://www.tcd.ie/Chemistry/outreach/prelim/</u>

Useful websites

- http://www.shodor.org/unchem/basic/ab/
- <u>http://chemistry.about.com/od/acidsbases</u>
 <u>/</u>
- <u>http://www.chem.neu.edu/Courses/1221P</u>
 <u>AM/acidbase/index.htm</u>
- <u>http://dbhs.wvusd.k12.ca.us/webdocs/Aci</u>
 <u>dBase/AcidBase.html</u>
- <u>http://www.sparknotes.com/chemistry/aci</u>
 <u>dsbases/fundamentals/section1.html</u>

Acids

- Have a sour taste.
 - Vinegar owes its taste to acetic acid.
 - Citrus fruits contain citric acid.
- React with certain metals to produce hydrogen gas.
- React with carbonates and bicarbonates to produce carbon dioxide gas.
 - Yeast free Baking

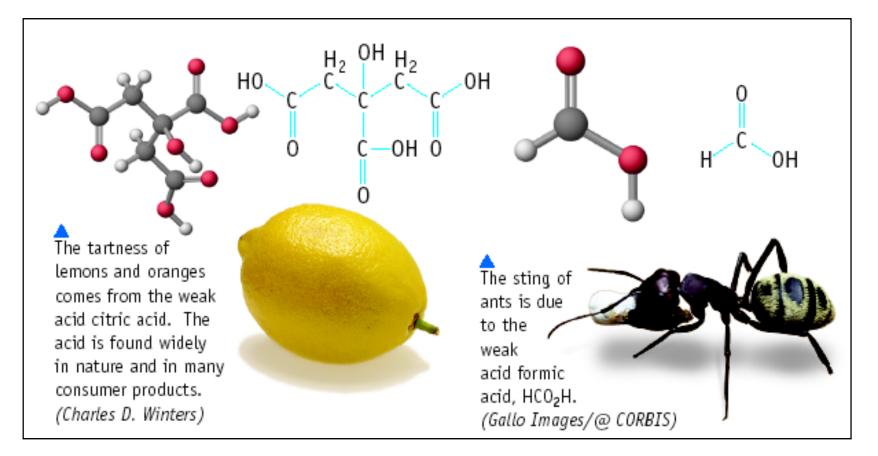
Bases

- Have a bitter taste.
 - Baking soda, dark unsweetened chocolate
- Feel slippery. Many soaps contain bases.



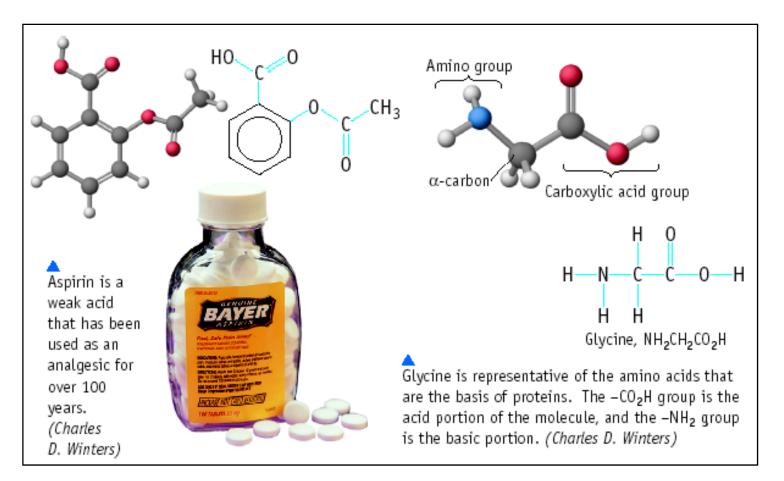


Acid and Bases

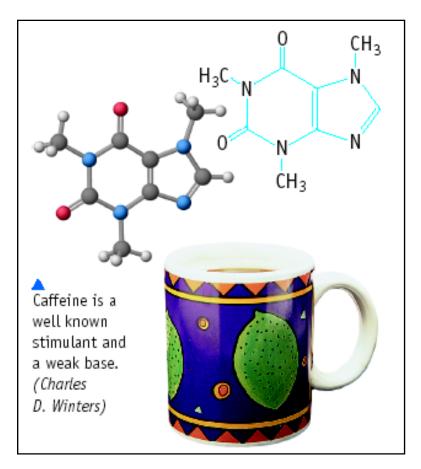


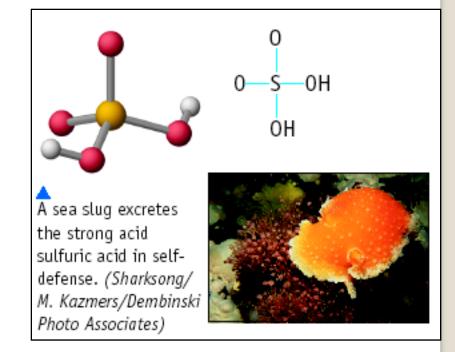
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Acid and Bases



Acid and Bases





Uses of Common Acids and Bases

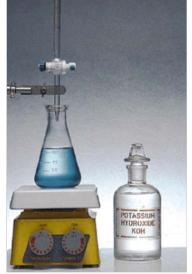
18.1 Some Common Acids and Bases and Their Household Uses

Substance	Formula	Use	
Acids			
Acetic acid (vinegar)	CH ₃ COOH (or HC ₂ H ₃ O ₂)	Flavoring, preservative	
Citric acid	H ₃ Č ₆ H ₅ O ₇	Flavoring	END STORES
Phosphoric acid	H ₃ PO₄	Rust remover	
Boric acid	B(OH) ₃ (or H ₃ BO ₃)	Mild antiseptic; insecticide	
Aluminum salts	NaAl(SO ₄) ₂ ·12H ₂ O	In baking powder, with sodium hydrogen carbonate	
Hydrochloric acid (muriatic acid)	HCI	Brick and ceramic tile cleaner	
Bases			
Sodium hydroxide (lye)	NaOH	Oven cleaner, unblocking plumbing	
Ammonia	NH ₃	Household cleaner	
Sodium carbonate	Na ₂ CO ₃	Water softener, grease remover	Pusons
Sodium hydrogen carbonate	NaHCO ₃	Fire extinguisher, rising agent in cake mixes (baking soda), mild antacid	
Trisodium phosphate	Na ₃ PO ₄	Cleaner for surfaces before painting or wallpapering	

Arrhenius (or Classical) Acid-Base Definition

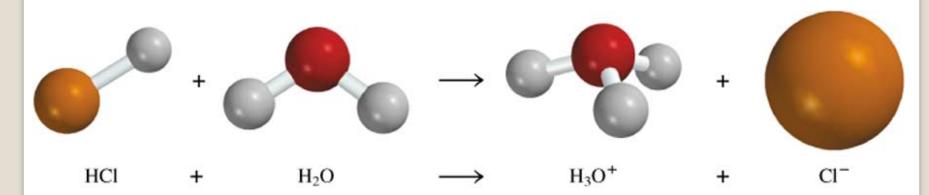
- Acid a neutral substance that contains hydrogen and dissociates or ionises in water to yield protons (H^+)or hydronium ions (H_3O^+).
- Base a neutral substance that contains the hydroxyl group and dissociates in water to yield hydroxide ions OH⁻.
- Neutralization the reaction of an H^+ (H_3O^+) ion from the acid and the OH ⁻ ion from the base to form water, H_2O .
- These definitions although correct are limited in that they are not very general and do not give a comprehensive idea of what acidity and basicity entails.

 $\begin{array}{ll} HCl \rightarrow H^{+}(aq) + Cl^{-}(aq) \\ NaOH \rightarrow Na^{+}(aq) + OH^{-}(aq) \end{array}$ $\begin{array}{ll} HCl + NaOH \rightarrow NaCl + H_{2}O \\ acid & base & salt & water \end{array}$

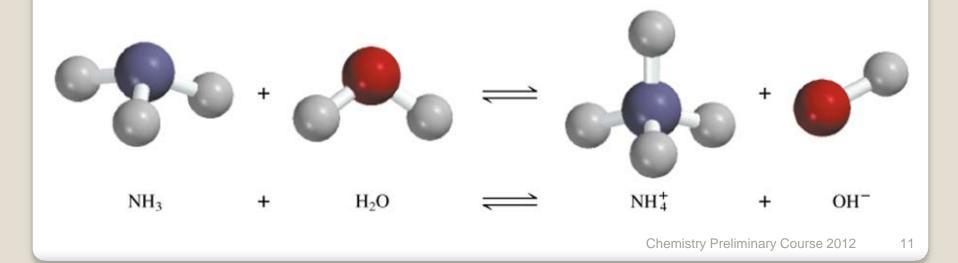


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Arrhenius acid is a substance that produces $H^+(H_3O^+)$ in water

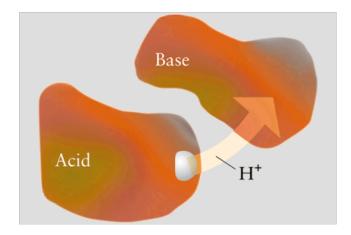


Arrhenius base is a substance that produces OH⁻ in water

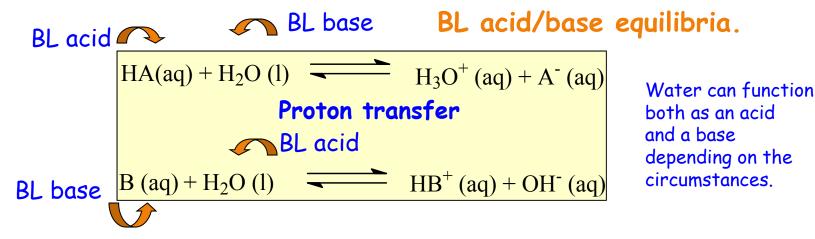


Acids and bases: Bronsted/Lowry definition.

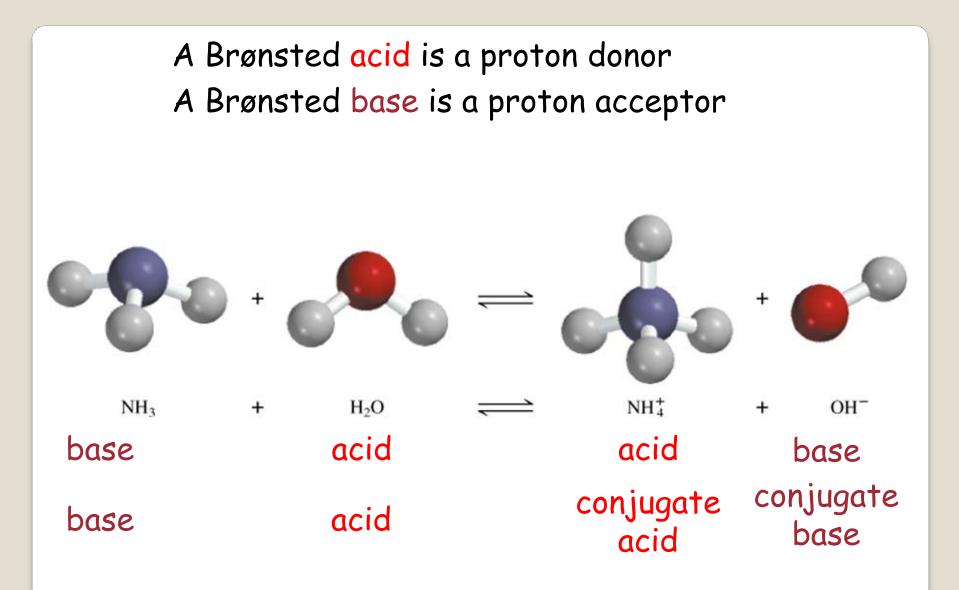
- Bronsted/Lowry Acid (HA): An acid is a species which <u>donates</u> a proton
- Bronsted/Lowry Base (B): A base is a species which <u>accepts</u> a proton.
- A more general definition and refer to the reaction between an acid and a base but not necessarily in water.
- An acid must contain H in its formula;
 - HNO_3 and $H_2PO_4^-$
- A base must contain a lone pair of electrons to bind the H⁺ ion;
 NH₃, CO₃²⁻, F⁻, as well as OH⁻.
- All Arrhenius acids/bases are Bronsted/Lowry acids/bases.



Bronsted/Lowry Perspective				
Acid: Proton Donor	Base: Proton Acceptor			
	n is the exchange of oton.			



- Proton donation and acceptance are dynamic processes
 proton transfer equilibrium is rapidly established in solution.
- The equilibrium reaction is described in terms of conjugate acid/base pairs.
- Conjugate base (CB) of a BL acid the base which forms when the acid has donated a proton.
- Conjugate acid (CA) of a BL base the acid which forms when the base has accepted a proton.
- A conjugate acid has one more proton than the base.
- A conjugate base has one less proton than the acid.
- If the acid of a conjugate acid/base pair is strong (good tendency to donate a proton) then the conjugate base will be weak (small tendency to accept a proton) and vice versa.

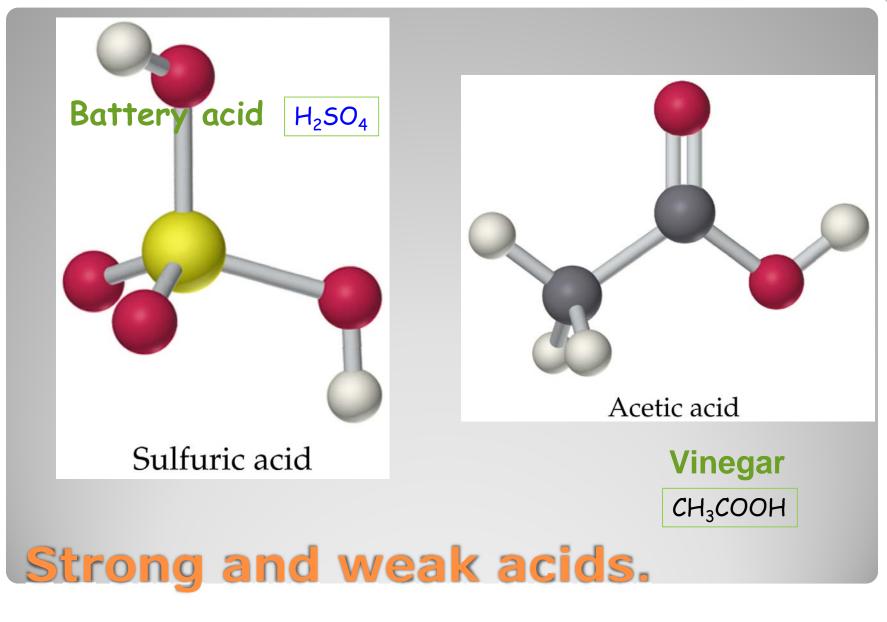


The Conjugate Pairs in Some Acid-Base Reactions							
	4	Conj	ugate Pair				
					_		
	Acid	+	Base	+	Base	+	Acid
				Conji	ugate Pair	7	
Reaction 1	HF	+	H₂O	\rightarrow	F⁻	+	H₃O⁺
Reaction 2	нсоон	+	CN⁻	+	HCOO-	+	HCN
Reaction 3	$\rm NH_4^+$	+	CO32-	+	NH_3	+	HCO3-
Reaction 4	H ₂ PO ₄ -	+	OH-	+	HPO42-	+	H ₂ O
Reaction 5	H_2SO_4	+	$N_2H_5^+$	+	HSO4-	+	N ₂ H ₆ ²⁺
Reaction 6	HPO42-	+	50 ₃ ²-	+	PO4 ³⁻	+	HSO₃ ⁻

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Quantifying acid/base strength.

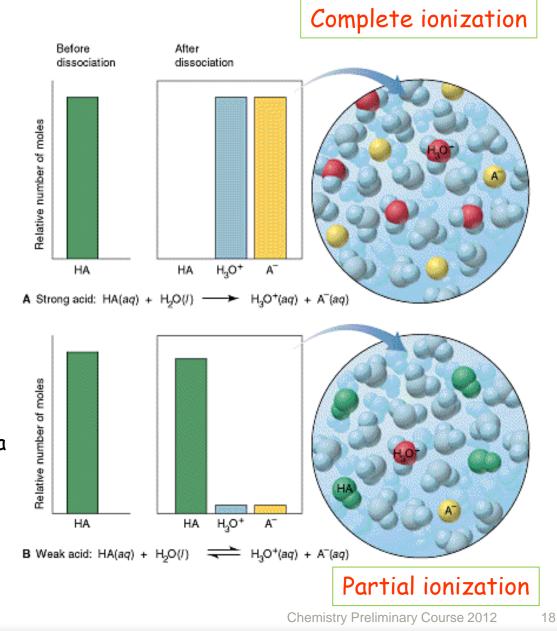
- How can acid and base strength be quantified?
 - 'Strong' acids vs 'weak' acids
 - 'Strong' bases vs 'weak' bases
 - Key concept is extent or degree of ionization/dissociation.
 - Correlation exists between acid/base strength, degree of ionization in solution and extent to which solution exhibits ionic conductivity.



The Extent of Dissociation for Strong and Weak Acids

Key concept : Acid/base strength quantified in terms of extent or degree of dissociation.

- A strong acid or base is fully ionized in solution
 - HCl
 - NaOH
- For a weak acid or base only a small fraction is ionized in solution
 - CH₃COOH,
 - NH₃



Reactivity of strong and weak acids.

Acids react with metals to produce hydrogen gas

1M HCl(aq)

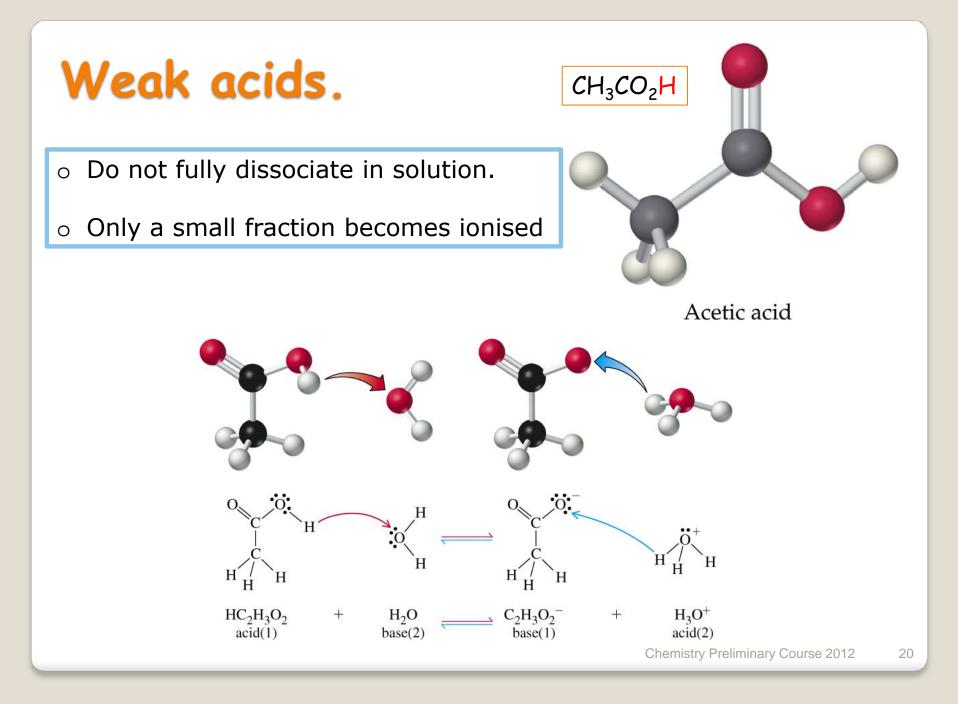
Strong acid: Extensive H₂ evolution



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1M CH₃COOH(aq)

Weak acid: H₂ evolution Not very extensive



Acids & Bases as Electrolytes

Strong Acids are strong electrolytes (100% dissociation)

HCl (aq) + H₂O (I) \longrightarrow H₃O⁺ (aq) + Cl⁻ (aq)

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

Weak Acids are weak electrolytes (not fully dissociated)

 $HF (aq) + H_2O (I) + H_3O^+ (aq) + F^- (aq)$

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

Acids & Bases as Electrolytes

Strong Bases are strong electrolytes (100% dissociated)

NaOH (s) H_2O Na⁺ (aq) + OH⁻ (aq)

KOH (s) $\xrightarrow{H_2O}$ K⁺ (aq) + OH⁻ (aq)

Weak Bases are weak electrolytes (not fully dissociated)

 $F^{-}(aq) + H_2O(1) \longrightarrow OH^{-}(aq) + HF(aq)$

 $NO_2^-(aq) + H_2O(l) \longrightarrow OH^-(aq) + HNO_2(aq)$

Weak acids/bases.

- Quantifying the extent of dissociation of a weak acid or a weak base in aqueous solution:
 - the acid dissociation constant K_a

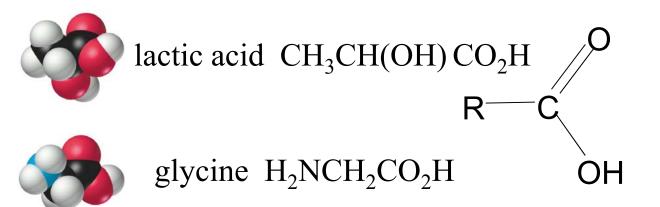
or

- the base dissociation constant K_b .
- Reflect acid or base strength
- Computed by determining the equilibrium concentrations of all relevant species in the solution.



$CH_3CO_2H_{(aq)} \rightleftharpoons CH_3CO_2^- + H_3O^+$

$$K_{a} = \frac{[CH_{3}CO_{2}^{-}][H_{3}O^{+}]}{[CH_{3}CO_{2}H]} = 1.8 \times 10^{-5}$$



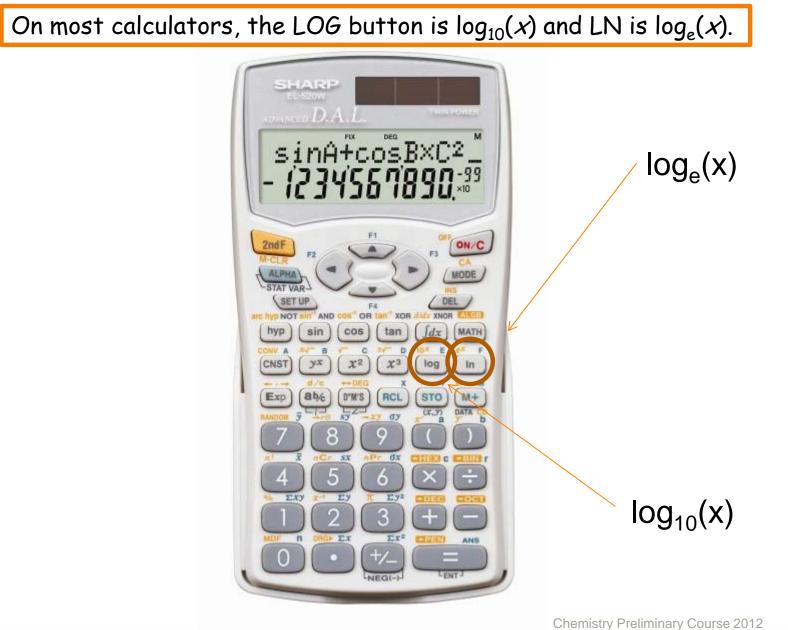
Mathematical interlude : the logarithm

Useful Resources:

- Paul Monk, Maths for Chemistry, Oxford University Press, 2006. http://mathworld.wolfram.com/Logarithm.html
- The logarithm is a mathematical operation that is the inverse of exponentiation.
- If $x = b^n$ then $log_b(x)=n$ where b is the base.
- If $10^{\times} = y$ then $\log_{10} y = x$,
- Example: $10^2 = 10 \times 10 = 100$, then $\log_{10}(100) = 2$.
- Logarithms are useful for making lengthy numerical operations easier to perform and for reducing large numbers to smaller ones.

Mathematical interlude : the logarithm

- The most widely used bases for logarithms are 10, the mathematical constant <u>e</u> ≈ 2.71828... and 2.
- When "log" is written without a base (b missing from log b), the intent can usually be determined from context:
 - <u>natural logarithm</u> (log<u>e</u>) in <u>mathematical analysis</u>
 - <u>common logarithm</u> (log10) in <u>engineering</u> and when logarithm <u>tables</u> are used to simplify hand calculations
 - binary logarithm (log2) in information theory and musical intervals .
- The notation " $\ln(x)$ " invariably means $\log_e(x)$, i.e., the natural logarithm of x, but the implied base for " $\log(x)$ " varies by discipline:
 - Mathematicians generally understand both "ln(x)" and "log(x)" to mean $log_e(x)$ and write " $log_{10}(x)$ " when the base-10 logarithm of x is intended.
 - Engineers, biologists, and some others write only " $\ln(x)$ " or " $\log_e(x)$ " when they mean the natural logarithm of x, and take " $\log(x)$ " to mean $\log_{10}(x)$ or, sometimes in the context of <u>computing</u>, $\log_2(x)$.



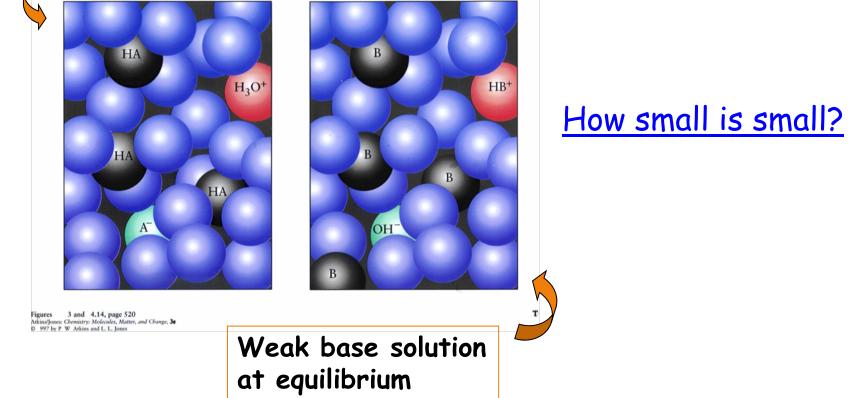
Logarithms are particularly useful when dealing with lengthy numerical operations as they reduce multiplication to addition, division to subtraction, exponentiation to multiplication, and roots to division.

Operations with numbers	Logarithmic identity
a .b	$\log(a.b) = \log(a) + \log(b)$
a/b	$\log(a/b) = \log(a) - \log(b)$
a^b	$\log(a^b) = b\log(a)$
$\sqrt[b]{a}$	$\log\left(\sqrt[b]{a}\right) = \log(a)/b$

Acid/base equilibria.

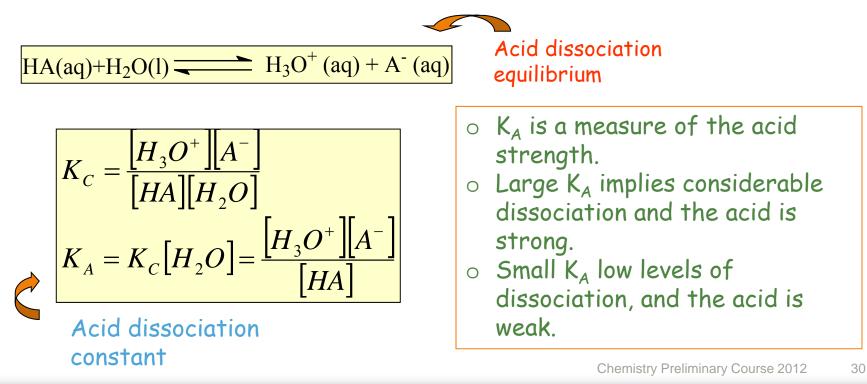
Weak acid solution at equilibrium

<u>Recall</u>: at equilibrium weak acids/bases only dissociate to a small degree.



Acid strength : the acid dissociation constant K_A .

- It is easy to quantify the strength of strong acids since they fully dissociate to ions in solution.
- For weak acids 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 .



The Relationship Between K_a and pK_a

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

 $pK_A = -\log_{10} K_A$

Note: 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.

Acid Name (Formula)	K _A at 298 K	р <i>К_А</i>
Hydrogen sulfate ion (HSO ₄ -)	1.02 × 10 ⁻²	1.991
Nitrous acid (HNO ₂)	7.1×10^{-4}	₄ ↓ 3.15
Acetic acid (CH ₃ COOH)	1.8 × 10 ⁻⁵ <i>pl</i>	K _A ↑ 4.74
Hypobromous acid (HBrO)	2.3 × 10 ⁻⁹	8.64
Phenol (C ₆ H ₅ OH)	1.0 × 10 ⁻¹⁰	10.00

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Acid dissociation constants.

TABLE 15.2	Acid–Dissociation Constants at 25°C					
	Acid	Molecular Formula	Structural Formula*	Ka	pKa [†]	
Stronger	Hydrochloric	HCl	H—Cl	$2 imes 10^{6}$	-6.3	
acid	Nitrous	HNO ₂	H - O - N = O	$4.5 imes10^{-4}$	3.35	
	Hydrofluoric	HF	H—F	$3.5 imes10^{-4}$	3.46	
Î	Acetylsalicylic (aspirin)	$C_9H_8O_4$	$H \sim C \sim CH_{3}$ $H \sim C \sim CH_{3}$ $H \sim C \sim C \sim CH_{3}$ $H \sim C \sim C \sim CH_{3}$ $H \sim C \sim C \sim CH_{3}$	$3.0 imes 10^{-4}$	3.52	
L	Formic Ascorbic	НСО ₂ Н С ₆ Н ₈ О ₆		$1.8 imes10^{-4}$ $8.0 imes10^{-5}$	3.74	
	(vitamin C) Benzoic	C ₆ H ₅ CO ₂ H	HO HO HO H H H H H C=C C C C C C OH H H H C C C C C OH OH H H C C C C C OH OH H H C C C C C C OH OH H H C C C C C C OH OH H H C C C C C C OH OH H H C C C C C OH OH H C C C C C OH OH H C C C C OH OH C C C OH OH C C C OH OH C C C OH OH C C C OH OH C C C OH OH C C C OH OH C C C OH C C C OH C C C C OH C C C C OH C C C C C OH C C C C C C OH C C C C C C OH C C C C C C C OH C C C C C C C C	$6.5 imes 10^{-5}$	4.19	
Weaker	Acetic Hypochlorous Hydrocyanic	CH3CO2H HOCl HCN	$H H H$ $CH_3 - C - O - H$ $H - O - CI$ $H - C \equiv N$	$egin{array}{c} 1.8 imes 10^{-5} \ 3.5 imes 10^{-8} \ 4.9 imes 10^{-10} \end{array}$	4.74 7.46 9.31	
acid	Methanol	CH ₃ OH	$CH_3 - O - H$	2.9×10^{-16}	15.54	

* The proton that is transferred to water when the acid dissociates is shown in color.

 $^{\dagger}pK_{a}=-\log K_{a}.$

Basicity Constant K_b.

$$B(aq) + H_2O(1) \longrightarrow BH^+(aq) + OH^-(aq)$$

$$K_c = \begin{bmatrix} BH^+ & OH^- \\ B & H_2O \end{bmatrix}$$

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

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

- Similarly, 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.

|B|

• If K_b is large then pK_b will be small, and the stronger the base.

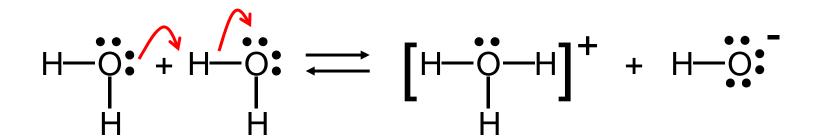
Ionization Constants of Weak Acids and Bases

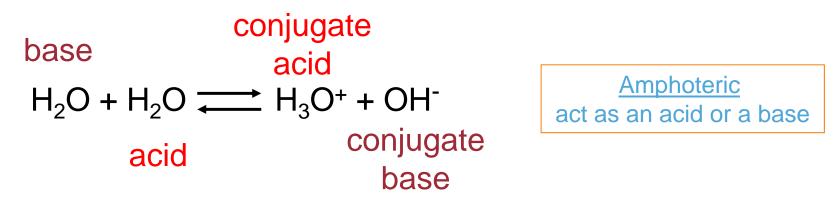
	Ionization Equilibrium	Ionization Constant K	p <i>K</i>	
Acid		$K_a =$	$pK_a =$	
Iodic acid	$HIO_3 + H_2O \implies H_3O^+ + IO_3^-$	1.6×10^{-1}	0.80	1
Chlorous acid	$HCIO_2 + H_2O \implies H_3O^+ + CIO_2^-$	1.1×10^{-2}	1.96	
Chloroacetic acid	$HC_2H_2CIO_2^- + H_2O \implies H_3O^+ + C_2H_2CIO_2^-$	1.4×10^{-3}	2.85	
Nitrous acid	$HNO_2 + H_2O \implies H_3O^+ + NO_2^-$	7.2×10^{-4}	3.14	
Hydrofluoric acid	$HF + H_2O \implies H_3O^+ + F^-$	$6.6 imes 10^{-4}$	3.18	÷
Formic acid	$HCHO_2 + H_2O \implies H_3O^+ + CHO_2^-$	$1.8 imes 10^{-4}$	3.74	Sug
Benzoic acid	$HC_7H_5O_2 + H_2O \implies H_3O^+ + C_7H_5O_2^-$	6.3×10^{-5}	4.20	stre
Hydrazoic acid	$HN_3 + H_2O \implies H_3O^+ + N_3^-$	1.9×10^{-5}	4.72	Acid strength
Acetic acid	$HC_2H_3O_2 + H_2O \implies H_3O^+ + C_2H_3O_2^-$	1.8×10^{-5}	4.74	A
Hypochlorous acid	$HOCI + H_2O \implies H_3O^+ + OCI^-$	$2.9 imes 10^{-8}$	7.54	
Hydrocyanic acid	$HCN + H_2O \implies H_3O^+ + CN^-$	$6.2 imes 10^{-10}$	9.21	
Phenol	$HOC_6H_5 + H_2O \implies H_3O^+ + C_6H_5O^-$	$1.0 imes 10^{-10}$	10.00	
Hydrogen peroxide	$H_2O_2 + H_2O \implies H_3O^+ + HO_2^-$	1.8×10^{-12}	11.74	
Base		$K_{\rm b} =$	$pK_b =$	\wedge
Diethylamine	$(C_2H_5)_2NH + H_2O \implies (C_2H_5)_2NH_2^+ + OH^-$	6.9×10^{-4}	3.16	1 - i
Ethylamine	$C_2H_5NH_2 + H_2O \implies C_2H_5NH_3^+ + OH^-$	4.3×10^{-4}	3.37	Base strength
Ammonia	$NH_3^2 + H_2^2O \implies NH_4^+ + OH^-$	1.8×10^{-5}	4.74	trei
Hydroxylamine	$HONH_2^{\vee} + H_2^{\vee}O \implies HONH_3^{+} + OH^{-}$	9.1×10^{-9}	8.04	se s
Pyridine	$C_5H_5N + H_2O \implies C_5H_5NH^+ + OH^-$	1.5×10^{-9}	8.82	Bas
Aniline	$C_6H_5NH_2 + H_2O \iff C_6H_5NH_3^+ + OH^-$	$7.4 imes 10^{-10}$	9.13	

Acid-Base Properties of Water

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

autoionization of water





The Ion Product of Water

$$H_2O(1) \stackrel{\longrightarrow}{\longrightarrow} H^+(aq) + OH^-(aq)$$
$$K_c = \frac{[H^+][OH^-]}{[H_2O]} \qquad [H_2O] = \text{constant}$$

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

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

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

The pH concept.

- Quantitatively acidity or alkalinity is measured using the concentration of hydrated protons $[H_3O^+]$ present in a solution.
- The [H₃O⁺] varies in magnitude over quite a large range in aqueous solution, typically from 1 M to 10⁻¹⁴ M.
- To make the numbers meaningful [H₃O⁺] is expressed in terms of a logarithmic scale called the pH scale.

$$pH = -\log_{10} \left[H_3 O^+ \right]$$
$$\left[H_3 O^+ \right] = 10^{-pH}$$

• The higher the $[H_3O^+]$, the more acidic the solution and the lower is the solution pH.

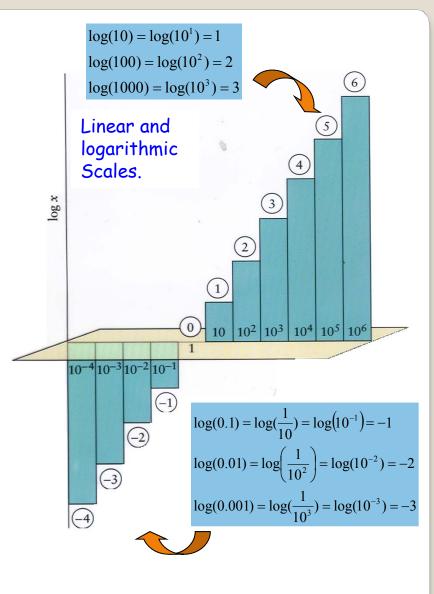
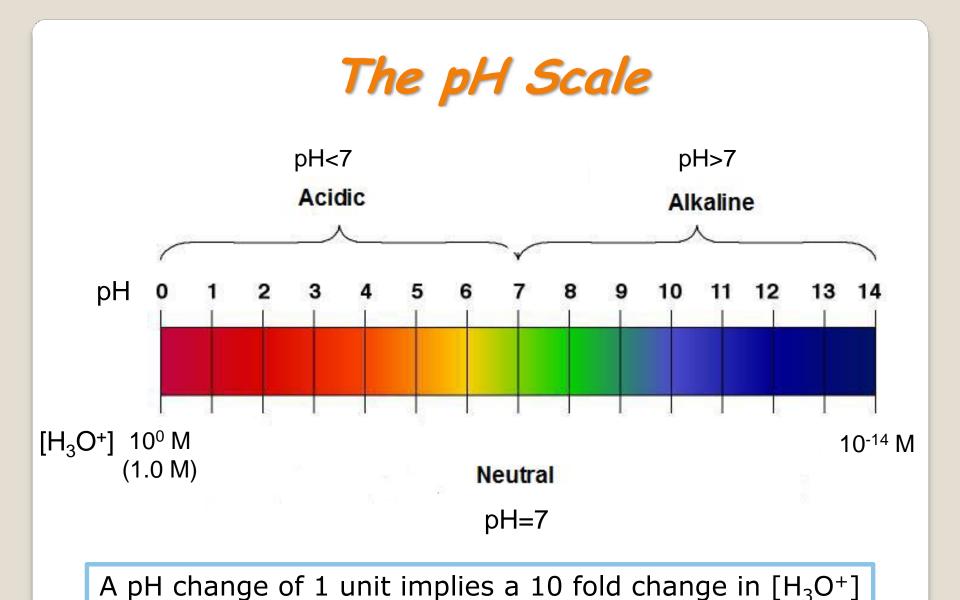
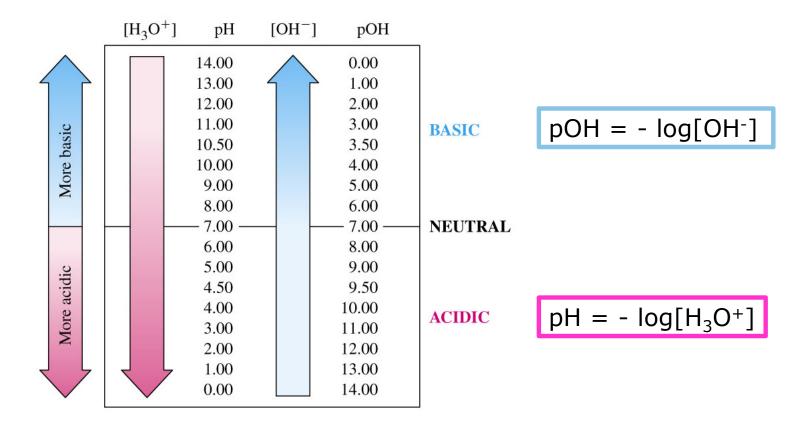


Figure 14.8, page 515 Atkins/Jones: Chemistry: Molecules, Matter. Change. © 1997 by P. W. Atkins and L. L. Jones



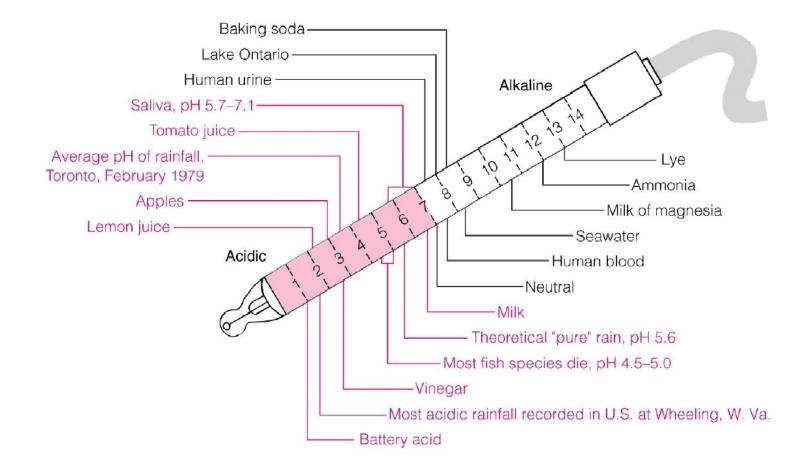
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pH & pOH Scales.



$$pH + pOH = pK_w = 14$$

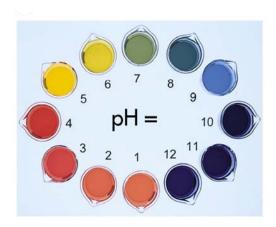
Typical pH values.



Measuring pH: Indicators, a visual estimation. $HIn(aq) + H_2O \rightarrow H_3O^+(aq) + In^-$

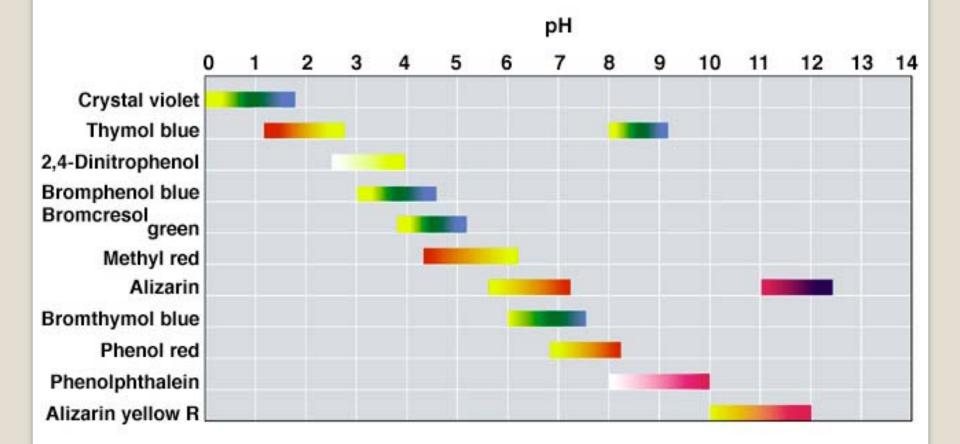
- Indictors are weak acids which change colour over a specific pH range when they donate protons.
- Used in acid/base titrations.
- Universal indicator used for pH measurements over a larger range.
 - Mixture of pH indicators
 - Different colours from red to purple







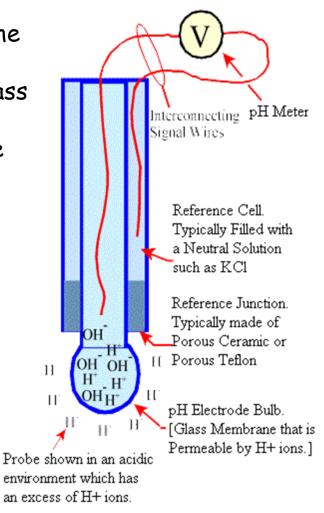
Colors and Approximate pH Range of Some Common Acid-Base Indicators



Measuring pH: The pH meter.

- The pH meter is a voltmeter connected to a chemical sensor probe which is sensitive to the concentration of H_3O^+ .
- Measures the electrical potential across a glass membrane in the probe.
- $_{\odot}$ The measured potential is proportional to the logarithm of [H_3O^+]
- A digital read out of the solution pH is given.





Summary. pH - A Measure of Acidity

<u>Solution Is</u>		<u>At 25°C</u>	
neutral	[H⁺] = [OH⁻]	[H ⁺] = 1 x 10 ⁻⁷	pH = 7
acidic	[H⁺] > [OH⁻]	[H⁺] > 1 × 10 ⁻⁷	pH < 7
basic	[H⁺] < [OH⁻]	[H⁺] < 1 × 10 ⁻⁷	pH > 7

рН [Н+]

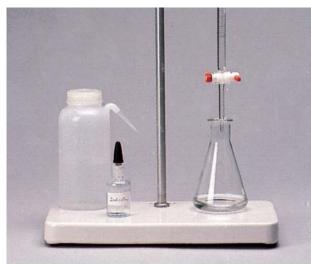
Titrations

In a *titration* a solution of accurately known concentration is added gradually added to another solution of unknown concentration until the chemical reaction between the two solutions is complete.

$HA + MOH \rightarrow MA + H_2O$

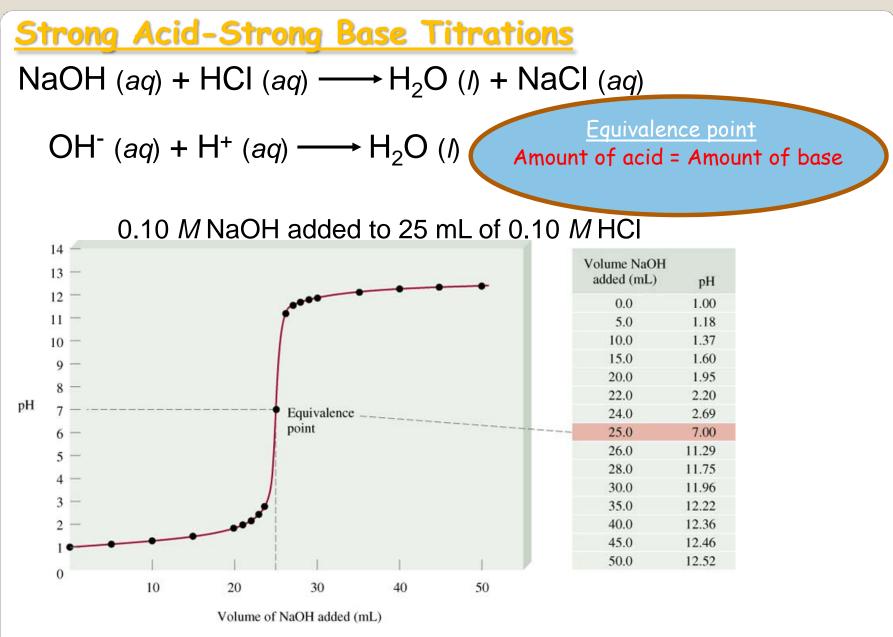
Equivalence point - the point at which the reaction is complete

Indicator – substance that changes color at (or near) the equivalence point



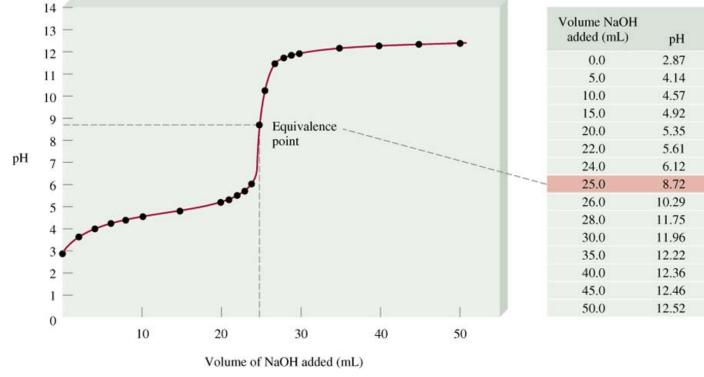
Slowly add base to unknown acid UNTIL The indicator changes color (pink)





Weak Acid-Strong Base Titrations

CH₃COOH (aq) + NaOH (aq) → CH₃COONa (aq) + H₂O (/) CH₃COOH (aq) + OH⁻ (aq) → CH₃COO⁻ (aq) + H2O (/) At equivalence point (pH > 7): CH₃COO⁻ (aq) + H₂O (/) \rightarrow OH⁻ (aq) + CH₃COOH (aq)



Concluding Comments

- Acid/base reactions represent an example of a fundamental class of chemical reactions.
- The process involves the transfer of a hydrated proton from a donor species (the acid) to an acceptor species (the base).
- The degree of proton transfer can be quantified and enables a distinction between strong and weak acids/bases to be made.
- The degree of acidity or alkalinity of a solution may be quantified in terms of the logarithmic pH scale. Acidic solutions have a low pH and basic solutions have a high pH.
- The solution pH can be measured via use of indicators or via use of pH meter.
- An acid/base reaction is termed a neutralization reaction and can be monitored by measuring the pH during the reaction. Chemistry Preliminary Course 2012