

JF Chemistry 1101 2011 Introduction to Physical Chemistry: Acid Base and Solution Equilibria.

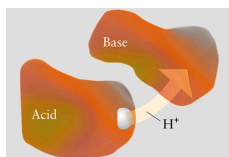


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Required Reading Material.

- 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 (Chemistry of Acids and Bases) & Chapter 18 (Principles of reactivity: other aspects of ionic equilibria), pp.760-859.
- Chemistry³, Burrows et al.
 - Chapter 6, Acids & bases, pp.263-299.



Review : Kotz Chapter 3 for simple acid/base definitions.

Lecture 13.

Acid/base chemistry :
Simple ideas: Arrhenius,
Bronsted-Lowry, Lewis.



Kotz: section 3.7, pp.131-139.
Section 17.1, pp.761-762.

Acid and Bases

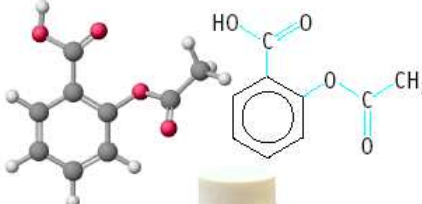
$HO-C(=O)-CH_2-C(OH)(CO_2H)-CH_2-C(=O)OH$

▲ The tartness of lemons and oranges comes from the weak acid citric acid. The acid is found widely in nature and in many consumer products.
(Charles D. Winters)

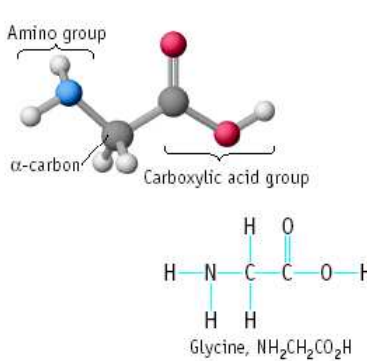
$H-C(=O)OH$

▲ The sting of ants is due to the weak acid formic acid, HCO_2H .
(Gallo Images/@ CORBIS)


Acid and Bases




▲ Aspirin is a weak acid that has been used as an analgesic for over 100 years. (Charles D. Winters)



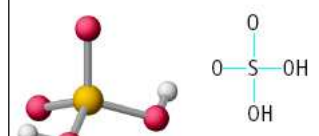
▲ Glycine is representative of the amino acids that are the basis of proteins. The $-CO_2H$ group is the acid portion of the molecule, and the $-NH_2$ group is the basic portion. (Charles D. Winters)




Acid and Bases




▲ Caffeine is a well known stimulant and a weak base. (Charles D. Winters)



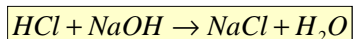
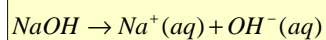
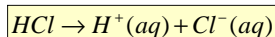
▲ A sea slug excretes the strong acid sulfuric acid in self-defense. (Sharksong/M. Kazmers/Dembinski Photo Associates)



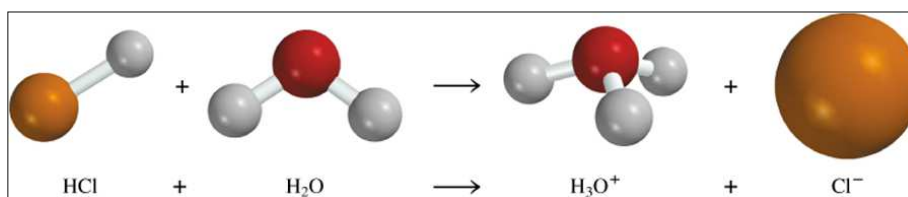


Arrhenius (or Classical) Acid-Base Definition

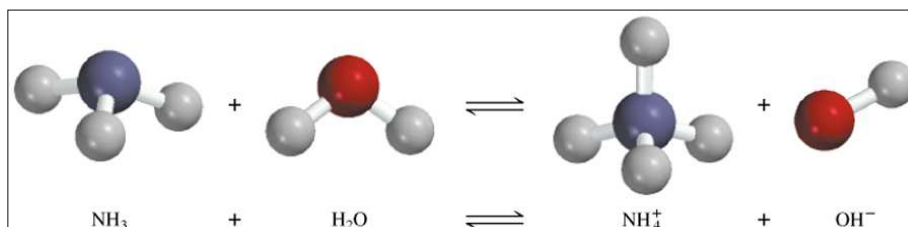
- An **acid** is a neutral substance that contains hydrogen and dissociates or ionizes in water to yield hydrated protons or hydronium ions H_3O^+ .
- A **base** is a neutral substance that contains the hydroxyl group and dissociates in water to yield hydrated hydroxide ions OH^- .
- **Neutralization** is 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.



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

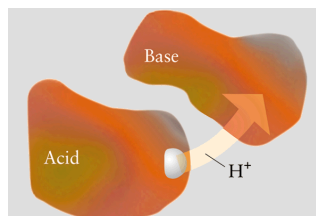


Arrhenius base is a substance that produces OH^- in water.



Acids and bases: Bronsted/Lowry definition.

- **Bronsted/Lowry Acid (HA):**
 - An acid is a species which **donates** a proton
- **Bronsted/Lowry Base (B):**
 - A base is a species which **accepts** a proton.
- These definitions are quite general and refer to the reaction between an acid and a base.
- An acid must contain H in its formula; HNO_3 and H_2PO_4^- are two examples, all Arrhenius acids are Bronsted-Lowry acids.
- A base must contain a lone pair of electrons to bind the H^+ ion; a few examples are NH_3 , CO_3^{2-} , F^- , as well as OH^- . Bronsted-Lowry bases are not Arrhenius bases, but all Arrhenius bases contain the Bronsted-Lowry base OH^- .

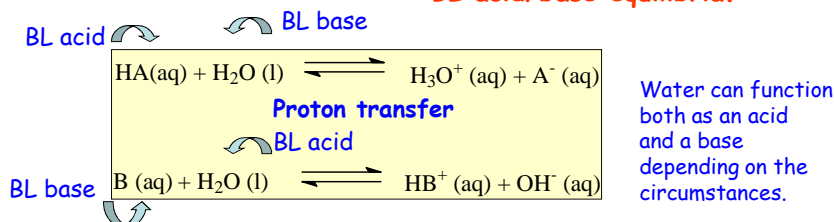


- In the Bronsted-Lowry perspective: *one species donates a proton and another species accepts it: an acid-base reaction is a proton transfer process.*

Chemistry³ section 6.1. pp.264-267.

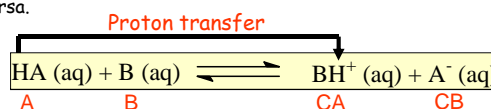
Kotz 7th ed. Section 17.1. pp.761-765

BL acid/base equilibria.



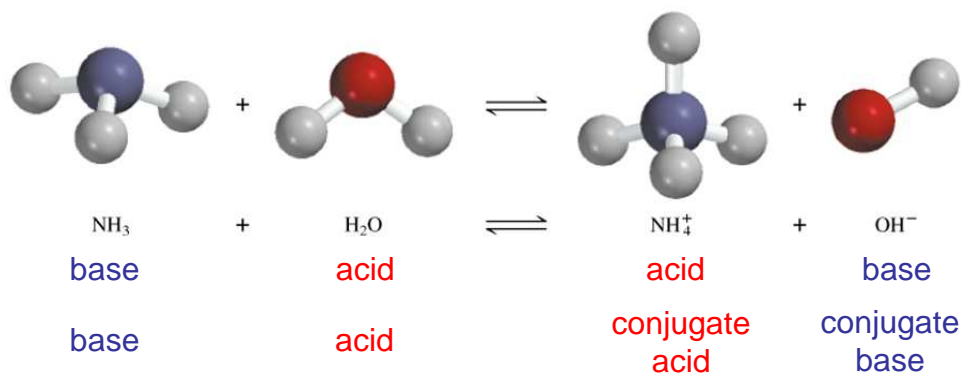
- Proton donation and acceptance are **dynamic** processes for all acids and bases. Hence a **proton transfer equilibrium** is rapidly established in solution.
- The equilibrium reaction is described in terms of conjugate acid/base pairs.
- The conjugate base (CB) of a BL acid is the base which forms when the acid has donated a proton.
- The conjugate acid (CA) of a BL base is the acid which forms when the base has accepted a proton.
- A conjugate acid has one more proton than the base has, and a conjugate base one less proton than the acid has.
- 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.

Acid : proton donor
Base : proton acceptor



A Brønsted **acid** is a proton donor

A Brønsted **base** is a proton acceptor



15.1

Brønsted-Lowry Acid-Base Definition

An acid is a proton donor, *any species which donates a H^+* .

A base is a proton acceptor, *any species which accepts a H^+* .

An acid-base reaction can now be viewed from the standpoint of the reactants AND the products.

An acid reactant will produce a base product and the two will constitute an acid-base conjugate pair.

Table 18.4 The Conjugate Pairs in Some Acid-Base Reactions

Conjugate Pair

Conjugate Pair

Reaction 1	HF	+	H ₂ O	⇌	F ⁻	+	H ₃ O ⁺
Reaction 2	HCOOH	+	CN ⁻	⇌	HCOO ⁻	+	HCN
Reaction 3	NH ₄ ⁺	+	CO ₃ ²⁻	⇌	NH ₃	+	HCO ₃ ⁻
Reaction 4	H ₂ PO ₄ ⁻	+	OH ⁻	⇌	HPO ₄ ²⁻	+	H ₂ O
Reaction 5	H ₂ SO ₄	+	N ₂ H ₅ ⁺	⇌	HSO ₄ ⁻	+	N ₂ H ₆ ²⁺
Reaction 6	HPO ₄ ²⁻	+	SO ₃ ²⁻	⇌	PO ₄ ³⁻	+	HSO ₃ ⁻

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Table 15.2 Relative Strengths of Conjugate Acid-Base Pairs

	Acid	Conjugate Base	
↑ Acid strength increases	{ HClO ₄ (perchloric acid) HI (hydroiodic acid) HBr (hydrobromic acid) HCl (hydrochloric acid) H ₂ SO ₄ (sulfuric acid) HNO ₃ (nitric acid) H ₃ O ⁺ (hydronium ion)	{ ClO ₄ ⁻ (perchlorate ion) I ⁻ (iodide ion) Br ⁻ (bromide ion) Cl ⁻ (chloride ion) HSO ₄ ⁻ (hydrogen sulfate ion) NO ₃ ⁻ (nitrate ion) H ₂ O (water)	
	{ HSO ₄ ⁻ (hydrogen sulfate ion) HF (hydrofluoric acid) HNO ₂ (nitrous acid) HCOOH (formic acid) CH ₃ COOH (acetic acid) NH ₄ ⁺ (ammonium ion) HCN (hydrocyanic acid) H ₂ O (water) NH ₃ (ammonia)	{ SO ₄ ²⁻ (sulfate ion) F ⁻ (fluoride ion) NO ₂ ⁻ (nitrite ion) HCOO ⁻ (formate ion) CH ₃ COO ⁻ (acetate ion) NH ₃ (ammonia) CN ⁻ (cyanide ion) OH ⁻ (hydroxide ion) NH ₂ ⁻ (amide ion)	
	↓ Base strength increases		

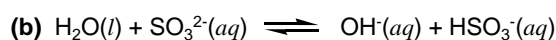
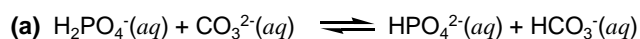
15.4

Table 6.1 The relative strengths of acids and their conjugate bases

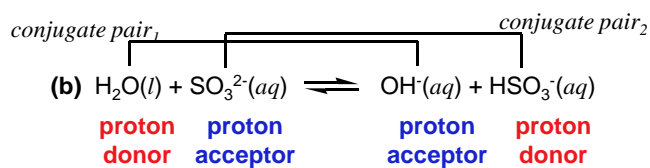
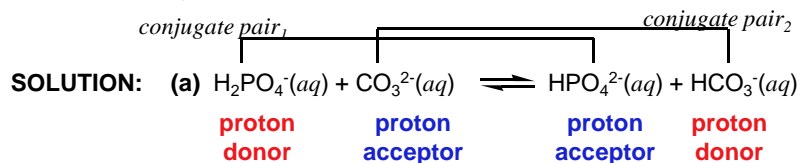
	Conjugate acid	Conjugate base	
Strongest acid	$\text{HClO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{ClO}_4^-(\text{aq})$ perchloric acid	$\text{H}_3\text{O}^+(\text{aq}) + \text{ClO}_4^-(\text{aq})$ perchlorate ion	Weakest base
Increasing acid strength	$\text{HCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ hydrochloric acid	$\text{H}_3\text{O}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ chloride ion	Increasing base strength
	$\text{H}_2\text{SO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HSO}_4^-(\text{aq})$ sulfuric acid	$\text{H}_3\text{O}^+(\text{aq}) + \text{HSO}_4^-(\text{aq})$ hydrogensulfate ion	
	$\text{H}_3\text{O}^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{H}_2\text{O}(\text{l})$ oxonium ion	$\text{H}_3\text{O}^+(\text{aq}) + \text{H}_2\text{O}(\text{l})$ water	
	$\text{CH}_3\text{CO}_2\text{H}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{CH}_3\text{CO}_2^-(\text{aq})$ ethanoic acid	$\text{H}_3\text{O}^+(\text{aq}) + \text{CH}_3\text{CO}_2^-(\text{aq})$ ethanoate ion	
	$\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{NH}_3(\text{aq})$ ammonium ion	$\text{H}_3\text{O}^+(\text{aq}) + \text{NH}_3(\text{aq})$ ammonia	
	$\text{H}_2\text{O}(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$ water	$\text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$ hydroxide ion	
Weakest acid	$\text{C}_2\text{H}_5\text{OH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{C}_2\text{H}_5\text{O}^-(\text{aq})$ ethanol	$\text{H}_3\text{O}^+(\text{aq}) + \text{C}_2\text{H}_5\text{O}^-(\text{aq})$ ethoxide ion	Strongest base

SAMPLE PROBLEM 18.4: Identifying Conjugate Acid-Base Pairs

PROBLEM: The following reactions are important environmental processes. Identify the conjugate acid-base pairs.

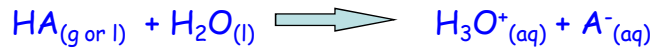


PLAN: Identify proton donors (acids) and proton acceptors (bases).



Strong and weak acids.

- Strong acids dissociate completely into ions in water:

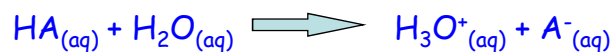


In a dilute solution of a strong acid, almost no HA molecules exist: $[H_3O^+] = [HA]_{init}$ or $[HA]_{eq} = 0$

$$Q_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]} \text{ at equilibrium, } Q_c = K_c \gg 1$$

Nitric acid is an example: $HNO_3(l) + H_2O(l) \rightleftharpoons H_3O^+_{(aq)} + NO_3^-_{(aq)}$

- Weak acids dissociate very slightly into ions in water:



In a dilute solution of a weak acid, the great majority of HA molecules are undissociated: $[H_3O^+] \ll [HA]_{init}$ or $[HA]_{eq} = [HA]_{init}$

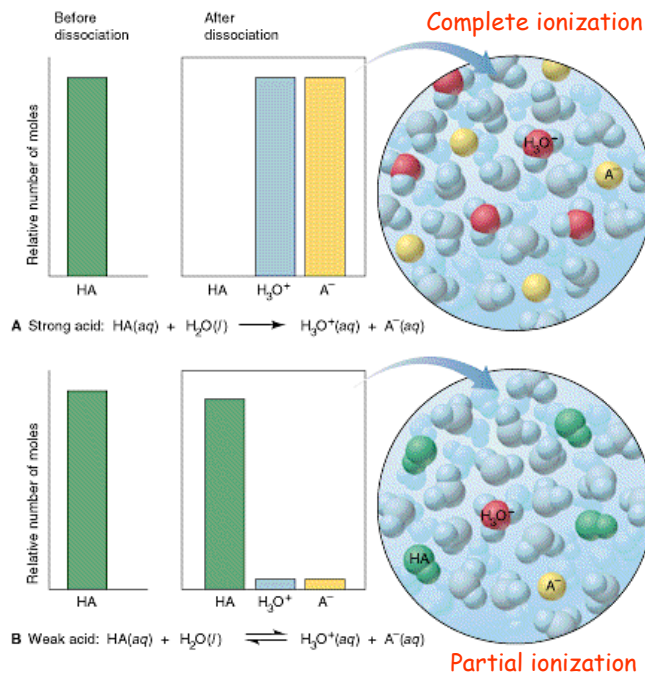
$$Q_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]} \text{ at equilibrium, } Q_c = K_c \ll 1$$

The Extent of Dissociation for Strong and Weak Acids

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

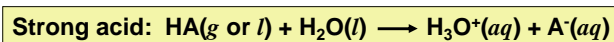
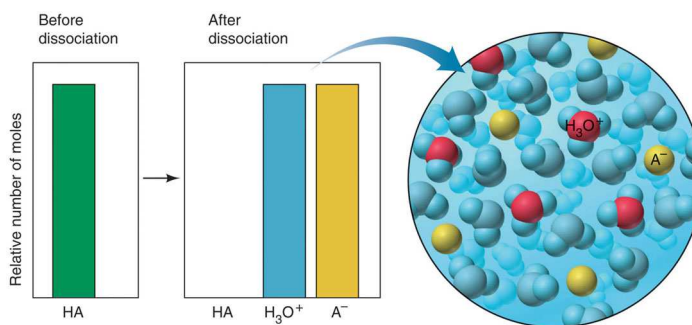
An acid or base is classified as **strong** if it is **fully ionized** in solution (e.g. HCl, NaOH).

An acid or base is classified as **weak** if only a **small fraction** is ionized in solution (e.g. CH_3COOH , NH_3).



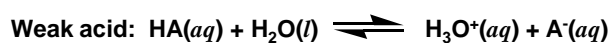
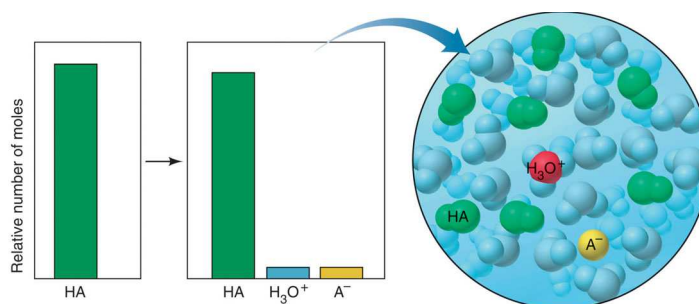
Extent of dissociation : strong acid.

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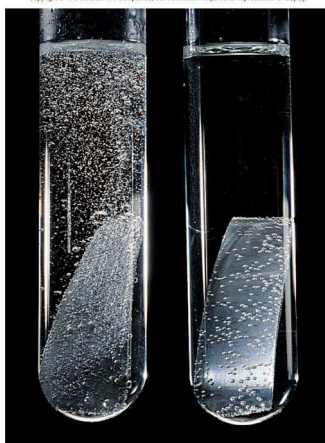
Extent of dissociation: weak acid.

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Reactivity of strong and weak acids.

1M HCl(aq)



1M CH₃COOH(aq)

Classifying the Relative Strengths of Acids.

Strong acids.

There are two types of strong acids:

- The hydrohalic acids HCl, HBr, and HI
- Oxoacids in which the number of O atoms exceeds the number of ionizable H atoms by two or more, such as HNO₃, H₂SO₄, HClO₄

Weak acids.

There are many more weak acids than strong ones. Four types, with examples, are:

- The hydrohalic acid HF
- Those acids in which H is bonded to O or to halogen, such as HCN and H₂S
- Oxoacids in which the number of O atoms equals or exceeds by one the number of ionizable H atoms, such as HClO, HNO₂, and H₃PO₄
- Organic acids (general formula RCOOH), such as CH₃COOH and C₆H₅COOH.

Classifying the Relative Strengths of Bases.

Strong bases.

- Soluble compounds containing O^{2-} or OH^- ions are strong bases. The cations are usually those of the most active metals: M_2O or MOH , where M = Group 1A(1) metals (Li, Na, K, Rb, Cs).
- MO or $M(OH)_2$, where M = Group 2A(2) metals (Ca, Sr, Ba) [MgO and $Mg(OH)_2$ are only slightly soluble, but the soluble portion dissociates completely.]

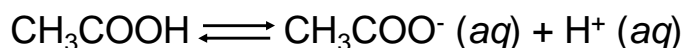
Weak bases.

- Many compounds with an electron-rich nitrogen are weak bases (none are Arrhenius bases). The common structural feature is an N atom that has a lone electron pair in its Lewis structure.
 - Ammonia (NH_3)
 - Amines (general formula RNH_2 , R_2NH , R_3N), such as $CH_3CH_2NH_2$, $(CH_3)_2NH$, $(C_3H_7)_3N$, and C_5H_5N

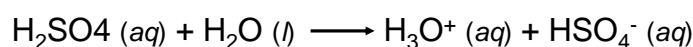
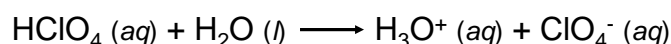
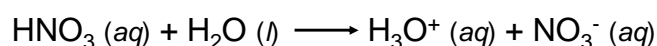
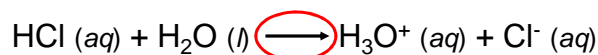
Strong Electrolyte - 100% dissociation



Weak Electrolyte - not completely dissociated

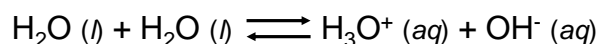
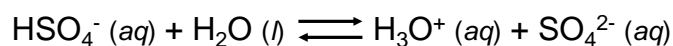
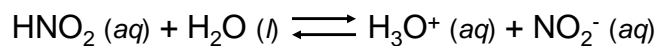


Strong Acids are strong electrolytes

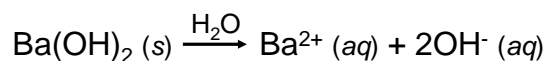
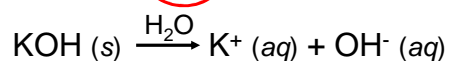


15.4

Weak Acids are weak electrolytes

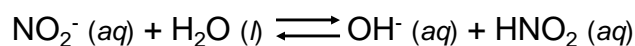


Strong Bases are strong electrolytes



15.4

Weak Bases are weak electrolytes



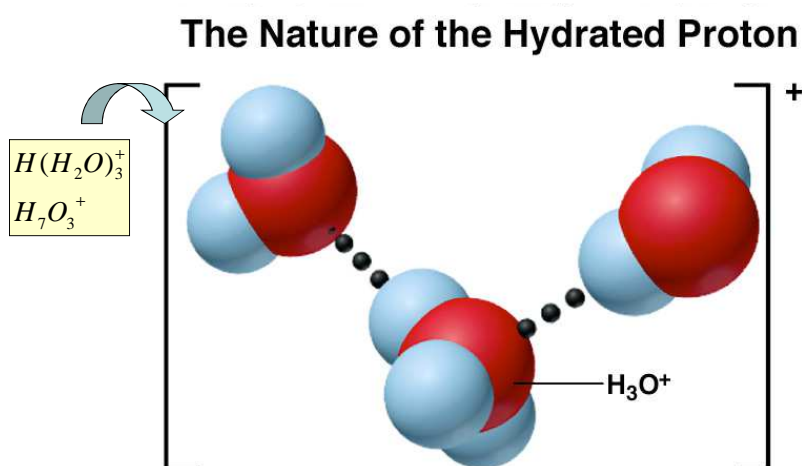
Conjugate acid-base pairs:

- The conjugate base of a strong acid has no measurable strength.
- H_3O^+ is the strongest acid that can exist in aqueous solution.
- The OH^- ion is the strongest base that can exist in aqueous solution.

15.4

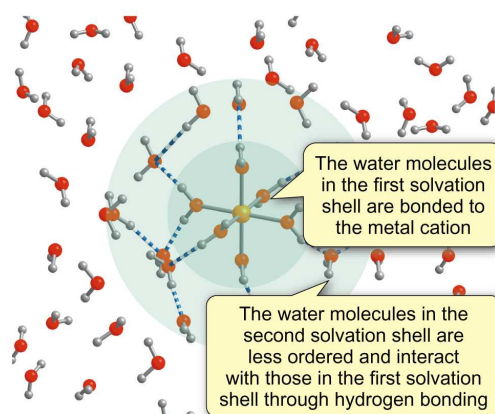
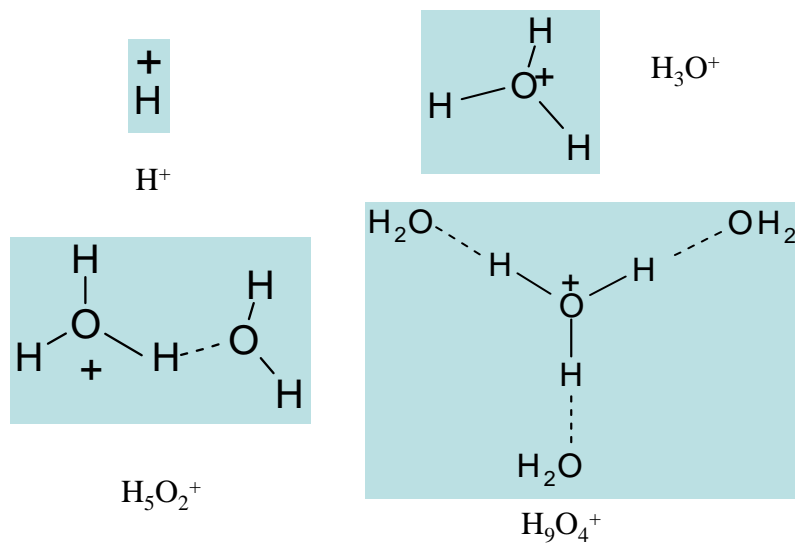
Representing Protons

- Both representations of the proton are equivalent.
- $H_5O_2^+$ (aq), $H_7O_3^+$ (aq), $H_9O_4^+$ (aq) have been observed.
- We will use H^+ (aq)!



The hydrated proton is quite a complex entity. It is usually represented in shorthand form as H^+ (aq). A better representation is in terms of the hydronium ion H_3O^+ . We will adopt this representation a lot. The real situation is more complex. The H_3O^+ ion binds to other water molecules forming a mixture of species with the general formula $H(H_2O)_n^+$. In fact the structural details of liquid water is still a hot item of research.

What is H^+ (aq)?



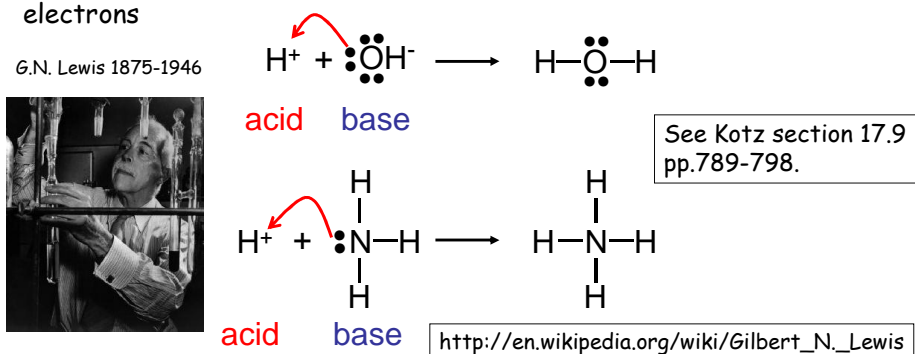
Yet more sophistication: Lewis acidity

An **Arrhenius acid** is defined as a substance that produces H^+ (H_3O^+) in water.

A **Brønsted acid** is defined as a proton donor

A **Lewis acid** is defined as a substance that can accept a pair of electrons.

A **Lewis base** is defined as a substance that can donate a pair of electrons

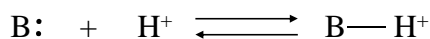


Electron-Pair Donation and the Lewis Acid-Base Definition

The Lewis acid-base definition :

- A **base** is any species that *donates* an electron pair.
- An **acid** is any species that *accepts* an electron pair.

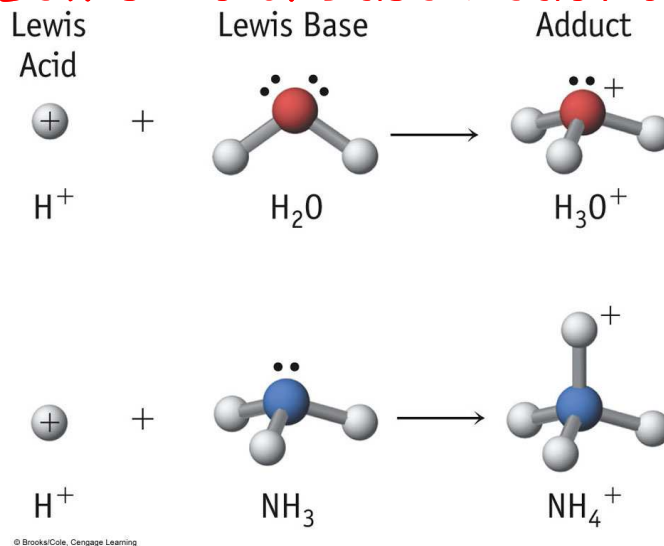
Protons act as Lewis acids in that they accept an electron pair in all reactions:



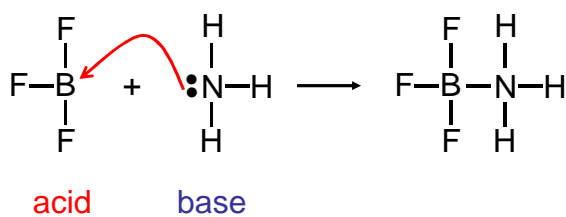
The product of any Lewis acid-base reaction is called an **adduct**, a single species that contains a new covalent bond.

- A Lewis base has a lone pair of electrons to donate.
- A Lewis acid has a vacant orbital

Lewis Acid/Base Reaction



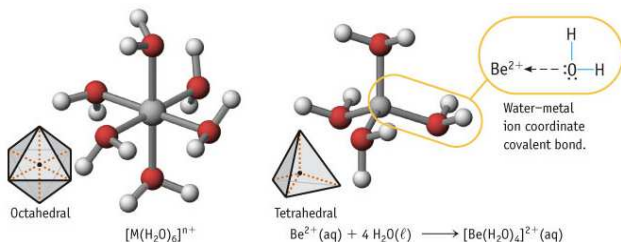
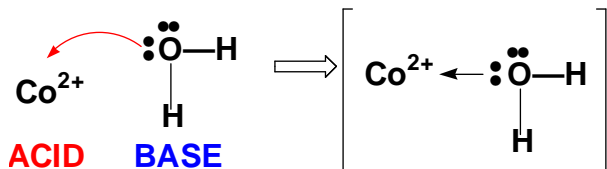
Lewis Acids and Bases



No protons donated or accepted!

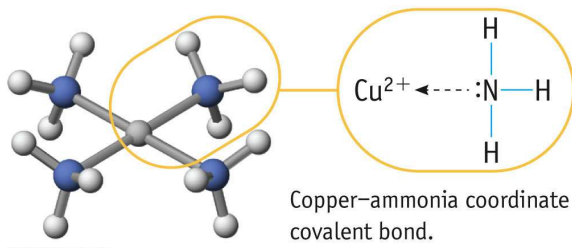
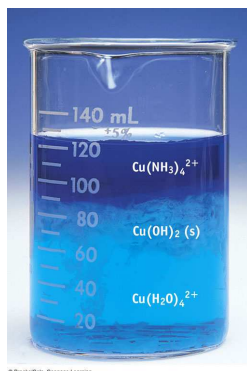
Lewis Acids & Bases

Other good examples involve metal ions.



Lewis Acids & Bases

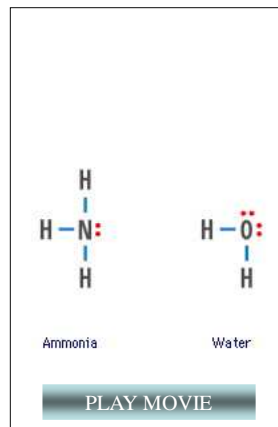
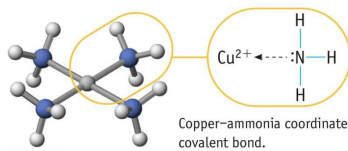
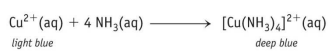
The combination of metal ions (Lewis acids) with Lewis bases such as H_2O and NH_3 leads to **COMPLEX IONS**



Reaction of NH_3 with $\text{Cu}^{2+}(\text{aq})$



PLAY MOVIE



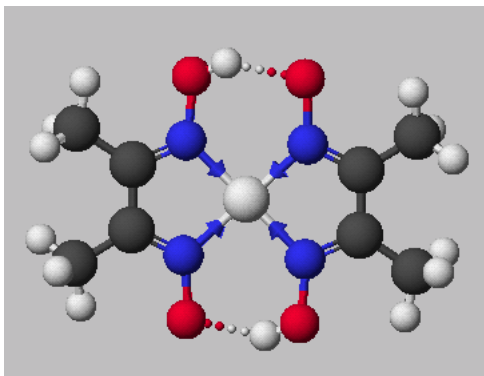
The Lewis Acid-Base Chemistry of Nickel(II)

Lewis Acids & Bases

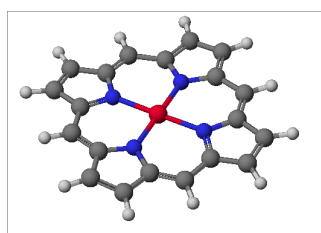
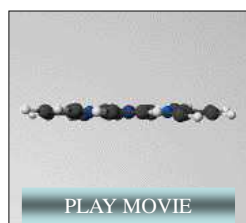


+ DMG

DMG =
dimethylglyoxime, a
standard reagent
to detect
nickel(II)



Lewis Acid-Base Interactions in Biology

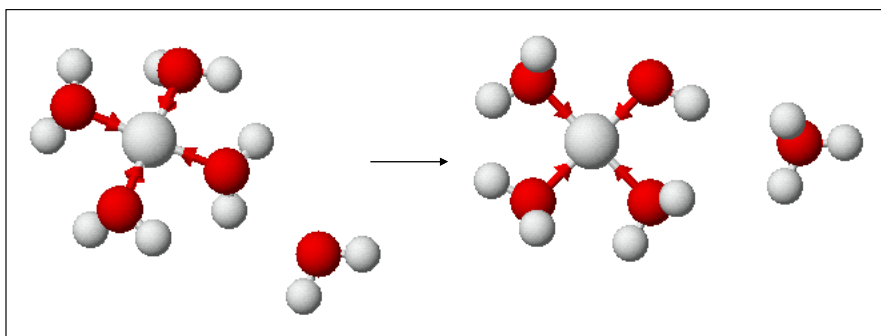


Heme group

- The heme group in hemoglobin can interact with O_2 and CO .
- The Fe ion in hemoglobin is a Lewis acid
- O_2 and CO can act as Lewis bases

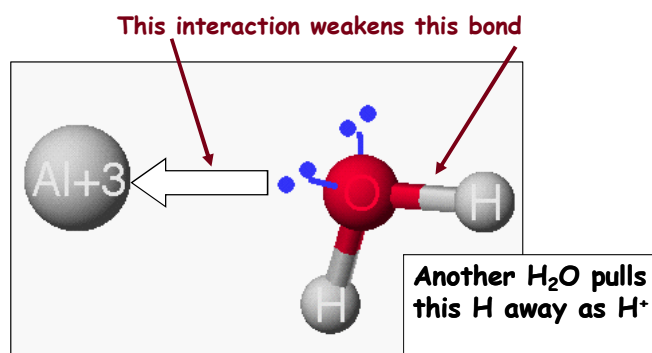
Lewis Acids & Bases

Many complex ions containing water undergo **HYDROLYSIS** to give acidic solutions.



Lewis Acids & Bases

This explains why water solutions of Fe^{3+} , Al^{3+} , Cu^{2+} , Pb^{2+} , etc. are acidic.



Amphoterism of $\text{Al}(\text{OH})_3$

(a) Add $\text{NH}_3(\text{aq})$

Adding aqueous ammonia to a soluble salt of Al^{3+} leads to a precipitate of $\text{Al}(\text{OH})_3$.

(b) Add $\text{NaOH}(\text{aq})$

Adding a strong base (NaOH) to $\text{Al}(\text{OH})_3$ dissolves the precipitate. Here, aluminum hydroxide acts as a Lewis acid toward the Lewis base OH^- and forms the soluble sodium salt of the complex ion $[\text{Al}(\text{OH})_4]^-$.

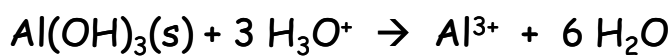
(c) Add $\text{HCl}(\text{aq})$

$\text{Al}(\text{OH})_3$ dissolves when a strong acid (HCl) is added. In this case, $\text{Al}(\text{OH})_3$ acts as a Brønsted base and forms a soluble aluminum salt and water.

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Lewis Acids & Bases

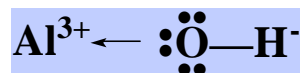
This explains **AMPHOTERIC** nature of some metal hydroxides.



Here $\text{Al}(\text{OH})_3$ is a Brønsted base.



Here $\text{Al}(\text{OH})_3$ is a Lewis acid.

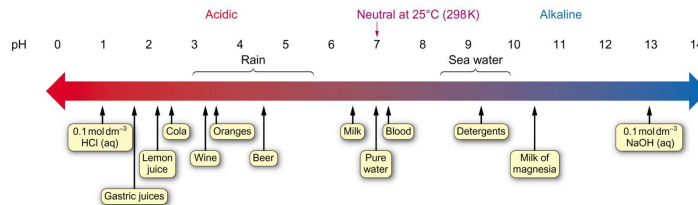
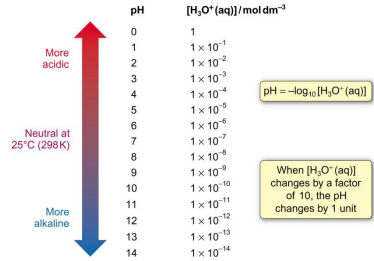




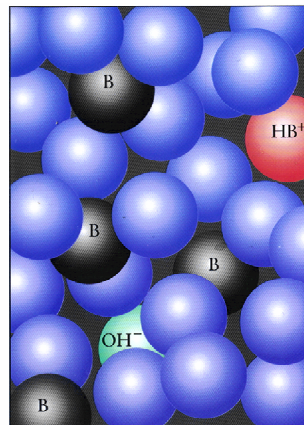
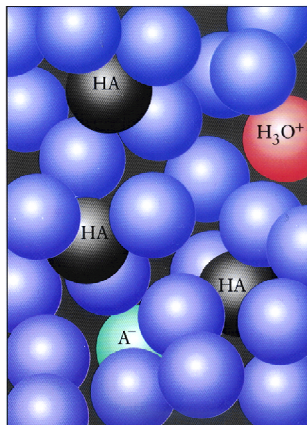
Lecture 14

Acid/base equilibria.

pK_a and pH



Acid/base equilibria.



Figures 3 and 4.14, page 520
Advanced Chemistry: Molecules, Matter, and Change, 2e
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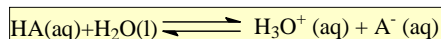
T

Acid strength : the acid dissociation constant K_A .

Chemistry³ Section 6.2. pp.268-270.

- 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 .

Acid dissociation equilibrium



$$K_C = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$$

$$K_A = K_C[\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

Acid dissociation constant

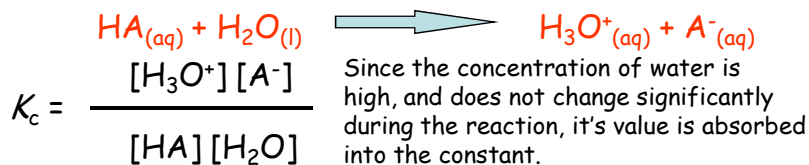
K_A is a measure of the acid strength. When K_A is large there is considerable dissociation and the acid is strong. When K_A is small there is a small degree of dissociation, and the acid is weak.

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:



Therefore:

$$K_A = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

The stronger the acid, the higher the $[\text{H}_3\text{O}^+]$ at equilibrium, and the larger the K_A :

Stronger acid

higher $[\text{H}_3\text{O}^+]$

larger K_A

For a weak acid with a relative high K_A ($\sim 10^{-2}$), a 1 M solution has $\sim 10\%$ of the HA molecules dissociated.

For a weak acid with a moderate K_A ($\sim 10^{-5}$), a 1 M solution has $\sim 0.3\%$ of the HA molecules dissociated.

For a weak acid with a relatively low K_A ($\sim 10^{-10}$), a 1 M solution has $\sim 0.001\%$ of the HA molecules dissociated.

Acid strengths and K_a value.

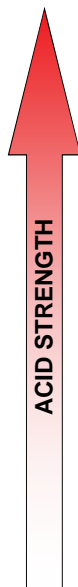


Table 18.2 K_a Values for Some Monoprotic Acids at 25°C

Name (Formula)	Lewis Structure*	K_a
Iodic acid (HIO ₃)		1.6×10^{-1}
Chlorous acid (HClO ₂)		1.12×10^{-2}
Nitrous acid (HNO ₂)		7.1×10^{-4}
Hydrofluoric acid (HF)		6.8×10^{-4}
Formic acid (HCOOH)		1.8×10^{-4}
Benzoic acid (C ₆ H ₅ COOH)		6.3×10^{-5}
Acetic acid (CH ₃ COOH)		1.8×10^{-5}
Propanoic acid (CH ₃ CH ₂ COOH)		1.3×10^{-5}
Hypochlorous acid (HClO)		2.9×10^{-8}
Hypobromous acid (HBrO)		2.3×10^{-9}
Hydrocyanic acid (HCN)		6.2×10^{-10}
Phenol (C ₆ H ₅ OH)		1.0×10^{-10}
Hypoiodous acid (HIO)		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		$K_a / \text{mol dm}^{-3}$	pK_a		
Hydriodic acid	HI	1×10^{10}	-10	Strongest acid	
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 ₂ SO ₄	1×10^3	-3		
Nitric acid [nitric(V) acid]	HNO ₃	25	-1.4		
Trichloroethanoic acid	CCl ₃ CO ₂ H	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 ₂ H	1.8×10^{-4}	3.75	Weak acids	
Benzoic acid	C ₆ H ₅ CO ₂ H	6.3×10^{-5}	4.20		
Ethanoic acid	CH ₃ CO ₂ H	1.7×10^{-5}	4.76		
Propanoic acid	CH ₃ CH ₂ CO ₂ H	1.3×10^{-5}	4.87		
Carbonic acid	H ₂ CO 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 ₆ H ₅ OH	1.0×10^{-10}	9.99		
					Weakest acid

The Relationship Between K_a and pK_a

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

Acid Name (Formula)	K_A at 298 K	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 ($\text{C}_6\text{H}_5\text{OH}$)	1.0×10^{-10}	10.00

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

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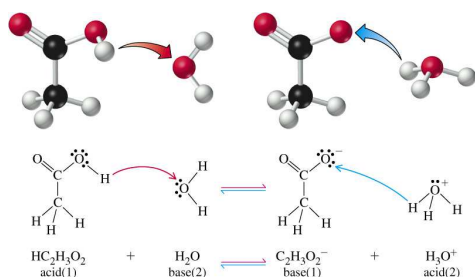
Table 18.3 The Relationship Between K_a and pK_a

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Hydrogen sulfate ion (HSO_4^-)	1.02×10^{-2}	1.991
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Acetic acid (CH_3COOH)	1.8×10^{-5}	4.74
Hypobromous acid (HBrO)	2.3×10^{-9}	8.64
Phenol ($\text{C}_6\text{H}_5\text{OH}$)	1.0×10^{-10}	10.00

↓
Acid Strength decreases

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

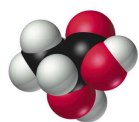
pK_a calculation



$$K_a = \frac{[\text{CH}_3\text{CO}_2^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CO}_2\text{H}]} = 1.8 \times 10^{-5}$$

$$\text{p}K_a = -\log(1.8 \times 10^{-5}) = 4.74$$

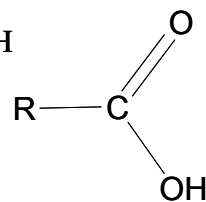
Weak acids



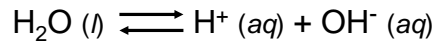
lactic acid $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}$



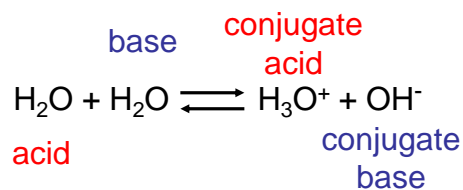
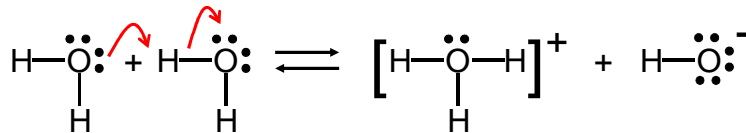
glycine $\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$



Acid-Base Properties of Water

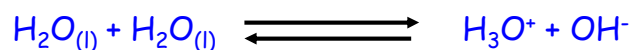


autoionization of water



15.2

Autoionization of Water



$$K_c = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

The ion-product for water, K_w :

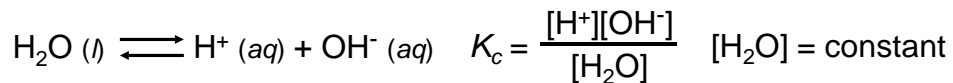
$$K_c[\text{H}_2\text{O}]^2 = K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ (at 298K)}$$

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

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} \text{ M (at 25}^\circ\text{C)}$$

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

The Ion Product of Water



$$K_c[\text{H}_2\text{O}] = K_w = [\text{H}^+][\text{OH}^-]$$

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

At 25°C
 $K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$

$$[\text{H}^+] = [\text{OH}^-]$$

$$[\text{H}^+] > [\text{OH}^-]$$

$$[\text{H}^+] < [\text{OH}^-]$$

Solution Is

neutral

acidic

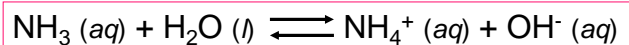
basic

15.2

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

Temperature / °C	Temperature / K	$K_w / \text{mol}^2 \text{dm}^{-6}$	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

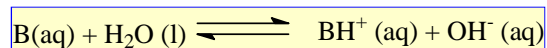
Weak Bases and Base Ionization Constants



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \quad K_b \uparrow \quad \text{weak base strength} \uparrow$$

K_b = base ionization constant

Basicity Constant K_b .



- 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 $[\text{OH}^-]$ instead of $[\text{H}^+]$.

$$K_c = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}][\text{H}_2\text{O}]}$$

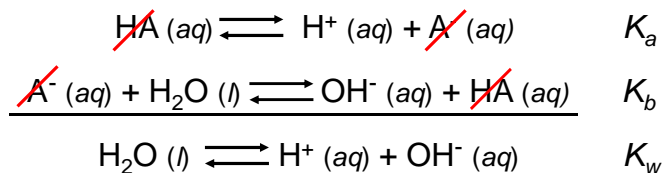
$$K_b = K_c[\text{H}_2\text{O}] = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

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

$$K_a K_b = K_w$$

$$pK_a + pK_b = pK_w$$

Ionization Constants of Conjugate Acid-Base Pairs



$$K_a K_b = K_w$$

Weak Acid and Its Conjugate Base

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

15.7

Acid and base dissociation constants

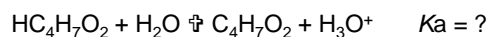
Ionization Equilibrium		Ionization Constant K	pK
Acid		$K_a =$	$pK_a =$
Iodic acid	$HIO_3 + H_2O \rightleftharpoons H_3O^+ + IO_3^-$	1.6×10^{-1}	0.80
Chlorous acid	$HClO_2 + H_2O \rightleftharpoons H_3O^+ + ClO_2^-$	1.1×10^{-2}	1.96
Chloroacetic acid	$HC_2H_2ClO_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_2ClO_2^-$	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

↑
Acid strength

↑
Base strength

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

Butyric acid, $\text{HC}_4\text{H}_7\text{O}_2$ (or $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$) is used to make compounds employed in artificial flavorings and syrups. A 0.250 M aqueous solution of $\text{HC}_4\text{H}_7\text{O}_2$ is found to have a pH of 2.72. Determine K_A for butyric acid.



For $\text{HC}_4\text{H}_7\text{O}_2$ K_A is likely to be much larger than K_W .

Therefore assume self-ionization of water is unimportant.

	$\text{HC}_4\text{H}_7\text{O}_2 + \text{H}_2\text{O}$	\rightleftharpoons	$\text{C}_4\text{H}_7\text{O}_2^- + \text{H}_3\text{O}^+$
Initial conc.	0.250 M		0 0
Changes	-x M		+x M +x M
Equilbrm. conc.	(0.250-x) M		x M x M

$$\text{Log}[\text{H}_3\text{O}^+] = -\text{pH} = -2.72$$

$$[\text{H}_3\text{O}^+] = 10^{-2.72} = 1.9 \times 10^{-3} = x$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_4\text{H}_7\text{O}_2^-]}{[\text{HC}_4\text{H}_7\text{O}_2]} = \frac{1.9 \times 10^{-3} \cdot 1.9 \times 10^{-3}}{(0.250 - 1.9 \times 10^{-3})}$$

$$K_a = 1.5 \times 10^{-5} \quad \text{Check assumption: } K_a \gg K_w.$$

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

PROBLEM: Propanoic acid ($\text{CH}_3\text{CH}_2\text{COOH}$, which we simplify and HPr) is an organic acid whose salts are used to retard mold growth in foods. What is the $[\text{H}_3\text{O}^+]$ of 0.10M HPr ($K_a = 1.3 \times 10^{-5}$)?

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

Assumptions: For $\text{HPr}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{Pr}^-(aq)$
 $x = [\text{HPr}]_{\text{diss}} = [\text{H}_3\text{O}^+]_{\text{from HPr}} = [\text{Pr}^-] \quad K_a = \frac{[\text{H}_3\text{O}^+][\text{Pr}^-]}{[\text{HPr}]}$

SOLUTION:

Concentration(M)	HPr(aq)	+ H ₂ O(l)	\rightleftharpoons	H ₃ O ⁺ (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 $x \ll 0.10$

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

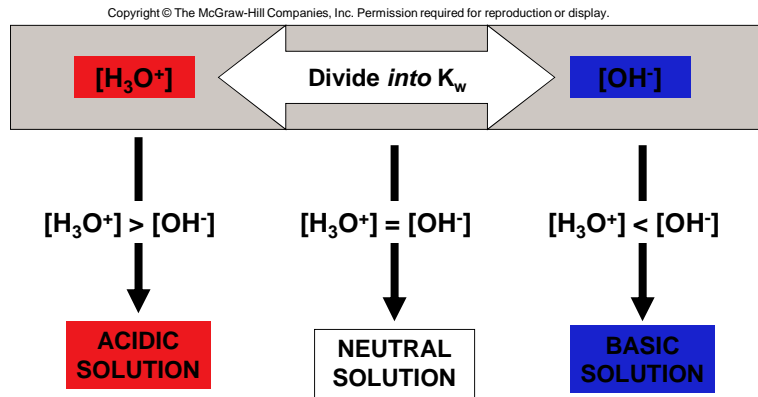
continued

$$1.3 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{Pr}^-]}{[\text{HPr}]} = \frac{(x)(x)}{0.10}$$

$$x = \sqrt{(0.10)(1.3 \times 10^{-5})} = 1.1 \times 10^{-3} \text{M} = [\text{H}_3\text{O}^+]$$

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

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

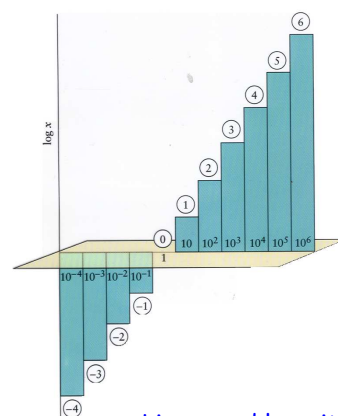


The pH concept.

- 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.

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

$$[H_3O^+] = 10^{-pH}$$



Linear and logarithmic Scales.

Figure 14.8, page 515
 Advanced Chemistry, Molecular Matter,
 © 1997 by P. W. Atkins and L. L. Jones

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 ₂ SO ₄ ^a	Mg(OH) ₂
	Ca(OH) ₂
	Sr(OH) ₂
	Ba(OH) ₂

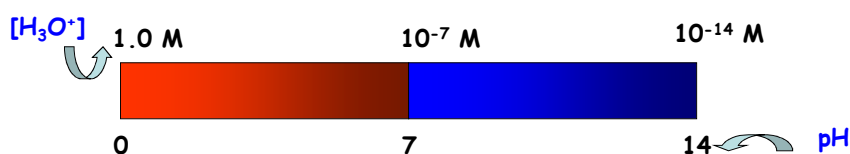
^aH₂SO₄ ionizes in two distinct steps. It is a strong acid only in its first ionization (see page 687).

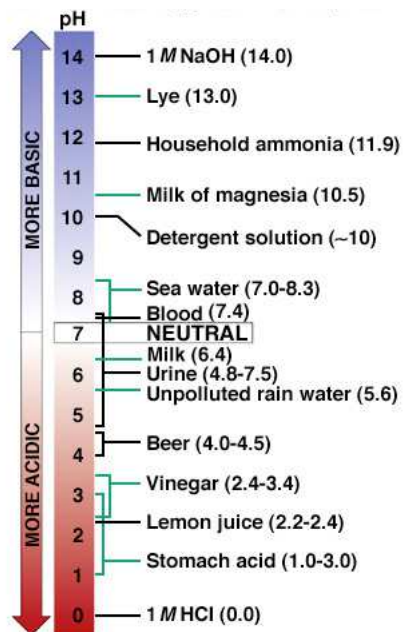


Thymol Blue Indicator
 $\text{pH} < 1.2 < \text{pH} < 2.8 < \text{pH}$

The pH Scale.

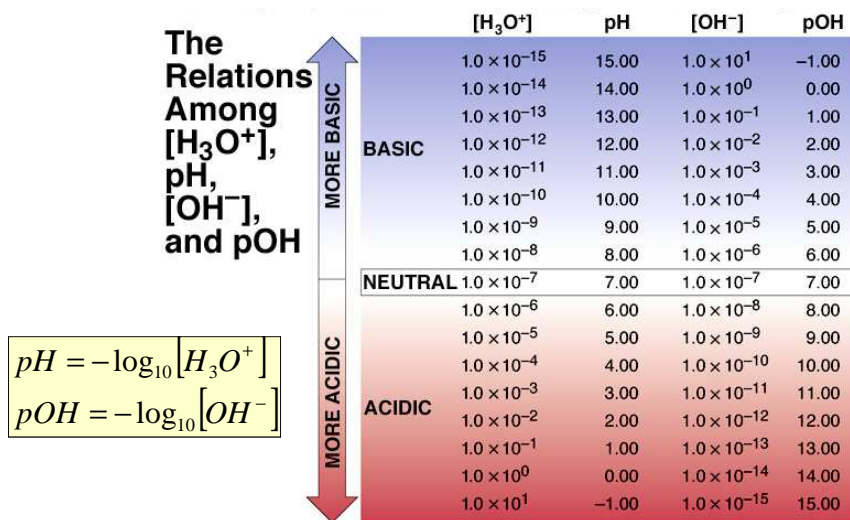
- pH is expressed on a numerical scale from 0 to 14.
- When $[\text{H}_3\text{O}^+] = 1.0 \text{ M}$ (i.e. 10^0M), $\text{pH} = 0$.
- When $[\text{H}_3\text{O}^+] = 10^{-14} \text{ M}$, $\text{pH} = 14$.
- $\text{pH value} < 7$ implies an acidic solution.
- $\text{pH value} > 7$ implies an alkaline solution.
- $\text{pH value} = 7$ 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



pH - A Measure of Acidity

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

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



Calculating $[\text{H}_3\text{O}^+]$, pH, $[\text{OH}^-]$, 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 $[\text{H}_3\text{O}^+]$, pH, $[\text{OH}^-]$, and pOH of the three solutions at 25°C.

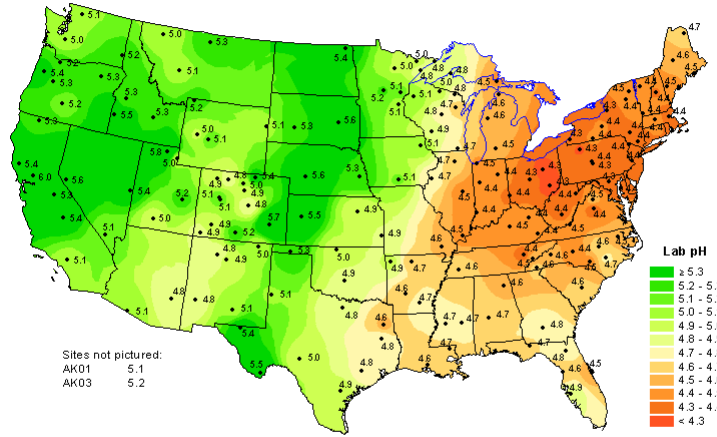
PLAN: HNO_3 is a strong acid so $[\text{H}_3\text{O}^+] = [\text{HNO}_3]$. Use K_w to find the $[\text{OH}^-]$ and then convert to pH and pOH.

SOLUTION: For 2.0M HNO_3 , $[\text{H}_3\text{O}^+] = 2.0\text{M}$ and $-\log [\text{H}_3\text{O}^+] = -0.30 = \text{pH}$
 $[\text{OH}^-] = K_w / [\text{H}_3\text{O}^+] = 1.0 \times 10^{-14} / 2.0 = 5.0 \times 10^{-15}\text{M}$; $\text{pOH} = 14.30$

For 0.3M HNO_3 , $[\text{H}_3\text{O}^+] = 0.30\text{M}$ and $-\log [\text{H}_3\text{O}^+] = 0.52 = \text{pH}$
 $[\text{OH}^-] = K_w / [\text{H}_3\text{O}^+] = 1.0 \times 10^{-14} / 0.30 = 3.3 \times 10^{-14}\text{M}$; $\text{pOH} = 13.48$

For 0.0063M HNO_3 , $[\text{H}_3\text{O}^+] = 0.0063\text{M}$ and $-\log [\text{H}_3\text{O}^+] = 2.20 = \text{pH}$
 $[\text{OH}^-] = K_w / [\text{H}_3\text{O}^+] = 1.0 \times 10^{-14} / 6.3 \times 10^{-3} = 1.6 \times 10^{-12}\text{M}$; $\text{pOH} = 11.80$

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



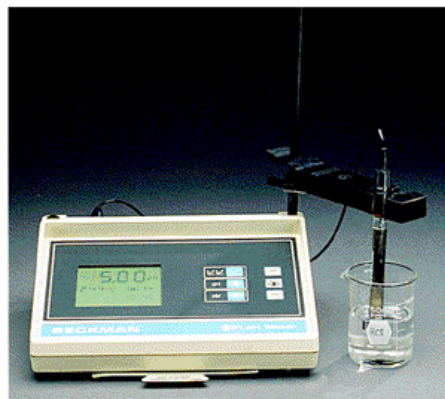
National Atmospheric Deposition Program/National Trends Network
<http://nadp.sws.uiuc.edu>

The problem of acid rain.

Methods for Measuring the pH of an Aqueous Solution



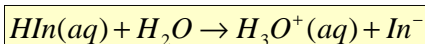
(a) pH paper



(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.
- 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 .

$$\begin{array}{l}
 \text{Weak acid case} \\
 \alpha = \sqrt{\frac{K_a}{c}} \\
 [H_3O^+] = \sqrt{cK_a} \\
 c = [HA] \\
 pH = \log_{10}[H_3O^+] = \log_{10}\{\sqrt{cK_a}\}
 \end{array}$$

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



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

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

$\alpha =$ degree of ionisation .

	$\text{HA(aq)} + \text{H}_2\text{O(l)}$	\rightleftharpoons	$\text{H}_3\text{O}^+(\text{aq}) + \text{A}^-(\text{aq})$	
Initial concentrations	c		0	0
Equilibrium concentrations	$(1-\alpha)c$		αc	αc
				$0 < \alpha < 1$

The acid dissociation constant is given by :

$$K_a = \frac{[\text{H}_3\text{O}^+]_{\text{eq}} [\text{A}^-]_{\text{eq}}}{[\text{HA}]_{\text{eq}}} = \frac{\alpha c \cdot \alpha c}{(1-\alpha)c} = \frac{\alpha^2 c}{1-\alpha}$$

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 $[\text{H}_3\text{O}^+]$ and hence the solution pH since :

$$[\text{H}_3\text{O}^+] = \alpha c = \sqrt{\frac{K_a^2}{4} + cK_a} - \frac{K_a}{2}$$

Useful approximation .

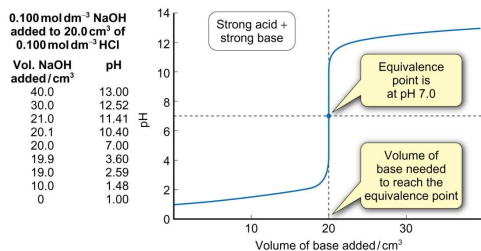
If α is small (valid if the acid is weak) then $\alpha \ll 1$

We set $1 - \alpha = 1$



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

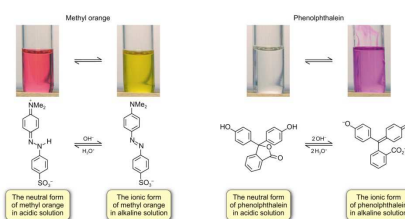
$$[\text{H}_3\text{O}^+] \cong \sqrt{cK_a}$$



Indicator	Colour		pK _a	pH range of colour change
	in acid	in base		
Thymol blue (acid range)	Red	Yellow	1.7	1.2–2.8
Methyl orange	Red	Yellow	3.4	3.2–4.4
Bromophenol blue	Yellow	Blue	3.9	3.0–4.6
Bromocresol green	Yellow	Blue	4.8	3.8–5.4
Methyl red	Red	Yellow	5.0	4.8–6.0
Litmus	Red	Blue	6.5	5.0–8.0
Phenol red	Yellow	Red	7.9	6.7–8.1
Thymol blue (base range)	Yellow	Blue	9.0	8.0–9.7
Phenolphthalein	Colourless	Pink	9.4	8.0–10.0
Alizarin yellow R	Yellow	Purple	11.2	10.1–12.0

Lecture 15

Acid/base reactions.
Equilibria in aqueous solutions.



COLÁISTE NA TRÍÓNÓIDE, BAILE ÁTHA CLIATH | TRINITY COLLEGE DUBLIN
Oilscoil Átha Cliath | The University of Dublin

Titration

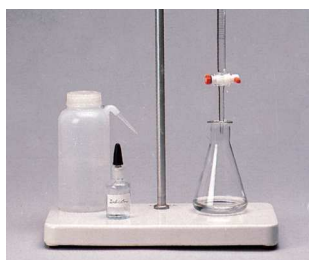
Kotz 7th ed. Section 18.3, pp.821-832.

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

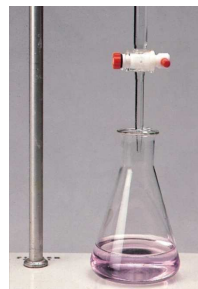
Titration is based on the acid/base neutralization reaction.

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)



4.7

Neutralization Reactions and Titration Curves

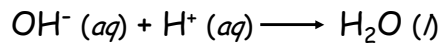
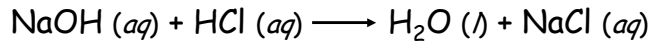
- Equivalence point:
 - The point in the reaction at which both acid and base have been consumed.
 - Neither acid nor base is present in excess.
- End point:
 - The point at which the indicator changes color.
- Titrant:
 - The known solution added to the solution of unknown concentration.
- Titration Curve:
 - The plot of pH vs. volume.

The millimole

- Typically:
 - Volume of titrant added is less than 50 mL.
 - Concentration of titrant is less than 1 mol/L.
 - Titration uses less than 1/1000 mole of acid and base.

$$M = \frac{\text{mol}}{\text{L}} = \frac{\text{mol}/1000}{\text{L}/1000} = \frac{\text{mmol}}{\text{mL}}$$

Strong Acid-Strong Base Titrations

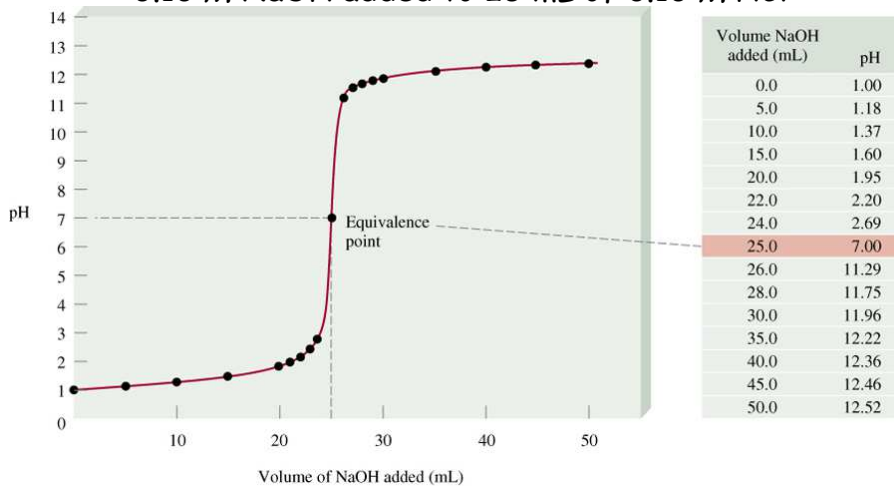


At equivalence point :
Amount of acid =
Amount of base

$$n_A = n_B$$

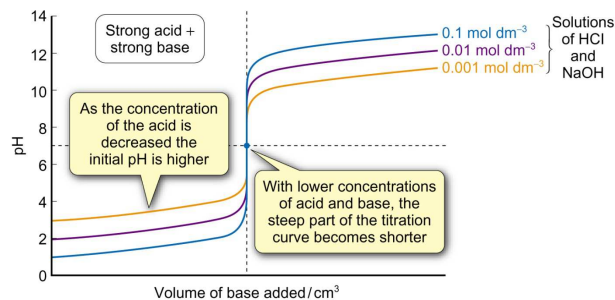
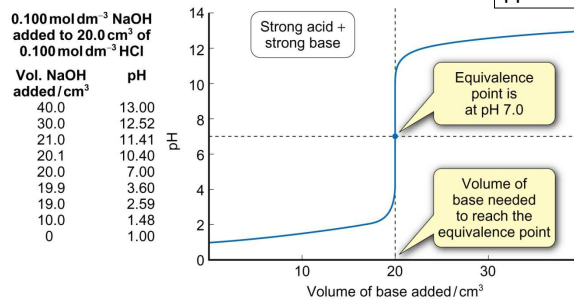
$$c_A V_A = c_B V_B$$

0.10 M NaOH added to 25 mL of 0.10 M HCl



Strong Acid/strong base titration

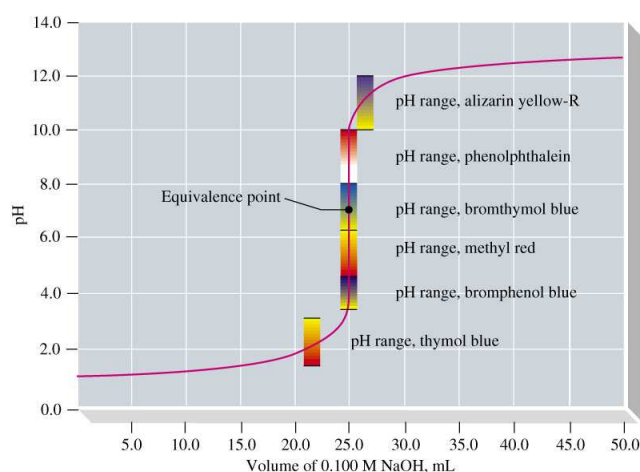
Chemistry³, section 6.4
pp.282-286.



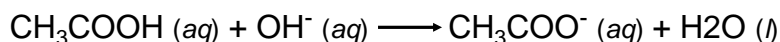
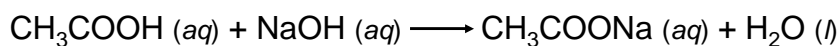
Titration of a Strong Acid with a Strong Base

- The pH has a low value at the beginning.
- The pH changes slowly
 - until just before the equivalence point.
- The pH rises sharply
 - perhaps 6 units per 0.1 mL addition of titrant.
- The pH rises slowly again.
- Any Acid-Base Indicator will do.
 - As long as color change occurs between pH 4 and 10.

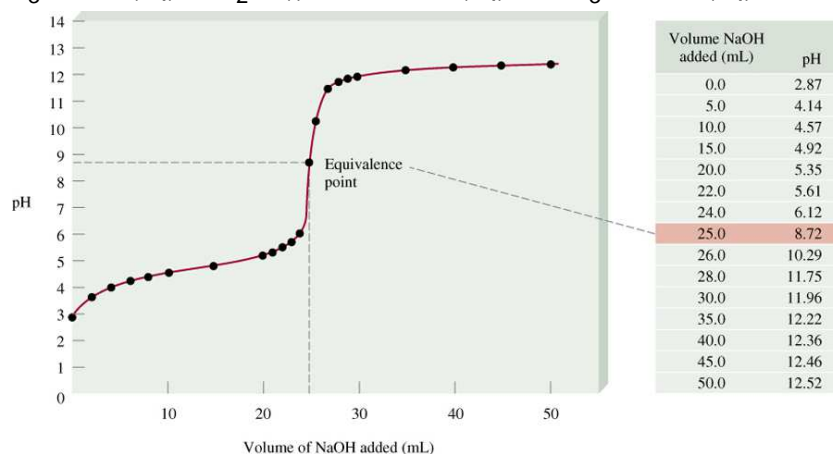
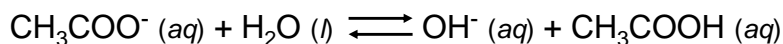
Titration of a Strong Acid with a Strong Base



Weak Acid-Strong Base Titrations



At equivalence point ($\text{pH} > 7$):

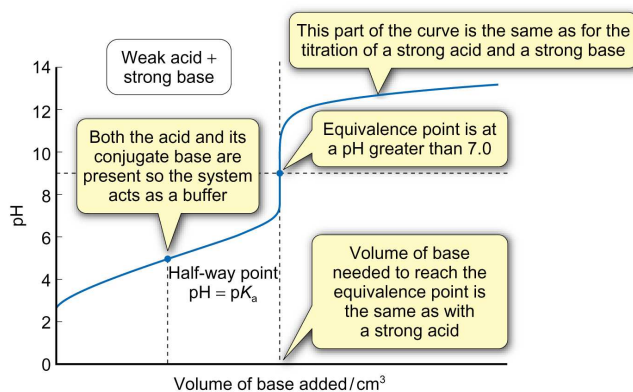


16.4

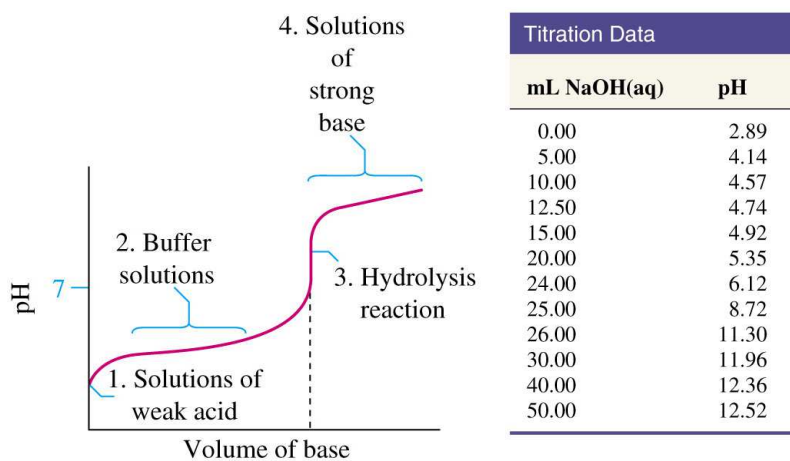
WA/SB Titration: Features of interest.

- Four regions in titration curve can be distinguished.
 - **Initial region:**
 - weak acid HA and H_2O only present.
 - **Buffer region:**
 - HA and A^- present; pH change is slow and its value is determined via Henderson-Hasselbalch equation. Buffer region contains midpoint of titration curve. From HH expression we determine that $\text{pH} = \text{pK}_a$ at $V = V_e/2$.
 - **Equivalence point region:**
 - Major species present is A^- and so pH is determined via hydrolysis expression. pH value at equivalence point is not 7 but will be greater than 7 due to anion hydrolysis.
 - **Post equivalence point region:**
 - Here both A^- and OH^- are main species present, but $[\text{OH}^-] \gg [\text{A}^-]$ and so pH is determined by concentration of excess OH^- ion.

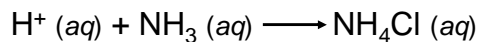
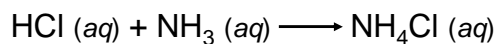
Weak acid/strong base titration



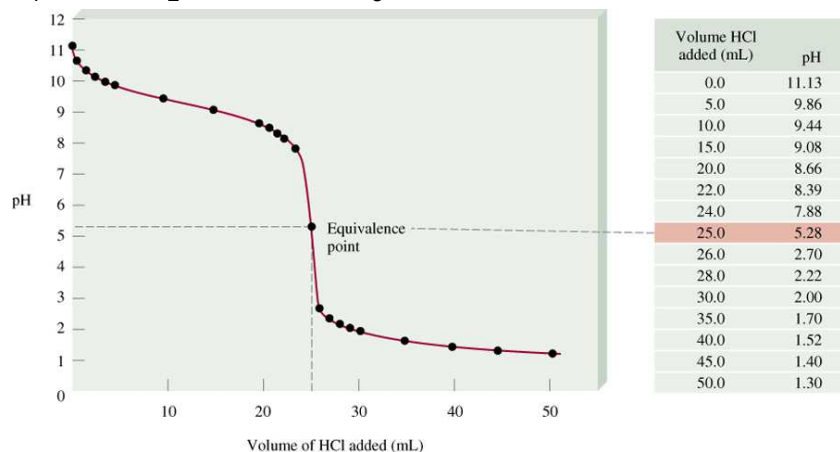
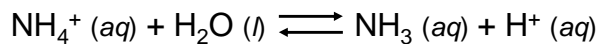
Titration of a Weak Acid with a Strong Base



Strong Acid-Weak Base Titrations

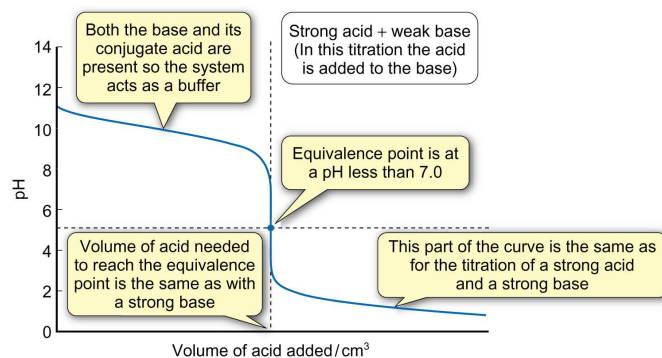


At equivalence point (pH < 7):

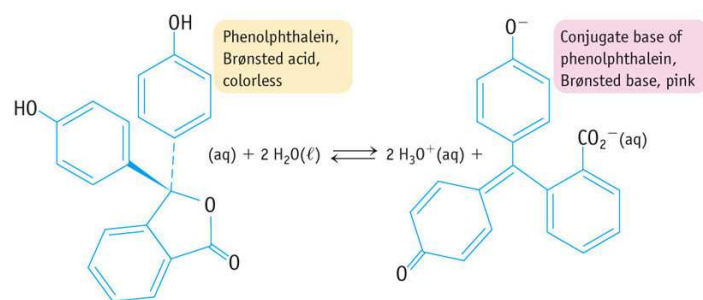
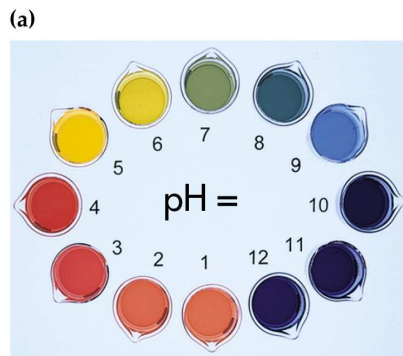


16.4

Strong acid/weak base titration



Indicators : a visual estimation of pH.



© Brooks/Cole, Cengage Learning

Acid/Base Indicators

Chemistry³ section 6.5, pp.287-289.

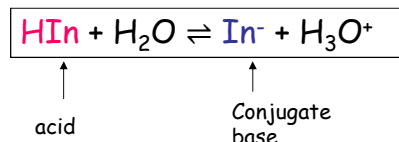
While it is possible to follow the course of an acid/base titration using a pH meter it is easier to use an indicator. At the end point of the titration

The indicator changes colour.

Kotz 7th ed. Section 18.3, pp.821-832.

Color of some substances depends on the pH.

An acid/base indicator is a weak organic acid (HIn) that has a different colour from its conjugate base (In⁻), with the colour change occurring over a relatively narrow pH range.



$$K_{in} = K_A = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]}$$

$$[\text{H}_3\text{O}^+] = K_{in} \left\{ \frac{[\text{HIn}]}{[\text{In}^-]} \right\}$$

$$\text{pH} = \text{p}K_{in} + \log \left\{ \frac{[\text{In}^-]}{[\text{HIn}]} \right\}$$

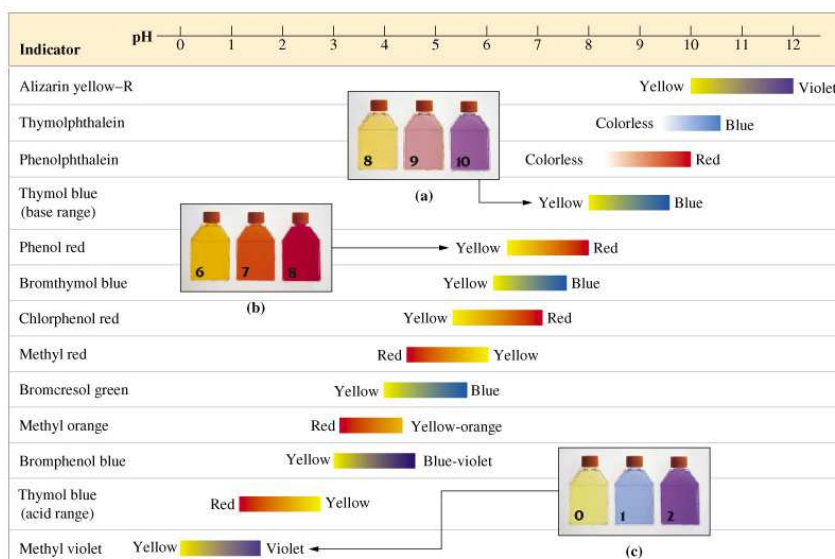
Since HIn is a weak acid the ratio of [HIn] to [In⁻] will be governed by [H₃O⁺] in the test solution.

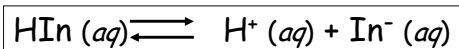
Indicator changes colour when reaction is half complete when [HIn] = [In⁻].

At this point pH = pK_{in}.

An indicator does not change colour instantaneously. Generally one can only see the colour of the neutral (or ionic) form if there is a 10:1 excess of that species present. Hence an indicator that is red in the neutral form and blue in the ionized form will appear completely red when [HIn] > 10[In⁻]. This means that the colour change appears over 2 pH units.

Indicator Colors and Ranges





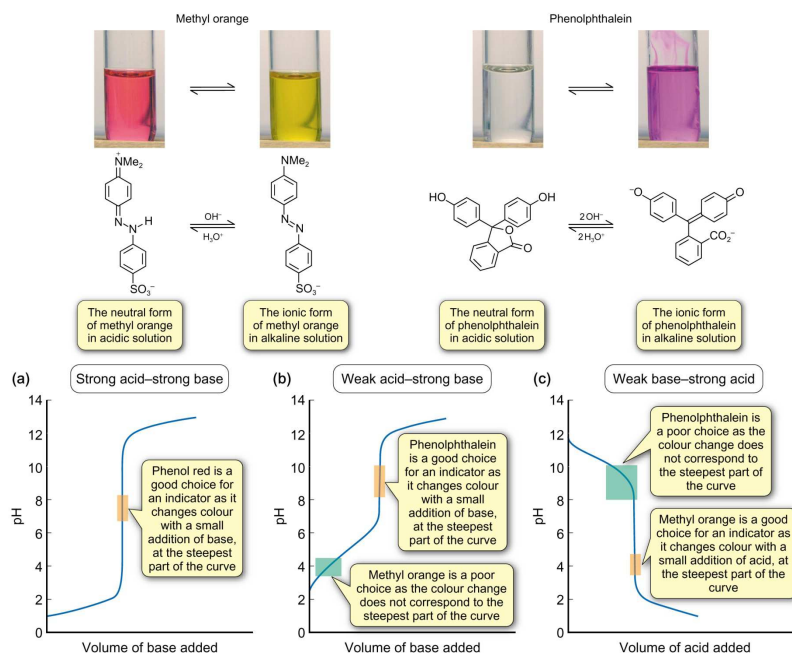
$\frac{[\text{HIn}]}{[\text{In}^-]} \geq 10$ Color of acid (HIn) predominates

$\frac{[\text{HIn}]}{[\text{In}^-]} \leq 10$ Color of conjugate base (In⁻) predominates

Table 16.1 Some Common Acid-Base Indicators

Indicator	C o l o r		pH Range*
	In Acid	In Base	
Thymol blue	Red	Yellow	1.2–2.8
Bromophenol blue	Yellow	Bluish purple	3.0–4.6
Methyl orange	Orange	Yellow	3.1–4.4
Methyl red	Red	Yellow	4.2–6.3
Chlorophenol blue	Yellow	Red	4.8–6.4
Bromothymol blue	Yellow	Blue	6.0–7.6
Cresol red	Yellow	Red	7.2–8.8
Phenolphthalein	Colorless	Reddish pink	8.3–10.0

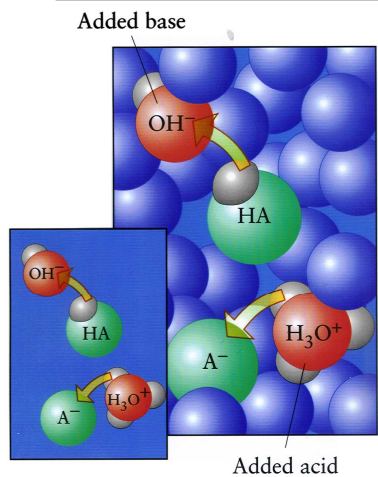
* The pH range is defined as the range over which the indicator changes from the acid color to the base color.



Specifics and mechanism of buffer action.

- A **buffer solution** resists changes in pH, when small amounts of acid or base are added. Buffers are used to keep the pH of a solution constant.
- A buffer solution consists of:
 - a mixture of a weak acid and its salt (the latter made via reaction of the weak acid and a strong base),
 - A mixture of a weak base and its salt (the latter made via reaction of the weak base and a strong acid).
- Hence the buffer solution consists of a weak acid HA (supplies protons to an added strong base), and its conjugate base A^- (accepts protons from added strong acid).
- Alternatively the buffer can consist of a weak base B (accepts protons from added strong acid) and its conjugate acid BH^+ (transfers protons to added strong base).
- A buffer solution contains a **sink** for protons supplied when a strong acid is added, and a **source** of protons to supply to a strong base that is added.
- The joint action of the source and sink keeps the pH constant when strong acid or strong base is added to the solution.

Chemistry³ Section 6.3 pp.279-281.



Kotz 7th Ed, section 18.1,18.2, pp.811-821.

Figure 16.29
Loreta Jones and Peter Atkins, CHEMISTRY: MOLECULES, MATTER, AND CHANGE, Fourth Edition
Copyright © 2000 by Loreta Jones and Peter Atkins

The Effect of Addition of Acid or Base to Un-buffered or Buffered Solutions

100 mL HCl unbuffered pH 5.

A

B Addition of 1mL of 1M HCl or 1M NaOH. Get large change in solution pH value.

100mL buffer solution. 1M acetic acid/1M sodium Acetate, pH5.

C

D Addition of 1mL of 1M HCl or 1M NaOH to buffer. Get little change in solution pH value.

Buffer Solutions

Kotz, section 18.2



PLAY MOVIE

HCl is added to pure water.



PLAY MOVIE

HCl is added to a solution of a weak acid H_2PO_4^- and its conjugate base HPO_4^{2-} .

Buffer Solutions

A buffer solution is a special case of the common ion effect.

The function of a buffer is to resist changes in the pH of a solution.

Buffer Composition

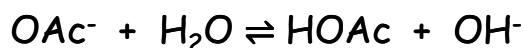
Weak Acid	+	Conj. Base
HOAc	+	OAc ⁻
H ₂ PO ₄ ⁻	+	HPO ₄ ²⁻
NH ₄ ⁺	+	NH ₃

Buffer Solutions

Consider HOAc/OAc⁻ to see how buffers work

ACID USES UP ADDED OH⁻

We know that



has $K_b = 5.6 \times 10^{-10}$

Therefore, the reverse reaction of the WEAK ACID with added OH⁻

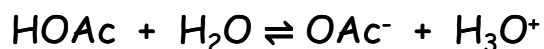
has $K_{\text{reverse}} = 1/K_b = 1.8 \times 10^9$

K_{reverse} is VERY LARGE, so HOAc completely eats up OH⁻ !!!!

Buffer Solutions

Consider HOAc/OAc⁻ to see how buffers work.

CONJ. BASE USES UP ADDED H⁺



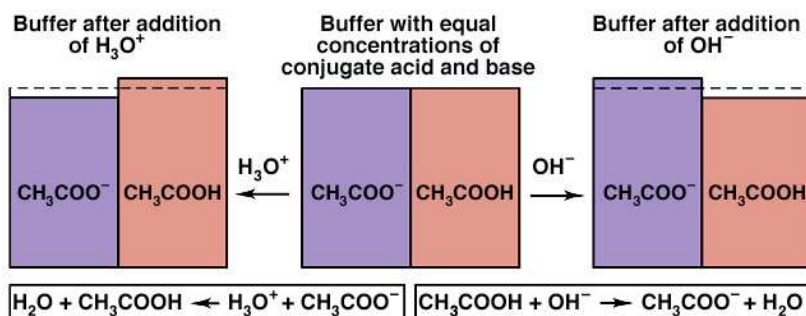
has $K_a = 1.8 \times 10^{-5}$

Therefore, the reverse reaction of the WEAK BASE with added H⁺

has $K_{\text{reverse}} = 1/K_a = 5.6 \times 10^4$

K_{reverse} is VERY LARGE, so OAc⁻ completely eats up H⁺ !

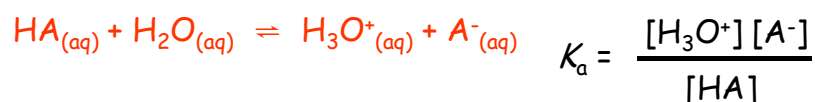
How a Buffer Works



A buffer consists of a solution that contains "high" concentrations of the acidic and basic components. This is normally a weak acid and the anion of that weak acid, or a weak base and the corresponding cation of the weak base. When small quantities of H_3O^+ or OH^- are added to the buffer, they cause *a small amount of one buffer component to convert into the other*. As long as the amounts of H_3O^+ and OH^- are small as compared to the concentrations of the acid and base in the buffer, the added ions will have little effect on the pH since they are consumed by the buffer components.

The Henderson-Hasselbalch Equation

Take the equilibrium ionization of a weak acid:



Solving for the hydronium ion concentration gives:

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]}$$

The pH is determined largely by the **pKa of the acid** and then **adjusted by the ratio of acid and conjugate base**.

Taking the negative logarithm of both sides:

$$-\log[\text{H}_3\text{O}^+] = -\log K_a - \log\left(\frac{[\text{HA}]}{[\text{A}^-]}\right) \quad \text{pH} = -\log K_a - \log\left(\frac{[\text{HA}]}{[\text{A}^-]}\right)$$

Generalizing for any conjugate acid-base pair :

Henderson-Hasselbalch equation

$$\text{pH} = \text{p}K_A + \log_{10} \left\{ \frac{[\text{salt}]}{[\text{acid}]} \right\}$$

$$\text{pH} = \text{p}K_A + \log_{10} \left\{ \frac{[\text{A}^-]}{[\text{HA}]} \right\}$$

Buffer Capacity and Buffer Range

Buffer capacity is the ability to resist pH change.

The more concentrated the components of a buffer, the greater the buffer capacity.

The pH of a buffer is distinct from its buffer capacity.

A buffer has the highest capacity when the component concentrations are equal.

Buffer range is the pH range over which the buffer acts effectively.

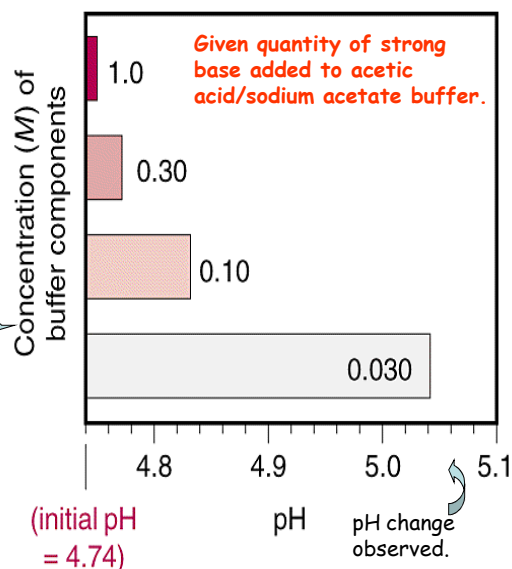
Buffers have a usable range within ± 1 pH unit of the pK_a of its acid component.

Buffer capacity.

- Buffer solutions resist a pH change as long as the concentrations of buffer components are large compared with the amount of strong acid or base added.
- Buffer capacity depends on the component concentrations and is a measure of the capacity to resist pH change.
- The more concentrated the components of the buffer, the greater the buffer capacity.
- Buffer capacity is also affected by the relative concentrations of the buffer components.
- For the best buffer capacity we must have

$$0.1 \leq \frac{[HA]}{[A^-]} \leq 10$$

Buffers have a useable range within ± 1 pH unit of the pK_a value.



The best choice of WA/CB pair for a buffer system is one in which $[HA] = [A^-]$. In this case the WA has a pK_a value equal to the desired solution pH.

More on buffer solutions.

Atkins & Jones p.562

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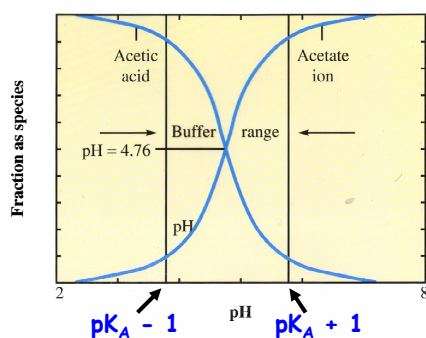
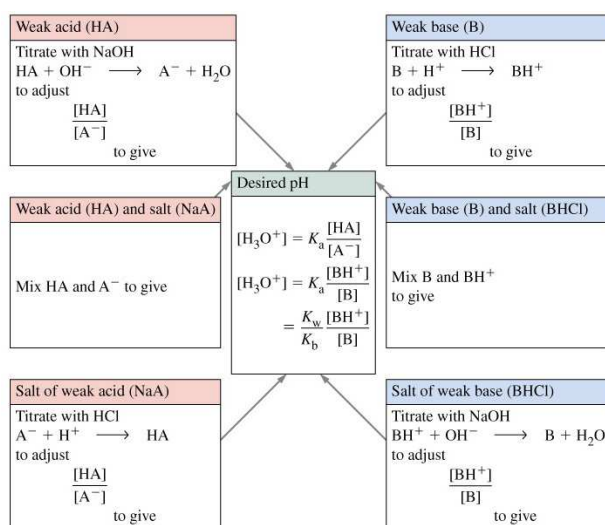


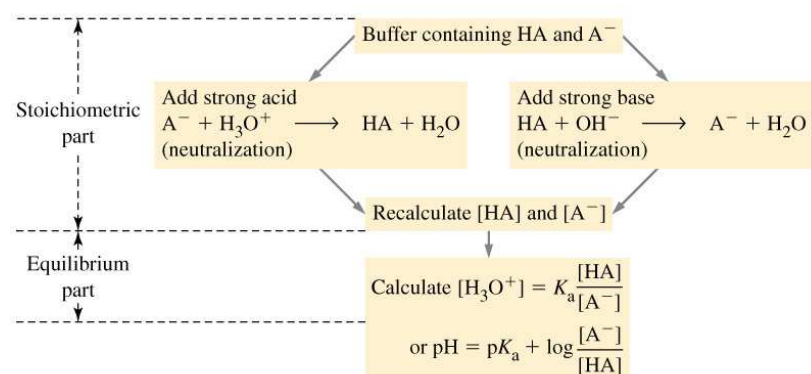
Table 15.4 Typical buffer systems

Composition	pK_a
ACID BUFFERS	
$\text{CH}_3\text{COOH}/\text{CH}_3\text{CO}_2^-$	4.74
$\text{HNO}_2/\text{NO}_2^-$	3.37
$\text{HClO}_2/\text{ClO}_2^-$	2.00
BASE BUFFERS	
$\text{NH}_4^+/\text{NH}_3$	9.25
$(\text{CH}_3)_3\text{NH}^+/(\text{CH}_3)_3\text{N}$	9.81
$\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$	7.21

Six Methods of Preparing Buffer Solutions



Calculating Changes in Buffer Solutions



Sample Problem 19.1

Calculating the Effect of Added H₃O⁺ or OH⁻ on Buffer pH

PROBLEM: Calculate the pH:

- (a) of a buffer solution consisting of 0.50M CH₃COOH and 0.50M CH₃COONa
- (b) after adding 0.020mol of solid NaOH to 1.0L of the buffer solution in part (a)
- (c) after adding 0.020mol of HCl to 1.0L of the buffer solution in part (a)

K_a of CH₃COOH = 1.8×10^{-5} . (Assume the additions cause negligible volume changes.)

PLAN: We know K_a and can find initial concentrations of conjugate acid and base. Make assumptions about the amount of acid dissociating relative to its initial concentration. Proceed step-wise through changes in the system.

SOLUTION: (a)

Concentration (M)	CH ₃ COOH(aq)	+ H ₂ O(l)	⇌	CH ₃ COO ⁻ (aq)	+ H ₃ O ⁺ (aq)
Initial	0.50	-		0.50	0
Change	- x	-		+ x	+ x
Equilibrium	0.50-x	-		0.50 + x	x

Sample Problem 19.1
Calculating the Effect of Added H₃O⁺ and OH⁻ on Buffer pH

continued (2 of 4)

$$[\text{H}_3\text{O}^+] = x \quad [\text{CH}_3\text{COOH}]_{\text{equil}} \approx 0.50\text{M} \quad [\text{CH}_3\text{COO}^-]_{\text{initial}} \approx 0.50\text{M}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \quad [\text{H}_3\text{O}^+] = x = K_a \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = 1.8 \times 10^{-5}\text{M}$$

 Check the assumption: $1.8 \times 10^{-5} / 0.50 \times 100 = 3.6 \times 10^{-3}\%$

(b) $[\text{OH}^-]_{\text{added}} = \frac{0.020 \text{ mol}}{1.0\text{L soln}} = 0.020\text{M NaOH}$

Concentration (M)	CH ₃ COOH(aq)	+ OH ⁻ (aq)	⇌	CH ₃ COO ⁻ (aq)	+ H ₂ O(l)
Before addition	0.50	-		0.50	-
Addition	-	0.020		-	-
After addition	0.48	0		0.52	-

Sample Problem 19.1
Calculating the Effect of Added H₃O⁺ and OH⁻ on Buffer pH

continued (3 of 4)

 Set up a *reaction table* with the new values.

Concentration (M)	CH ₃ COOH(aq)	+ H ₂ O(l)	⇌	CH ₃ COO ⁻ (aq)	+ H ₃ O ⁺ (aq)
Initial	0.48	-		0.52	0
Change	- x	-		+ x	+ x
Equilibrium	0.48 - x	-		0.52 + x	x

$$[\text{H}_3\text{O}^+] = 1.8 \times 10^{-5} \frac{0.48}{0.52} = 1.7 \times 10^{-5} \quad \text{pH} = 4.77$$

(c) $[\text{H}_3\text{O}^+]_{\text{added}} = \frac{0.020 \text{ mol}}{1.0\text{L soln}} = 0.020\text{M H}_3\text{O}^+$

Concentration (M)	CH ₃ COO ⁻ (aq)	+ H ₃ O ⁺ (aq)	⇌	CH ₃ COOH(aq)	+ H ₂ O(l)
Before addition	0.50	-		0.50	-
Addition	-	0.020		-	-
After addition	0.48	0		0.52	-

Sample Problem 19.1**Calculating the Effect of Added H₃O⁺ and OH⁻ on Buffer pH**

continued (4 of 4)

Set up a *reaction table* with the new values.

Concentration (M)	CH ₃ COOH(aq)	+ H ₂ O(l)	⇌	CH ₃ COO ⁻ (aq)	+ H ₃ O ⁺ (aq)
Initial	0.52	-		0.48	0
Change	- x	-		+ x	+ x
Equilibrium	0.52 - x	-		0.48 + x	x

$[\text{H}_3\text{O}^+] = 1.8 \times 10^{-5} \frac{0.52}{0.48} = 2.0 \times 10^{-5}$
pH = 4.70

Acid/base properties of salts.

- A salt is an ionic compound formed by the reaction between an acid and a base.
- Salts are strong electrolytes that completely dissociate into ions in water.
- The term **salt hydrolysis** describes the reaction of an anion or a cation of a salt, or both, with water.
- Salt hydrolysis usually affects the pH of a solution.
- Salts can produce **acidic** solutions, **basic** solutions or **neutral** solutions.

Behavior of Salts in Water

Table 18.8 The Behavior of Salts in Water

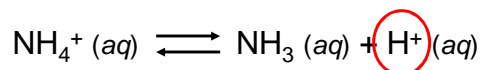
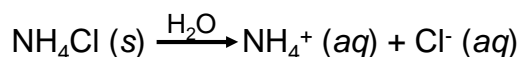
Salt Solution (Examples)	pH	Nature of Ions	Ion That Reacts with Water
Neutral [NaCl, KBr, Ba(NO ₃) ₂]	7.0	Cation of strong base Anion of strong acid	None
Acidic [NH ₄ Cl, NH ₄ NO ₃ , CH ₃ NH ₃ Br]	<7.0	Cation of weak base Anion of strong acid	Cation
Acidic [Al(NO ₃) ₃ , CrCl ₃ , FeBr ₃]	<7.0	Small, highly charged cation Anion of strong acid	Cation
Basic [CH ₃ COONa, KF, Na ₂ CO ₃]	>7.0	Cation of strong base Anion of weak acid	Anion

© McGraw-Hill Higher Education/Stephen Frisch, photographer

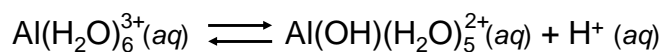
Acid-Base Properties of Salts

Acid Solutions:

Salts derived from a strong acid and a weak base.



Salts with small, highly charged metal cations (e.g. Al³⁺, Cr³⁺, and Be²⁺) and the conjugate base of a strong acid.

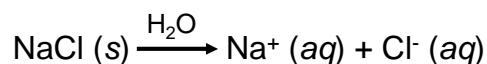


15.10

Acid-Base Properties of Salts

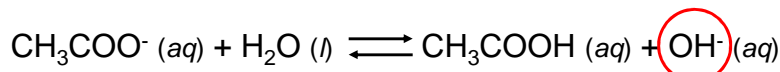
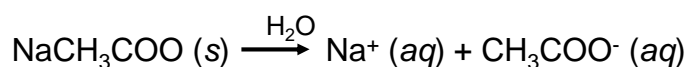
Neutral Solutions:

Salts containing an alkali metal or alkaline earth metal ion (except Be^{2+}) **and** the conjugate base of a **strong** acid (e.g. Cl^- , Br^- , and NO_3^-).



Basic Solutions:

Salts derived from a strong base **and** a **weak** acid.



15.10

Acid-Base Properties of Salts

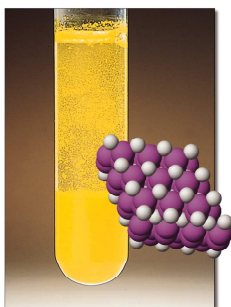
Solutions in which both the cation and the anion hydrolyze:

- K_b for the anion $>$ K_a for the cation, solution will be basic
- K_b for the anion $<$ K_a for the cation, solution will be acidic
- K_b for the anion \approx K_a for the cation, solution will be neutral

Table 15.7 Acid-Base Properties of Salts

Type of Salt	Examples	Ions That Undergo Hydrolysis	pH of Solution
Cation from strong base; anion from strong acid	NaCl , KI , KNO_3 , RbBr , BaCl_2	None	≈ 7
Cation from strong base; anion from weak acid	CH_3COONa , KNO_2	Anion	> 7
Cation from weak base; anion from strong acid	NH_4Cl , NH_4NO_3	Cation	< 7
Cation from weak base; anion from weak acid	NH_4NO_2 , $\text{CH}_3\text{COONH}_4$, NH_4CN	Anion and cation	< 7 if $K_b < K_a$ ≈ 7 if $K_b \approx K_a$ > 7 if $K_b > K_a$
Small, highly charged cation; anion from strong acid	AlCl_3 , $\text{Fe}(\text{NO}_3)_3$	Hydrated cation	< 7

15.10



Lecture 15

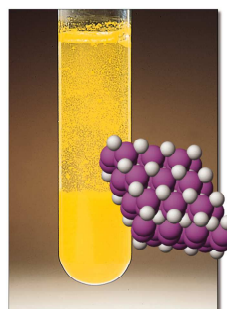
Solubility Equilibria

PRECIPITATION REACTIONS Solubility of Salts

Kotz section 18.4, pp. 832-842



PLAY MOVIE



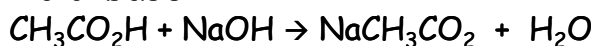
Lead(II) iodide

Types of Chemical Reactions

- EXCHANGE REACTIONS:



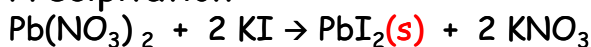
- Acid-base:



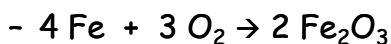
- Gas forming:



- Precipitation:

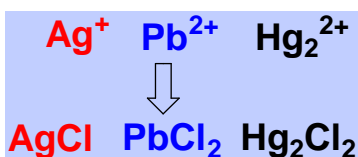


- OXIDATION REDUCTION



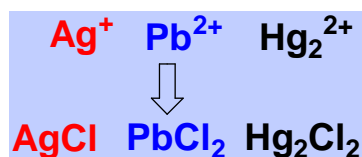
- *Apply equilibrium principles to acid-base and precipitation reactions.*

Analysis of Silver Group



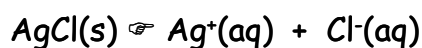
PLAY MOVIE

All salts formed in this experiment are said to be **INSOLUBLE** and form when mixing moderately concentrated solutions of the metal ion with chloride ions.

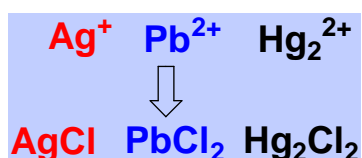


Analysis of Silver Group

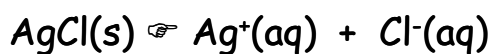
Although all salts formed in this experiment are said to be insoluble, they do dissolve to some SLIGHT extent.



When equilibrium has been established, no more AgCl dissolves and the solution is **SATURATED**.



Analysis of Silver Group

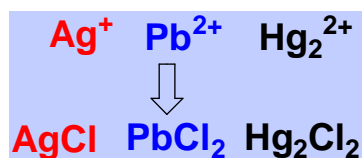


$$K_c = [\text{Ag}^+][\text{Cl}^-] = 2.79 \times 10^{-10}$$

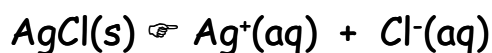
Because this is the product of "solubilities", we call it

K_{sp} = solubility product constant

• See Kotz, Table 18.2 and Appendix J



Analysis of Silver Group



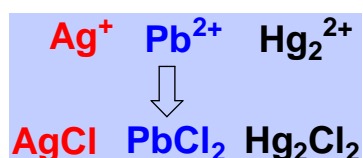
When solution is **SATURATED**, expt. shows that

$$[\text{Ag}^+] = 1.67 \times 10^{-5} \text{ M.}$$

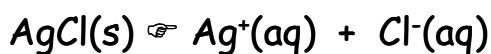
This is equivalent to the **SOLUBILITY** of AgCl.

What is $[\text{Cl}^-]$?

$$[\text{Cl}^-] = [\text{Ag}^+] = 1.67 \times 10^{-5} \text{ M}$$



Analysis of Silver Group



Saturated solution has

$$[\text{Ag}^+] = [\text{Cl}^-] = 1.67 \times 10^{-5} \text{ M}$$

Use this to calculate K_c

$$K_c = [\text{Ag}^+][\text{Cl}^-]$$

$$= (1.67 \times 10^{-5})(1.67 \times 10^{-5})$$

$$= 2.79 \times 10^{-10}$$

Some Values of K_{sp} Table 18.2 and Appendix J

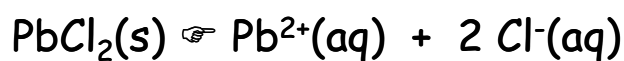
TABLE 18.2 Some Common Insoluble Compounds and Their K_{sp} Values*

Formula	Name	K_{sp} (25 °C)	Common Names/Uses
CaCO ₃	Calcium carbonate	3.4×10^{-9}	Calcite, iceland spar
MnCO ₃	Manganese(II) carbonate	2.3×10^{-11}	Rhodochrosite (forms rose-colored crystals)
FeCO ₃	Iron(II) carbonate	3.1×10^{-11}	Siderite
CaF ₂	Calcium fluoride	5.3×10^{-11}	Fluorite (source of HF and other inorganic fluorides)
AgCl	Silver chloride	1.8×10^{-10}	Chlorargyrite
AgBr	Silver bromide	5.4×10^{-13}	Used in photographic film
CaSO ₄	Calcium sulfate	4.9×10^{-5}	The hydrated form is commonly called gypsum
BaSO ₄	Barium sulfate	1.1×10^{-10}	Barite (used in "drilling mud" and as a component of paints)
SrSO ₄	Strontium sulfate	3.4×10^{-7}	Celestite
Ca(OH) ₂	Calcium hydroxide	5.5×10^{-5}	Slaked lime

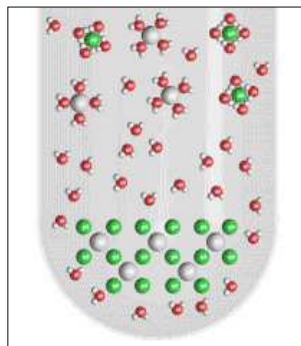
* The values in this table were taken from *Lange's Handbook of Chemistry*, 15th edition, McGraw-Hill Publishers, New York, NY (1999). Additional K_{sp} values are given in Appendix J.

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Lead(II) Chloride



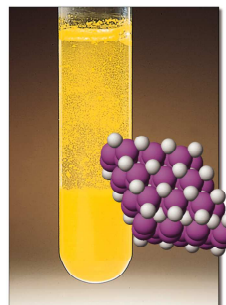
$$K_{sp} = 1.9 \times 10^{-5} = [\text{Pb}^{2+}][\text{Cl}^{-}]^2$$



PLAY MOVIE

Solubility of Lead(II) Iodide

Consider PbI_2 dissolving in water
 $\text{PbI}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2 \text{I}^{-}(\text{aq})$
Calculate K_{sp}
if solubility = 0.00130 M



Solution

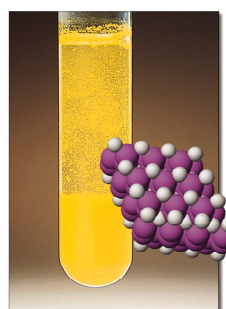
1. Solubility = $[\text{Pb}^{2+}] = 1.30 \times 10^{-3} \text{ M}$

$$[\text{I}^{-}] = ?$$

$$[\text{I}^{-}] = 2 \times [\text{Pb}^{2+}] = 2.60 \times 10^{-3} \text{ M}$$

Solubility of Lead(II) Iodide

Consider PbI_2 dissolving in water
 $\text{PbI}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2 \text{I}^{-}(\text{aq})$
Calculate K_{sp}
if solubility = 0.00130 M



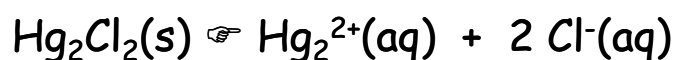
Solution

2. $K_{\text{sp}} = [\text{Pb}^{2+}] [\text{I}^{-}]^2$
 $= [\text{Pb}^{2+}] \{2 \cdot [\text{Pb}^{2+}]\}^2$

$$K_{\text{sp}} = 4 [\text{Pb}^{2+}]^3 = 4 (\text{solubility})^3$$

$$K_{\text{sp}} = 4 (1.30 \times 10^{-3})^3 = 8.79 \times 10^{-9}$$

Precipitating an Insoluble Salt

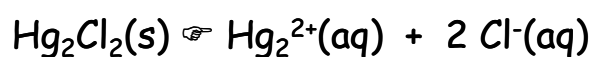


$$K_{\text{sp}} = 1.1 \times 10^{-18} = [\text{Hg}_2^{2+}] [\text{Cl}^-]^2$$

If $[\text{Hg}_2^{2+}] = 0.010 \text{ M}$, what $[\text{Cl}^-]$ is req'd to just begin the precipitation of Hg_2Cl_2 ?

That is, what is the maximum $[\text{Cl}^-]$ that can be in solution with $0.010 \text{ M Hg}_2^{2+}$ without forming Hg_2Cl_2 ?

Precipitating an Insoluble Salt

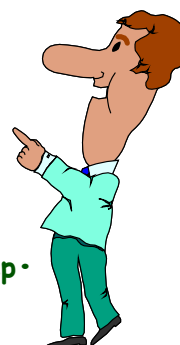


$$K_{\text{sp}} = 1.1 \times 10^{-18} = [\text{Hg}_2^{2+}] [\text{Cl}^-]^2$$

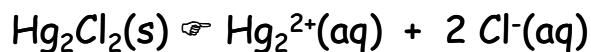
Recognize that

K_{sp} = product of
maximum ion concs.

Precip. begins when product of
ion concs. EXCEEDS the K_{sp} .



Precipitating an Insoluble Salt



$$K_{\text{sp}} = 1.1 \times 10^{-18} = [\text{Hg}_2^{2+}] [\text{Cl}^-]^2$$

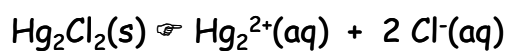
Solution

$[\text{Cl}^-]$ that can exist when $[\text{Hg}_2^{2+}] = 0.010 \text{ M}$,

$$[\text{Cl}^-] = \sqrt{\frac{K_{\text{sp}}}{0.010}} = 1.1 \times 10^{-8} \text{ M}$$

If this conc. of Cl^- is just exceeded, Hg_2Cl_2 begins to precipitate.

Precipitating an Insoluble Salt



$$K_{\text{sp}} = 1.1 \times 10^{-18}$$

Now raise $[\text{Cl}^-]$ to 1.0 M. What is the value of $[\text{Hg}_2^{2+}]$ at this point?

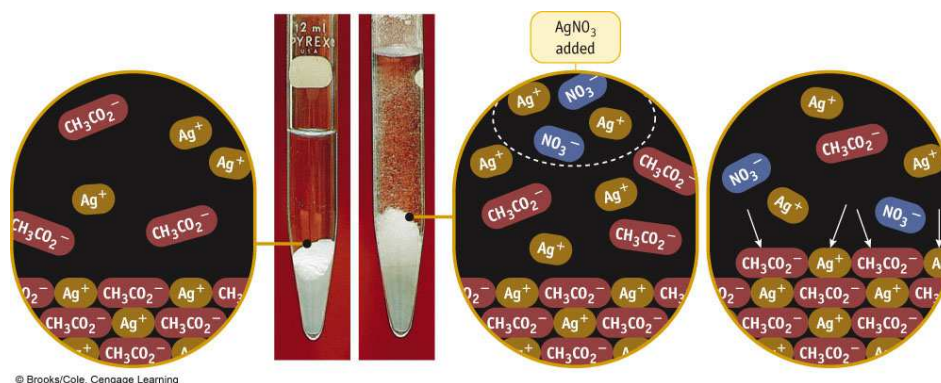
Solution

$$\begin{aligned} [\text{Hg}_2^{2+}] &= K_{\text{sp}} / [\text{Cl}^-]^2 \\ &= K_{\text{sp}} / (1.0)^2 = 1.1 \times 10^{-18} \text{ M} \end{aligned}$$

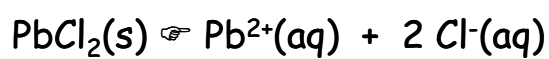
The concentration of Hg_2^{2+} has been reduced by 10^{16} !

The Common Ion Effect

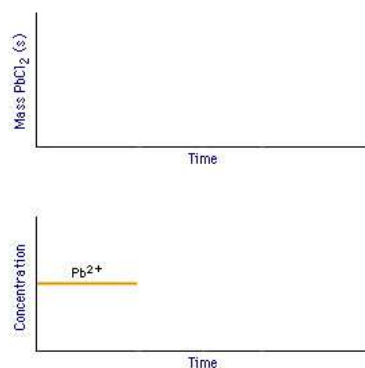
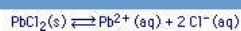
Adding an ion "common" to an equilibrium causes the equilibrium to shift back to reactant.



Common Ion Effect



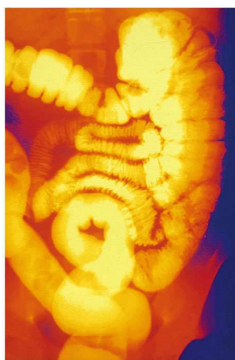
$$K_{\text{sp}} = 1.9 \times 10^{-5}$$



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(a)
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(b)

Barium Sulfate

$$K_{sp} = 1.1 \times 10^{-10}$$

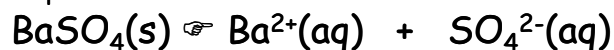
(a) BaSO_4 is a common mineral, appearing a white powder or colorless crystals.

(b) BaSO_4 is opaque to x-rays. Drinking a BaSO_4 cocktail enables a physician to exam the intestines.

The Common Ion Effect

Calculate the solubility of BaSO_4 in (a) pure water and (b) in 0.010 M $\text{Ba}(\text{NO}_3)_2$.

$$K_{sp} \text{ for } \text{BaSO}_4 = 1.1 \times 10^{-10}$$



Solution (a)

$$\text{Solubility in pure water} = [\text{Ba}^{2+}] = [\text{SO}_4^{2-}] = x$$

$$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = x^2$$

$$x = (K_{sp})^{1/2} = 1.1 \times 10^{-5} \text{ M}$$

$$\text{Solubility in pure water} = 1.0 \times 10^{-5} \text{ mol/L}$$

The Common Ion Effect

Calculate the solubility of BaSO_4 in (a) pure water and (b) in $0.010 \text{ M Ba(NO}_3)_2$.
 K_{sp} for $\text{BaSO}_4 = 1.1 \times 10^{-10}$
 $\text{BaSO}_4(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$

Solution (b)

Solubility in pure water = $1.1 \times 10^{-5} \text{ mol/L}$.

Now dissolve BaSO_4 in water already containing 0.010 M Ba^{2+} .

Which way will the "common ion" shift the equilibrium?

Will solubility of BaSO_4 be less than or greater than in pure water?

The Common Ion Effect

Solution (b) cont.

	$[\text{Ba}^{2+}]$	$[\text{SO}_4^{2-}]$
initial	0.010	0
change	+ y	+ y
equilib.	0.010 + y	y

$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = (0.010 + y)(y)$$

Because $y < 1.1 \times 10^{-5} \text{ M}$ (= x, the solubility in pure water), this means $0.010 + y$ is about equal to 0.010 . Therefore,

$$K_{\text{sp}} = 1.1 \times 10^{-10} = (0.010)(y)$$

$$y = 1.1 \times 10^{-8} \text{ M} = \text{solubility in presence of added } \text{Ba}^{2+} \text{ ion.}$$

SUMMARY

Solubility in pure water = $x = 1.1 \times 10^{-5} \text{ M}$

Solubility in presence of added $\text{Ba}^{2+} = 1.1 \times 10^{-8} \text{ M}$

Le Chatelier's Principle is followed!

Separating Metal Ions Cu^{2+} , Ag^+ , Pb^{2+}



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K_{sp} Values

AgCl	1.8×10^{-10}
PbCl_2	1.7×10^{-5}
PbCrO_4	1.8×10^{-14}

Kotz, section 18.5, pp. 842-845

Separating Salts by Differences in K_{sp}

A solution contains 0.020 M Ag^+ and Pb^{2+} . Add CrO_4^{2-} to precipitate red Ag_2CrO_4 and yellow PbCrO_4 . Which precipitates first?

$$K_{sp} \text{ for } \text{Ag}_2\text{CrO}_4 = 9.0 \times 10^{-12}$$

$$K_{sp} \text{ for } \text{PbCrO}_4 = 1.8 \times 10^{-14}$$

Solution

The substance whose K_{sp} is first exceeded precipitates first.

The ion requiring the lesser amount of CrO_4^{2-} ppts. first.

Separating Salts by Differences in K_{sp}

A solution contains 0.020 M Ag^+ and Pb^{2+} . Add CrO_4^{2-} to precipitate red Ag_2CrO_4 and yellow PbCrO_4 . Which precipitates first?

$$K_{sp} \text{ for } \text{Ag}_2\text{CrO}_4 = 9.0 \times 10^{-12}$$

$$K_{sp} \text{ for } \text{PbCrO}_4 = 1.8 \times 10^{-14}$$

Solution

Calculate $[\text{CrO}_4^{2-}]$ required by each ion.

$$\begin{aligned} [\text{CrO}_4^{2-}] \text{ to ppt. } \text{PbCrO}_4 &= K_{sp} / [\text{Pb}^{2+}] \\ &= 1.8 \times 10^{-14} / 0.020 = 9.0 \times 10^{-13} \text{ M} \end{aligned}$$

$$\begin{aligned} [\text{CrO}_4^{2-}] \text{ to ppt. } \text{Ag}_2\text{CrO}_4 &= K_{sp} / [\text{Ag}^+]^2 \\ &= 9.0 \times 10^{-12} / (0.020)^2 = 2.3 \times 10^{-8} \text{ M} \end{aligned}$$

PbCrO_4 precipitates first

Forming and dissolving precipitates: insoluble compounds often dissolve on Adding a suitable complexing agent.

Kotz, section 18.6, pp.846-848

$\text{AgCl}(s)$,
 $K_{sp} = 1.8 \times 10^{-10}$

(a) AgCl precipitates on adding $\text{NaCl}(aq)$ to $\text{AgNO}_3(aq)$ (see Figure 3.7).

$[\text{Ag}(\text{NH}_3)_2]^+(aq)$

(b) The precipitate of AgCl dissolves on adding aqueous NH_3 to give water-soluble $[\text{Ag}(\text{NH}_3)_2]^+$.

$\text{AgBr}(s)$,
 $K_{sp} = 5.4 \times 10^{-13}$

(c) The silver-ammonia complex ion is changed to insoluble AgBr on adding $\text{NaBr}(aq)$.

$[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}(aq)$

(d) Solid AgBr is dissolved on adding $\text{Na}_2\text{S}_2\text{O}_3(aq)$. The product is the water-soluble complex ion $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$.

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