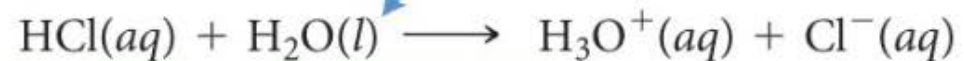


Amphoteric Nature of Water

Water acting
as a base



Acid
(proton donor)

Base
(proton acceptor)

Water acting
as an acid



Base
(proton acceptor)

Acid
(proton donor)

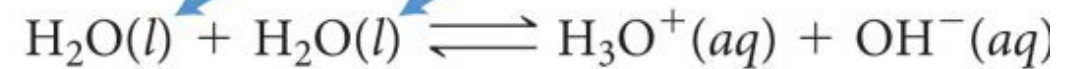
The pH scale in water depends upon this

Autoionization

A self-ionization process which depends upon the amphoteric nature of the solvent.. It is exactly this process which defines what acidity and basicity in a particular solvent is (via the autoionization reaction of the solvent).

of water:

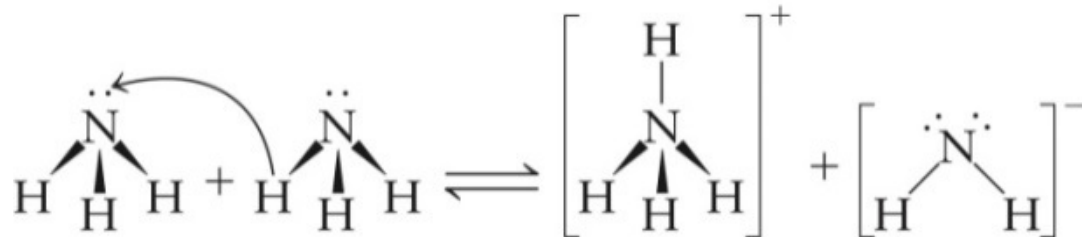
Water acting as both
an acid and a base



Acid
(proton donor)

Base
(proton acceptor)

of ammonia:



base

acid

conjugate acid

conjugate base

Strong Acids and Bases to Know

seven strong acids to know

hydrochloric acid	HCl
hydrobromic acid	HBr
hydroiodic acid	HI
perchloric acid	HClO ₄
chloric acid	HClO ₃
sulfuric acid	H ₂ SO ₄
nitric acid	HNO ₃

soluble strong bases to know

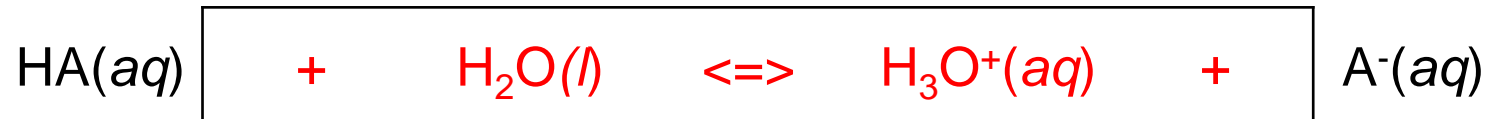
lithium hydroxide	LiOH
sodium hydroxide	NaOH
potassium hydroxide	KOH
rubidium hydroxide	RbOH
cesium hydroxide	CsOH
barium hydroxide	Ba(OH) ₂

strong bases - all Group I and Group II hydroxides except Be

Acid Strength

HA – generic way of writing a monoprotic acid (one acidic hydrogen)

acid strength – determined by extent of reaction of acid with water to form $\text{H}_3\text{O}^+(\text{aq})$, or the extent of its ionization or dissociation, as shown by the magnitude of its equilibrium constant, K_a – then for any hydrogen-containing compound, HA



EQUATION FOR ACIDITY FOR ANY HA

EQUILIBRIUM CONSTANT

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

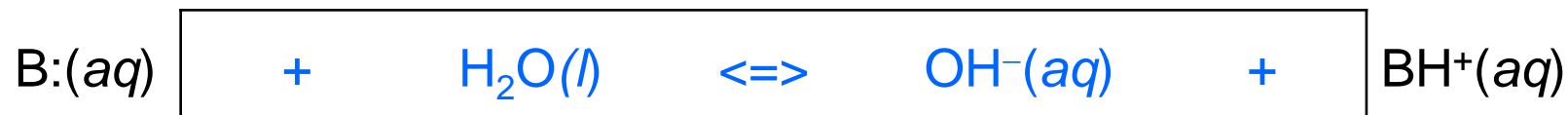
Various Ways to Describe Acid Strength

Property	Strong Acid	Weak Acid
K_a value	K_a is large	K_a is small
Position of the dissociation equilibrium	Far to the right	Far to the left
Equilibrium concentration of H^+ compared with original concentration of HA	$[\text{H}^+] \approx [\text{HA}]_0$	$[\text{H}^+] \ll [\text{HA}]_0$
Strength of conjugate base compared with that of water	A^- much weaker base than H_2O	A^- much stronger base than H_2O

Base Strength

B: – generic way of writing a monobasic base (one basic site)

base strength – (aside from Group I and II hydroxides) determined by extent of reaction of base with water to form $\text{OH}^-(aq)$, or extent of its ionization, as shown by the magnitude of its equilibrium constant, K_b – then for any base B:



EQUATION FOR BASICITY FOR ANY B:

EQUILIBRIUM CONSTANT

$$K_b = \frac{[\text{OH}^-][\text{BH}^+]}{[\text{B:}]}$$

Various Ways to Describe Base Strength

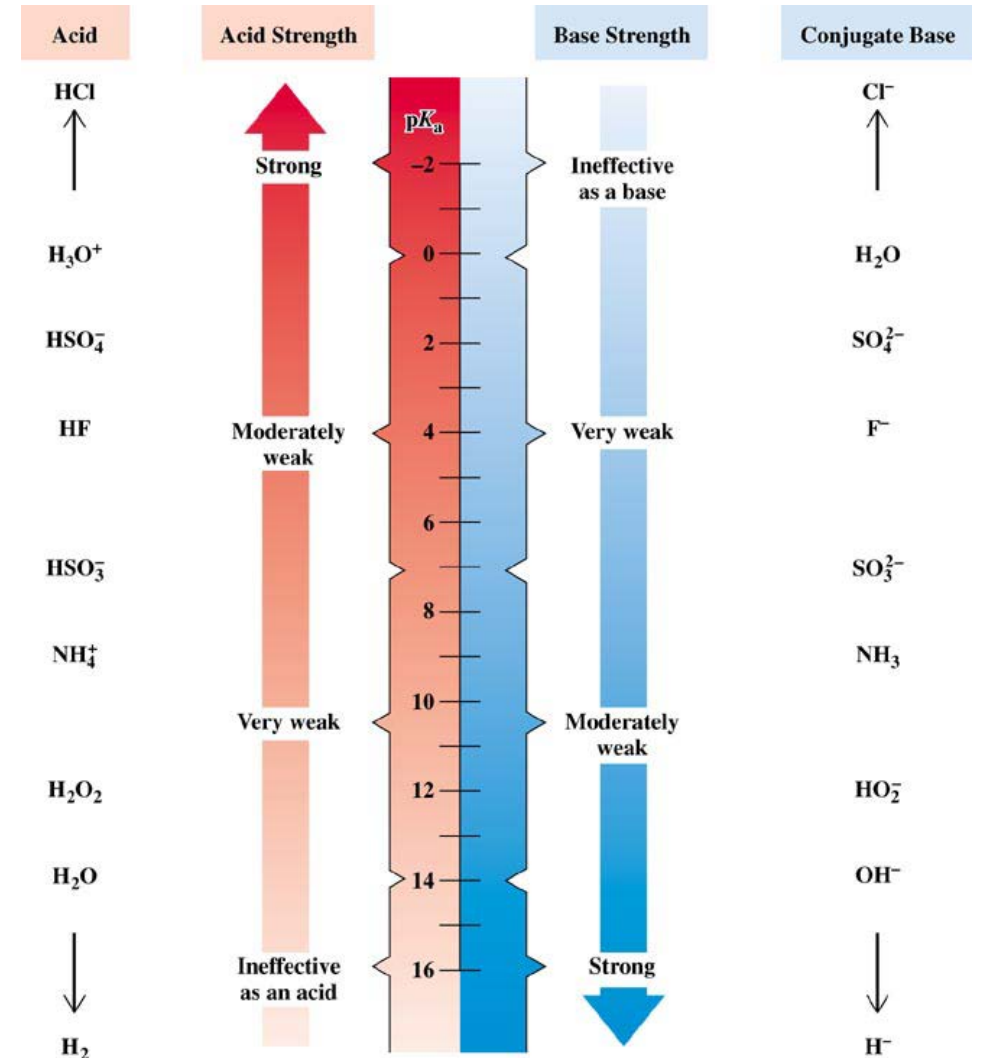
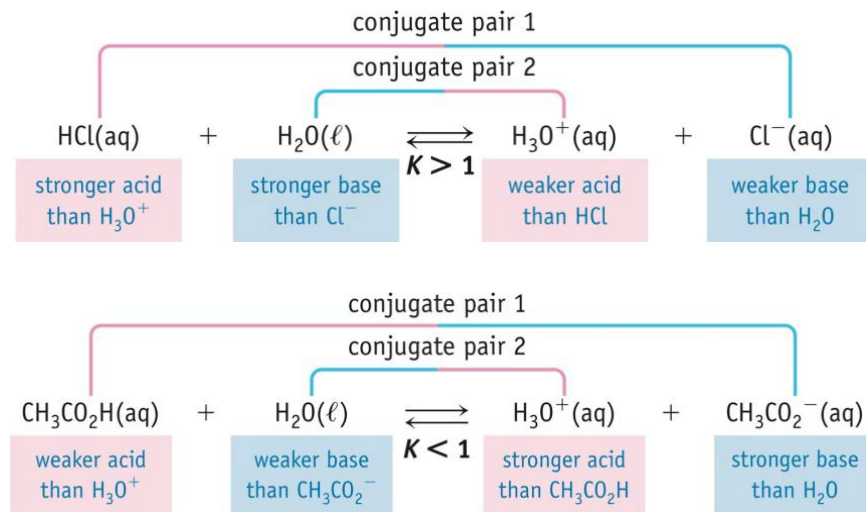
Property	Strong Base	Weak Base
K_b value	either 1) dissociates to give OH^- ions to the solution or 2) reacts with water in either case: $[\text{OH}^-] = [\text{B:}]_0$	K_b is small
Position of the dissociation equilibrium		Far to the left
Equilibrium concentration of OH^- compared with original concentration of B:		$[\text{OH}^-] \ll [\text{B:}]_0$
Strength of conjugate acid compared with that of water		BH^+ much stronger acid than water

Conjugate Acid/Base Pairs

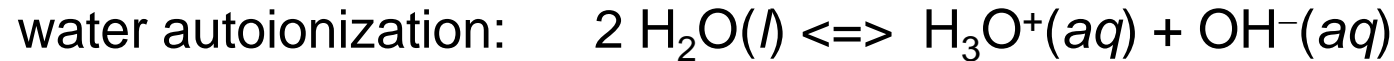
The conjugate base of a weak acid is a weak base. The weaker the acid, the stronger the base. However, if one member of a conjugate pair is weak, so is its conjugate.

The relation between K_a for an acid and K_b for its conjugate base in aqueous solution is $K_w = K_a \times K_b$.

When a strong acid (or base) is added to a weak base (or acid), they react nearly completely.



Water and the pH Scale



$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.01 \times 10^{-14} \text{ (at } 25^\circ\text{C)}$$

K_w is an equilibrium constant which depends upon temperature.

pH is temperature dependent

condition	concentrations	pH (only at 25°C)
acidic	$[\text{H}_3\text{O}^+] > [\text{OH}^-]$	pH < 7
neutral	$[\text{H}_3\text{O}^+] = [\text{OH}^-]$	pH = 7
basic	$[\text{H}_3\text{O}^+] < [\text{OH}^-]$	pH > 7

Temperature (°C)	K_w
0	0.114×10^{-14}
10	0.292×10^{-14}
20	0.681×10^{-14}
25	1.01×10^{-14}
30	1.47×10^{-14}
40	2.92×10^{-14}
50	5.47×10^{-14}
60	9.61×10^{-14}

EX 6. $K_w = 2.4 \times 10^{-14}$ at body temperature ($98.6^\circ\text{C} = 37.0^\circ\text{C}$).

a) What is the hydrogen ion concentration?

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = x^2 \Rightarrow x = [\text{H}_3\text{O}^+] = \sqrt{K_w} = \sqrt{2.4 \times 10^{-14}} = \mathbf{1.5 \times 10^{-7} \text{ M}}$$

b) What is the pH?

$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+] = -\log_{10} (1.549 \times 10^{-7}) = 6.80989 \Rightarrow \mathbf{6.81}$$

significant figures for logarithms:

3 significant digits

3 decimal places

$$\log(1.00 \times 10^{-3}) = 3.000$$

Water and the pH Scale

other "p" functions:

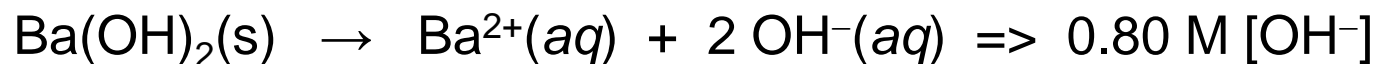
$$\begin{array}{ll} \text{pH} = -\log_{10}[\text{H}_3\text{O}^+] & \text{p}K_a = -\log_{10}K_a \\ \text{pOH} = -\log_{10}[\text{OH}^-] & \text{p}K_b = -\log_{10}K_b \\ \text{p}K_w = -\log_{10}K_w & \text{p}K_{\text{sp}} = -\log_{10}K_{\text{sp}} \end{array}$$

EX 7. Answer each of the following

a) pH = 9.3, $[\text{H}_3\text{O}^+] = ?$

$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+] \Rightarrow [\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-9.3} = 5.01 \times 10^{-10} \Rightarrow \mathbf{5 \times 10^{-10}}$$

b) 0.40 moles of $\text{Ba}(\text{OH})_2$ is dissolved in a liter of water, pOH?



Water and the pH Scale

other "p" functions:

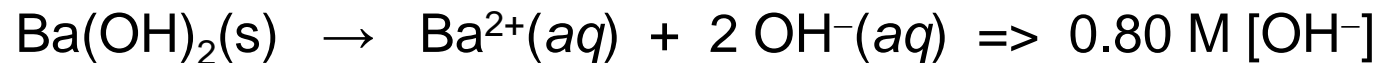
$$\begin{array}{ll} \text{pH} = -\log_{10}[\text{H}_3\text{O}^+] & \text{p}K_a = -\log_{10}K_a \\ \text{pOH} = -\log_{10}[\text{OH}^-] & \text{p}K_b = -\log_{10}K_b \\ \text{p}K_w = -\log_{10}K_w & \text{p}K_{sp} = -\log_{10}K_{sp} \end{array}$$

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b) 0.40 moles of $\text{Ba}(\text{OH})_2$ is dissolved in a liter of water, pOH?



$$\text{pH} = -\log_{10} [\text{OH}^{-}] = -\log_{10} [0.08] = 0.0969 \Rightarrow \mathbf{0.097}$$

c) pH = 9.3, $[\text{OH}^{-}] = ?$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^{-}] = 1.01 \times 10^{-14} \Rightarrow \text{p}K_w = \text{pH} + \text{pOH} = -\log_{10} (1.01 \times 10^{-14}) = 13.9956$$

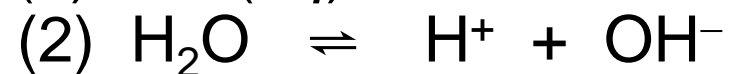
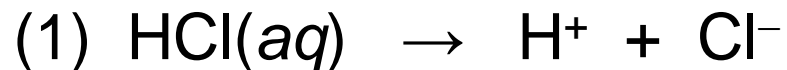
$$\text{pOH} = 13.9956 - 9.3 = 4.6956 \Rightarrow [\text{OH}^{-}] = 10^{-4.6956} = 2.015 \times 10^{-5} \Rightarrow \mathbf{2.0 \times 10^{-5}}$$

Systematic Treatment of Equilibrium – HARRIS text

What is the pH of 1.0×10^{-8} M HCl?

Answer: It cannot be pH 8.00. It should be an acidic solution with a pH lower than 7.00!

There are two reactions that are important.



Use the systematic treatment of equilibrium

Systematic Treatment of Equilibrium – HARRIS text

What is the pH of a 1.0×10^{-8} M solution of HCl?

GOAL - account for the concentration of all species present in a solution once equilibrium has been reached. The equations to do this derive from

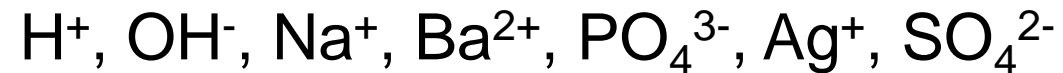
1. **charge balance** - solution must be electrically neutral
2. **material balance** - conservation of matter; what happens to initial concentrations
3. equilibrium expressions and their equilibrium constants

Systematic Treatment of Equilibrium – HARRIS text

GOAL - account for the concentration of all species present in a solution once equilibrium has been reached. The equations to do this derive from

1. **charge balance** - solution must be electrically neutral

EX 1. Write the charge balance for a solution containing only the following:



Systematic Treatment of Equilibrium – Charge Balance

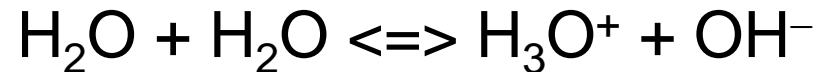
salt

EX 2. Write the charge balance for a solution containing $(\text{NH}_4)_3\text{PO}_4$. Be sure to consider all possible equilibrium reactions.

NH_4^+ is an acid but its equilibrium reaction produces its neutral conjugate base, NH_3 ; PO_4^{3-} is a base whose equilibrium reactions produce



in aqueous solution autoionization of water must always be considered:



$$[\text{NH}_4^+] + [\text{H}^+] = [\text{OH}^-] + [\text{H}_2\text{PO}_4^-] + 2[\text{HPO}_4^{2-}] + 3[\text{PO}_4^{3-}]$$

Systematic Treatment of Equilibrium – HARRIS text

GOAL - account for the concentration of all species present in a solution once equilibrium has been reached. The equations to do this derive from

1. **charge balance** - solution must be electrically neutral
2. **material balance** - conservation of matter; what happens to initial concentrations
3. equilibrium expressions

Molarity and Formality

These two types of concentration are identical for a species which does not dissociate into ions in solution or does not react with water to produce ions

Molarity is the concentration of the species that is actually present in solution such as 1.0 M Cl^- .

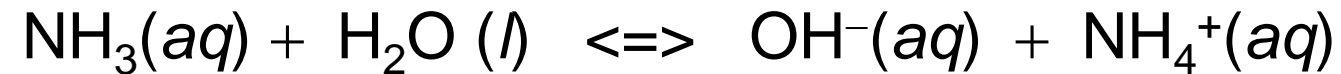
Consider a species which forms ions in solution such as acetic acid, CH_3COOH . You might try to place exactly 1.0 mole in a liter of water to form a 1.0 M solution but the solution will have partially dissociated into CH_3COO^- . Such a solution is 1.0 F = $[\text{CH}_3\text{COOH}] + [\text{CH}_3\text{COO}^-]$. So **formality** represents the concentration of the different “pieces” that acetic acid forms in solution or the concentration originally placed in water (before dissociation).

Harris uses formality

Systematic Treatment of Equilibrium – Mass Balance

EX 3. What is the mass balance equation for a solution prepared by adding 0.100 moles of ammonia to 1.000 L?

NH_3 is a weak base and reacts with water:



so the mass balance is

$$0.100 \text{ F} = [\text{NH}_3]_0 = [\text{NH}_3] + [\text{NH}_4^+]$$

Systematic Treatment of Equilibrium

equations needed for solution for unknown

General approach includes

1. write down the pertinent chemical reactions and their **equilibrium constant expressions**
2. write down all species present in solution according to #1
3. set up the **charge balance equation** (the solution must be electrically neutral so the number of positive charges = the number of negative charges)
4. apply the **material balance equation** (conservation of matter) – may be more than one
5. are there enough equations to solve for the unknowns?

Systematic Treatment – Dilute Strong Acid

EX 4. What is the pH of a 1.0×10^{-8} M solution of HBr?

1. reactions, K ($\text{HBr} \rightarrow \text{H}^+ + \text{Br}^-$)



2. species: H^+ , OH^- , Br^-

3. charge balance: $[\text{H}^+] = [\text{OH}^-] + [\text{Br}^-]$

substitute for $[\text{OH}^-]$

4. mass balance: $[\text{Br}^-] = 1.0 \times 10^{-8}$

substitute for $[\text{Br}^-]$

$$K_w = [\text{H}^+][\text{OH}^-] = [\text{H}^+] \{ [\text{H}^+] - [\text{Br}^-] \} = [\text{H}^+]^2 - [\text{H}^+] [\text{Br}^-]$$

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$$\text{quadratic: } [\text{H}^+]^2 - [\text{H}^+][\text{Br}^-] - K_w = 0$$

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$$[\text{H}^+] = \{ -10^{-8} \pm \sqrt{[(10^{-8})^2 + 4(1.01 \times 10^{-14})] } \} / 2$$

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$$= 1.05 \times 10^{-8} \text{ M}$$

$$\Rightarrow \text{pH} = 6.978 \Rightarrow \mathbf{6.98}$$