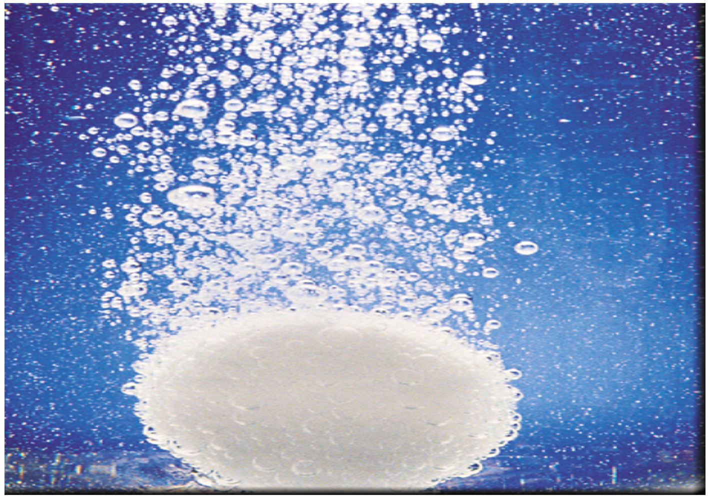
Acids and Bases

The pH Scale



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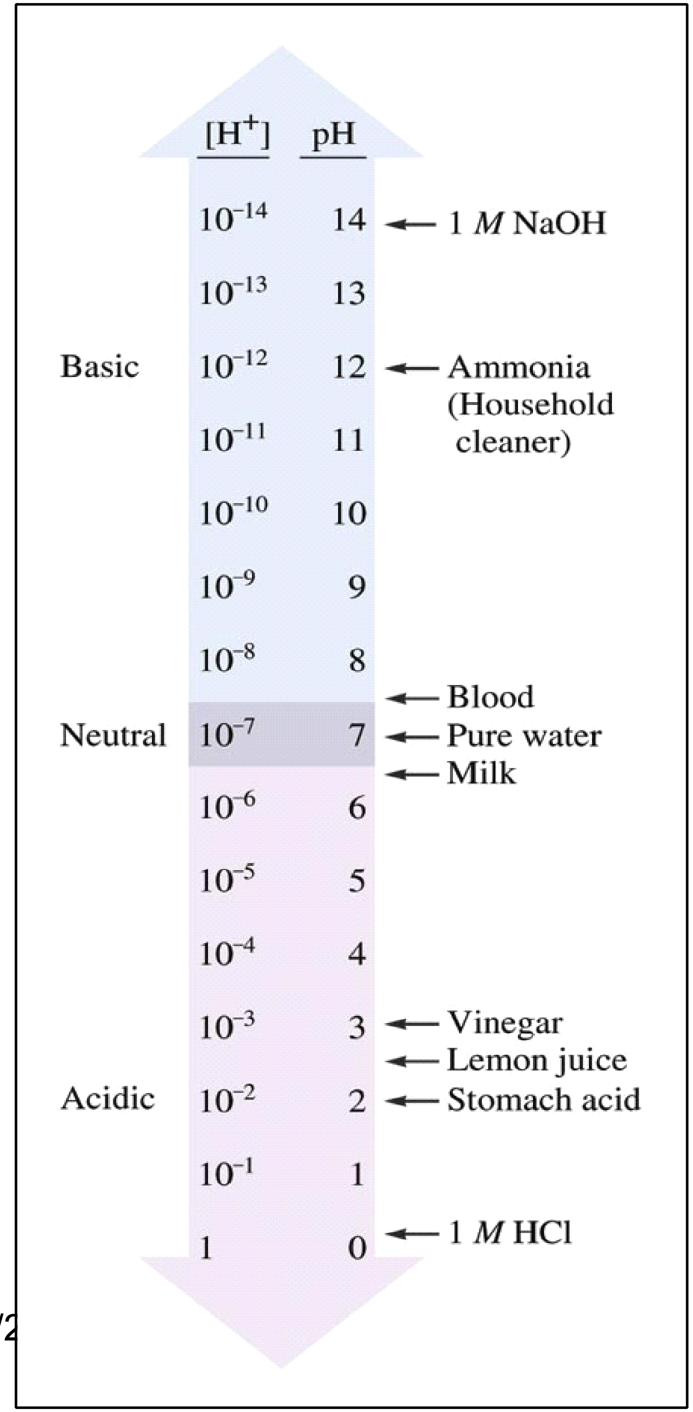
Ammonia
12.063
25.0
2.477
25.0

pH – A Measure of Acidity

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

Solution Is		**At 25^0C**	
neutral	$[H^+] = [OH^-]$	$[H^+] = 1 \times 10^{-7}$	$pH = 7$
acidic	$[H^+] > [OH^-]$	$[H^+] > 1 \times 10^{-7}$	$pH < 7$
basic	$[H^+] < [OH^-]$	$[H^+] < 1 \times 10^{-7}$	$pH > 7$

pH $\uparrow$ $[H^+]$ $\downarrow$



$$pOH = -\log [OH^-]$$

$$[H^+][OH^-] = K_w = 1.0 \times 10^{-14}$$

$$-\log [H^+] - \log [OH^-] = 14.00$$

$$pH + pOH = 14.00$$

The pH Scale

- The number of **decimal places** in the *log* is equal to the **number of significant figures** in the *original number*

$[H^+] = 1.0 \times 10^{-9}$ (2 significant figures)

pH = 9.00 (2 decimal places)

- The pH changes by 1 for every **power of 10** change in $[H^+]$
- The pH **decrease** as $[H^+]$ **increase**

1 The pH of rainwater collected in a certain region of the northeastern United States on a particular day was 4.82. What is the H^+ ion concentration of the rainwater?

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

$$[H^+] = 10^{-pH} = 10^{-4.82} \boxed{= 1.5 \times 10^{-5}\ M}$$

2 The OH^- ion concentration of a blood sample is 2.5×10^{-7} *M*. What is the pH of the blood?

$$pH + pOH = 14.00$$

$$pOH = -\log [OH^-] = -\log (2.5 \times 10^{-7}) = 6.60$$

$$\boxed{pH = 14.00 - pOH = 14.00 - 6.60 = 7.40}$$

Calculating the pH of Strong Acid Solutions

To deal with acid-base equilibria focus on the solution components and their chemistry

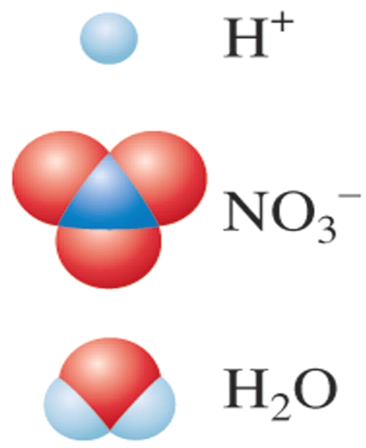
Example

0.1 M HCl solution

Determine which components are significant and which can be ignored. Focus on the major species

3

What is the pH of a 2 x 10^{-3} *M* HNO_3 solution?



HNO_3 is a strong acid – 100% dissociation.
The major species are H^+, NO_3^- and H_2O

Start 0.002 *M* 0.0 *M* 0.0 *M*

$$\boxed{HNO_3\,(aq) + H_2O\,(l) \longrightarrow H_3O^+\,(aq) + NO_3^-\,(aq)}$$

End 0.0 *M* 0.002 *M* 0.002 *M*

$$\boxed{pH = -\log [H^+] = -\log [H_3O^+] = -\log(0.002) = 2.7}$$

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

HCl is a strong acid – 100% dissociation but the amount of HCl in this solution is so small.
So it has no effect.
The only major species is H_2O
H^+ from H_2O

$$\boxed{\mathbf{pH = 7.00}}$$

Calculating the pH of Weak Acid Solutions

Solving **weak acid** ionization problems:

1. Identify the **major species** that can affect the pH.
   - In most cases, you can ignore the autoionization of water.
   - Ignore $[OH^-]$ because it is determined by $[H^+]$.
2. Use **ICE** to express the equilibrium concentrations in terms of single unknown *x*.

I Initial concentration, **C Change**, **E Equilibrium concentration**

3. Write K_a in terms of equilibrium concentrations. Solve for *x* by the approximation method $[HA]_0 - x \approx [HA]_0$.
4. Use 5% rule to verify whether the approximation is valid
5. Calculate concentrations of all species and/or pH of the solution.

5

What is the pH of a 0.5 *M* HF solution (at 25°C)?

$HF\ (aq) \rightleftharpoons H^+\ (aq) + F^-\ (aq)$ $\qquad K_a = \dfrac{[H^+][F^-]}{[HF]} = 7.1 \times 10^{-4}$

	$HF\ (aq) \rightleftharpoons$	$H^+\ (aq)$ +	$F^-\ (aq)$
Initial (*M*)	0.50	0.00	0.00
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.50 - x$	x	x

$K_a = \dfrac{x^2}{0.50 - x} = 7.1 \times 10^{-4}$ $\qquad K_a << 1 \qquad 0.50 - x \approx 0.50$

$K_a \approx \dfrac{x^2}{0.50} = 7.1 \times 10^{-4}$ $\qquad x^2 = 3.55 \times 10^{-4} \qquad x = 0.019\ M$

When can I use the approximation?

$K_a << 1 \quad 0.50 - x \approx 0.50$

When x is less than 5% of the value from which it is subtracted.

$x = 0.019 \qquad \frac{0.019\ M}{0.50\ M} \times 100\% = 3.8\%$

Less than 5%

Approximation ok.

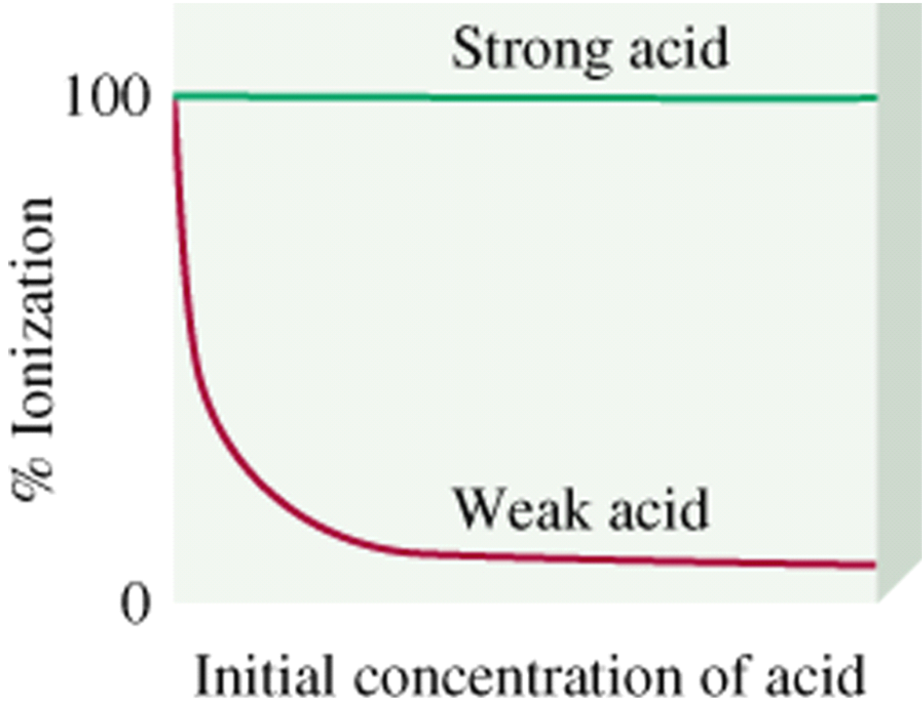
$[H^+] = [F^-] = 0.019\ M \qquad pH = -\log [H^+] = 1.72$

$[HF] = 0.50 - x = 0.48\ M$

$$\textit{\textbf{percent dissociation}} = \frac{\text{Amount dissociated at equilibrium (mol/ L)}}{\text{Initial concentration of acid (mol/ L)}} \times 100\%$$

For a monoprotic acid HA

$$\textbf{Percent dissociation} = \frac{[H^+]}{[HA]_0} \times 100\% \qquad [HA]_0 = \text{initial concentration}$$



The pH of Weak Acid Mixtures

Calculate the pH of a solution that contains 1.00 M HCN ($K_a = 6.2 \times 10^{-10}$) and 5.00 M HNO_2 ($K_a = 4.00 \times 10^{-4}$. Also calculate the concentration of cyanide ion (CN^-) in this solution at equilibrium.

6

What is the pH of a 0.122 *M* monoprotic acid whose K_a is 5.7×10^{-4}?

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

	HA (*aq*)	H^+ (*aq*)	A^- (*aq*)
Initial (*M*)	0.122	0.00	0.00
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.122 - x$	x	x

$$K_a = \frac{x^2}{0.122 - x} = 5.7 \times 10^{-4}$$

$K_a \ll 1 \quad 0.122 - x \approx 0.122$

$$K_a \approx \frac{x^2}{0.122} = 5.7 \times 10^{-4}$$

$x^2 = 6.95 \times 10^{-5} \qquad x = 0.0083\ M$

$$\frac{0.0083\ M}{0.122\ M} \times 100\% = 6.8\%$$

More than 5%

Approximation **not** ok.

$$K_a = \frac{x^2}{0.122 - x} = 5.7 \times 10^{-4}$$

$$x^2 + 0.00057x - 6.95 \times 10^{-5} = 0$$

$$ax^2 + bx + c = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

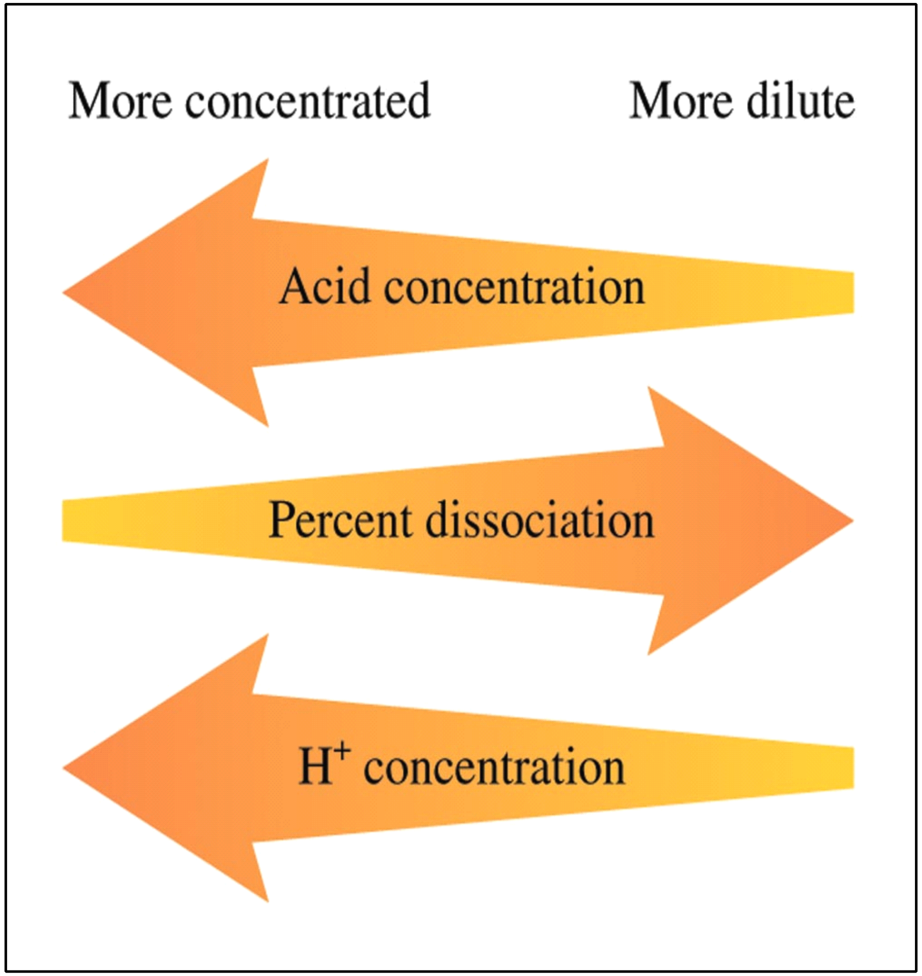
$x = 0.0081$

~~$x = -0.0081$~~

	HA (*aq*) $\rightleftharpoons$	H^+ (*aq*) +	A^- (*aq*)
Initial (*M*)	0.122	0.00	0.00
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.122 - x$	x	x

$[H^+] = x = 0.0081\ M$

$\text{pH} = -\log[H^+] = 2.09$



For solutions of any weak acid HA

- [H+] **decreases** as [HA] **decreases**
- However the percent dissociation **increases** as [HA] **decreases**

Figure 14.10 The Effect of Dilution on the Percent Dissociation and [H+] of a Weak Acid Solution

Calculating K_a from precent Dissociation

Example

In a 0.100 M aqueous solution, lactic acid is 3.7% dissociated. Calculate the value of K_a for this acid.

Bases

- According to Arrhenius concept, base is a substance that **produce OH^-**
- According to the Bronsted- Lowry model, a base is **a proton acceptor**
- Strong bases dissociate completely and are strong electrolytes
- Al the hydroxides of the Group 1A elements are **strong bases** e.g. NaOH, KOH, CsOH and RbOH
- The alkaline earth (Group 2A) hydroxides are also strong bases. $Ca(OH)_2$ and $Ba(OH)_2$

7

What is the pH of a 1.8 x 10-2 *M* Ba(OH)2 solution?

$Ba(OH)_2$ is a strong base – 100% dissociation.

	$Ba(OH)_2\ (s)$	$\longrightarrow$	$Ba^{2+}\ (aq)$	+	$2OH^-\ (aq)$
Start	0.018 *M*		0.0 *M*		0.0 *M*
End	0.0 *M*		0.018 *M*		0.036 *M*

$$pH = 14.00 - pOH = 14.00 + \log(0.036) = 12.56$$

Weak Bases and Base Ionization Constants

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

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

K_b is the ***base ionization constant***

K_b ↑ weak base strength ↑

Solve weak base problems like weak acids ***except*** solve for [OH-] instead of [H^+].

Table 14.3 Values of K_b for Some Common Weak Bases

TABLE 14.3 Values of K_b for Some Common Weak Bases

Name	Formula	Conjugate Acid	K_b
Ammonia	NH_3	NH_4^+	1.8×10^{-5}
Methylamine	CH_3NH_2	$CH_3NH_3^+$	4.38×10^{-4}
Ethylamine	$C_2H_5NH_2$	$C_2H_5NH_3^+$	5.6×10^{-4}
Aniline	$C_6H_5NH_2$	$C_6H_5NH_3^+$	3.8×10^{-10}
Pyridine	C_5H_5N	$C_5H_5NH^+$	1.7×10^{-9}

Polyprotic Acids

- H_3PO_4
- H_2SO_4
- H_2CO_3
- $H_2C_2O_4$

Polyprotic Acids

- Some acids can furnish more than one proton e.g. H_2SO_4 and H_3PO_4 and are called polyprotic acids
- A polyprotic acid always dissociate in a *stepwise* manner
- H_2SO_4 is a diprotic acid
- H_3PO_4 is a triprotic acid

Table 14.4 Stepwise dissociation Constants for Several Common Polyprotic Acids

TABLE 14.4 Stepwise Dissociation Constants for Several Common Polyprotic Acids

Name	Formula	K_{a_1}	K_{a_2}	K_{a_3}
Phosphoric acid	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
Arsenic acid	H_3AsO_4	5×10^{-3}	8×10^{-8}	6×10^{-10}
Carbonic acid	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Sulfuric acid	H_2SO_4	Large	1.2×10^{-2}	
Sulfurous acid	H_2SO_3	1.5×10^{-2}	1.0×10^{-7}	
Hydrosulfuric acid*	H_2S	1.0×10^{-7}	$\sim 10^{-19}$	
Oxalic acid	$H_2C_2O_4$	6.5×10^{-2}	6.1×10^{-5}	
Ascorbic acid (vitamin C)	$H_2C_6H_6O_6$	7.9×10^{-5}	1.6×10^{-12}	

*The K_{a_2} value for H_2S is very uncertain. Because it is so small, the K_{a_2} value is very difficult to measure accurately.

The pH Of a Polyprotic Acid

8 Calculate the pH of 5.0 M H_3PO_4 solution and the equilibrium concentrations of the species H_3PO_4, $H_2PO_4^-$, HPO_4^{-2}, PO_4^{-3}.

Solution

The major species in solution are

H_3PO_4 and H_2O ...The ICE table

ICE table

$$H_3PO_4\ (aq) \rightleftharpoons H^+\ (aq) + H_2PO_4^-\ (aq)$$

	H_3PO_4	H^+	$H_2PO_4^-$
• Initial (*M*)	5.0	0.00	0.00
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$5.0 - x$	x	x

$$K_{a1} = \frac{x^2}{5.0 - x} = 7.5 \times 10^{-3} \qquad K_b << 1 \qquad 5.0 - x \approx 5.0$$

$$K_{a1} \approx \frac{x^2}{5.0} = 7.5 \times 10^{-3} \quad x = 1.9 \times 10^{-1} \qquad [H^+] = 0.19\ M$$

$[H^+] = [H_2PO_4^-] = 0.19\ M$

[H3PO4] = 5.0 – x = 4.8M

The concentration of HPO_4^{-2}

$$K_{a2} = \frac{[H^+][HPO_4^{-2}]}{[H_2PO_4^-]} = 6.2 \times 10^{-8}$$

$[H^+] = [H_2PO_4^-] = 0.19M$

$[HPO_4^{-2}] = K_{a2} = 6.2 \times 10^{-8}M$

$$K_{a3} = \frac{[H^+]\,[PO_4^{-3}]}{[H_2PO_4^-]} = 4.8 \times 10^{-13}$$

$$[PO_4^{-3}] = \frac{(4.8 \times 10^{-13})(6.2 \times 10^{-8})}{0.19} = 1.6 \times 10^{-19}M$$

The pH of Sulfuric Acid

- Calculate the pH of 0.1 M H_2SO_4 solution.

Ostwald Dilution law

- "For a dilute solution of a weak electrolyte, the degree of dissociation is inversely proportional to the squar root of the molarity i.e. it is proportional to $\sqrt{1/M}$
- $\alpha = \frac{\sqrt{K_a}}{C}$ $\quad\quad K_a = \alpha^2 C$

α is degree of ionization

$$\alpha = \frac{[\text{amount dissociated}]}{[\text{initial conc}]} = \frac{[H^+]}{[HA]_o}$$

9 Calculate degree of ionization of 0.1M ethanoic acid CH_3COOH, using Ostwald Dilution Law
$K_a = 1.8 \times 10^{-5}$ mol/dm^3 at 298K

Solution

$$K_a = \alpha^2 C$$

$$1.8 \times 10^{-5} = \alpha^2 \times 0.1$$

$$\alpha^2 = \frac{1.8 \times 10^{-5}}{0.1}$$

$$\alpha = 0.0134$$

Relation between α and pH

10 Calculate the pH of propanoic acid at 298 K given that the Concentration is 0.1M $K_a = 1.35 \times 10^{-5}$

$$\alpha = \frac{\sqrt{K_a}}{C} = \frac{\sqrt{1.35 \times 10^{-}}}{0.1} = 0.0116$$

Find $[H^+] = ?$ $\alpha = [H^+] / [HA]_o$

$[H^+] = \alpha \times [HA]_o = 0.0116 \times 0.1 = 1.16 \times 10^{-3}$

$pH = -\log 1.16 \times 10^{-3} = 2.935$