Calculation of pH for weak acids and bases

Unlike strong acids and bases, weak acids and bases are only partially dissociated in aqueous solution and establish an equilibrium.

Generic acid HA $HA + H_2O \rightleftarrows H_3O^+ + A^-$ $K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}$

$[H_2O]$ is omitted because it is constant.

Generic base B $B + H_2O \rightleftarrows HB^+ + OH^-$ $K_b = \frac{[HB^+]\,[OH^-]}{[B]}$

https://www.youtube.com/watch?v=x-nI3Ws7nxQ

In practice, all acid with Ka>>1 are considered strong acids, while weak acids have Ka<1.

NB: $K_a(H_3O^+)=1$

The same is for the basics, but considering the Kb

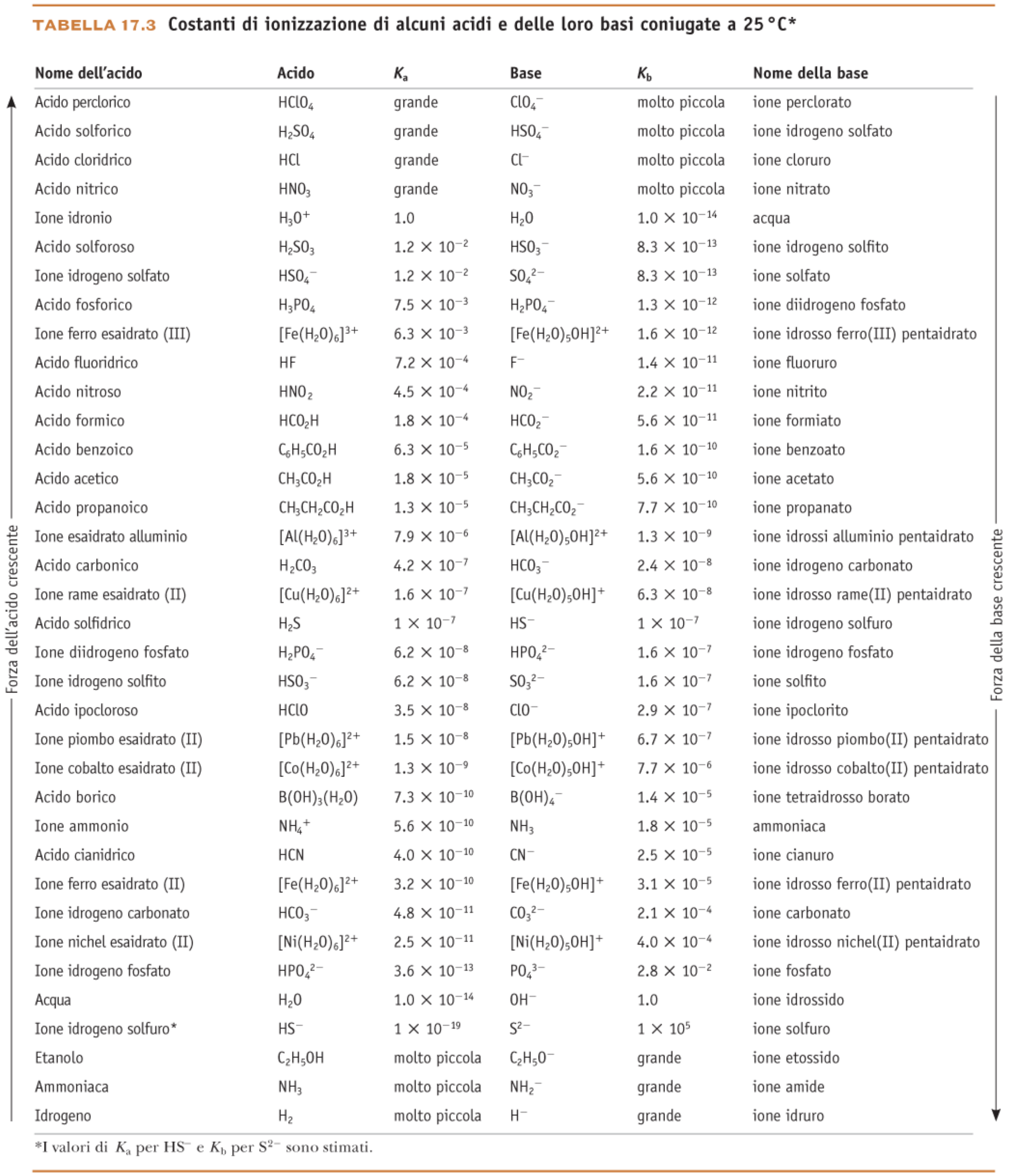


TABELLA 17.3 Costanti di ionizzazione di alcuni acidi e delle loro basi coniugate a 25 °C*

Nome dell'acido	Acido	K_a	Base	K_b	Nome della base
Acido perclorico	$HClO_4$	grande	ClO_4^-	molto piccola	ione perclorato
Acido solforico	H_2SO_4	grande	HSO_4^-	molto piccola	ione idrogeno solfato
Acido cloridrico	HCl	grande	Cl^-	molto piccola	ione cloruro
Acido nitrico	HNO_3	grande	NO_3^-	molto piccola	ione nitrato
Ione idronio	H_3O^+	1.0	H_2O	1.0×10^{-14}	acqua
Acido solforoso	H_2SO_3	1.2×10^{-2}	HSO_3^-	8.3×10^{-13}	ione idrogeno solfito
Ione idrogeno solfato	HSO_4^-	1.2×10^{-2}	SO_4^{2-}	8.3×10^{-13}	ione solfato
Acido fosforico	H_3PO_4	7.5×10^{-3}	$H_2PO_4^-$	1.3×10^{-12}	ione diidrogeno fosfato
Ione ferro esaidrato (III)	$[Fe(H_2O)_6]^{3+}$	6.3×10^{-3}	$[Fe(H_2O)_5OH]^{2+}$	1.6×10^{-12}	ione idrosso ferro(III) pentaidrato
Acido fluoridrico	HF	7.2×10^{-4}	F^-	1.4×10^{-11}	ione fluoruro
Acido nitroso	HNO_2	4.5×10^{-4}	NO_2^-	2.2×10^{-11}	ione nitrito
Acido formico	HCO_2H	1.8×10^{-4}	HCO_2^-	5.6×10^{-11}	ione formiato
Acido benzoico	$C_6H_5CO_2H$	6.3×10^{-5}	$C_6H_5CO_2^-$	1.6×10^{-10}	ione benzoato
Acido acetico	CH_3CO_2H	1.8×10^{-5}	$CH_3CO_2^-$	5.6×10^{-10}	ione acetato
Acido propanoico	$CH_3CH_2CO_2H$	1.3×10^{-5}	$CH_3CH_2CO_2^-$	7.7×10^{-10}	ione propanato
Ione esaidrato alluminio	$[Al(H_2O)_6]^{3+}$	7.9×10^{-6}	$[Al(H_2O)_5OH]^{2+}$	1.3×10^{-9}	ione idrossi alluminio pentaidrato
Acido carbonico	H_2CO_3	4.2×10^{-7}	HCO_3^-	2.4×10^{-8}	ione idrogeno carbonato
Ione rame esaidrato (II)	$[Cu(H_2O)_6]^{2+}$	1.6×10^{-7}	$[Cu(H_2O)_5OH]^+$	6.3×10^{-8}	ione idrosso rame(II) pentaidrato
Acido solfidrico	H_2S	1×10^{-7}	HS^-	1×10^{-7}	ione idrogeno solfuro
Ione diidrogeno fosfato	$H_2PO_4^-$	6.2×10^{-8}	HPO_4^{2-}	1.6×10^{-7}	ione idrogeno fosfato
Ione idrogeno solfito	HSO_3^-	6.2×10^{-8}	SO_3^{2-}	1.6×10^{-7}	ione solfito
Acido ipocloroso	$HClO$	3.5×10^{-8}	ClO^-	2.9×10^{-7}	ione ipoclorito
Ione piombo esaidrato (II)	$[Pb(H_2O)_6]^{2+}$	1.5×10^{-8}	$[Pb(H_2O)_5OH]^+$	6.7×10^{-7}	ione idrosso piombo(II) pentaidrato
Ione cobalto esaidrato (II)	$[Co(H_2O)_6]^{2+}$	1.3×10^{-9}	$[Co(H_2O)_5OH]^+$	7.7×10^{-6}	ione idrosso cobalto(II) pentaidrato
Acido borico	$B(OH)_3(H_2O)$	7.3×10^{-10}	$B(OH)_4^-$	1.4×10^{-5}	ione tetraidrosso borato
Ione ammonio	NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}	ammoniaca
Acido cianidrico	HCN	4.0×10^{-10}	CN^-	2.5×10^{-5}	ione cianuro
Ione ferro esaidrato (II)	$[Fe(H_2O)_6]^{2+}$	3.2×10^{-10}	$[Fe(H_2O)_5OH]^+$	3.1×10^{-5}	ione idrosso ferro(II) pentaidrato
Ione idrogeno carbonato	HCO_3^-	4.8×10^{-11}	CO_3^{2-}	2.1×10^{-4}	ione carbonato
Ione nichel esaidrato (II)	$[Ni(H_2O)_6]^{2+}$	2.5×10^{-11}	$[Ni(H_2O)_5OH]^+$	4.0×10^{-4}	ione idrosso nichel(II) pentaidrato
Ione idrogeno fosfato	HPO_4^{2-}	3.6×10^{-13}	PO_4^{3-}	2.8×10^{-2}	ione fosfato
Acqua	H_2O	1.0×10^{-14}	OH^-	1.0	ione idrossido
Ione idrogeno solfuro*	HS^-	1×10^{-19}	S^{2-}	1×10^{5}	ione solfuro
Etanolo	C_2H_5OH	molto piccola	$C_2H_5O^-$	grande	ione etossido
Ammoniaca	NH_3	molto piccola	NH_2^-	grande	ione amide
Idrogeno	H_2	molto piccola	H^-	grande	ione idruro

*I valori di K_a per HS^- e K_b per S^{2-} sono stimati.

Tabella 14.1 K_a e K_b di alcune coppie coniugate acido-base

STRONG acids

Weak acids

K_a

	K_a		K_b
$HClO_4$	> 1	ClO_4^-	$< 10^{-14}$
HBr	> 1	Br^-	$< 10^{-14}$
H_2SO_4	> 1	HSO_4^-	$< 10^{-14}$
HCl	> 1	Cl^-	$< 10^{-14}$
HNO_3	> 1	NO_3^-	$< 10^{-14}$
H_3O^+ (*)	1	H_2O(*)	$1{,}0 \cdot 10^{-14}$
HSO_4^-	$2{,}0 \cdot 10^{-2}$	SO_4^{2-}	$5{,}0 \cdot 10^{-13}$
SO_2	$1{,}7 \cdot 10^{-2}$	HSO_3^-	$5{,}9 \cdot 10^{-13}$
H_3PO_4	$7{,}5 \cdot 10^{-3}$	$H_2PO_4^-$	$1{,}3 \cdot 10^{-12}$
$ClCH_2COOH$	$1{,}4 \cdot 10^{-3}$	$ClCH_2OOO^-$	$7{,}1 \cdot 10^{-12}$
HF	$7{,}1 \cdot 10^{-4}$	F^-	$1{,}4 \cdot 10^{-11}$
HNO_2	$4{,}5 \cdot 10^{-4}$	NO_2^-	$2{,}2 \cdot 10^{-11}$
$HCOOH$	$2{,}1 \cdot 10^{-4}$	$HCOO^-$	$4{,}8 \cdot 10^{-11}$
CH_3COOH	$1{,}8 \cdot 10^{-5}$	CH_3COO^-	$5{,}6 \cdot 10^{-10}$
$Al(H_2O)_6^{3+}$	$1{,}3 \cdot 10^{-5}$	$Al(OH)(H_2O)_5^{2+}$	$7{,}7 \cdot 10^{-10}$
CO_2	$4{,}2 \cdot 10^{-7}$	HCO_3^-	$2{,}4 \cdot 10^{-8}$
H_2S	$1{,}0 \cdot 10^{-7}$	HS^-	$1{,}0 \cdot 10^{-7}$
$H_2PO_4^-$	$6{,}0 \cdot 10^{-8}$	HPO_4^{2-}	$1{,}7 \cdot 10^{-7}$
HSO_3^-	$5{,}6 \cdot 10^{-8}$	SO_3^{2-}	$1{,}8 \cdot 10^{-7}$
$HClO$	$3{,}2 \cdot 10^{-8}$	ClO^-	$3{,}1 \cdot 10^{-7}$
H_3BO_3	$6{,}0 \cdot 10^{-10}$	$H_2BO_3^-$	$1{,}7 \cdot 10^{-5}$
NH_4^+	$5{,}6 \cdot 10^{-10}$	NH_3	$1{,}8 \cdot 10^{-5}$
HCN	$4{,}0 \cdot 10^{-10}$	CN^-	$2{,}5 \cdot 10^{-5}$
HCO_3^-	$4{,}8 \cdot 10^{-11}$	CO_3^{2-}	$2{,}1 \cdot 10^{-4}$
H_2O_2	$2{,}6 \cdot 10^{-12}$	HO_2^-	$3{,}8 \cdot 10^{-3}$
HPO_4^{2-}	$4{,}4 \cdot 10^{-13}$	PO_4^{3-}	$2{,}3 \cdot 10^{-2}$
HS^-	$1{,}1 \cdot 10^{-13}$	S^{2-}	$9{,}1 \cdot 10^{-2}$
H_2O (*)	$1{,}0 \cdot 10^{-14}$	OH^- (*)	1
CH_3OH	$< 10^{-14}$	CH_3O^-	> 1
NH_3	$< 10^{-14}$	NH_2^-	> 1
OH^-	$< 10^{-14}$	O^{2-}	> 1
H_2	$< 10^{-14}$	H^-	> 1

(*) I valori di $K_a(H_3O^+) = K_b(OH^-) = 1$ e di $K_a(H_2O) = K_b(H_2O) = 1{,}0 \cdot 10^{-14}$ de-rivano dall'aver assunto $[H_2O] = 1$. In alcuni testi la concentrazione dello stato standard di riferimento del solvente è 1 mol dm^{-3}, e pertanto $[H_2O]$ è preso uguale a 55,5. Con queste assunzioni $K_a(H_3O^+) = K_b(OH^-) = 55{,}5$ e $K_a(H_2O) = K_b(H_2O) = 1{,}8 \cdot 10^{-16}$. Naturalmente K_a e K_b di tutti gli altri acidi e basi restano invariate né cambia tutto ciò che riguarda i calcoli stechiometrici.

Weak bases

K_b

STRONG bases

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

$$*K_b = \frac{[HB^+]\,[OH^-]}{[B]}$$

*

K>> 1, more products

K<< 1, more reagents

Generic dissociation reaction at equilibrium

Known **K_a** for a weak acid it is possible to easily calculate the equilibrium concentrations of HA, H_3O^+, and A^- for a solution with known HA concentration using the general methods of equilibria.

	$HA(aq)$	$\rightleftharpoons$	$H^+(aq)$ +	$A^-(aq)$
Starting Conc.	C_a		0	0
Variation	$-x$		$+x$	$+x$
Equilibria concentration	$C_a - x$		x	x

From the equation of the equilibrium constant we have:

$$K_a = \frac{[H^+]\,[A^-]}{[HA]} \qquad K_a = \frac{[x]\,[x]}{c_a - [x]} \qquad K_a = \frac{[x]^2}{c_a - [x]}$$

$$\boxed{K_a = \frac{[H_3O^+]^2}{c_a - [H_3O^+]}}$$

Calculation of pH for weak acids and bases

Consider a generic ***weak acid HA***, with initial concentration c_a

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

its ionization constant or acid constant is

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

In this case it is an equilibrium reaction, so the K that regulates dissociation must be taken into account.

K_a = constant equilibrium / acid constant / acidity constant

K_b = constant equilibrium / basic constant

Calculation of pH for weak acids and bases

Depending on the starting concentration (of the acid or base) and the K we have two types of equations to calculate pH

So to decide which equation to use you need to evaluate:

1) **The starting concentration of the acid (C_a) or of the base (C_b)**
2) **The equilibration constant of the acid (K_a) or of the base (K_b)**

Calculation of pH for weak acids and bases

To calculate the pH we should know the [H_3O^+].

The H_3O^+ ions come both from the dissociation of the weak acid and from the self-ionization of water (as for the strong acids)

1) If the acid is sufficiently concentrated, I have:

Fairly high acid concentration (**$c_a > 10^{-3}$**)

Quite weak acid, i.e. small K_a, it is very poorly dissociated (**$K_a < 10^{-3}$**)

the dissociation of water is negligible, so we can consider that all H_3O^+ present in solution come only from the weak acid.

Calculation of pH for weak acids and bases

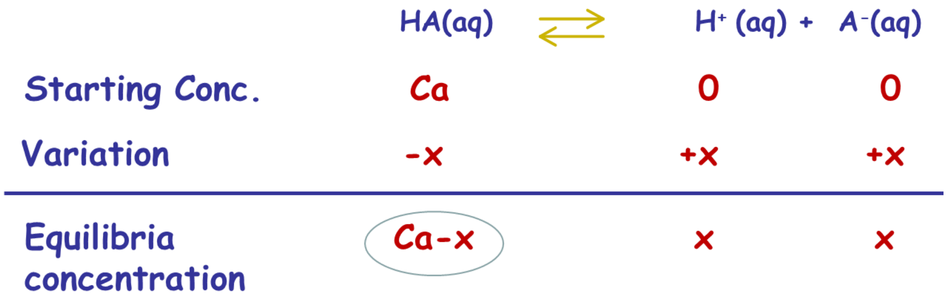
Then, based on the stoichiometric equation we can write

$$HA + H_2O \rightleftarrows H_3O^+ + A^- \qquad [H_3O^+] = [A^-]$$

Then derive the equilibrium constant:

Since all $[H_3O^+]$ come from HA the

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]} \qquad K_a = \frac{[H_3O^+]^2}{[HA]}$$



	$HA(aq)$	$\rightleftarrows$	$H^+(aq)$ +	$A^-(aq)$
Starting Conc.	Ca		0	0
Variation	-x		+x	+x
Equilibria concentration	Ca-x		x	x

I derive the concentration of undissociated acid (HA) at equilibrium

$$[HA] = c_a - [H_3O^+]$$

Negligible

the **HA** concentration, at equilibrium, is given by the difference of the initial concentration (**c_a**) and the part that dissociated, which is equal to the concentration of **H_3O^+ ions that were formed (in the product)**

Then being sufficiently concentrated ($c_a > 10^{-3}$) and few dissociated the starting acid ($K_a < 10^{-3}$)

$[HA] = c_a - [H_3O^+] \longleftarrow$ Negligible because the HA is sufficiently concentrated And poorly dissociated

I can approximate

$$\mathbf{[HA] \cong c_a}$$

$$K_a = \frac{[H_3O^+]^2}{c_a - \cancel{[H_3O^+]}}$$

And then write the Ka (form eq. Constant):

$$K_a = \frac{[H_3O^+]^2}{[HA]} \quad \text{as} \quad K_a \cong \frac{[H_3O^+]^2}{c_a}$$

Deriving the $[H_3O^+]$:

$$[H_3O^+]^2 \cong K_a\, c_a$$

$$\boxed{[H_3O^+] \cong \sqrt{K_a\, c_a}}$$

Simplified expression to calculate the pH of weak acids

It must satisfy both:

$c_a > 10^{-3}$ $\quad$ $K_a < 10^{-3}$

2) If the acid is not concentrated enough and I have:

Low acid concentration (**$c_a < 10^{-3}$**)

Very dissociated acid (**$K_a > 10^{-3}$**)

(ONE of these 2 condition IS ENOUGH!)

Water dissociation is NOT negligible, so we need to consider H_3O^+ from the acid and self-ionization of water

The **quadratic formula** is used (see next page).

⇩ ⇩

Attention !! How to choose formula to use

The simplified is used if and only if $c_a > 10^{-3}$ and $K_a < 10^{-3}$

$$\boxed{[H_3O^+] \cong \sqrt{K_a\, c_a}}$$

If one of the two condition is not satisfied ($c_a < 10^{-3}$ or **$K_a > 10^{-3}$)**, the quadratic formula is used (see next page).

If it is not possible to approximate, then if **$K_a > 10^{-3}$**, or **$c_a < 10^{-3}$**

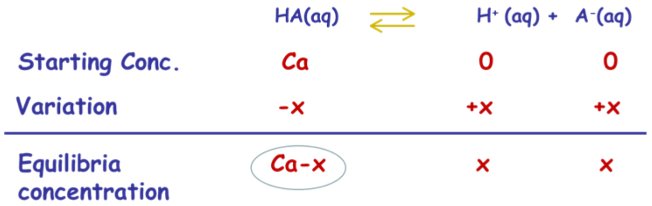
$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

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

$$K_a = \frac{[H_3O^+]^2}{[HA]}$$

$$\boxed{K_a = \frac{[H_3O^+]^2}{c_a - [H_3O^+]}}$$

$$[HA] = c_a - [H_3O^+]$$



	$HA(aq)$	$\rightleftharpoons$	$H^+(aq)$ +	$A^-(aq)$
Starting Conc.	Ca		0	0
Variation	-x		+x	+x
Equilibria concentration	Ca-x		x	x

Non-negligible

$$K_a = \frac{[H_3O^+]^2}{c_a - [H_3O^+]}$$

the **HA** concentration, at equilibrium, is given by the difference of the initial concentration (**c_a**) and the part that has dissociated

(because low concentration, and very dissociated)

$$K_a (c_a - [H_3O^+]) = [H_3O^+]^2$$

$$K_a c_a - K_a [H_3O^+] = [H_3O^+]^2$$

$$\boxed{[H_3O^+]^2 + K_a [H_3O^+] - K_a c_a = 0}$$

quadratic expression to calculate the pH of weak acid

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

The same considerations are for a generic ***weak base B***, with initial concentration, are completely similar c_b

$$B + H_2O \rightleftarrows HB^+ + OH^-$$

$$K_b = \frac{[HB^+]\,[OH^-]}{[B]}$$

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

$[B] = c_b - [OH^-]$

$$K_b = \frac{[OH^-]^2}{c_b - [OH^-]}$$

$$\boxed{[OH^-] \cong \sqrt{K_b\, c_b}}$$

simplified expression to calculate the pH of weak bases, if ***$c_b > 10^{-3}$*** *and* ***$K_b < 10^{-3}$***

$$\boxed{[OH^-]^2 + K_b\,[OH^-] - K_b\, c_b = 0}$$

quadratic expression to calculate the pH of weak bases

*(**if at least one of the two conditions above is not met: i.e., $c_b < 10^{-3}$** and **$K_b > 10^{-3}$**)*

Exercise. Calculate the pH of a 0.15 M solution of acetic acid (CH3 COOH), a weak acid having $K_a = 1.8\times10^{-5}$.

$$CH_3COOH \rightleftarrows H^+ + CH_3COO^-$$

Due to $K_a<10^{-3}$ and $c_a>10^{-3}$ it is possible to use the simplified equation

$$[H^+] = \sqrt{K_a\ c_a}$$

$$[H^+] = \sqrt{1.8\times10^{-5}\ \ 0.15} = 1.64\times10^{-3}$$

$pH = -\log[H^+] = \mathbf{2.79}$

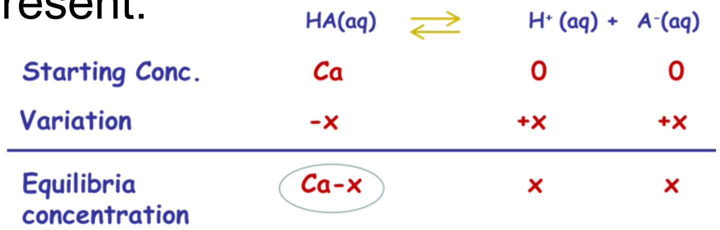
Once calculated the H^+ concentration

Proof that negligible $[H^+]$ contribution compared to Ca of the acid (and therefore ok to use simplified formula)

Let's calculate the concentration of all the species present:

$[CH_3COO^-] = [H^+] = 1.64\times10^{-3}$ (form pH)

$[CH_3COOH] = c_a - [H^+] = 0.15 - 1.64\times10^{-3} \cong 0.15$



	$HA(aq)$	$\rightleftarrows$	$H^+(aq)$ +	$A^-(aq)$
Starting Conc.	Ca		0	0
Variation	-x		+x	+x
Equilibria concentration	Ca-x		x	x

Let's now calculate the pH by applying the quadratic equation, **to check whether the approximation made is acceptable**:

$$[H^+]^2 + K_a[H^+] - K_a c_a = 0$$

$$[H^+]^2 + 1.8\times10^{-5}[H^+] - 1.8\times10^{-5}\ 0.15 = 0$$

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

$$x_1 = \frac{-b + \sqrt{b^2 - 4ac}}{2a},$$

$$x_2 = \xcancel{\frac{-b - \sqrt{b^2 - 4ac}}{2a}}$$

$$[H^+]^2 + 1.8\times10^{-5}[H^+] - 2.7\times10^{-6} = 0$$

$$[H^+] = \frac{-1.8\times10^{-5} \pm \sqrt{(1.8\times10^{-5})^2 - 4(-\,2.7\times10^{-6})}}{2} = 1.63\times10^{-3} \qquad pH = 2.79$$

The result obtained is <u>identical</u> to that calculated by applying the approximate equation, so it is permissible to use the simplified equation, when **<u>BOTH</u>** the conditions are verified $K_a<10^{-3}$ e $c_a>10^{-3}$.

Exercise. Calculate the pH of a 0.015 M solution of periodic acid (HIO_4) whose ionization constant is $K_a = 2.30\times10^{-2}$.

$$HIO_4 \rightleftarrows H^+ + IO_4^-$$

The approximate equation **cannot be used** because both conditions must be satisfied $K_a<10^{-3}$ e $c_a>10^{-3}$; in this case in fact $K_a>10^{-3}$, so we need to solve the quadratic equation

$$[H^+]^2 + K_a[H^+] - K_a c_a = 0$$

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

$$x_1 = \frac{-b+\sqrt{b^2-4ac}}{2a},$$

$$\cancel{x_2 = \frac{-b-\sqrt{b^2-4ac}}{2a}}$$

$$[H^+]^2 + 2.30\times10^{-2}[H^+] - 2.30\times10^{-2}\ 0.015 = 0$$

$$[H^+]^2 + 2.30\times10^{-2}[H^+] - 3.45\times10^{-4} = 0$$

$$[H^+] = \frac{-2.30\times10^{-2} \pm \sqrt{(2.30\times10^{-2})^2 - 4(-3.45\times10^{-4})}}{2} = 1.03\times10^{-2}$$

pH = **1.99**

For comparison let's see the value we would have obtained if we had used the approximate formula (Wrong!)

$$[H^+] = \sqrt{K_a\ c_a}$$

$$[H^+] = \sqrt{2.30\times10^{-2}\ 0.015} = 1.86\times10^{-2} \qquad \text{pH} = 1.73$$

The value obtained is significantly different from that obtained with the quadratic equation, demonstrating that if the conditions are not satisfied both for K_a and/or c_a no approximations can be made.

Exercise. Calculate the pH of a solution 1.12×10^{-2} M of aniline, a weak base (generic formula B) having $K_b = 3.82\times10^{-10}$.

Due to $K_b<10^{-3}$ and $c_b>10^{-3}$ it is possible to use the approximated equation

$$[OH^-] = \sqrt{K_b\, c_b}$$

$$[OH^-] = \sqrt{3.82\times10^{-10}\ 1.12\times10^{-2}} = 2.07\times10^{-6}$$

$$pOH = -\log[OH^-] = 5.68$$

$$pH = 14 - pOH = 8.32$$

Exercise. Calculate the pH at equilibrium in a 5.32×10^{-2} M solution of nitrous acid (HNO_2) knowing that its $K_a = 4.6 \times 10^{-4}$.

1) pH calculation

Due to $K_a < 10^{-3}$ and $c_a > 10^{-3}$ it is possible to use the approximated equation

$$[H^+] = \sqrt{K_a\, c_a}$$

$$[H^+] = \sqrt{(4.6 \times 10^{-4})\,(5.32 \times 10^{-2})} = 4.95 \times 10^{-3}$$

$pH = -\log[H^+] = \mathbf{2.30}$

Exercise for study.

1) Calculate the pH of a 0.125 M solution of a generic weak acid HA, having K_a = 1.28 x 10^{-5} , Using the approximate and quadratic formula. Can the approximate formula be used? (pH = 2.90)

2) Calculate the pH of a 1.12 x 10^{-2} M solution of aniline, a weak base having K_b = 3.82 x 10^{-10}. (pH = 8.31)

3) Calculate the pH of a 0.075 M propanoic acid (C_2H_5COOH) solution, knowing that K_a = 1.32 x 10^{-5}. Using the approximate and quadratic formula. Can the approximate formula be used? (pH = 3.00)

4) Calculate the pH of a cinnamic acid solution (C_8H_7COOH) 1.0 x 10^{-3} (K_a = 4.0 x 10^{-5}). (pH = 3.74)

5) Calculate the pH of a solution containing a 1.0 x 10 $^{-2}$ M monoprotic weak base (K_b = 4.0 x 10^{-5}). Check if the approximate formula can be used, also performing the exercise with the quadratic formula. (pH = 10.9)

6) Calculate the pH and pOH of a solution of CH_3COOH 10^{-3} M kwowing that K_a = 1,8 x 10^{-5}

7) Calculate the pH of a 0.100 M solution of NH_3 knowing that K_b = 1.8 x 10^{-5}

Polyprotic acids

Some acids contain two or more dissociable hydrogens such as protons and are called polyprotic acids.

Sulfuric acid H_2SO_4, for example, can lose two protons:

$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$ complete (strong acid; $K_a > 1$)

$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ $K_a = 1.7 \times 10^{-2}$ (weak acid; $K_a < 1$)

In general, a polyprotic acid is a weak acid and involves two or more simultaneous equilibria. For example for carbonic acid H_2CO_3:

$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

$K_{a1} = 4.3 \times 10^{-7}$

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

$K_{a2} = 4.8 \times 10^{-11}$

In general the second acid constant of a polyprotic acid is much smaller than the first

$K_{a2} << K_{a1}$

Polyprotic bases

Similarly, some bases can also accept two or more protons and are called polyprotic bases.
Typically, they are either organic polyamines, with two or more nitrogens each with a lone doublet, or inorganic polyanions.

For example the carbonate ion CO_3^{2-}:

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- \qquad K_{b1} = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} \qquad K_{b1}=2.4\times10^{-4}$$

$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^- \qquad K_{b2} = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]} \qquad K_{b2}=2.8\times10^{-8}$$

The second basic constant of a polyprotic base is also typically much smaller than the first, $K_{b2} << K_{b1}$, and the pH calculation is similar to that for a polyprotic acid

Calculation of pH for polyprotic acids

They are acids that contain two or more protons, which ionize in successive phases, each characterized by an equilibrium constant

e.g. phosphoric acid H_3PO_4

$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^-$ $$K_{a1} = \frac{[H^+]\,[H_2PO_4^-]}{[H_3PO_4]} = 7.4 \times 10^{-3}$$ Medium acid force

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

$HPO_4^{2-} \rightleftarrows H^+ + PO_4^{3-}$ $$K_{a3} = \frac{[H^+]\,[PO_4^{3-}]}{[HPO_4^{2-}]} = 4.8 \times 10^{-13}$$ Acid very weak

The three constants differ from each other by several orders of magnitude (at least 10^5), in particular between K_{a1} and K_{a2} there is 5 orders of magnitude difference.

For this reason, in calculating the pH one can limit oneself to considering only the first ionization

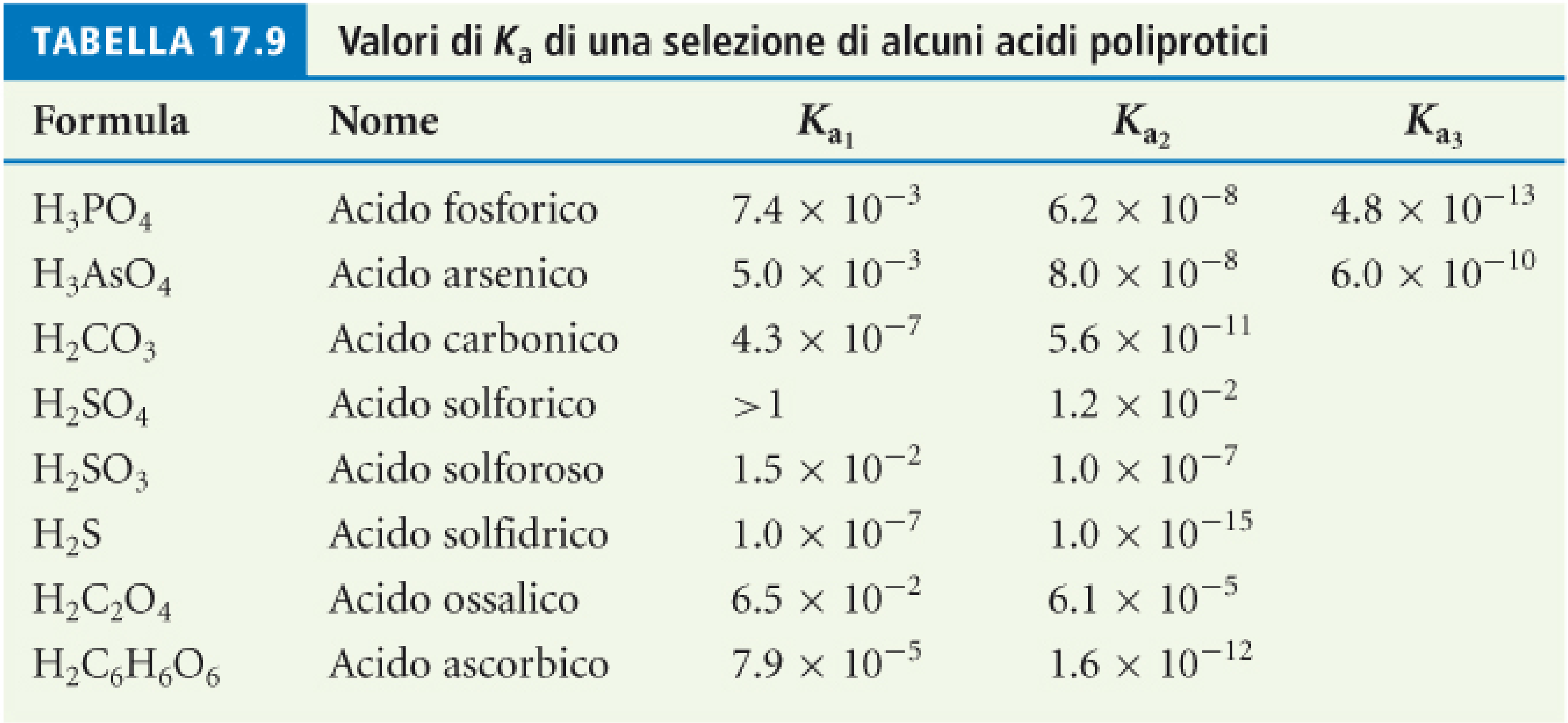


TABELLA 17.9 Valori di K_a di una selezione di alcuni acidi poliprotici

Formula	Nome	K_{a_1}	K_{a_2}	K_{a_3}
H_3PO_4	Acido fosforico	7.4×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
H_3AsO_4	Acido arsenico	5.0×10^{-3}	8.0×10^{-8}	6.0×10^{-10}
H_2CO_3	Acido carbonico	4.3×10^{-7}	5.6×10^{-11}	
H_2SO_4	Acido solforico	>1	1.2×10^{-2}	
H_2SO_3	Acido solforoso	1.5×10^{-2}	1.0×10^{-7}	
H_2S	Acido solfidrico	1.0×10^{-7}	1.0×10^{-15}	
$H_2C_2O_4$	Acido ossalico	6.5×10^{-2}	6.1×10^{-5}	
$H_2C_6H_6O_6$	Acido ascorbico	7.9×10^{-5}	1.6×10^{-12}	

For pH calculation:

only the first ionization is considered, as if it act as a monoprotic acid because more significant.

Exercise. Calculate the H^+ (and pH) of a 0.02 M solution of carbonic acid (H_2CO_3, $K_{a1} = 4.3\times10^{-7}$, $K_{a2} = 5.6\times10^{-11}$)

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^- \qquad K_{a1} = \frac{[H^+]\,[HCO_3^-]}{[H_2CO_3]} = 4.3 \times 10^{-7}$$

$$HCO_3^- \rightleftarrows H^+ + CO_3^{2-} \qquad K_{a2} = \frac{[H^+]\,[CO_3^{2-}]}{[HCO_3^-]} = 5.6 \times 10^{-11}$$

For the pH calculation we consider only the first dissociation. We have a weak acid with $c>10^{-3}$ and $K_{a1}<10^{-3}$, so we can use the simplified expression

$$[H^+] = \sqrt{K_{a1}\, c_a}$$

$$[H^+] = \sqrt{4.3\times10^{-7}\ 0.02} = 9.27\times10^{-5}$$

pH = 4.03

$[HCO_3^-] = [H^+] =$ 9.27×10^{-5}, considering the second dissociation negligible (NOT SIGNIFICANT CONTRIBUTE)

Exercise for study.

1) Calculate the pH of a hydrogen sulfide solution H_2S 5.0 x 10^{-2} ($K_{a1} = 1.0\times10^{-7}$; $K_{a2} = 1.0\times10^{-19}$). (pH = 4.15)

2) Calculate the pH of a 0.1 M solution of oxalic acid $H_2C_2O_4$, knowing that $K_{a1}=5.6\times10^{-2}$ and $K_{a2}=5.25\times10^{-5}$. (pH=1.28)

3) Calculate the pH in a 0.10 M solution of H_2Se having $K_{a1} = 1.9\times10^{-4}$ and $K_{a2} = 10^{-14}$. (pH=2.36)

4) Calculate the pH of a solution containing in 150 ml 3.87 g of H_2SeO_3, a weak diprotic acid having $K_{a1} = 3.0\times10^{-3}$ e $K_{a2} = 5.0\times10^{-8}$. (A.W.: H=1, Se=79, O=16)

(pH = 1.64)