

ACID-BASE EQUILIBRIUM

1: EQUILIBRIUM CONSTANT

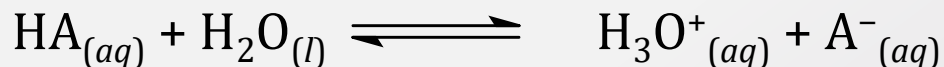
K_a , K_b AND pH

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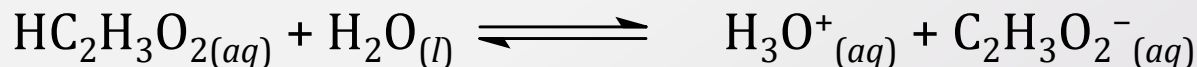
ACID BASE EQUILIBRIUM

Acid base **equilibrium** occurs when we deal with **weak acids and bases**. There is incomplete ionization of the acid.

We can write an acid equilibrium reaction for the generic acid, HA.



Acetic acid is a weak acid. It reacts with water as follows ($\text{HA} = \text{HC}_2\text{H}_3\text{O}_2$)*



Equilibrium constant, K_c can be calculated as in any equilibria (products over reactants); however here K_c is referred to as K_a as it is specific for acids.

Water is not part of the equilibrium as water is a liquid and has no concentration.

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

Note: the higher the K_a value – the more the concentration of hydronium ion and the stronger the acid.

**Acetic acid can also be written as CH_3COOH , but then the acidic proton is the last one, so it is more convenient to write it as $\text{HC}_2\text{H}_3\text{O}_2$.*

K_a FOR WEAK ACIDS

Acid ionization Constants at 25 °C

Acid	Formula	Constant K_a
Acetic acid	$\text{HC}_2\text{H}_3\text{O}_2$	1.7×10^{-5}
Benzoic acid	$\text{HC}_7\text{H}_5\text{O}_2$	6.3×10^{-5}
Boric acid	H_3BO_3	5.9×10^{-10}
Carbonic acid	H_2CO_3	4.3×10^{-7}
	HBO_3	4.8×10^{-11}
Cyanic acid	HOCN	3.5×10^{-4}
Formic acid	HCHO_2	1.7×10^{-4}
Hydrocyanic acid	HCN	4.9×10^{-10}
Hydrofluoric acid	HF	6.8×10^{-2}
Hydrogen sulfate ion	HSO_4^-	1.1×10^{-4}
Hydrogen sulfide	H_2S	8.9×10^{-4}
	HS^-	1.2×10^{-13}

EXAMPLE 1: QUICK CHECK: K_a FOR SOME ACIDS

You have prepared dilute solutions of equal molar concentrations of $\text{HC}_2\text{H}_3\text{O}_2$ (acetic acid), HNO_2 , HF , and HCN . Rank the solutions from the highest pH to the lowest pH using the K_a values given.

Answer:

Acid	K_a	pH
HF	6.8×10^{-4}	highest
HNO_2	4.5×10^{-4}	
$\text{HC}_2\text{H}_3\text{O}_2$	1.7×10^{-5}	
HCN	4.9×10^{-10}	lowest

CALCULATIONS USING K_a

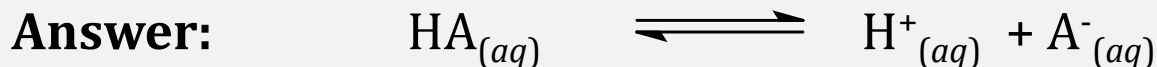
From the K_a values and concentrations of acids, one can calculate the concentrations of all ions at equilibrium, and then the pH of the acid.

- Remember in weak acids and bases, the ionization is not complete, so not all the hydronium ions will be in solution.
- If the pH of the solution is given, then x or concentration of product ions can be calculated from it.
- This setup is similar to equilibrium setup. Remember again that water is not part of the equilibrium as it is a liquid. (*I may not be writing water in future equations*).

	$\text{HA}_{(aq)}$	$\text{H}_2\text{O}_{(l)} \rightleftharpoons$	$\text{H}_3\text{O}^+_{(aq)}$	$\text{A}^-_{(aq)}$
Initial	C_1		0	0
Change	$-x$		$+x$	$+x$
Equilibrium	$C_1 - x$		x	x

EXAMPLE 2: CALCULATING pH

Calculate the pH of a 0.18 M solution of a weak acid that has $K_a = 9.2 \times 10^{-6}$.



Initial	0.18 M		0		0
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Change	-x		+x		+x
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At Eq.	0.18-x		x		x
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$$9.2 \times 10^{-6} = \frac{(x)(x)}{0.18 \text{ M} - x}$$

$$9.2 \times 10^{-6} = \frac{x^2}{0.18 \text{ M}}$$

$$x = \sqrt{(9.2 \times 10^{-6})(0.18)} = 1.29 \times 10^{-3} \text{ M}$$

$$1.29 \times 10^{-3} \text{ M} = x$$

$$\text{pH} = -\log(1.3 \times 10^{-3} \text{ M}) = \boxed{2.89}$$

Do we ignore x?

$$\frac{0.18 \text{ M}}{9.2 \times 10^{-6}} > 100, \text{ so yes, ignore } x$$

Check % ionization to make sure ignoring x was valid.

$$\frac{1.3 \times 10^{-3} \text{ M}}{0.18 \text{ M}} \times 100 = 0.72\%$$

$$0.72\% < 5\%$$

So ignoring x was okay

WHEN TO IGNORE X

For the equilibrium conc. of C_1 ($C_1 - x$); x can usually be ignored because in weak acids and bases “ x ” is very small. To know when to ignore x use either of the two equations below. (*I prefer the first one*).

- Divide the molarity (M) of the **initial** acid/base solution by the K_a or K_b . If value is more than 100 then ignore x .

$$\frac{M}{K_a} > 100$$

- Alternatively, you can also use the formula below for percent ionization **after** you have calculated the molarity of the solution. If the percent ionization is less than 5% then ignoring x was fine.

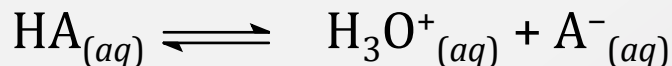
$$\frac{K_a}{M} \times 100\% < 5\%$$

- Another clue is that if K_a or K_b 10^{-5} or less then don't worry with calculations, just ignore x .

EXAMPLE 3: CALCULATING pH

Para-hydroxybenzoic acid is used to make certain dyes. What are the concentrations of this acid, of hydronium ion, and of para-hydroxybenzoate ion in a **0.200 M** aqueous solution at 25 °C? What is the pH of the solution? The K_a of this acid is **2.6×10^{-5}** .

Answer: (use HA as a generic acid)



Initial	0.200	0	0
Change	-x	+x	+x
Equilibrium	0.200 - x	x	x

Step 1

Do we ignore x?

$$\frac{0.200 \text{ M}}{2.6 \times 10^{-5}} > 100, \text{ so yes, ignore } x$$

Step 2

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

$$2.6 \times 10^{-5} = \frac{x^2}{0.200 - x}$$

$$2.6 \times 10^{-5} = \frac{x^2}{0.200}$$

$$2.6 \times 10^{-5} \times 0.200 = x^2$$

$$x = \sqrt{(2.6 \times 10^{-5})(0.2)} = 2.3 \times 10^{-3} \text{ M}$$

[H₃O⁺] and [A⁻]

$$0.200 - 2.6 \times 10^{-3} = 0.197 \text{ M [HA]}$$

$$\text{pH} = -\log(2.3 \times 10^{-3})$$

$$\text{pH} = 2.64$$

EXAMPLE 4: CALCULATING K_a , % IONIZATION

Sore-throat medications sometimes contain the weak acid phenol, $\text{HC}_6\text{H}_5\text{O}$. A **0.10 M** solution of phenol has a pH of **5.43** at 25 °C.

- a) What is the acid-ionization constant, K_a , for phenol at 25 °C?
- b) What is the degree of ionization?

Answer:

	$\text{HC}_6\text{H}_5\text{O}_{(aq)} \rightleftharpoons$	$\text{H}_3\text{O}^+_{(aq)} +$	$\text{C}_6\text{H}_5\text{O}^-_{(aq)}$
Initial	0.10	0	0
Change	-x	+x	+x
Equilibrium	$0.10 - x$	x	x

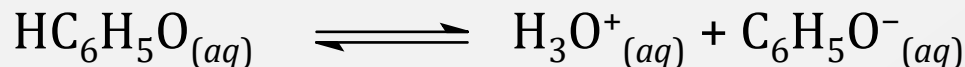
a) If pH = 5.43 then $[\text{H}_3\text{O}^+] = 3.7 \times 10^{-6} \text{ M} = x = [\text{C}_6\text{H}_5\text{O}^-]$.

$[\text{HC}_6\text{H}_5\text{O}] = 0.10 - x = 0.10 \text{ M}$. (*x is a very small amount so its subtraction from the original conc. will give almost the same original conc.*)

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EXAMPLE 4: CONTD...

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$$[\text{HC}_6\text{H}_5\text{O}] = 0.10 \text{ M}$$

$$[\text{H}_3\text{O}^+] = [\text{C}_6\text{H}_5\text{O}^-] = 3.7 \times 10^{-6} \text{ M}$$

Once we have all the values we can calculate K_a .

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_5\text{O}^-]}{[\text{HC}_6\text{H}_5\text{O}]} = \frac{(3.7 \times 10^{-6})^2}{0.10}$$

$$K_a = 1.4 \times 10^{-10}$$

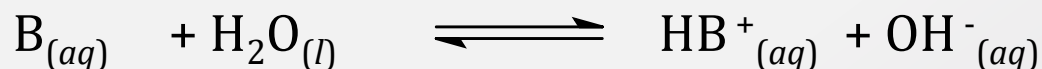
b) Degree of ionization is ratio of ionized to original concentrations.

$$\text{Degree of ionization} = \frac{x}{0.10} \times 100\% = \frac{3.7 \times 10^{-6}}{0.10} \times 100\% = 3.7 \times 10^{-3}\%$$

CALCULATING pH FOR WEAK BASES

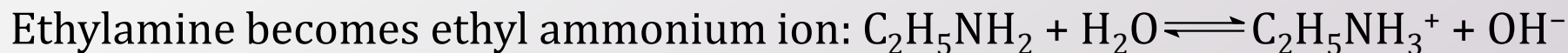
The degree to which a weak base ionizes depends on

- the concentration of the base.
- the equilibrium constant for the ionization called the base ionization constant, K_b . H_2O is the acid here.



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

- Solving for x gives the hydroxide ion conc. – **not** the hydronium ion conc., so one more calculation is needed to get the pH: calculate $[H_3O^+]$ using K_w .
- Example of some weak base equations:



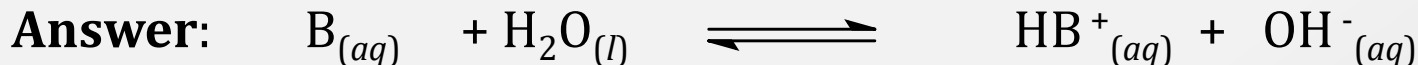
K_b FOR WEAK BASES

Base ionization Constants at 25 °C.

Base	Formula	Constant K_b
Ethylamine	$C_2H_5NH_2$	5.6×10^{-4}
Methylamine	CH_3NH_2	4.5×10^{-4}
Ammonia	NH_3	1.8×10^{-9}
Pyridine	C_5H_5N	1.7×10^{-10}
Aniline	$C_6H_5NH_2$	3.8×10^{-10}
Urea	H_2NCONH_2	1.5×10^{-14}

EXAMPLE 5: CALCULATE pH FOR WEAK BASE

Calculate the pH of a 0.0142 M weak base with K_b of 5.6×10^{-6} at 25 °C.



Initial	0.0142		0	0
Change	-x		+x	+x
Eq.	0.0142 - x		x	x

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

Step 1

$$5.6 \times 10^{-6} = \frac{x^2}{0.0142 - x}$$

$$5.6 \times 10^{-6} \times 0.0142 = x^2$$

$$x = \sqrt{(5.6 \times 10^{-6})(0.0142)} = 2.82 \times 10^{-4} M$$

$$= [OH^-]$$

Step 3

Two ways to do calculate pH: either calc. $[H_3O^+]$ using K_w or calc pOH.

$$K_w = [H_3O^+][OH^-] \quad [H_3O^+] = \frac{1 \times 10^{-14}}{2.82 \times 10^{-4}} = 3.546 \times 10^{-11} \quad pH = -\log(1.258 \times 10^{-6}) = 10.5$$

Step 2

Do we ignore x?

$$\frac{0.0142 M}{5.6 \times 10^{-6}} = 2535$$

> 100, ignore x

OR $pOH = -\log(2.82 \times 10^{-4}) = 3.55$

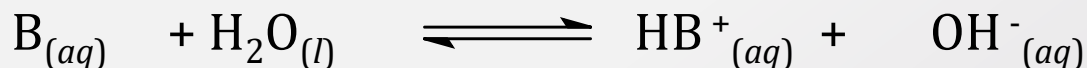
$pH = 14 - pOH = 14 - 3.55 = 10.5$

EXAMPLE 6: CALCULATE K_b

Determine the K_b of a weak base if a 0.350 M solution of the base has a pH of 10.6 at 25°C.

Answer:

$$\text{pOH} = 14.00 - 10.6 = 3.4 \quad [\text{OH}^-] = 10^{-3.4} = 3.89 \times 10^{-4} \text{ M}$$



Initial 0.350 M

Change $-3.89 \times 10^{-4} \text{ M}$ $+3.89 \times 10^{-4} \text{ M}$ $+3.89 \times 10^{-4} \text{ M}$

Eq. conc. 0.350^* $3.89 \times 10^{-4} \text{ M}$ $3.89 \times 10^{-4} \text{ M}$
M

* $3.89 \times 10^{-4} \text{ M}$ is too small – so it does not have to be subtracted

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

$$K_b = \frac{(3.89 \times 10^{-4} \text{ M})^2}{0.350 \text{ M}} = 4.53 \times 10^{-7}$$

POLYPROTIC ACIDS

A polyprotic acid has more than one acidic proton—for example, H_2SO_4 , H_2SO_3 , H_2CO_3 , H_3PO_4 .

These acids have successive ionization reactions with K_{a1} , K_{a2} , ...

The calculations of the pH includes ionization of all the protons and then adding all the concentrations to calculate the final pH.

K_a FOR POLYPROTIC ACIDS

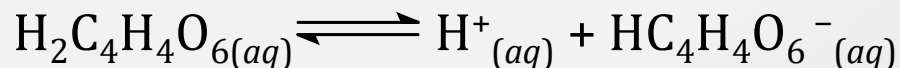
Some acid ionization Constants for di and triprotic acids at 25 °C

Acid	Formula	K_{a1}	K_{a2}	K_{a3}
Sulfuric acid	H_2SO_4	Very large	1.3×10^{-2}	
Oxalic acid	$H_2C_2O_4$	6.5×10^{-4}	6.1×10^{-5}	
Sulfurous acid	H_2SO_3	1.3×10^{-9}	6.3×10^{-8}	
Ascorbic acid (Vit.C)	$H_2C_6H_6O_6$	8.0×10^{-10}	1.6×10^{-12}	
Carbonic acid	H_2CO_3	4.2×10^{-10}	4.8×10^{-11}	
Hydrosulfuric acid	H_2S	9.5×10^{-14}	1.0×10^{-19}	
Phosphoric acid	H_3PO_4	7.5×10^{-4}	6.2×10^{-8}	4.2×10^{-13}

EXAMPLE 7: POLYPROTIC ACID pH

Tartaric acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, is a diprotic acid used in food products. What is the pH of a **0.10 M solution**? What is the concentration of the $\text{C}_4\text{H}_4\text{O}_6^{2-}$ ion in the same solution? $K_{a1} = 9.2 \times 10^{-4}$; $K_{a2} = 4.3 \times 10^{-5}$.

Answer: Find the first and second ionizations...



Initial	0.10	0	0
Change	-x	+x	+x
Equilibrium	0.10 - x	x	x

$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HA}^-]}{[\text{H}_2\text{A}]}$$

$$9.2 \times 10^{-4} = \frac{x^2}{0.10 - x}$$

Check ionization

$$\frac{0.100 \text{ M}}{9.2 \times 10^{-4}} = 108 \text{ which is just about } 100, \text{ so cannot ignore } x$$

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EXAMPLE 7: POLYPROTIC ACID CONTD....1

- Use the quadratic equation.

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

$$9.2 \times 10^{-4}(0.10 - x) = x^2$$

$$9.2 \times 10^{-5} - 9.2 \times 10^{-4}x = x^2$$

$$x^2 + 9.2 \times 10^{-4}x - 9.2 \times 10^{-5} = 0$$

$$a = 1 \quad b = 9.2 \times 10^{-4} \quad c = -9.2 \times 10^{-5}$$

$$x = \frac{-(9.2 \times 10^{-4}) \pm \sqrt{(9.2 \times 10^{-4})^2 - 4(1)(-9.2 \times 10^{-5})}}{2(1)}$$

$$x = \frac{-(9.2 \times 10^{-4}) \pm (1.92 \times 10^{-2})}{2} = -4.6 \times 10^{-4} \pm 9.6 \times 10^{-3}$$

$$x = 9.1 \times 10^{-3} \quad \text{and} \quad x = -1.0 \times 10^{-2}$$

- At the end of the first acid ionization equilibrium, the concentrations are

- $[\text{H}_3\text{O}^+] = 9.1 \times 10^{-3} \text{ M}$
- $[\text{HA}^-] = 9.1 \times 10^{-3} \text{ M}$
- $[\text{H}_2\text{A}] = 9.0 \times 10^{-4} \text{ M}$

- Use these to calculate the 2nd conc. of hydronium ion.

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EXAMPLE 7: POLYPROTIC ACID CONTD....2

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	$\text{HC}_4\text{H}_4\text{O}_6^- (aq)$	$\rightleftharpoons$	$\text{H}^+ (aq) +$	$\text{C}_4\text{H}_4\text{O}_6^{2-} (aq)$
Initial	0.0091		0.0091	0
Change	$-x$		$+x$	$+x$
Equilibrium	$0.0091 - x$		$0.0091 + x$	x

$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{A}^{2-}]}{[\text{HA}^-]} \quad 4.3 \times 10^{-5} = \frac{(0.0091 + x)x}{(0.0091 - x)}$$

Check again if we can subtract $x = \frac{.0091}{4.3} = 211, > 100$, so ignore x

- Calculating the final pH.

$$[\text{C}_4\text{H}_4\text{O}_6^{2-}] = 4.3 \times 10^{-5} \text{ M}$$

$$[\text{HC}_4\text{H}_4\text{O}_6^-] = 9.1 \times 10^{-3} \text{ M}$$

Use this for pH $\longrightarrow [\text{H}_3\text{O}^+] = 9.1 \times 10^{-3} \text{ M}$

$$[\text{H}_2\text{C}_4\text{H}_4\text{O}_6] = 9.0 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log(9.1 \times 10^{-3}) = 2.04$$

KEY CONCEPTS

- Calculation of pH and pOH of weak acids and bases
- Calculation of K_a and K_b of weak acids and bases
- Calculation of pH for diprotic acids.