

ACIDS AND BASES – 3

WEAK ACID BASE

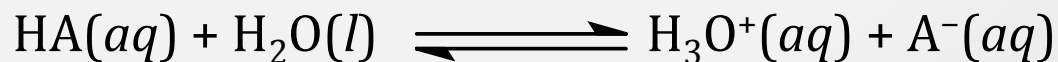
EQUILIBRIUM

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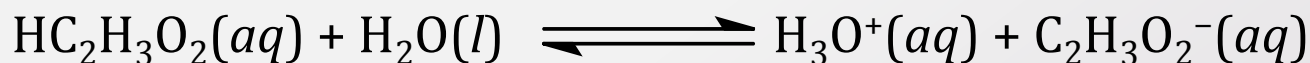
ACID BASE EQUILIBRIUM

Acid base **equilibrium** occurs when we deal with **weak acids and bases**.

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



Acetic acid is a weak acid. It reacts with water as follows (HA = HC₂H₃O₂)



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. Liquid water is not part of the equilibrium as water 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.

K_a FOR SOME ACIDS

Table 16.1 Acid-Ionization Constants at 25°C*

Substance	Formula	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}
	HCO_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^{-4}
Hydrogen sulfate ion	HSO_4^-	1.1×10^{-2}
Hydrogen sulfide	H_2S	8.9×10^{-8}
	HS^-	$1.2 \times 10^{-13\dagger}$

EXAMPLE: 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. Use data table given before or your text book.

Solution:

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

- Given the K_a values and concentrations of acids, one can calculate the concentrations of all ions at equilibrium, and then pH of the acid.
- Remember for 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 can be calculated from it.
- These setup is similar to equilibrium setup.

	HA(aq)	H ₂ O(l)	H ₃ O ⁺ (aq)	A ⁻ (aq)
Initial	C_1		0	0
Change	$-x$		$+x$	$+x$
Equilibrium	$C_1 - x$		x	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 the equation shown. If the percent is less than 5% then ignore x .

$$5\% \leq \frac{x}{C_i} \times 100$$

EXAMPLE: 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

Change -x +x +x

At Eq. 0.18-x x x

Ignore -x for equilibrium conc.

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

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

Check % ionization

$$1.3 \times 10^{-3} \text{ M} = x$$

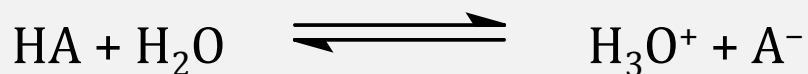
$$\frac{1.3 \times 10^{-3} \text{ M}}{0.18 \text{ M}} \times 100 = 0.72\% \qquad 0.72\% < 5\%$$

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

EXAMPLE: 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 and the degree of ionization of the acid? The K_a of this acid is **2.6×10^{-5}** .

Solution: (use HA as a generic acid)



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

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

$$\frac{0.200}{2.6 \times 10^{-5}} > 1000, \text{ so } 0.200 - x \approx 0.200$$

$$K_a = \frac{x^2}{0.200}$$

$$5.2 \times 10^{-6} = x^2$$

	HA(aq) +	H ₂ O(l) □	H ₃ O ⁺ (aq) +	A ⁻ (aq)
Initial	0.200		0	0
Change	-x		+x	+x
Equilibrium	0.200 - x		x	x

$$x = 2.3 \times 10^{-3} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.3 \times 10^{-3})$$

$$\text{pH} = 2.64$$

EXAMPLE: 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 .

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

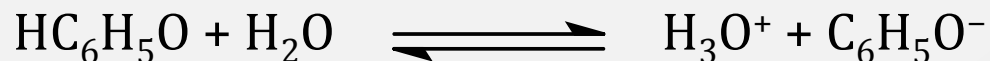
Solution:

	$\text{HC}_6\text{H}_5\text{O}(aq) +$	$\text{H}_2\text{O}(l)$	$\text{H}_3\text{O}^+(aq) +$	$\text{C}_6\text{H}_5\text{O}^-(aq)$
Initial	0.10		0	0
Change	$-x$		$+x$	$+x$
Equilibrium	$0.10 - x$		x	x

If $\text{pH} = 5.43$ 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.*)

EXAMPLE...CONTD...



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

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

Once we have all the values we can calculate K_a .

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_5\text{O}^-]}{[\text{HC}_6\text{H}_5\text{O}]}$$

$$K_a = \frac{(3.7 \times 10^{-6})^2}{0.10}$$

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

Degree of ionization is ratio of ionized to original concentrations.

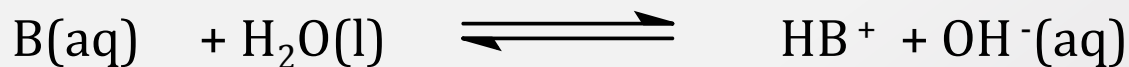
$$\text{Degree of ionization} = \frac{x}{0.10} = \frac{3.7 \times 10^{-6}}{0.10}$$

$$\text{Degree of ionization} = 3.7 \times 10^{-5}$$

$$\text{Percent ionization} = 3.7 \times 10^{-3}\% \text{ or } 0.0037\%$$

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 .

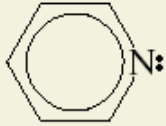
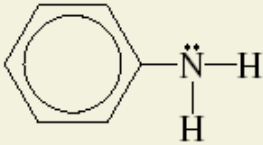


$$K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$$

- Solving for x gives the hydroxide ion conc. – not the hydronium ion conc., so one more calculation is needed to get the pH – calculate $[\text{H}_3\text{O}^+]$ using K_w .
- Example of some weak base equations:



SOME K_b FOR WEAK BASES

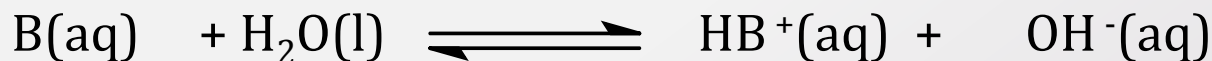
TABLE 16.7		Ionization Constants of Some Weak Bases at 25°C	
Name of Base	Formula	Structure	K_b
Ethylamine	$C_2H_5NH_2$	$CH_3-CH_2-\overset{\cdot\cdot}{N}-H$ H	5.6×10^{-4}
Methylamine	CH_3NH_2	$CH_3-\overset{\cdot\cdot}{N}-H$ H	4.4×10^{-4}
Ammonia	NH_3	$H-\overset{\cdot\cdot}{N}-H$ H	1.8×10^{-5}
Pyridine	C_5H_5N		1.7×10^{-9}
Aniline	$C_6H_5NH_2$		3.8×10^{-10}
Urea	H_2NCONH_2	$H-\overset{\cdot\cdot}{N}-\overset{O}{\parallel}C-\overset{\cdot\cdot}{N}-H$ H H	1.5×10^{-14}

EXAMPLE: USING pH TO CALCULATE K_b

Determine the K_b of a weak base if a 0.50 M solution of the base has a pH of 9.59 at 25°C.

Solution:

$$\text{pOH} = 14.00 - 9.59 = 4.41 \quad [\text{OH}^-] = 10^{-4.41} = 3.89 \times 10^{-5} \text{ M}$$



Initial 0.050 M

Change $-3.89 \times 10^{-5} \text{ M}$ $+3.89 \times 10^{-5} \text{ M}$ $+3.89 \times 10^{-5} \text{ M}$

Eq. conc 0.050^* $3.89 \times 10^{-5} \text{ M}$ $3.89 \times 10^{-5} \text{ M}$

* $3.89 \times 10^{-5} \text{ M}$ is too small – so it does not have to be subtracted

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

$$K_b = \frac{(3.89 \times 10^{-5} \text{ M})^2}{0.50 \text{ M}} = 3.0 \times 10^{-9}$$

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.

SOME K_a S FOR POLYPROTIC ACIDS

TABLE 16.8

Ionization Constants for Some Diprotic and Polyprotic Acids at 25°C

Name of Acid	Formula	Structure	K_{a_1}	K_{a_2}	K_{a_3}
Sulfuric acid	H_2SO_4	$\begin{array}{c} O \\ \\ H-O-S-O-H \\ \\ O \end{array}$	Very large	1.3×10^{-2}	
Oxalic acid	$H_2C_2O_4$	$\begin{array}{c} O \quad O \\ \quad \\ H-O-C-C-O-H \end{array}$	6.5×10^{-2}	6.1×10^{-5}	
Sulfurous acid	H_2SO_3	$\begin{array}{c} O \\ \\ H-O-S-O-H \end{array}$	1.3×10^{-2}	6.3×10^{-8}	
Ascorbic acid (vitamin C)	$H_2C_6H_6O_6$	$\begin{array}{c} H-O \quad \quad O-H \\ \quad \quad \quad \diagdown \quad \diagup \\ \quad \quad \quad C=C \\ \quad \quad \quad / \quad \quad \backslash \\ H \quad \quad \quad O \\ \quad \quad \quad \\ -C \quad \quad \quad C=O \\ \quad \quad \quad \\ -CH_2OH \quad -O- \\ \\ -CHOH \\ \\ -CH_2OH \end{array}$	8.0×10^{-5}	1.6×10^{-12}	
Carbonic acid	H_2CO_3	$\begin{array}{c} O \\ \\ H-O-C-O-H \end{array}$	4.2×10^{-7}	4.8×10^{-11}	
Hydrosulfuric acid*	H_2S	$H-S-H$	9.5×10^{-8}	1×10^{-19}	
Phosphoric acid	H_3PO_4	$\begin{array}{c} O \\ \\ H-O-P-O-H \\ \\ O \\ \\ H \end{array}$	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}

EXAMPLE: 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? $K_{a1} = 9.2 \times 10^{-4}$; $K_{a2} = 4.3 \times 10^{-5}$.

Solution: Find the first and second ionizations...

	$\text{H}_2\text{A}(aq) +$	$\text{H}_2\text{O}(l) \rightleftharpoons$	$\text{H}_3\text{O}^+(aq)$ +	$\text{HA}^-(aq)$
Initial	0.10		0	0
Change	-x		+x	+x
Equilibrium	$0.10 - x$		x	x

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

Cannot ignore "x"

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

EXAMPLE:...CONTD....1

- Use the quadratic equation.

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

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

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

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

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

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

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

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

- 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.

EXAMPLE:....CONTD....2

	$\text{HA}^-(aq) +$	$\text{H}_2\text{O}(l)$	$\text{H}_3\text{O}^+(aq) +$	$\text{A}^{2-}(aq)$
Initial	0.0091		0.0091	0
Change	-x		+x	+x
Equilibrium	$0.0091 - x$		$0.0091 + x$	x

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

We can assume that

$$0.0091 + x \approx 0.0091 \quad \text{and} \quad 0.0091 - x \approx 0.0091$$

- So $x = 4.3 \times 10^{-5} \text{ M}$ ($4.3 \times 10^{-5} / 0.0091 \times 100\% = 0.47\%$) so x is insignificant

- 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 $[\text{H}_3\text{O}^+] = 9.1 \times 10^{-3} \text{ M}$ ←

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

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

$$\text{pH} = 2.04$$

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.