

**ACID-BASE EQUILIBRIA**
**Solutions of a Weak Acid or Base**

- Weak acids ionize (dissociate) partially in water



?????

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

- [H<sub>2</sub>O]      ➤ can be considered constant for dilute solutions  
 ➤ can be included in K<sub>c</sub>

$$\frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = K_c \times [\text{H}_2\text{O}] = \mathbf{K_a = ACID IONIZATION CONSTANT}$$

- K<sub>a</sub>**      ➤ expresses the extent of ionization of a weak acid  
 ➤ is a measure of the relative strength of weak acids

<u>Weak Acids</u>	<u>Acid-Ionization Constant (at 25<sup>0</sup>C)</u>
HF	K <sub>a</sub> = 6.8 x 10 <sup>-4</sup> ← <b>strongest weak acid</b>
HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	K <sub>a</sub> = 1.7 x 10 <sup>-5</sup>
HClO	K <sub>a</sub> = 3.5 x 10 <sup>-8</sup>
HCN	K <sub>a</sub> = 4.9 x 10 <sup>-10</sup> ← <b>weakest weak acid</b>

 ↑  
**Strength  
Of  
Weak  
Acids  
Increases**
**Experimental Determination of K<sub>a</sub>:**

- Two methods are commonly used:

**1. Experimental Quantitative Determination of Electrical Conductivity**

- From the numerical value of the Electrical Conductivity, the Degree of Ionization is obtained.
- Degree of Ionization is the fraction of molecules that react with water to give ions.
- Degree of ionization is usually expressed in Percent Ionization

**2. Experimental Quantitative Determination of pH**

- Once the pH is known, the concentration of [H<sub>3</sub>O<sup>+</sup>] is calculated:      [H<sub>3</sub>O<sup>+</sup>] = antilog (- pH)
- From [H<sub>3</sub>O<sup>+</sup>], the concentration of the other species can be calculated.

**CALCULATIONS WITH  $K_a$** 
**Examples:**

1. Lactic acid,  $\text{HC}_3\text{H}_5\text{O}_3$ , is a weak acid found in sour milk. A 0.025 M solution of lactic acid has a pH of 2.75. What is the ionization constant,  $K_a$  for this acid? What is the degree of ionization?

	$\text{HC}_3\text{H}_5\text{O}_3 (\text{l}) + \text{H}_2\text{O} (\text{l}) \rightleftharpoons \text{H}_3\text{O}^+ (\text{aq}) + \text{C}_3\text{H}_5\text{O}_3^- (\text{aq})$			
Initial	0.025 M	----	0	0
$\Delta$	-x	----	+x	+x
Equilibrium	0.025-x	-----	x	x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_3\text{H}_5\text{O}_3^-]}{[\text{HC}_3\text{H}_5\text{O}_3]} = \frac{x^2}{0.025 - x}$$

$$[\text{H}_3\text{O}^+] = x = \text{antilog}(-\text{pH}) = \text{antilog}(-2.75) = 1.78 \times 10^{-3}$$

$$[\text{C}_3\text{H}_5\text{O}_3^-] = X = 1.78 \times 10^{-3}$$

$$[\text{HC}_3\text{H}_5\text{O}_3] = 25 \times 10^{-3} - 1.78 \times 10^{-3} = 23.2 \times 10^{-3}$$

$$K_a = \frac{(1.78 \times 10^{-3})^2}{23.2 \times 10^{-3}} = 1.4 \times 10^{-4}$$

$$\text{Degree of Ionization} = \frac{\text{Molar concentration of Ionized Acid}}{\text{Total Molar concentration of Acid}}$$

$$\text{Degree of Ionization} = \frac{1.78 \times 10^{-3}}{25 \times 10^{-3}} = 0.071 \quad \text{or} \quad 7.1\%$$



## EFFECT OF DILUTION ON pH AND DEGREE OF IONIZATION OF WEAK ACIDS

(Example: Acetic Acid,  $\text{HC}_2\text{H}_3\text{O}_2$ ,  $K_a = 1.7 \times 10^{-5}$ )

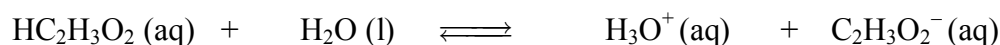
Concentration of $\text{HC}_2\text{H}_3\text{O}_2$ (M)	0.10	0.010	0.0010	0.00010	0.000010
	$1.0 \times 10^{-1}$	$1.0 \times 10^{-2}$	$1.0 \times 10^{-3}$	$1.0 \times 10^{-4}$	$1.0 \times 10^{-5}$
[ $\text{H}_3\text{O}^+$ ]	$1.3 \times 10^{-3}$	$4.1 \times 10^{-4}$	$1.3 \times 10^{-4}$	$4.1 \times 10^{-5}$	$1.3 \times 10^{-5}$
Degree of Ionization (%)	1.3%	4.1%	13%	41%	$\approx 100\%$
pH	2.89	3.39	3.89	4.39	4.89

### NOTES:

- Weak Acids: A **100 fold** dilution of the acid brings the pH 1 unit closer to 7
- Strong Acids: A **10 fold** dilution of the acid brings the pH 1 unit closer to 7
- Dilution causes the pH of all acidic solution to increase (approaching 7). This effect is 10 times stronger for strong acids.
- Consider: solutions of  $\text{HCl}(\text{aq})$  and  $\text{HC}_2\text{H}_3\text{O}_2$  of different concentrations:

	HCl (aq) – Strong Acid			HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> (aq) – Weak Acid		
Concentration of acid (M)	0.1	0.01	0.001	0.1	0.01	0.001
pH	1	2	3	2.89	3.39	3.89
Degree of Ionization (%)	100%	100%	100%	1.3%	4.1%	13%

- What causes the different effect of dilution on strong versus weak acids?
- The equilibrium ionization of the weak acid provides the explanation:



Stress: increased

Response: Equilibrium shifts to the right →

Result: - A higher % of  $\text{HC}_2\text{H}_3\text{O}_2$  molecules will ionize (degree of ionization increases)  
 - The concentration of  $\text{H}_3\text{O}^+$  decreases with dilution, but not proportionally.

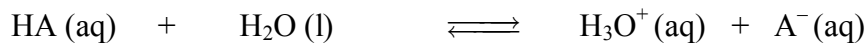
- **CONCLUSION: FOR WEAK ACIDS, FOR A GIVEN  $K_a$ :**

The more dilute the solution:

- The smaller the [ $\text{H}_3\text{O}^+$ ] ⇨ the greater the pH (the less acidic the solution) (the decrease in the [ $\text{H}_3\text{O}^+$ ] is not proportional to the decrease in dilution)
- The greater the degree of ionization

**EFFECT OF  $K_a$  ON pH OF WEAK ACIDS**

- Consider an 1.0 M aqueous solution of a weak acid, HA:



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \quad [\text{H}_3\text{O}^+]^2 = K_a \times [\text{HA}] = K_a \times 1.0 = K_a \quad [\text{H}_3\text{O}^+] = \sqrt{K_a}$$

- Consider several weak acids of the same molar concentration: 1.0 M

Weak Acid	HF (hydrofluoric acid)	HC <sub>7</sub> H <sub>5</sub> O <sub>2</sub> (benzoic acid)	HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> (acetic acid)	HClO (hypochlorous acid)	HCN (hydrocyanic acid)
<b><math>K_a</math></b>	<b><math>6.8 \times 10^{-4}</math></b>	<b><math>6.3 \times 10^{-5}</math></b>	<b><math>1.7 \times 10^{-5}</math></b>	<b><math>3.5 \times 10^{-8}</math></b>	<b><math>4.9 \times 10^{-10}</math></b>
[H <sub>3</sub> O <sup>+</sup> ]	$2.6 \times 10^{-2}$	$7.9 \times 10^{-3}$	$4.1 \times 10^{-3}$	$1.9 \times 10^{-4}$	$2.2 \times 10^{-5}$
<b>pH</b>	<b>1.59</b>	<b>2.10</b>	<b>2.39</b>	<b>3.72</b>	<b>4.66</b>

**Conclusion:**

- For a given concentration:
  - The larger the  $K_a$ :
    - the greater the [H<sub>3</sub>O<sup>+</sup>]
    - the lower the pH (the more acidic the solution)

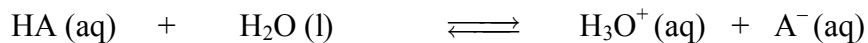
**Examples:**

Rank the following 0.1 M solutions of acids in order of decreasing pH (highest to lowest):



**EFFECT OF  $K_a$  ON DEGREE IONIZATION OF WEAK ACIDS**

- Consider an 1.0 M aqueous solution of a weak acid, HA:



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \quad [\text{H}_3\text{O}^+]^2 = K_a \times [\text{HA}] = K_a \times 1.0 = K_a \quad [\text{H}_3\text{O}^+] = \sqrt{K_a}$$

- Consider several weak acids of the same molar concentration: 1.0 M

Weak Acid	HF (hydrofluoric acid)	HC <sub>7</sub> H <sub>5</sub> O <sub>2</sub> (benzoic acid)	HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> (acetic acid)	HClO (hypochlorous acid)	HCN (hydrocyanic acid)
<b><math>K_a</math></b>	<b><math>6.8 \times 10^{-4}</math></b>	<b><math>6.3 \times 10^{-5}</math></b>	<b><math>1.7 \times 10^{-5}</math></b>	<b><math>3.5 \times 10^{-8}</math></b>	<b><math>4.9 \times 10^{-10}</math></b>
$[\text{H}_3\text{O}^+]$	$2.6 \times 10^{-2}$	$7.9 \times 10^{-3}$	$4.1 \times 10^{-3}$	$1.9 \times 10^{-4}$	$2.2 \times 10^{-5}$
Concentration of ionized molecules	$2.6 \times 10^{-2}$	$7.9 \times 10^{-3}$	$4.1 \times 10^{-3}$	$1.9 \times 10^{-4}$	$2.2 \times 10^{-5}$
<b>Degree of Ionization (%)</b>	<b>2.6</b>	<b>0.79</b>	<b>0.49</b>	<b>0.019</b>	<b>0.022</b>

**Conclusion:**

- For a given concentration:
  - The larger the  $K_a$ :
    - the greater the concentration of ionized molecules
    - the greater the degree of ionization

**Examples:**

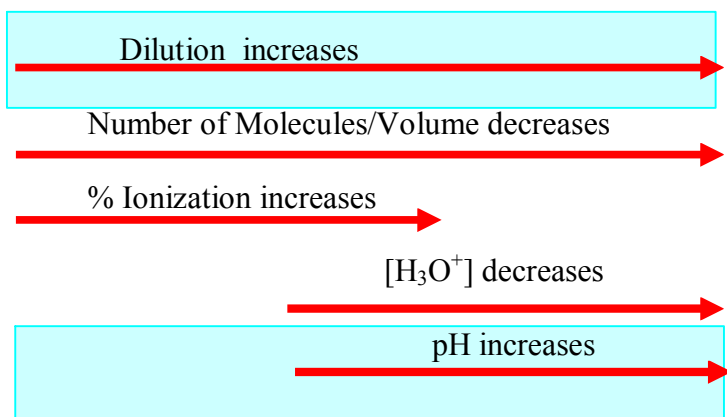
Rank the following 0.1 M solutions of acids in order of increasing ionization (from lowest to highest):



**SUMMARY OF EFFECT OF DILUTION AND  $K_a$   
ON THE pH AND DEGREE OF IONIZATION OF WEAK ACIDS**

**I. Effect of Dilution (decreasing concentration)**

(for a given  $K_a$ ):



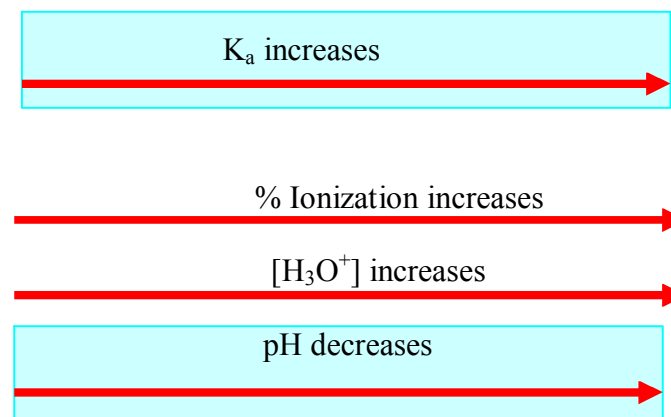
- Decreasing the concentration increases the pH, but not proportionally.

Reason:

- The increase in dilution (more  $H_2O$ ) increases the degree of ionization of the weak acid (more  $H_3O^+$ )
- The pH increases with dilution, but not proportionally

**II. Effect of  $K_a$**

(for a given concentration):



- A higher  $K_a$  (stronger acid) indicates a proportionally increased degree of ionization and increased  $[H_3O^+]$
- The pH decreases proportionally with increasing values of  $K_a$

**CALCULATING CONCENTRATIONS OF SPECIES IN A WEAK  
ACID SOLUTION USING  $K_a$** 
**(Quadratic Formula)**
**Examples:**

1. What is the pH of an aqueous solution that is 0.0030 M pyruvic acid,  $\text{HC}_3\text{H}_3\text{O}_3$ ? ( $K_a = 1.4 \times 10^{-4}$ )

**Step 1:**

Assemble a reaction table. (Abbreviate the formula for pyruvic acid as HPy)

	HPy	+	H <sub>2</sub> O (l)	$\rightleftharpoons$	H <sub>3</sub> O <sup>+</sup> (aq)	+	Py <sup>-</sup> (aq)
Initial			----				
$\Delta$			----				
Equilibrium			-----				

**Step 2:**

 Substitute the equilibrium concentrations and the value of  $K_a$  into the equilibrium constant equation:

$$K_a =$$

**Step 3:** Try approximation method and solve for x

**Step 4:** Check if the approximation is valid:

**NOTE:**

- As a general Rule: If the ratio:  $\frac{\text{Conc. acid}}{K_a} > 100$ , the approximation can be used
- If the ratio:  $\frac{\text{Conc. acid}}{K_a} < 100$  the approximation cannot be used  
(the quadratic formula must be used)



**CALCULATING THE CONCENTRATION OF VARIOUS SPECIES  
IN A SOLUTION OF A POLYPROTIC ACID**

Ascorbic acid ( $\text{H}_2\text{Asc}$ ) is a diprotic acid with  $K_{a1} = 7.9 \times 10^{-5}$  and  $K_{a2} = 1.6 \times 10^{-12}$ . What is the pH of a 0.10 M solution of ascorbic acid? What is the concentration of the ascorbate ion ( $\text{Asc}^{2-}$ ), in the solution?

**First Part: Calculate the pH of the solution:**

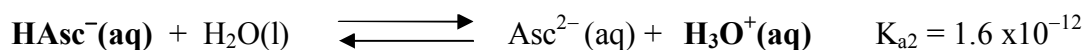
- Note that  $K_{a2} (1.6 \times 10^{-12}) \lllllllllll K_{a1} (7.9 \times 10^{-5})$
- As such:
  - the 2<sup>nd</sup> ionization can be neglected
  - any  $\text{H}^+$  produced by the 2<sup>nd</sup> ionization can be ignored.

	$\text{H}_2\text{Asc (aq)}$	$+$	$\text{H}_2\text{O (l)}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+ \text{(aq)}$	$+$	$\text{HAsc}^- \text{(aq)}$
Initial	0.10 M		----		0		0
$\Delta$	-x		----		+x		+x
Equilibrium	0.10-x		-----		x		x

$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HAsc}^-]}{[\text{H}_2\text{Asc}]} = \frac{x^2}{0.10-x} = 7.9 \times 10^{-5}$$

$$x^2 = (0.10)(7.9 \times 10^{-5}) = 7.9 \times 10^{-6} \quad x = [\text{H}_3\text{O}^+] = 2.8 \times 10^{-3}$$

$$\text{pH} = -\log(2.8 \times 10^{-3}) = 2.55$$

**Second Part: Calculate the concentration of the sulfite ion ( $\text{SO}_3^{2-}$ ):**


	$\text{HAsc}^- \text{(aq)}$	$+$	$\text{H}_2\text{O (l)}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+ \text{(aq)}$	$+$	$\text{Asc}^{2-} \text{(aq)}$
Initial	0.0028		----		0.0028		0
$\Delta$	-y		----		+y		+y
Equilibrium	0.0028 - y		-----		0.0028 + y		y

$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{Asc}^{2-}]}{[\text{HAsc}^-]} = \frac{(0.0028 + y)(y)}{0.0028 - y} = 1.6 \times 10^{-12}$$

- Assume that:  $y \lllllll 0.0028$
- Therefore:  $0.0028 + y \approx 0.0028$  and  $0.0028 - y \approx 0.0028$

$$K_{a2} = \frac{(0.0028 + y)(y)}{0.0028 - y} = \frac{(0.0028)(y)}{0.0028} = 1.6 \times 10^{-12}$$

$$y = [A^{2-}] = 1.6 \times 10^{-12} \text{ M}$$

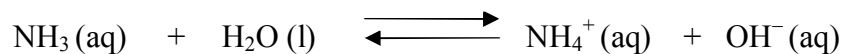
- **General Rule: The concentration of the ion  $A^{2-}$  equals the second ionization constant,  $K_{a2}$**

**Examples:**

1. Carbonic acid ( $H_2CO_3$ ) is a weak acid with  $K_{a1} = 4.3 \times 10^{-7}$  and  $K_{a2} = 4.8 \times 10^{-11}$ . Calculate the pH and the carbonate ion concentration of a 0.050M solution of carbonic acid.

**BASE-IONIZATION EQUILIBRIA**

- Weak bases ionize (dissociate) partially in water.




$$K_c = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3][\text{H}_2\text{O}]}$$

- [H<sub>2</sub>O]      ➤ can be considered constant for dilute solutions  
                  ➤ can be included in K<sub>c</sub>

$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = K_c \times [\text{H}_2\text{O}] = \mathbf{K_b = \text{BASE IONIZATION CONSTANT}}$$

- K<sub>b</sub>**      ➤ expresses the extent of ionization of a weak base  
                  ➤ is a measure of the relative strength of weak bases

<u>Weak Bases</u>	<u>Formula</u>	<u>Base-Ionization Constant (at 25 °C)</u>	
Dimethylamine	(CH <sub>3</sub> ) <sub>2</sub> NH	K <sub>b</sub> = 5.1 × 10 <sup>-4</sup>	← <b>strongest weak base</b>
Ammonia	NH <sub>3</sub>	K <sub>b</sub> = 1.8 × 10 <sup>-5</sup>	
Aniline	C <sub>6</sub> H <sub>5</sub> -NH <sub>2</sub>	K <sub>b</sub> = 4.2 × 10 <sup>-10</sup>	
Urea	NH <sub>2</sub> -CO-NH <sub>2</sub>	K <sub>b</sub> = 1.5 × 10 <sup>-14</sup>	← <b>weakest weak base</b>



**Strength  
Of  
Weak  
Bases  
Increases**

**CALCULATIONS WITH  $K_b$** 
**Examples:**

1. Quinine is an alkaloid, or naturally occurring base, used to treat malaria. A 0.0015 M solution of quinine has a pH of 9.84. What is  $K_b$  of quinine?

**Step 1: Convert the pH to pOH, and then to  $[\text{OH}^-]$** 

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 9.84 = 4.16$$

$$[\text{OH}^-] = \text{antilog}(-4.16) = 6.92 \times 10^{-5} \text{ M}$$

**Step 2: Using the symbol Qu for quinine, assemble reaction table**

	Qu (aq)	+	H <sub>2</sub> O (l)	$\rightleftharpoons$	HQu <sup>+</sup> (aq)	+	OH <sup>-</sup> (aq)
Initial	0.0015 M		----		0		0
$\Delta$	-x		----		+x		+x
Equilibrium	0.0015-x		-----		x		x

$$K_b = \frac{[\text{HQu}^+][\text{OH}^-]}{[\text{Qu}]} = \frac{x^2}{0.0015 - x} = \frac{(6.92 \times 10^{-5})^2}{(0.0015 - 6.92 \times 10^{-5})} = 3.3 \times 10^{-6}$$

2. What is the pH of a 0.20 M solution of ammonia in water ( $K_b = 1.8 \times 10^{-5}$ )?

	NH <sub>3</sub> (aq)	+	H <sub>2</sub> O (l)	$\rightleftharpoons$	NH <sub>4</sub> <sup>+</sup> (aq)	+	OH <sup>-</sup> (aq)
Initial	0.20 M		----		0		0
$\Delta$	-x		----		+x		+x
Equilibrium	0.20-x		-----		x		x

- Assume that x is small enough to neglect compared with 0.20.

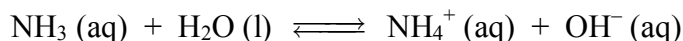
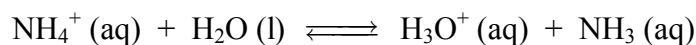
$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{0.20 - x} = \frac{x^2}{0.20} = 1.8 \times 10^{-5} \quad x^2 = 3.6 \times 10^{-6}$$

$$x = [\text{OH}^-] = 1.89 \times 10^{-3} \text{ M} \quad (\text{Note that } x \text{ is negligible compared to } 0.20)$$

$$[\text{H}_3\text{O}^+] = \frac{1.0 \times 10^{-14}}{1.89 \times 10^{-3}} = 5.3 \times 10^{-12} \quad \text{pH} = -\log(5.3 \times 10^{-12}) = \mathbf{11.28}$$

**RELATIONSHIP BETWEEN  $K_a$  AND  $K_b$** 

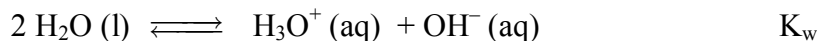
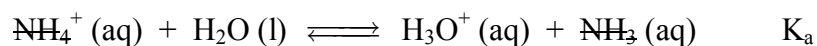
- The quantitative relationship between an acid and its conjugate base can be seen in the examples below:



- Each of these equilibria can be expressed by an ionization constant:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} \quad \text{and} \quad K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

- Addition of the two equations above results the following:



- Recall that when two reactions are added to form a third reaction, the equilibrium constant for the third reaction is the products of the two added reactions. Therefore,

$$K_w = K_a \times K_b$$

- Note that  $K_a$  and  $K_b$  are inversely proportional for an acid-base conjugate pair. This is expected, since as the strength of an acid increases (larger  $K_a$ ), the strength of its conjugate base decreases (smaller  $K_b$ ).

**Examples:**

- Hydrofluoric acid (HF) has  $K_a = 6.8 \times 10^{-4}$ . What is  $K_b$  for the fluoride ion?

$$K_b = \frac{K_w}{K_a}$$

- Which of the following anions has the largest  $K_b$  value:  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{HCO}_3^-$ ?