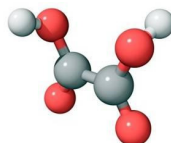
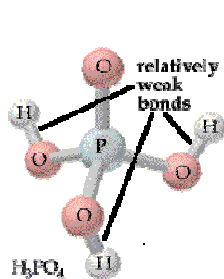


Chapter 9: POLYPROTIC ACID-BASE EQUILIBRIA



Oxalic acid,
rhubarb and
rhubarb pie

Images available at http://www.800mainstreet.com/acid_base/0000-01a-oxyacids-.html and¹ <http://www.sciencephoto.com/images/>

Understanding Polyprotic Species

Diprotic acids, H_2A
 ➤ Can donate 2 H^+
 Ex. H_2SO_4 , H_2CO_3

vs. **Dibasic species**, A^{2-}
 ➤ Can accept 2 H^+
 Ex. SO_4^{2-} , CO_3^{2-}

Triprotic acids, H_3A
 ➤ Can donate 3 H^+
 Ex. H_3PO_4 ,
 $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$ (Citric acid)

vs. **Tribasic species**, A^{3-}
 ➤ Can accept 3 H^+
 Ex. PO_4^{3-} ,
 $\text{C}_6\text{H}_5\text{O}_7^{3-}$

Diprotic Acids and Bases

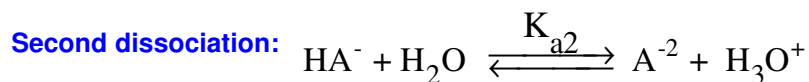
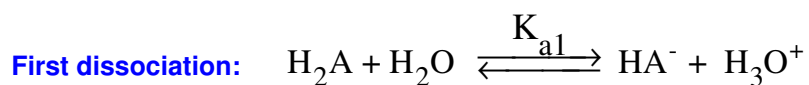
General formulas:

- ❖ H_2A = fully acidic form
- ❖ HA^- = intermediate form; amphoteric
- ❖ A^{2-} = fully basic or fully deprotonated form

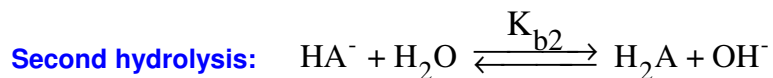
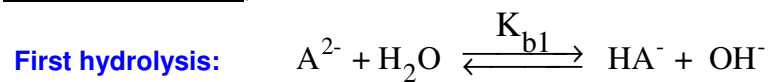
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Equilibria involved: Diprotic Acids and Bases

Diprotic Acid, H_2A



Dibasic species, A^{2-}



Q. How do we calculate K_{b1} and K_{b2} from K_a values?

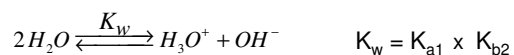
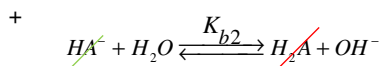
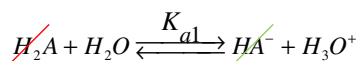
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Note that H_2A and HA^- species in the K_{a1} expression both appear in the K_{b2} expression. Similarly, the conjugates HA^- and A^{2-} in the K_{a2} expression both appear in the K_{b1} expression.

Thus, $K_{a1} \cdot K_{b2} = K_w$

$$K_{a2} \cdot K_{b1} = K_w$$

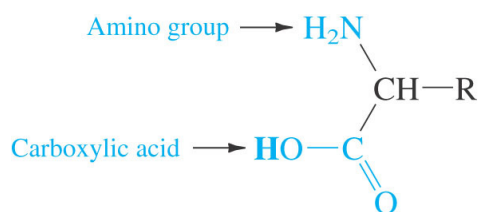
Proof:



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Polyprotic acids: Amino Acids



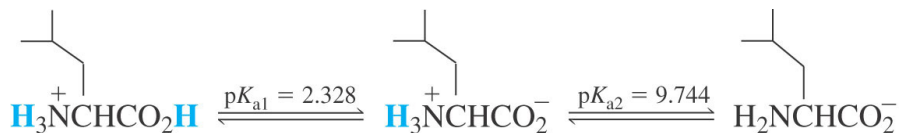
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NOTE: - **COOH** group is much **more acidic** (higher K_a ; first to dissociate) than the $-NH_3^+$ group.

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Diprotic Acids

Example: Leucine, H_2L



Fully protonated form =
fully acidic, H_2A^+

Fully dissociated
form = fully basic, A^-

Stepwise dissociation:

➤ Start with the fully acidic form, $H_2A^+ = H_2L^+$



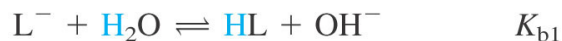
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Dibasic Species

Stepwise hydrolysis of leucine:

➤ Start with the fully basic form, $A^- = L^-$



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pH Calculations: Diprotic Acids and Bases

Problem: Find the pH and concentrations of H_2SO_3 , HSO_3^- and SO_3^{2-} in each of the following solutions:

- (a) 0.050 M H_2SO_3
- (b) 0.050 M NaHSO_3 , and
- (c) 0.050 M Na_2SO_3

Note that for **diprotic acids and bases**, there are **3 species** in solution (i.e. 3 unknowns: H_2A , HA^- and A^{2-}) so we need 3 independent equations to solve the problem.

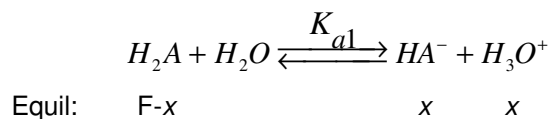
9

pH Calculation: Diprotic Acids and Bases

1. The fully acidic form, H_2A

Approximation: In a solution of H_2A (Ex. 0.050 M H_2SO_3), the 2nd dissociation is usually negligible that H_2A behaves as a **monoprotic acid**. Also, $[\text{A}^{2-}] \approx 0$ M.

Calculation of pH and [species]

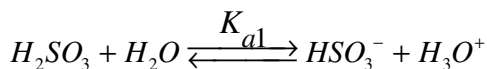


$$K_{a1} = \frac{x^2}{F - x}$$

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Fully acidic form (H_2A) – *Cont.*

Problem (a): Find the pH and $[H_2SO_3]$, $[HSO_3^-]$ and $[SO_3^{2-}]$ in a 0.050 M H_2SO_3 solution. $K_{a1} = 1.23 \times 10^{-2}$; $K_{a2} = 6.6 \times 10^{-8}$



Equil: $0.050-x$ x x

$$K_{a1} = 1.23 \times 10^{-2} = \frac{x^2}{(0.050-x)}$$

x cannot be ignored since K_{a1} isn't too small

$$x^2 + 1.23 \times 10^{-2}x - 6.15 \times 10^{-4}$$

Solve for x using quadratic equation

$$x = 1.94 \times 10^{-2} M = [H_3O^+] = [HSO_3^-]$$

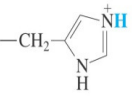
$pH = 1.71$ $[H_2SO_3] = 0.031 M$ $[HSO_3^-] = 1.9 \times 10^{-2} M$

↙ 0.050 M - x

$[SO_3^{2-}] \approx 0 M$


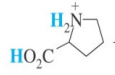
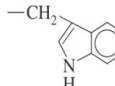

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TABLE 9-1 Acid dissociation constants of amino acids

Amino acid ^a	Substituent ^a	Carboxylic acid ^b pK_a	Ammonium ^b pK_a	Substituent ^b pK_a	Formula mass
Alanine (A)	$-CH_3$	2.344	9.868		89.09
Arginine (R)	$-CH_2CH_2CH_2NHC \begin{matrix} \diagup NH_2 \\ \diagdown NH_2 \end{matrix}$	1.823	8.991	(12.1 ^c)	174.20
Asparagine (N)	$-CH_2C \begin{matrix} O \\ \\ NH_2 \end{matrix}$	2.16 ^c	8.73 ^c		132.12
Aspartic acid (D)	$-CH_2CO_2H$	1.990	10.002	3.900	133.10
Cysteine (C)	$-CH_2SH$	(1.7)	10.74	8.36	121.16
Glutamic acid (E)	$-CH_2CH_2CO_2H$	2.16	9.96	4.30	147.13
Glutamine (Q)	$-CH_2CH_2C \begin{matrix} O \\ \\ NH_2 \end{matrix}$	2.19 ^c	9.00 ^c		146.15
Glycine (G)	$-H$	2.350	9.778		75.07
Histidine (H)	$-CH_2$ 	(1.6)	9.28	5.97	155.16

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TABLE 9-1 Acid dissociation constants of amino acids

Amino acid ^a	Substituent ^a	Carboxylic acid ^b p <i>K</i> _a	Ammonium ^b p <i>K</i> _a	Substituent ^b p <i>K</i> _a	Formula mass
Leucine (L)	—CH ₂ CH(CH ₃) ₂	2.328	9.744		131.17
Lysine (K)	—CH ₂ CH ₂ CH ₂ CH ₂ NH ₃ ⁺	(1.77)	9.07	10.82	146.19
Methionine (M)	—CH ₂ CH ₂ SCH ₃	2.18 ^c	9.08 ^c		149.21
Phenylalanine (F)	—CH ₂ — 	2.20	9.31		165.19
Proline (P)	 ← Structure of entire amino acid	1.952	10.640		115.13
Serine (S)	—CH ₂ OH	2.187	9.209		105.09
Threonine (T)	—CH(CH ₃)(OH)	2.088	9.100		119.12
Tryptophan (W)	—CH ₂ — 	2.37 ^c	9.33 ^c		204.23
Tyrosine (Y)	—CH ₂ — 	2.41 ^c	8.67 ^c	11.01 ^c	181.19
Valine (V)	—CH(CH ₃) ₂	2.286	9.719		117.15

a. The acidic protons are shown in **bold** type. Each amino acid is written in its fully protonated form. Standard abbreviations are shown in parentheses.
b. p*K*_a values refer to 25°C and zero ionic strength unless marked by c. Values considered to be uncertain are enclosed in parentheses. Appendix G gives p*K*_a for μ = 0.1 M.
c. For these entries, the ionic strength is 0.1 M, and the constant refers to a product of concentrations instead of activities.

SOURCE: A. E. Martell and R. J. Motekaitis, NIST Database 46 (Gaithersburg, MD: National Institute of Standards and Technology, 2001).

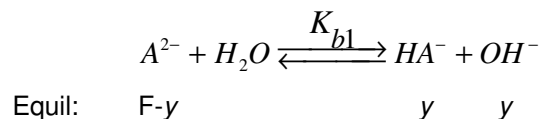
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pH Calculations: Diprotic systems – Cont.

2. The fully basic form, A²⁻

Approximation: In a solution of A²⁻ (Ex. 0.050 M Na₂SO₃), the 2nd hydrolysis is usually negligible that A²⁻ *behaves* as a *monobasic species*. Also, [H₂A] ≈ 0 M.

Calculation of pH and [species]



$$K_{b1} = \frac{y^2}{F - y} \quad \begin{array}{l} \text{pOH} = -\log(y) \\ \text{pH} = 14 - \text{pOH} \end{array}$$

Recall: $K_{b1} = K_w/K_{a2}$

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Problem: Find the pH and concentrations of H_2SO_3 , HSO_3^- and SO_3^{2-} in each of the following solutions:

$$K_{a1} = 1.23 \times 10^{-2};$$

$$K_{a2} = 6.6 \times 10^{-8}$$

(a) 0.050 M H_2SO_3 - DONE!

(b) 0.050 M NaHSO_3 , and

✓ (c) **0.050 M Na_2SO_3**

Answer: pH = 9.94; $[\text{H}_2\text{SO}_3] \approx 0 \text{ M}$; $[\text{SO}_3^{2-}] = 0.04991 \text{ M} \approx 0.050 \text{ M}$ and $[\text{HSO}_3^-] =$
 $[\text{OH}^-] = 8.7 \times 10^{-5} \text{ M}$ 15

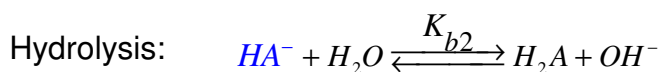
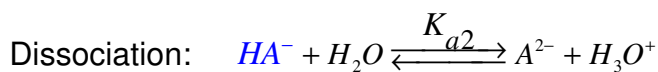
pH Calculations: Diprotic systems – Cont.

3. The intermediate (amphoteric) form, HA^-

➤ HA^- can act as an acid or a base

Q. What is the predominant species in a solution of HA^- ?

Compare K_{a2} and K_{b2} equilibria:



➤ HA^- will dissociate/hydrolyze to form A^{2-} and H_2A

Approximation: $[\text{HA}^-] \approx F_{\text{HA}^-} = F_{\text{NaHA}}$ or F_{KHA}

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The intermediate form, HA^- (Cont.)

Calculation of pH and [species]

$$[H^+] \approx \sqrt{\frac{K_1 K_2 F + K_1 K_w}{K_1 + F}}$$

Where

$$K_1 = K_{a1}$$

$$K_2 = K_{a2}$$

$$F = F_{HA^-}$$

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

Quick check: $pH = \frac{1}{2} (pK_1 + pK_2)$

- Solve for $[H_2A]$ and $[A^{2-}]$ using $[H^+]$ above and K_1 & K_2 equilibria

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The intermediate form, HA^- (Cont.)

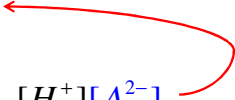
- Solving for $[H_2A]$ and $[A^{2-}]$:

$$K_1 = K_{a1} = \frac{[H^+][HA^-]}{[H_2A]}$$

Thus $[H_2A] = \frac{[H^+][HA^-]}{K_1}$

Likewise, $[A^{2-}] = \frac{K_2 [HA^-]}{[H^+]}$

From 2nd dissociation: $K_2 = K_{a2} = \frac{[H^+][A^{2-}]}{[HA^-]}$



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Problem: Find the pH and concentrations of H_2SO_3 , HSO_3^- and SO_3^{2-} in each of the following solutions:

(a) 0.050 M H_2SO_3 - DONE!

✓(b) 0.050 M NaHSO_3 , and

(c) 0.050 M Na_2SO_3 - DONE!

$$K_{a1} = 1.23 \times 10^{-2};$$

$$K_{a2} = 6.6 \times 10^{-8}$$

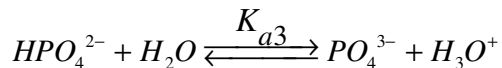
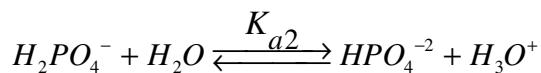
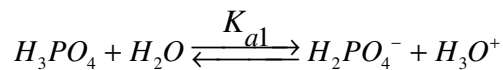
Answer: pH = 4.59; $[\text{HSO}_3^-] \approx 0.050 \text{ M}$, $[\text{H}_2\text{SO}_3] = 1.1 \times 10^{-4} \text{ M}$; $[\text{SO}_3^{2-}] = 1.3 \times 10^{-4} \text{ M}$

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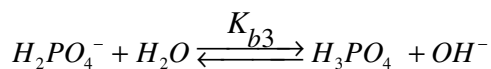
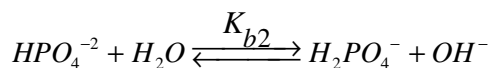
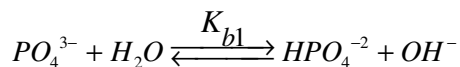
Tripotric Acids and Bases

Example: H_3PO_4 ; PO_4^{3-}

Successive dissociation:



Successive hydrolysis:



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Use handout on **pH calculations** involving **triprotic systems**

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Treatment of triprotic systems

1. H_3A is treated as monoprotic weak acid. $K_{a1} = K_1$.
2. H_2A^- is treated as the intermediate form of a diprotic acid.

$$[H^+] \approx \sqrt{\frac{K_1 K_2 F + K_1 K_w}{K_1 + F}}$$

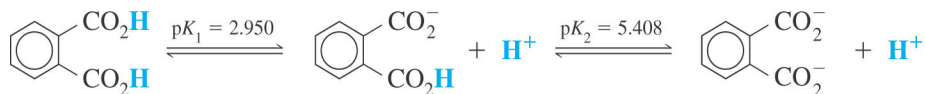
3. HA^{2-} is also treated as the intermediate form of a diprotic acid. However, HA^{2-} is "surrounded" by H_2A^- and A^{3-} , so the equil. constants to use are K_{a2} ($= K_2$) and K_{a3} ($= K_3$)

$$[H^+] \approx \sqrt{\frac{K_2 K_3 F + K_2 K_w}{K_2 + F}}$$

4. A^{3-} is treated as monobasic. $K_{b1} = K_w/K_{a3}$

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What is the **major species** at a given pH?



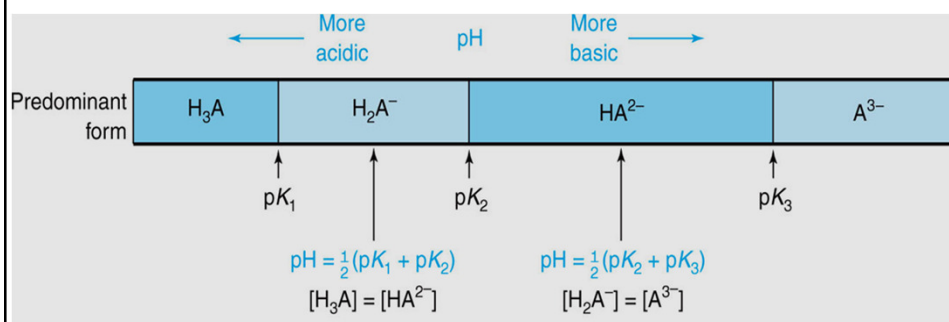
1. When $\text{pH} < \text{p}K_1$, H_2A predominates
2. When $\text{pH} = \text{p}K_1$, $[\text{H}_2\text{A}] = [\text{HA}^-]$
3. When $\text{p}K_1 > \text{pH} < \text{p}K_2$, $[\text{HA}^-]$ predominates
4. When $\text{pH} = \text{p}K_2$, $[\text{HA}^-] = [\text{A}^{2-}]$
5. When $\text{pH} > \text{p}K_2$, $[\text{A}^{2-}]$ predominates

Q. Which of the species above predominate at pH 6.50?
pH 4.00? pH 2.00?

Answer: A^{2-} , HA^- , H_2A

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FIGURE 9-2 The predominant molecular form of a triprotic system (H_3A) in the various pH intervals.



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