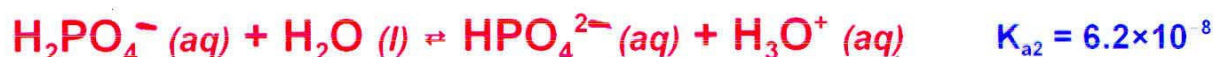
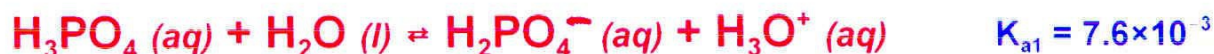


Topic 6E - Polyprotic Acids and Bases

Polyprotic Acids and Bases

Capable of donating (acids) or accepting (bases) more than one proton, in succession:



where, typically,

$$\frac{K_{\text{a}2}}{K_{\text{a}1}} \approx \frac{K_{\text{a}3}}{K_{\text{a}2}} \approx 10^{-5}$$

All polyprotic acids are weak, except for H_2SO_4 (first H^+ donation only):

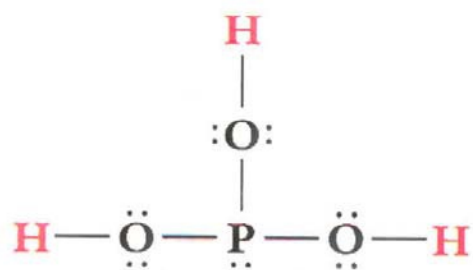


Table 12.3: Stepwise Equilibrium Constants for Selected Polyprotic Acids

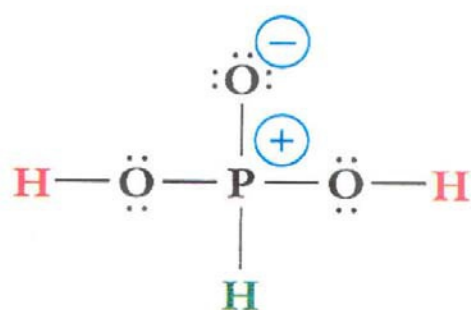
TABLE 12.3

Stepwise equilibrium constants for selected polyprotic acids

Acid name	Formula	pK_{a1}	pK_{a2}	pK_{a3}
Hydrosulfuric	H_2S	7.04	13.89	
Hydroselenic	H_2Se	3.89	11.	
Sulfurous	H_2SO_3	1.81	6.99	
Sulfuric	H_2SO_4	−2.	1.92	
Selenous	H_2SeO_3	2.46	7.31	
Selenic	H_2SeO_4	−2.	1.92	
Phosphorous	H_3PO_3	2.00	6.59	
Phosphoric	H_3PO_4	2.12	7.21	12.67
Arsenic	H_3AsO_4	2.25	6.77	11.60
Carbonic	H_2CO_3	6.37	10.32	
Silicic	H_4SiO_4	9.66	11.7	12.
Chromic	H_2CrO_4	0.74	6.49	
Oxalic	$HOOC-COOH$	1.23	4.19	
Malonic	$HOOCCH_2COOH$	2.83	5.69	
Succinic	$HOOC(CH_2)_2COOH$	4.16	5.61	
Glutaric	$HOOC(CH_2)_3COOH$	4.31	5.41	
Adipic	$HOOC(CH_2)_4COOH$	4.43	5.41	
Phthalic	$C_6H_4(COOH)_2$	2.89	5.51	
Citric	$C_3H_4(OH)(COOH)_3$	3.14	4.77	6.39
Ascorbic (vitamin C)	$C_6H_6O_4(OH)_2$	4.10	11.79	



(a)



(b)

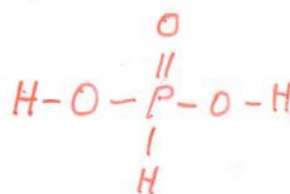
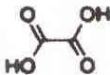
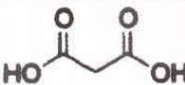
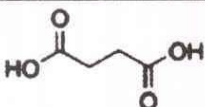

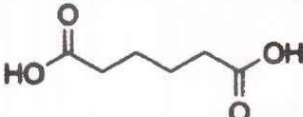

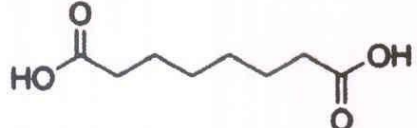
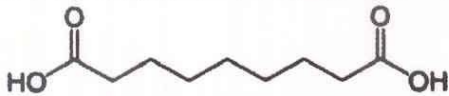
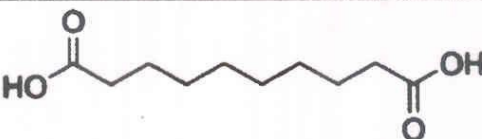


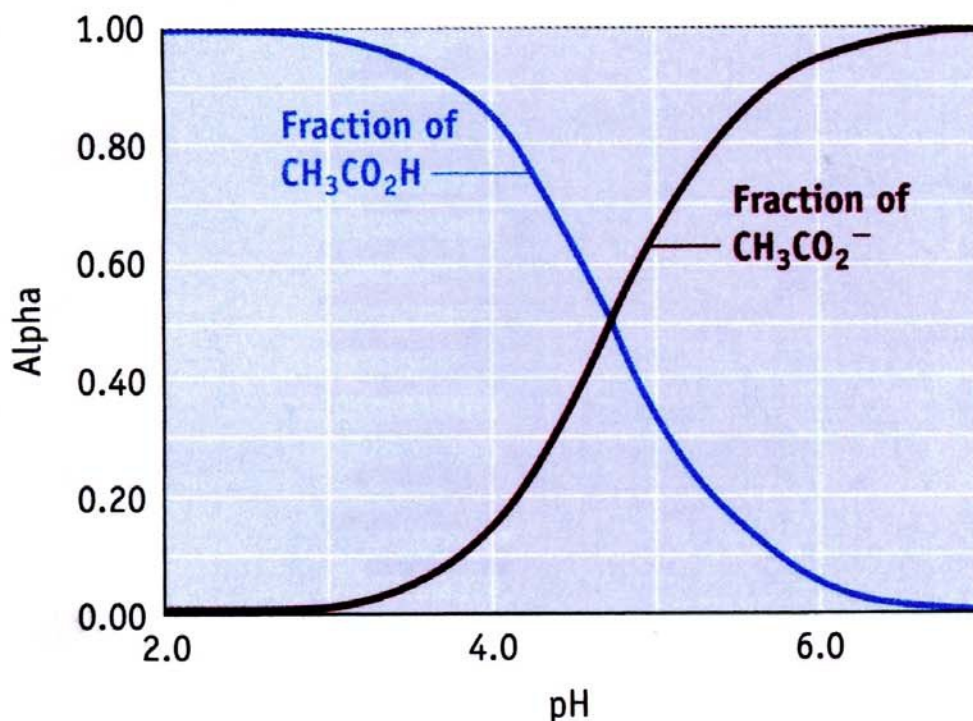
FIGURE 10.7 (a) The simplest Lewis diagram that can be drawn for H_3PO_3 gives an incorrect structure. This acid would be triprotic, like H_3PO_4 . (b) The observed structure of H_3PO_3 requires assigning formal charge to the P atom and the lone O atom. The hydrogen atom attached to the P is not released into acid solution, so the acid is diprotic.

Elementary saturated dicarboxylic acids^[1]

Common name	IUPAC name	Chemical formula	Structural formula	pK _a 1	pK _a 2
Oxalic acid	ethanedioic acid	HOOC-COOH		1.27	4.27
Malonic acid	propanedioic acid	HOOC-(CH ₂)-COOH		2.85	5.70
Succinic acid	butanedioic acid	HOOC-(CH ₂) ₂ -COOH		4.21	5.41
Glutaric acid	pentanedioic acid	HOOC-(CH ₂) ₃ -COOH		4.34	5.41
Adipic acid	hexanedioic acid	HOOC-(CH ₂) ₄ -COOH		4.41	5.41
Pimelic acid	heptanedioic acid	HOOC-(CH ₂) ₅ -COOH		4.50	5.43
Suberic acid	octanedioic acid	HOOC-(CH ₂) ₆ -COOH		4.62	5.41
Azelaic acid	nonanedioic acid	HOOC-(CH ₂) ₇ -COOH		4.54	5.41
Sebacic acid	decanedioic acid	HOOC-(CH ₂) ₈ -COOH			
	undecanedioic acid	HOOC-(CH ₂) ₉ -COOH			
	dodecanedioic acid	HOOC-(CH ₂) ₁₀ -COOH			

Alpha Plots

So-called “alpha plots” depict how the fractions (α) of the species in solutions of weak acids and bases vary with the pH. The α -plot below, for example, is for a 0.1 M solution of acetic acid:



With increasing pH (brought about, for example, by gradual addition of a strong base), the fraction of the protonated species (acetic acid) decreases, and the fraction of the deprotonated species (acetate ion) increases.

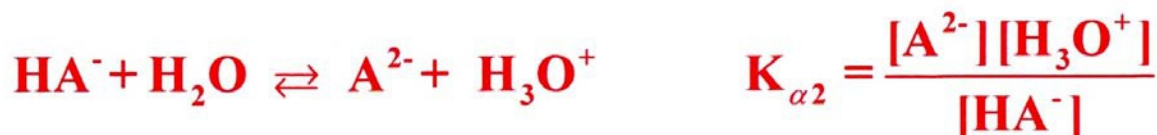
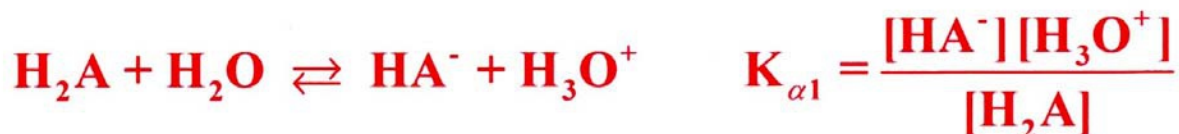
The pH at the point where the two curves cross (for which $[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-]$) equals the pK_a (4.75) of acetic acid, since:



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = [\text{H}_3\text{O}^+]$$

$$\text{pK}_a = -\log[\text{H}_3\text{O}^+] = \text{pH}$$

For a diprotic acid (H_2A), *e.g.*, H_2CO_3 , it can be shown by using mass balance considerations and the two acid equilibrium expressions:



that the variations with pH of the fractions (α) of the three species in solution (H_2A , HA^- , and A^{2-}) are given by:

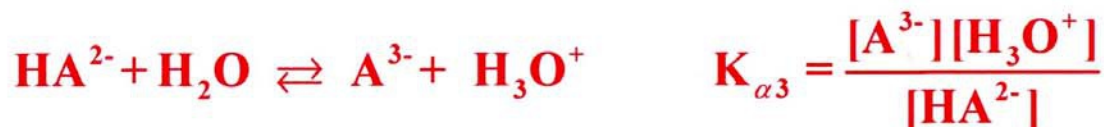
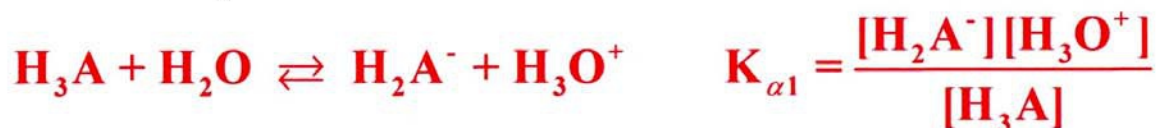
$$\alpha_{H_2A} = \frac{[H_3O^+]^2}{[H_3O^+]^2 + [H_3O^+]K_{\alpha 1} + K_{\alpha 1}K_{\alpha 2}}$$

$$\alpha_{HA^-} = \frac{[H_3O^+]K_{\alpha 1}}{[H_3O^+]^2 + [H_3O^+]K_{\alpha 1} + K_{\alpha 1}K_{\alpha 2}}$$

$$\alpha_{A^{2-}} = \frac{K_{\alpha 1}K_{\alpha 2}}{[H_3O^+]^2 + [H_3O^+]K_{\alpha 1} + K_{\alpha 1}K_{\alpha 2}}$$

For a typical diprotic acid, the term $K_{\alpha 1}K_{\alpha 2}$ is negligibly small compared to the other two terms in the denominators of these expressions.

For a triprotic acid (H_3A), *e.g.*, H_3PO_4 , it can similarly be shown by using mass balance considerations and the three acid equilibrium expressions:



that the variations with pH of the fractions (α) of the four species in solution (H_3A , H_2A^- , HA^{2-} , and A^{3-}) are given by:

$$\alpha_{H_3A} = \frac{[H_3O^+]^3}{[H_3O^+]^3 + K_{\alpha 1}[H_3O^+]^2 + K_{\alpha 1}K_{\alpha 2}[H_3O^+] + K_{\alpha 1}K_{\alpha 2}K_{\alpha 3}}$$

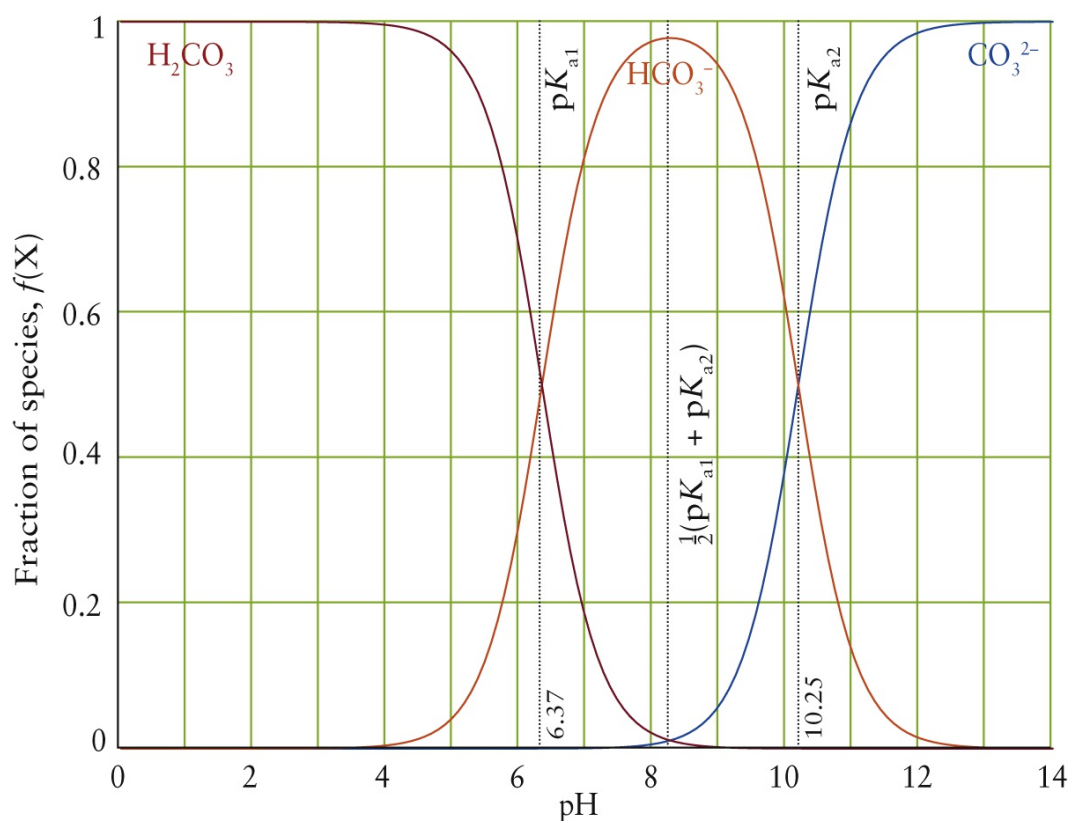
$$\alpha_{H_2A^-} = \frac{K_{\alpha 1}[H_3O^+]^2}{[H_3O^+]^3 + K_{\alpha 1}[H_3O^+]^2 + K_{\alpha 1}K_{\alpha 2}[H_3O^+] + K_{\alpha 1}K_{\alpha 2}K_{\alpha 3}}$$

$$\alpha_{HA^{2-}} = \frac{K_{\alpha 1}K_{\alpha 2}[H_3O^+]}{[H_3O^+]^3 + K_{\alpha 1}[H_3O^+]^2 + K_{\alpha 1}K_{\alpha 2}[H_3O^+] + K_{\alpha 1}K_{\alpha 2}K_{\alpha 3}}$$

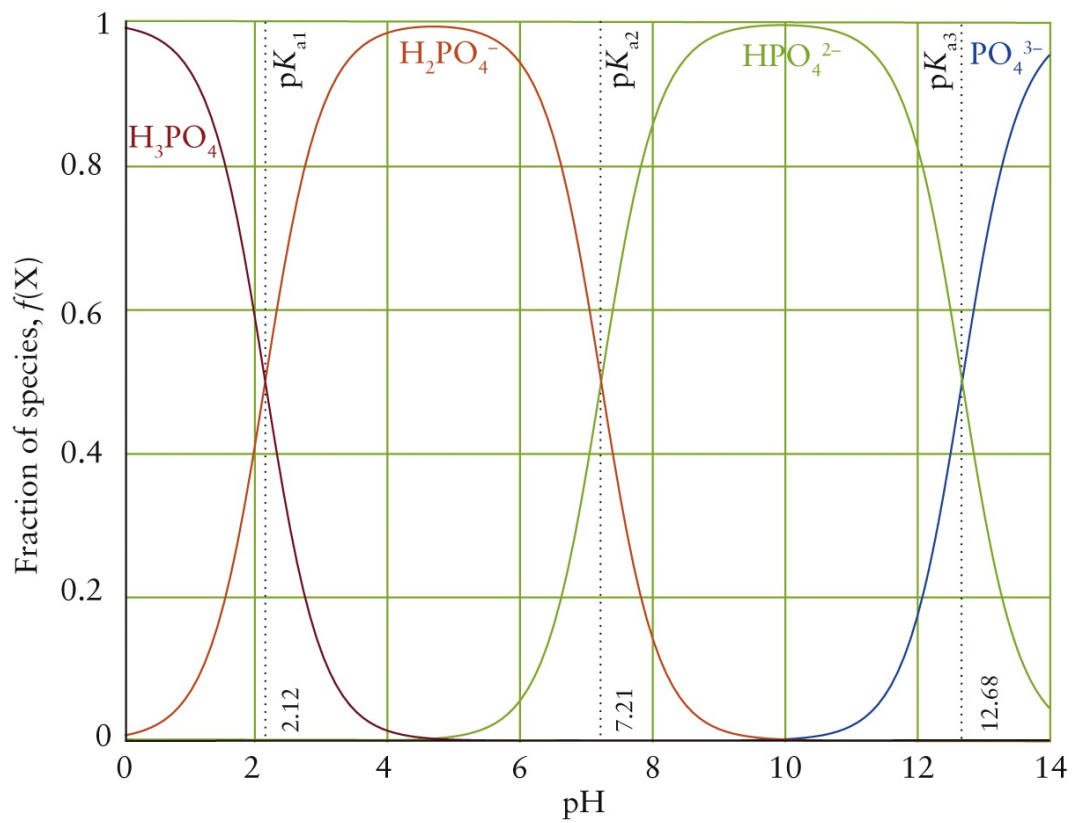
$$\alpha_{A^{3-}} = \frac{K_{\alpha 1}K_{\alpha 2}K_{\alpha 3}}{[H_3O^+]^3 + K_{\alpha 1}[H_3O^+]^2 + K_{\alpha 1}K_{\alpha 2}[H_3O^+] + K_{\alpha 1}K_{\alpha 2}K_{\alpha 3}}$$

For a typical triprotic acid, the term $K_{\alpha 1}K_{\alpha 2}K_{\alpha 3}$ is negligibly small compared to the other three terms in the denominators of these expressions. The relative contributions of these other three terms are strongly dependent on the pH of the solution.

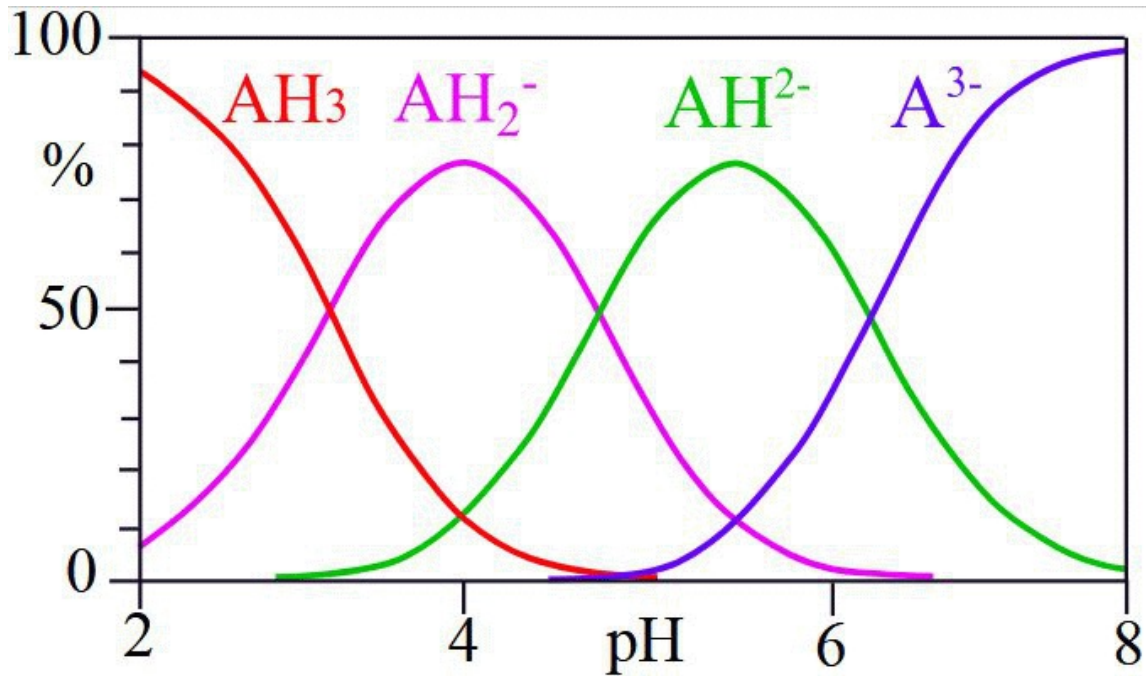
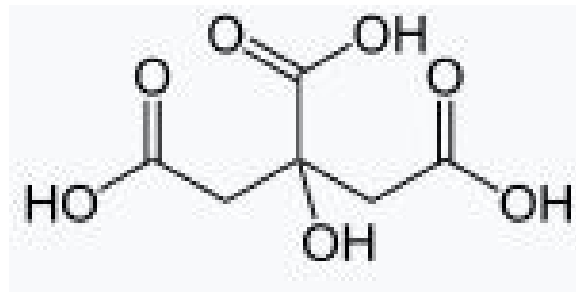
Carbonic Acid: (H_2CO_3)



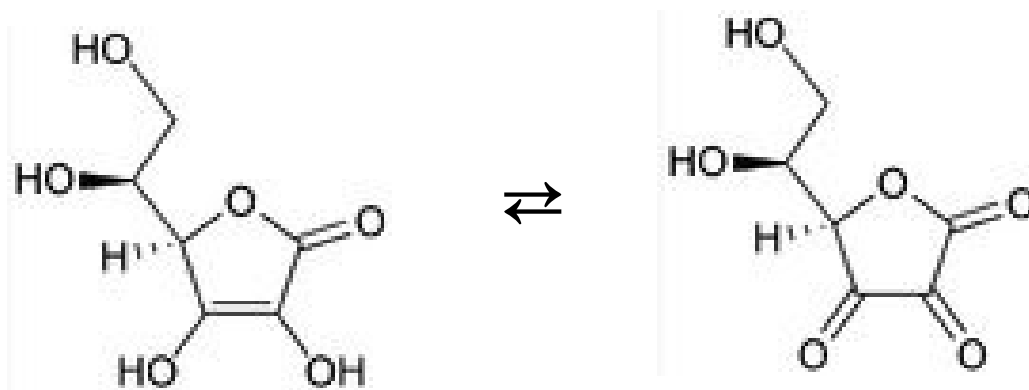
Phosphoric Acid: (H_3PO_4)



Citric Acid:



Ascorbic Acid: (Vitamin C)



Reduced Form

Oxidized Form