

Topic 6D. The pH of Aqueous Solutions

- 6D.1 Solutions of Weak Acids
- 6D.2 Solutions of Weak Bases
- 6D.3 The pH of Salt Solutions

Solutions of Weak Acids



- $K_a = [\text{H}_3\text{O}^+][\text{A}^-] / [\text{HA}]$
- Percentage deprotonated = $\frac{[\text{H}_3\text{O}^+]}{[\text{HA}]_{\text{initial}}} \times 100\%$
- Calculation method

	HA	H_3O^+	A^-
Initial	$[\text{HA}]_{\text{initial}}$	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$[\text{HA}]_{\text{initial}} - x$	$+x$	$+x$

Solutions of Weak Bases

- Weak base: $B(aq) + H_2O(l) \leftrightarrow HB^+(aq) + OH^-(aq)$
 - $K_b = [HB^+][OH^-] / [B]$
 - Percentage protonated = $\frac{[HB^+]}{[B]_{initial}} \times 100\%$
 - Calculation method

	B	HB ⁺	OH ⁻
Initial	[B] _{initial}	0	0
Change	- x	+ x	+ x
Equilibrium	[B] _{initial} - x	+ x	+ x

pH of Salt Solution

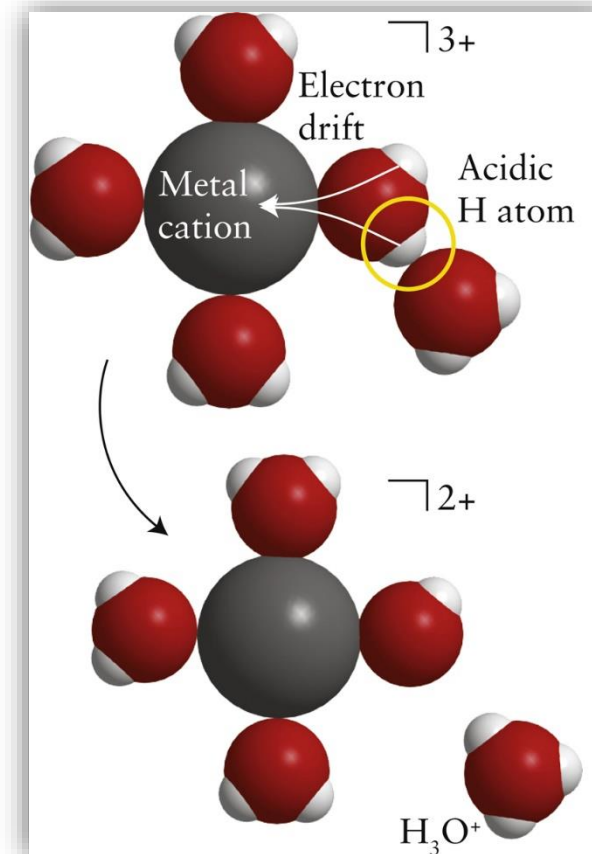
- A salt is produced by the neutralization of a base by an acid.
However, if the pH of a solution of a salt is not in general found to have the “neutral” value.
- The pH of a solution of a salt depends on the relative acidity and basicity of its ions.

pH of Salt Solution

■ Cations and their acidities in water

TABLE 6D.1 Acidic Character and K_a Values of Common Cations in Water*

Character	Examples	K_a	pK_a
Acidic			
conjugate acids of weak bases	anilinium ion, $C_6H_5NH_3^+$ pyridinium ion, $C_5H_5NH^+$ ammonium ion, NH_4^+ methylammonium ion, $CH_3NH_3^+$	2.3×10^{-5} 5.6×10^{-6} 5.6×10^{-10} 2.8×10^{-11}	4.64 5.24 9.25 10.56
small, highly charged metal cations	Fe^{3+} as $Fe(H_2O)_6^{3+}$ Cr^{3+} as $Cr(H_2O)_6^{3+}$ Al^{3+} as $Al(H_2O)_6^{3+}$ Cu^{2+} as $Cu(H_2O)_6^{2+}$ Ni^{2+} as $Ni(H_2O)_6^{2+}$ Fe^{2+} as $Fe(H_2O)_6^{2+}$	3.5×10^{-3} 1.3×10^{-4} 1.4×10^{-5} 3.2×10^{-8} 9.3×10^{-10} 8×10^{-11}	2.46 3.89 4.85 7.49 9.03 10.1
Neutral			
Group 1 and 2 cations metal cations with charge +1	Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ag^+		
Basic	none		



pH of Salt Solution

- Anions and their acidic/basic character

TABLE 6D.2 Acidic and Basic Character of Common Anions in Water

Character	Examples
Acidic very few	HSO_4^- , H_2PO_4^-
Neutral conjugate bases of strong acids	Cl^- , Br^- , I^- , NO_3^- , ClO_4^-
Basic conjugate bases of weak acids	F^- , O^{2-} , OH^- , S^{2-} , HS^- , CN^- , CO_3^{2-} , PO_4^{3-} , NO_2^- , CH_3CO_2^- , other carboxylate ions

Topic 6E. Polyprotic Acids and Bases

- 6E.1 The pH of a Polyprotic Acid Solution
- 6E.2 Solutions of Salts of Polyprotic Acids
- 6E.3 The Concentrations of Solute Species
- 6E.4 Composition and pH

The pH of a Polyprotic Acid Solution

- **Polyprotic acid:** a compound that can donate more than one proton.
 H_2SO_4 , H_2CO_3 , H_3PO_4 , etc
- Polyprotic base: a species that can accept more than one proton.
- Polyprotic acids donate protons successively, with the acidity constant decreasing significantly, usually by a factor of about 10^3 or more : $K_{a1} \gg K_{a2} \gg K_{a3}$
→ It is harder to separate a positively charged proton from a negatively charged ion.



The pH of a Polyprotic Acid Solution

TABLE 6E.1 Acidity Constants of Polyprotic Acids at 25 °C

Acid	K_{a1}	pK_{a1}	K_{a2}	pK_{a2}	K_{a3}	pK_{a3}
sulfuric acid, H_2SO_4	strong		1.2×10^{-2}	1.92		
oxalic acid, $(COOH)_2$	5.9×10^{-2}	1.23	6.5×10^{-5}	4.19		
sulfurous acid, H_2SO_3	1.5×10^{-2}	1.81	1.2×10^{-7}	6.91		
phosphorous acid, H_3PO_3	1.0×10^{-2}	2.00	2.6×10^{-7}	6.59		
phosphoric acid, H_3PO_4	7.6×10^{-3}	2.12	6.2×10^{-8}	7.21	2.1×10^{-13}	12.68
tartaric acid, $C_2H_4O_2(COOH)_2$	6.0×10^{-4}	3.22	1.5×10^{-5}	4.82		
carbonic acid, H_2CO_3	4.3×10^{-7}	6.37	5.6×10^{-11}	10.25		
hydrosulfuric acid, H_2S	1.3×10^{-7}	6.89	7.1×10^{-15}	14.15		

- Estimating the pH of a polyprotic acid: consideration of only first deprotonation is enough (exception: H_2SO_4)

Solution of Salts of Polyprotic Acids

- The conjugate base of a polyprotic acid is amphiprotic.

- Case of HS^- (deprotonated form of H_2S)



- For salts of polyprotic acids, HA^-

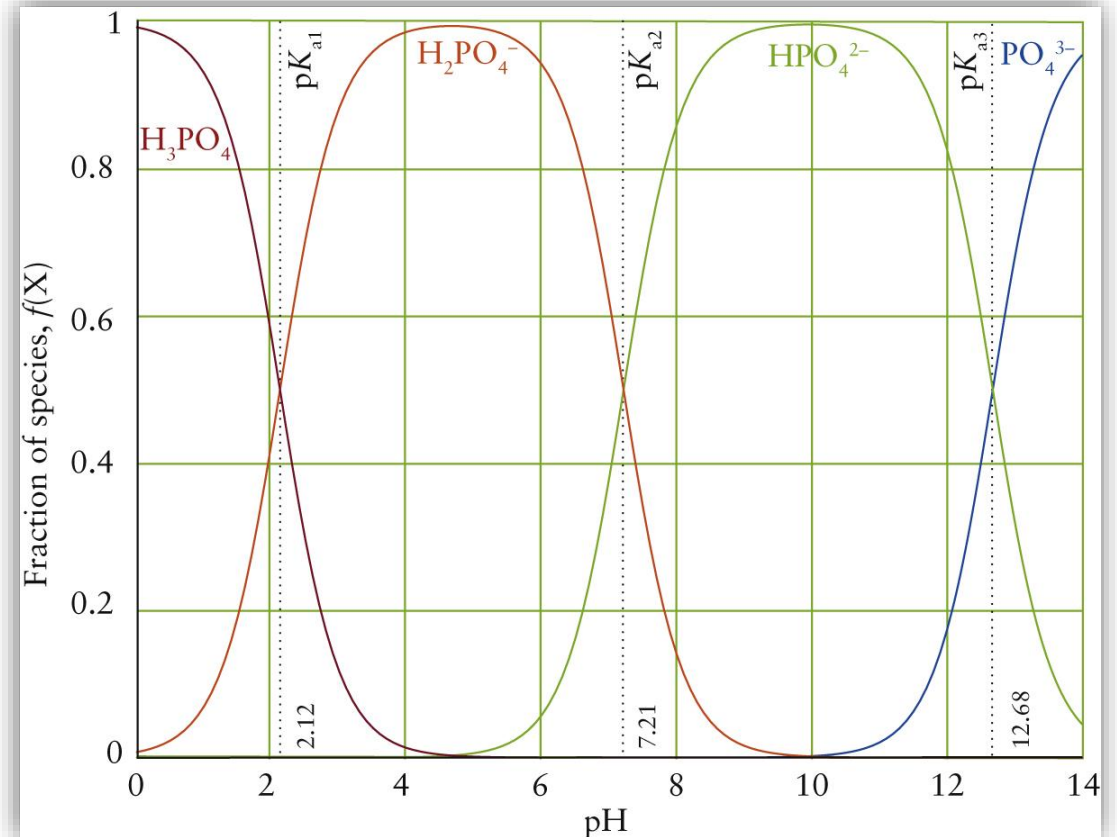
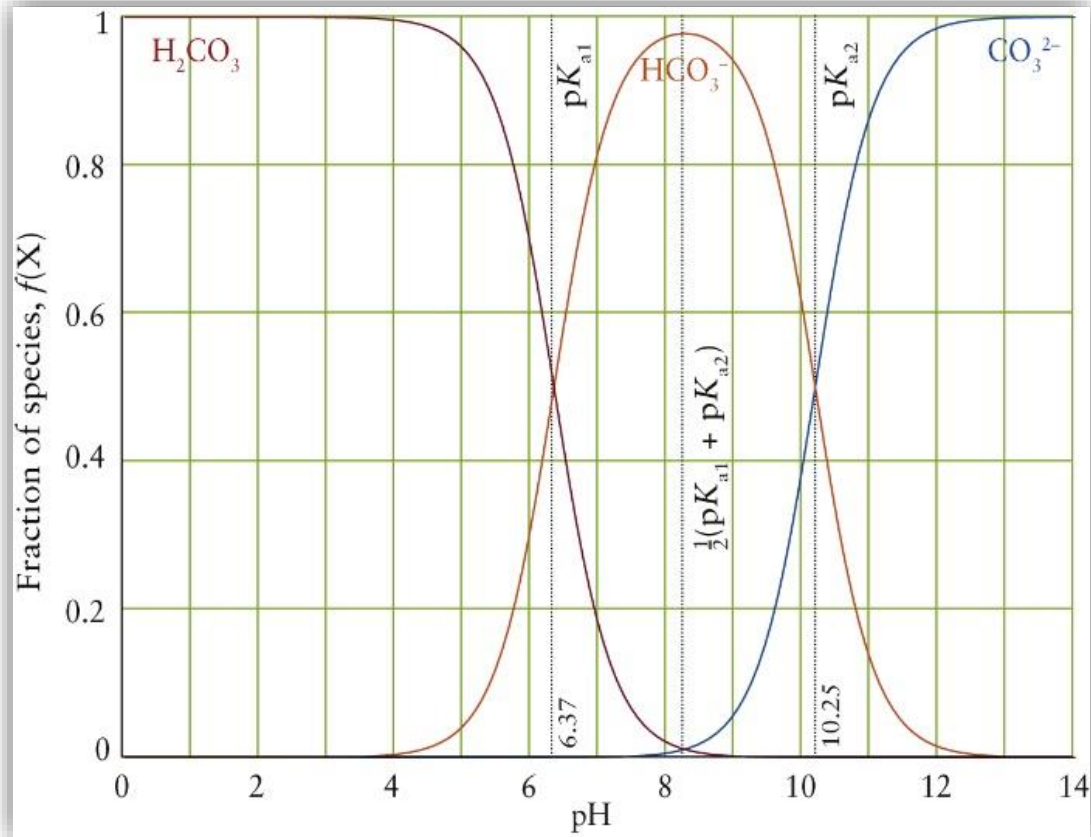
$$\text{pH} = \frac{1}{2} (\text{p}K_{\text{a}1} + \text{p}K_{\text{a}2})$$

Valid if $S \gg K_{\text{w}}/K_{\text{a}2}$ and $S \gg K_{\text{a}1}$, where S is the initial concentration of the salt

Concentrations of Solute Species

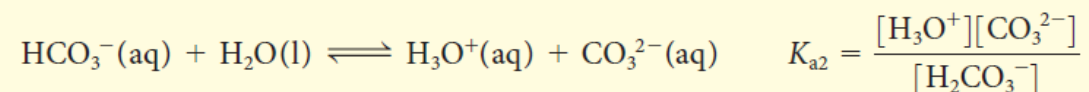
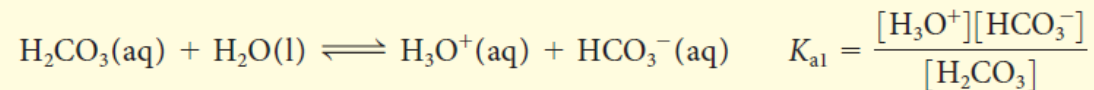
- The concentrations of all species in a solution of a polyprotic acid can be calculated by assuming that species present in smaller amounts do not affect the concentrations of species present in larger amounts.
- H_3PO_4 : H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-}
- Example 6E.2) Calculate the concentrations of all solute species in 0.10 m H_3PO_4 (aq).

Composition and pH



Composition and pH

To see how the concentrations of species present in a solution vary with pH, take the carbonic acid system as an example. Consider the following proton transfer equilibria:



Express the composition of the solution in terms of the fraction, $f(X)$, of each species X present, where X could be H_2CO_3 , HCO_3^- , or CO_3^{2-} , and

$$f(X) = \frac{[X]}{[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]}$$

It will turn out to be helpful to express $f(X)$ in terms of the ratio of each species to the intermediate species, HCO_3^- . So divide the numerator and denominator by $[\text{HCO}_3^-]$ and get

$$f(X) = \frac{[X]/[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]/[\text{HCO}_3^-] + 1 + [\text{CO}_3^{2-}]/[\text{HCO}_3^-]}$$

All three concentration ratios can be written in terms of the hydronium ion concentration. To do so, simply rearrange the expressions for the first and second acidity constants:

$$\frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]} = \frac{[\text{H}_3\text{O}^+]}{K_{a1}} \quad \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{K_{a2}}{[\text{H}_3\text{O}^+]}$$

then substitute them into the expression for $f(X)$ and rearrange it to obtain

$$\begin{aligned} f(\text{H}_2\text{CO}_3) &= \frac{[\text{H}_3\text{O}^+]^2}{[\text{H}_3\text{O}^+]^2 + [\text{H}_3\text{O}^+]K_{a1} + K_{a1}K_{a2}} \\ f(\text{HCO}_3^-) &= \frac{[\text{H}_3\text{O}^+]K_{a1}}{[\text{H}_3\text{O}^+]^2 + [\text{H}_3\text{O}^+]K_{a1} + K_{a1}K_{a2}} \\ f(\text{CO}_3^{2-}) &= \frac{K_{a1}K_{a2}}{[\text{H}_3\text{O}^+]^2 + [\text{H}_3\text{O}^+]K_{a1} + K_{a1}K_{a2}} \end{aligned}$$

Topic 6F. Autoprotolysis and pH

6F.1 Very Dilute Solutions of Strong Acids and Bases

6F.2 Very Dilute Solutions of Weak Acids

Very Dilute Solutions of Strong Acids and Bases

- Think about pH of 1.0×10^{-8} M HCl: pH = 8 ?
- When the concentration of strong acid or base $< 10^{-6}$ M, the contribution of **autoprotolysis** to pH must be taken into account.
- Consider a dilute solution of HCl
 - Charge balance: $[\text{OH}^-] = [\text{H}_3\text{O}^+] - [\text{Cl}^-]$
 - Materials balance: $[\text{Cl}^-] = [\text{HCl}]_{\text{initial}}$; $[\text{OH}^-] = [\text{H}_3\text{O}^+] - [\text{HCl}]_{\text{initial}}$
 - $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}_3\text{O}^+] ([\text{H}_3\text{O}^+] - [\text{HCl}]_{\text{initial}})$
- Consider a dilute solution of NaOH
 - Charge balance: $[\text{OH}^-] = [\text{H}_3\text{O}^+] + [\text{Na}^+]$
 - Materials balance: $[\text{Na}^+] = [\text{NaOH}]_{\text{initial}}$; $[\text{OH}^-] = [\text{H}_3\text{O}^+] + [\text{NaOH}]_{\text{initial}}$
 - $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}_3\text{O}^+] ([\text{H}_3\text{O}^+] + [\text{NaOH}]_{\text{initial}})$

Very Dilute Solutions of Weak Acids

The calculation of pH for very dilute solutions of a weak acid HA is similar to that for strong acids. It is based on the fact that, apart from water, there are four species in solution—namely, HA, A^- , H_3O^+ , and OH^- . Because there are four unknowns, four equations are needed to find their concentrations. Two of the relations are the autoprotolysis constant of water and the acidity constant of the acid HA:

$$K_w = [H_3O^+][OH^-] \quad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Charge balance implies that

$$[H_3O^+] = [OH^-] + [A^-]$$

Material balance provides the fourth equation: the total concentration of “A” groups (the acid itself and any conjugate base it forms; for instance, F^- ions if the acid added is HF) must be equal to the initial concentration of the acid:

$$[HA]_{\text{initial}} = [HA] + [A^-]$$

To find an expression for the concentration of hydronium ions in terms of the initial concentration of the acid, rearrange the charge-balance relation to express the concentration of A^- in terms of $[H_3O^+]$:

$$[A^-] = [H_3O^+] - [OH^-]$$

Then express $[OH^-]$ in terms of the hydronium ion concentration by using the autoprotolysis expression:

$$[A^-] = [H_3O^+] - \frac{K_w}{[H_3O^+]}$$

Very Dilute Solutions of Weak Acids

When this expression for $[A^-]$ is substituted into the material-balance equation in the form $[HA] = [HA]_{\text{initial}} - [A^-]$, that equation becomes

$$[HA] = [HA]_{\text{initial}} - \overbrace{\left([H_3O^+] - \frac{K_w}{[H_3O^+]} \right)}^{[A^-]}$$

Now substitute these expressions for $[HA]$ and $[A^-]$ into K_a to obtain

$$K_a = \frac{[H_3O^+] \left([H_3O^+] - \frac{K_w}{[H_3O^+]} \right)}{[HA]_{\text{initial}} - [H_3O^+] + \frac{K_w}{[H_3O^+]}}$$