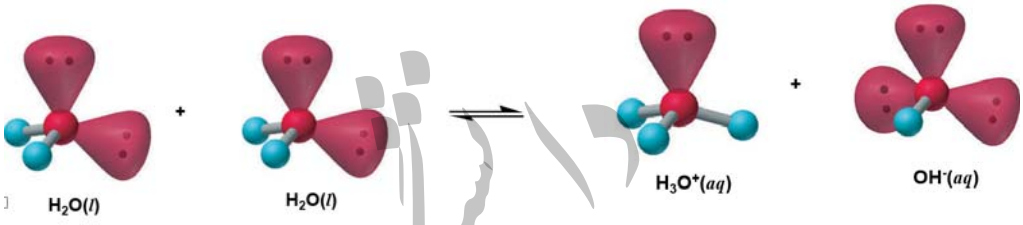
یونش خود به خودی آب و مقیاس pH:



$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

$$K_c = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

The Ion-Product Constant for Water

$$K_c[H_2O]^2 = K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25^oC$$

A change in $[H_3O^+]$ causes an inverse change in $[OH^-]$.

In an acidic solution, $[H_3O^+] > [OH^-]$

In a basic solution, $[H_3O^+] < [OH^-]$

In a neutral solution, $[H_3O^+] = [OH^-]$

$[H_3O^+] > [OH^-]$ → **ACIDIC SOLUTION**

$[H_3O^+] = [OH^-]$ → **NEUTRAL SOLUTION**

$[H_3O^+] < [OH^-]$ → **BASIC SOLUTION**

محاسبه غلظت یونهای هیدرونیوم و هیدروکسید در محلول آبی

Sample Problem 18.2 **Calculating $[H_3O^+]$ and $[OH^-]$ in an Aqueous Solution**

PROBLEM: A research chemist adds a measured amount of HCl gas to pure water at 25°C and obtains a solution with $[H_3O^+] = 3.0\times10^{-4}$ *M*. Calculate $[OH^-]$. Is the solution neutral, acidic, or basic?

PLAN: Use the K_w at 25°C and the $[H_3O^+]$ to find the corresponding $[OH^-]$.

SOLUTION: $K_w = 1.0\times10^{-14} = [H_3O^+]\,[OH^-]$ so

$[OH^-] = K_w / [H_3O^+] = 1.0\times10^{-14}/3.0\times10^{-4} =$ 3.3×10^{-11} *M*

$[H_3O^+]$ is > $[OH^-]$ and the solution is acidic.

تعریف pH و مقیاس آن

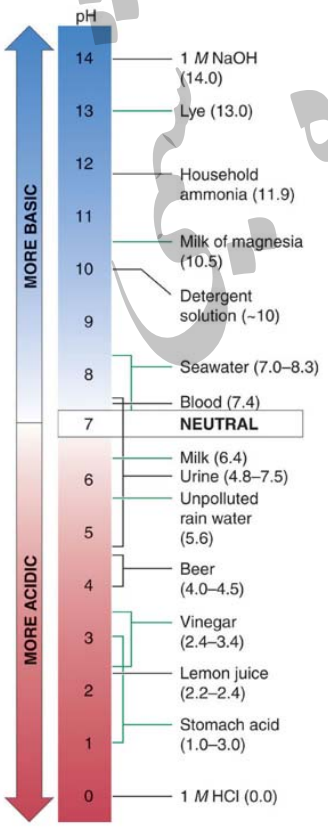


Figure 18.5

The pH values of some familiar aqueous solutions.

$$pH = -\log [H_3O^+]$$

محاسبه غلظت یونهای هیدرونیوم و هیدروکسید و تابع p آنها در محلول اسید قوی

به عنوان مثال برای محلولهای اسیدی که برای کنده کاری روی صفحات مسی در آثار هنری به کار می رود:

Sample Problem 18.3 **Calculating $[H_3O^+]$, pH, $[OH^-]$, and pOH**

PROBLEM: In an art restoration project, a conservator prepares copper-plate etching solutions by diluting concentrated HNO_3 to 2.0 *M*, 0.30 *M*, and 0.0063 *M* HNO_3. Calculate $[H_3O^+]$, pH, $[OH^-]$, and pOH of the three solutions at 25°C.

PLAN: HNO_3 is a strong acid so $[H_3O^+] = [HNO_3]$. Use K_w to find the $[OH^-]$ and then convert to pH and pOH.

SOLUTION: For 2.0 *M* HNO_3, $[H_3O^+]$ = 2.0 *M* and -log $[H_3O^+]$ = -0.30 = pH

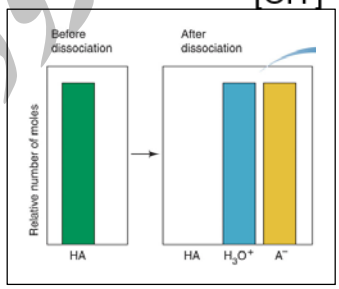
$[OH^-] = K_w / [H_3O^+] = 1.0\times10^{-14}/2.0 = 5.0\times10^{-15}$ *M*; pOH = 14.30

For 0.3 *M* HNO_3, $[H_3O^+]$ = 0.30 *M* and -log $[H_3O^+]$ = 0.52 = pH

$[OH^-] = K_w / [H_3O^+] = 1.0\times10^{-14}/0.30 = 3.3\times10^{-14}$ *M*; pOH = 13.48

For 0.0063 *M* HNO_3, $[H_3O^+]$ = 0.0063 *M* and -log $[H_3O^+]$ = 2.20 = pH

$[OH^-] = K_w / [H_3O^+] = 1.0\times10^{-14}/6.3\times10^{-3} = 1.6\times10^{-12}$ *M*; pOH = 11.80



محاسبه pH محلول باز قوی

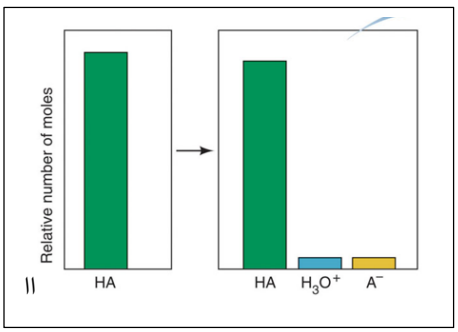
تمرین:

محاسبه pH محلولی از سود با غلظت 0/02 مولار

$$NaOH \longrightarrow Na^+ + OH^-$$

اسیدهای ضعیف

- اسید ضعیف مانند استیک اسید
- اسید مزدوج بازهای ضعیف مانند یون آمونیوم



Weak acid: $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$

$$\text{Percent HA dissociation} = \frac{[HA]_{dissociated}}{[HA]_{initial}} \times 100$$

% dissociated = 4/(5 + 4) x 100 = 44%

دو رویکرد در مسائل مربوط به تعادل اسید ضعیف:

- یافتن K_a از pH محلول

نمونه مسئله 18-7: یافتن K_a محلول 0/12 مولار فنیل استیک اسید با pH =2.62.

Sample Problem 18.7 **Finding the K_a of a Weak Acid from the Solution pH**

PROBLEM: Phenylacetic acid ($C_6H_5CH_2COOH$, simplified here as HPAc) builds up in the blood of persons with phenylketonuria, an inherited disorder that, if untreated, causes mental retardation and death. A study of the acid shows that the pH of 0.12 *M* HPAc is 2.62. What is the K_a of phenylacetic acid?

Concentration (*M*)	$HPAc(aq)$ +	$H_2O(l)$ $\rightleftharpoons$	$H_3O^+(aq)$ +	$PAc^-(aq)$
Initial	0.12	-	0	0
Change	$-x$	-	$+x$	$+x$
Equilibrium	$0.12 - x$	-	x	x

$[H_3O^+] = 10^{-pH} = 2.4\times10^{-3}\ M$ which is >> 10^{-7} (the $[H_3O^+]$ from water)

$x \approx 2.4\times10^{-3}\ M \approx [H_3O^+] \approx [PAc^-]$ $\quad [HPAc]_{equilibrium} = 0.12 - x \approx 0.12\ M$

$$\text{So } K_a = \frac{(2.4\times10^{-3})(2.4\times10^{-3})}{0.12} = 4.8\times10^{-5}$$

- یافتن غلظتهای تعادلی با داشتن K_a و غلظت اولیه اسید

نمونه مسئله 18-8 پروپانوئیک اسید:

Sample Problem 18.8 **Determining Concentrations from K_a and Initial [HA]**

PROBLEM: Propanoic acid (CH_3CH_2COOH, which we simplify as HPr) is a organic acid whose salts are used to retard mold growth in foods. What is the $[H_3O^+]$ of 0.10 *M* HPr ($K_a = 1.3x10^{-5}$)?

PLAN: Write out the dissociation equation and expression; make whateve assumptions about concentration which are necessary; substitute.

Assumptions: For $HPr(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Pr^-(aq)$

$x = [HPr]_{diss} = [H_3O^+]_{from\ HPr} = [Pr^-]$ $\qquad K_a = \dfrac{[H_3O^+][Pr^-]}{[HPr]}$

SOLUTION:

Concentration (*M*)	**$HPr(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Pr^-(aq)$**			
Initial	0.10	-	0	0
Change	$-x$	-	$+x$	$+x$
Equilibrium	0.10 - x	-	x	x

Since K_a is small, we will assume that $x << 0.10$

$$1.3x10^{-5} = \frac{[H_3O^+][Pr^-]}{[HPr]} = \frac{(x)(x)}{0.10}$$

تقریب.

$$x = \sqrt{(0.10)(1.3x10^{-5})} = 1.1x10^{-3}\ M = [H_3O^+]$$

Check: $[HPr]_{diss} = 1.1x10^{-3}\ M/0.10\ M \times 100 = 1.1\%$

اسیدهای چند پروتونی:

در این اسیدها هر مرحله یونش در pH موثر است ولی اگر ثابت های تعادل دوم و سوم خیلی کوچکتر از ثابت تفکیک اول باشد از مراحل بعدی صرفنظر می شود.

Polyprotic acids

acids with more than one ionizable proton

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq) \qquad K_{a1} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = 7.2\times10^{-3}$$

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq) \qquad K_{a2} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.3\times10^{-8}$$

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons PO_4^{3-}(aq) + H_3O^+(aq) \qquad K_{a3} = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.2\times10^{-13}$$

$K_{a1} > K_{a2} > K_{a3}$

نمونه مسئله 18-10: تعیین غلظتهای تعادلی در محلول آسکوربیک اسید0/050 مولار

(اسید دو ظرفیتی)

Sample Problem 18.10 **Calculating Equilibrium Concentrations for a Polyprotic Acid**

PROBLEM: Ascorbic acid ($H_2C_6H_6O_6$; H_2Asc for this problem), known as vitamin C, is a diprotic acid ($K_{a1} = 1.0\times10^{-5}$ and $K_{a2} = 5\times10^{-12}$) found in citrus fruit. Calculate [H_2Asc], [$HAsc^-$], [Asc^{2-}], and the pH of 0.050 *M* H_2Asc.

PLAN: Write out expressions for both dissociations and make assumptions.

$K_{a1} >> K_{a2}$ so the first dissociation produces virtually all of the H_3O^+.

K_{a1} is small so $[H_2Asc]_{initial} \approx [H_2Asc]$

دو فرض در نظر می گیریم.

After finding the concentrations of various species for the first dissociation, we can use them as initial concentrations for the second dissociation.

SOLUTION:

$$H_2Asc(aq) + H_2O(l) \rightleftharpoons HAsc^-(aq) + H_3O^+(aq) \qquad K_{a1} = \frac{[HAsc^-][H_3O^+]}{[H_2Asc]} = 1.0\times10^{-5}$$

$$HAsc^-(aq) + H_2O(l) \rightleftharpoons Asc^{2-}(aq) + H_3O^+(aq) \qquad K_{a2} = \frac{[Asc^{2-}][H_3O^+]}{[HAsc^-]} = 5\times10^{-12}$$

Sample Problem 18.10 **Calculating Equilibrium Concentrations for a Polyprotic Acid**

Concentration (*M*)	$H_2Asc(aq) + H_2O(l) \rightleftharpoons HAsc^-(aq) + H_3O^+(aq)$			
Initial	0.050	-	0	0
Change	$-x$	-	$+x$	$+x$
Equilibrium	$0.050 - x$	-	x	x

$K_{a1} = [HAsc^-][H_3O^+]/[H_2Asc] = 1.0\times10^{-5} = (x)(x)/0.050\ M$

تقریب.

$x = \sqrt{(0.050)(1.0\times10^{-5})}$ $x = 7.1\times10^{-4}\ M$

$pH = -\log(7.1\times10^{-4}) = 3.15$

Concentration (*M*)	$HAsc^-(aq) + H_2O(l) \rightleftharpoons Asc^{2-}(aq) + H_3O^+(aq)$			
Initial	7.1×10^{-4}M	-	0	$7.1\times10^{-4}\ M$
Change	$-x$	-	$+x$	$+x$
Equilibrium	$7.1\times10^{-4} - x$	-	x	$7.1\times10^{-4} + x$

$K_{a2} = [Asc^{2-}][H_3O^+]/[HAsc^-] = 5\times10^{-12} = (x)(7.1\times10^{-4} + x)/(7.1\times10^{-4} - x)\ M = x$

تقریب بزنید

اصلاح کنید