Question 41. The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it.
Answer:
pH = - log [H^+] or log [H^+] = - pH = - 3.76 = 4.24
∴ [H^+] = Antilog 4.24 = 1.738 x 10^{-4} = 1.74 x 10^{-4} M

Question 42. The ionization constant of HF, HCOOH and HCN at 298 K are is 6.8 x 10^{-4} , 1.8 x 10^{-4} and 4.8 x 10^{-9} respectively, Calculate the ionization constant of the corresponding conjugate base.
Answer:
For F^- , K_b =K_w/K_a= 10^{-14}/(6.8 x 10^{-4}) = 1.47 x 10^{-11} = 1.5 x 10^{-11}.
For HCOO-, K_b = 10^{-14}/(1.8 x 10^{-4}) = 5.6 x 10^{-11}
For CN^-, K_b= 10^{-14}/(4.8 X 10^{-9}) = 2.08 x 10^{-6}

Question 43. The ionization constant of phenol is 1.0 x 10^{10}. What is the concentration of phenolate ion in 0.05 M solution of phenol? What will be its degree of ionization if the solution is also 0.01 M in sodium phenolate?
Answer:

	$C_6H_5OH \rightleftharpoons C_6H_5O^- + H^+$	
Initial	0.05 M	
After disso.	$0.05 - x$	x x

$$\therefore \quad K_a = \frac{x \times x}{0.05 - x} = 1.0 \times 10^{-10} \text{ (Given)} \quad \text{or} \quad \frac{x^2}{0.05} = 1.0 \times 10^{-10}$$

or $x^2 = 5 \times 10^{-12}$ or $x = \mathbf{2.2 \times 10^{-6}}$ **M**

In presence of 0.01 C_6H_5ONa, suppose y is the amount of phenol dissociated, then at equilibrium

$$[C_6H_5OH] = 0.05 - y \simeq 0.05,$$
$$[C_6H_5O^-] = 0.01 + y \simeq 0.01 \text{ M}, [H^+] = y \text{ M}$$

$$\therefore \quad K_a = \frac{(0.01)(y)}{0.05} = 1.0 \times 10^{-10} \text{ (Given)} \quad \text{or} \quad y = 5 \times 10^{-10}$$

$$\therefore \quad \alpha = \frac{y}{c} = \frac{5 \times 10^{-10}}{5 \times 10^{-2}} = \mathbf{10^{-8}}.$$

Question 44. The-first ionization constant of H_2S is 9.1 x 10^{-8}.
Calculate the concentration of HS^- ions in its 0.1 M solution and how will this concentration be affected if the solution is 0.1 M in HCl also? If the second dissociation constant of H_2S is 1.2 x 10^{-13}, calculate the concentration of S^{2-}under both conditions.
Answer:
To calculate [HS^-]

	$H_2S \rightleftharpoons$	H^+ +	HS^-
Initial	0.1 M		
After disso.	$0.1 - x$ $\simeq 0.1$	x	x

$$K_a = \frac{x \times x}{0.1} = 9.1 \times 10^{-8} \quad \text{or} \quad x^2 = 9.1 \times 10^{-9} \quad \text{or} \quad x = \mathbf{9.54 \times 10^{-5}}.$$

In presence of 0.1 M HCl, suppose H_2S dissociated is y. Then at equilibrium,
$[H_2S] = 0.1 - y \simeq 0.1$, $[H^+] = 0.1 + y \simeq 0.1$, $[HS^-] = y$ M

$$K_a = \frac{0.1 \times y}{0.1} = 9.1 \times 10^{-8} \ (Given) \quad or \quad y = \mathbf{9.1 \times 10^{-8}\ M}$$

To calculate $[S^{2-}]$

$$H_2S \xrightleftharpoons{K_{a_1}} H^+ + HS^- \ ; \qquad HS^- \xrightleftharpoons{K_{a_2}} H^+ + S^{2-}$$

For the overall reaction,

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

$$K_a = K_{a_1} \times K_{a_2} = 9.1 \times 10^{-8} \times 1.2 \times 10^{-13} = 1.092 \times 10^{-20}$$

$$K_a = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

In the absence of 0.1 MHCl, $[H^+] = 2\,[S^{2-}]$
Hence, if $[S^{2-}] = x$, $[H^+] = 2x$

$$\therefore \quad \frac{(2x)^2 x}{0.1} = 1.092 \times 10^{-20} \quad or \quad 4x^3 = 1.092 \times 10^{-21} = 273 \times 10^{-24}$$

$$3 \log x = \log 273 - 24 = 2.4362 - 24$$

$$\log x = 0.8127 - 8 = \bar{8}.8127,$$

$$or \quad x = \text{Antilog } \bar{8}.8127 = 273 \times 10^{-24} = 6.497 \times 10 = \mathbf{6.5 \times 10^{-8}\ M.}$$

In presence of 0.1 M HCl, suppose $[S^{2-}] = y$, then

$$[H_2S] = 0.1 - y \simeq 0.1\ M, \quad [H^+] = 0.1 + y \simeq 0.1\ M$$

$$K_a = \frac{(0.1)^2 \times y}{0.1} = 1.09 \times 10^{-20} \quad or \quad y = \mathbf{1.09 \times 10^{-19}\ M.}$$

Question 45. The ionization constant of acetic acid is 1.74×10^5. Calculate the degree of dissociation of acetic acid in its 0.05 M solution. Calculate the concentration of acetate ions in the solution and its pH.

Answer:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{[H^+]^2}{[CH_3COOH]}$$

$$or \quad [H^+] = \sqrt{K_a\,[CH_3COOH]} = \sqrt{(1.74 \times 10^{-5})(5 \times 10^{-2})} = 9.33 \times 10^{-4}\ M$$

$$[CH_3COO^-] = [H^+] = \mathbf{9.33 \times 10^{-4}\ M}$$

$$pH = -\log(9.33 \times 10^{-4}) = 4 - 0.9699 = 4 - 0.97 = \mathbf{3.03}$$

Question 46. It has been found that the pH of a 0.01 M solution of an organic acid is 4.15. Calculate the concentration of the anion, the ionization constant of the acid and its PK_a.

Answer:

$$HA \rightleftharpoons H^+$$

$$pH = -\log[H^+] \quad or \quad \log[H^+] = -4.15 = \bar{5}.85$$

$$\therefore \quad [H^+] = 7.08 \times 10^{-5}\ M = 7.08 \times 10^{-5}\ M$$

$$[A^-] = [H^+] = 7.08 \times 10^{-5}\ M$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(7.08 \times 10^{-5})(7.08 \times 10^{-5})}{10^{-2}} = \mathbf{5.0 \times 10^{-7}}$$

$$pK_a = -\log K_a = -\log(5.0 \times 10^{-7}) = 7 - 0.699 = \mathbf{6.301}$$

Question 47. Assuming complete dissociation, calculate the pH of the following solutions:
(a) 0.003 M HCl
(b) 0.005 M NaOH
(c) 0.002 M HBr
(d) 0.002 M KOH

Answer:

(a) $HCl + aq \rightarrow H^+ + Cl^-$, $\therefore [H^+] = [HCl] = 3 \times 10^{-3}$ M, $pH = -\log(3 \times 10^{-3}) = 2.52$

(b) $NaOH + aq \rightarrow Na^+ + OH^-$

$$\therefore \quad [OH^-] = 5 \times 10^{-3}\ M, [H^+] = 10^{-14}/(5 \times 10^{-3}) = 2 \times 10^{-12}\ M$$

$$pH = -\log(2 \times 10^{-12}) = \mathbf{11.70}$$

(c) $HBr + aq \rightarrow H^+ + Br^-$, $\therefore$ $[H^+] = 2 \times 10^{-3}$ M, $pH = -\log(2 \times 10^{-3}) = 2.70$

(d) $KOH + aq \rightarrow K^+ + OH^-$,

$$\therefore \quad [OH^+] = 2 \times 10^{-3}\ M, [H^+] = 10^{-14}/(2 \times 10^{-3}) = 5 \times 10^{-12}$$

$$pH = -\log(5 \times 10^{-12}) = \mathbf{11.30}$$

Question 48. Calculate the pH of the following solutions:
(a) 2g ofTlOH dissolved in water to give 2 litre of the solution
(b) 0.3 g of $Ca(OH)_2$ dissolved in water to give 500 mL of the solution
(c) 0.3 g of NaOH dissolved in water to give 200 mL of the solution

(d) I mL of 13.6 M HCl is diluted with water to give 1 litre of the solution.
Answer:

(a) Molar conc. of TlOH $= \dfrac{2g}{(204+16+1)\,g\ mol^{-1}} \times \dfrac{1}{2\,L} = 4.52 \times 10^{-3}$ M

$$[OH^-] = [TlOH] = 4.52 \times 10^{-3}\ M$$
$$[H^+] = 10^{-14}/\ (4.52 \times 10^{-3}) = 2.21 \times 10^{-12}\ M$$
$$\therefore \quad pH = -\log (2.21 \times 10^{-12}) = 12 - (0.3424) = 11.66$$

(b) Molar conc. of $Ca(OH)_2 = \dfrac{0.3\,g}{(40+34)g\ mol^{-1}} \times \dfrac{1}{0.5\,L} = 8.11 \times 10^{-3}$ M

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$$
$$[OH^-] = 2[Ca(OH)_2] = 2 \times (8.11 \times 10^{-3})\ M = 16.22 \times 10^{-3}\ M$$
$$pOH = -\log (16.22 \times 10^{-3}) = 3 - 1.2101 = 1.79$$
$$pH = 14 - 1.79 = \mathbf{12.21}$$

(c) Molar conc. of NaOH $= \dfrac{0.3\,g}{40\,g\ mol^{-1}} \times \dfrac{1}{0.2\,L} = 3.75 \times 10^{-2}$ M

$$[OH^-] = 3.75 \times 10^{-2}\ M$$
$$pOH = -\log (3.75 \times 10^{-2}) = 2 - 0.0574 = 1.43$$
$$pH = 14 - 1.43 = \mathbf{12.57}$$

(d) $M_1V_1 = M_2V_2 \therefore 13.6\ M \times 1m\ L = M_2 \times 1000\ mL \quad \therefore M_2 = 1.36 \times 10^{-2}\ M$

$$[H^+] = [HCl] = 1.36 \times 10^{-2}\ M,\ pH = -\log (1.36 \times 10^{-2}) = 2 - 0.1335 \simeq \mathbf{1.87}$$

Question 49. The degree of ionization of a 0.1 M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the PK_a of bromoacetic acid.
Answer:

	$CH_2(Br)\ COOH$	$\rightleftharpoons$	$CH_2(Br)COO^-$	+	H^+
Initial conc.	C		0		0
Conc. at eqm.	$C - C\alpha$		$C\alpha$		$C\alpha$

$$K_a = \frac{C\alpha . C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} \simeq C\alpha^2 = 0.1 \times (0.132)^2 = 1.74 \times 10^{-3}$$
$$pK_a = -\log (1.74 \times 10^{-3}) = 3 - 0.2405 = \mathbf{2.76}$$
$$[H^+] = C\alpha = 0.1 \times 0.132 = 1.32 \times 10^{-2}\ M$$
$$pH = -\log (1.32 \times 10^{-2}) = 2 - 0.1206 = \mathbf{1.88}$$

Question 50. The pH of0.005 M codeine ($C_{18}H_{21}NO_3$) solution is 9.95. Calculate the ionization constant and PK_b.
Answer:

$$Cod + H_2O \rightleftharpoons Cod\ H^+ + OH^-$$
$$pH = 9.95 \quad \therefore pOH = 14 - 9.95 = 4.05, \quad i.e., -\log [OH^-] = 4.05$$
$$\text{or} \quad \log [OH^-] = -4.05 = \bar{5}.95 \quad \text{or} \quad [OH^-] = 8.913 \times 10^{-5}\ M$$
$$K_b = \frac{[CodH^+][OH^-]}{[Cod]} = \frac{[OH^-]^2}{[Cod]} = \frac{(8.91 \times 10^{-5})^2}{5 \times 10^{-3}} = \mathbf{1.588 \times 10^{-6}}$$
$$pK_b = -\log (1.588 \times 10^{-6}) = 6 - 0.1987 = \mathbf{5.8}$$

*********** END **********