VMC Vidyamandir Classes SINCE 1986

IIT JEE | MEDICAL | FOUNDATION

Ionic equilibrium

self ionisation of water ⟶

Complex Rxⁿ.

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

$$H_2O_{(l)} + 2H_2O_{(l)} \rightleftharpoons H_5O_2^+{}_{(aq)} + OH^-_{(aq)}$$

B.A. B.B.

$$2H_2O_{(l)} + 2H_2O_{(l)} \rightleftharpoons H_5O_2^+{}_{(aq)} + H_3O_2^-{}_{(aq)}$$

B.A. B.B.

Hydrated hydronium ion ⇒ $H_3O^+(H_2O)_n$

$n = 1, 2, 3, 4, \ldots$

Hydrated hydroxyl ion ⇒ $OH^-(H_2O)_n$

$n = 1, 2, 3, 4, \ldots$

Ionic Product of water (K_w) ⟶

Simple Rxⁿ ⟶ $H_2O \rightleftharpoons H^+ + OH^-$

	H_2O	H^+	OH^-
t=0	c mol/lit.	0	0
t=eq.	$c - c\alpha$	$c\alpha$	$c\alpha$

where c = initial conc. of water

α = degree of ionisation

(Ionization const. of H_2O) $(K_i)_{H_2O} = \dfrac{[H^+]^1\,[OH^-]^1}{[H_2O]^1}$

$d_{H_2O} = 1\ gm/ml$

$V_{H_2O} = V\ ml$

$w_{H_2O} = V\ gm$

Molarity of pure H_2O = $\dfrac{\text{No. of moles of } H_2O}{\text{Vol. of } H_2O \text{ in lit}}$

$$c = \frac{V/18}{V/1000} = \frac{1000}{18} = 55.55M$$

At 25°C, $[H^+]$ and $[OH^-]$ obtained from $H_2O = 10^{-7}\ M$

$c\alpha = 10^{-7}$

$[H_2O]_{eq.} = c - c\alpha$

$= (55.55) - (10^{-7})$

$= 55.55\ M$ = const.

$(K_i)_{H_2O} \times [H_2O] = [H^+] \times [OH^-]$

$$\boxed{K_w = [H^+] \times [OH^-]}$$

↓

Ionic Product of H_2O or self ionisation const. of H_2O or Auto protolysis const. of H_2O

at 25°c, $K_w = 10^{-7} \times 10^{-7} = 10^{-14}$

$$\log \frac{K_{w_2}}{K_{w_1}} = \frac{\Delta H^\circ_{ionisation}}{2.303\ R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\Delta H^\circ_{ionisation} = +13.7\ Kcal./mol$$
$$= +57.1\ KJ/mol$$

All Ionisation Rx^n are endothermic so K_w, $(K_i)_{H_2O}$, K_a, K_b, K_h, K_{sp} etc. increase on increasing the temp.

at 90°c, $K_w = 10^{-12} \Rightarrow [H^+] = [OH^-] = 10^{-6}\ M$

$\Rightarrow$ degree of Ionisation ↑

Q. Calculate % Ionisation of H_2O at 25°c ?

Soln → $[H^+] = [OH^-] = 10^{-7}\ M$ at 25°c

$$c\alpha = 10^{-7}$$

$$\frac{1000}{18}\alpha = 10^{-7}$$

$$\alpha = 18 \times 10^{-10} = 1.8 \times 10^{-9}$$

$$\% \text{ Ionisation} = 1.8 \times 10^{-7}\ \%$$

Q. Calculate Ionisation const. of H_2O at 25°c ?

Soln → $(K_i)_{H_2O} = \frac{[H^+] \times [OH^-]}{[H_2O]} = \frac{10^{-7} \times 10^{-7}}{1000} \times 18 = 1.8 \times 10^{-16}$

pH scale → It was developed by sorensen. It is used to express the conc. of H^+ ions.

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

$$pOH = -\log [OH^-]$$

$$pK_w = -\log K_w$$

$$pK_i = -\log (K_i)$$

Note → (1) $\log (AB) = \log A + \log B$

(2) $\log \left(\frac{A}{B}\right) = \log A - \log B$

(3) $\log (x^y) = y \log x$

(4) $\log 2 = 0.3$, $\log 3 = 0.48$

$\log 5 = 0.7$, $\log 7 = 0.85$

$\log 10 = 1$

Imp. (5) $-\log (a \times 10^{-b}) = -\log a - \log 10^{-b}$

$= -\log a + b$

Relation b/w pH and pOH ⟶

$$[H^+] \times [OH^-] = K_w$$

$$-\log\{[H^+] \times [OH^-]\} = -\log K_w$$

$$-\log[H^+] - \log[OH^-] = -\log K_w$$

$$\boxed{pH + pOH = pK_w}$$

at 25°C, $K_w = 10^{-14} \Rightarrow pK_w = 14$

$$\boxed{pH + pOH = 14}$$

* If temp. is not given in question then take 25°C.

Q. If pH = 2 for a soln then calculate ratio of conc. of H^+ and OH^- ion for given soln ?

Soln ⟶ $pH = 2 \Rightarrow [H^+] = 10^{-2}$ M

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{10^{-2}} = 10^{-12} \text{ M}$$

$$\frac{[H^+]}{[OH^-]} = \frac{10^{-2}}{10^{-12}} = 10^{10}$$

Q. If $[OH^-]$ for a basic sol^n is 3×10^{-4} M then Calculate pH for given basic sol^n ?

Sol^n →

$$pOH = -\log[OH^-] = -\log(3\times10^{-4})$$

$$= 4 - \log 3 = 3.52$$

$$pH = 14 - 3.52 = 10.48$$

Method-2

$$[H^+] = \frac{10^{-14}}{3\times10^{-4}} = \frac{10^{-10}}{3} \text{ M}$$

$$pH = -\log\left(\frac{1}{3}\times10^{-10}\right) = 10 - \log\frac{1}{3}$$

$$= 10 + \log 3 = 10.48$$

Nature of resulting sol^n →

If $[H^+] = [OH^-] = \sqrt{K_w}$ or $pH = pOH = \frac{1}{2}pK_w$ → Neutral sol^n

at 25°C, $pH = pOH = 7$

If $[H^+] > [OH^-]$ or $[H^+] > \sqrt{K_w}$, $[OH^-] < \sqrt{K_w}$ or $pH < \frac{1}{2}pK_w$, $pOH > \frac{1}{2}pK_w$ → Acidic sol^n

at 25°C, $pH < 7$, $pOH > 7$

If $[H^+] < [OH^-]$

or

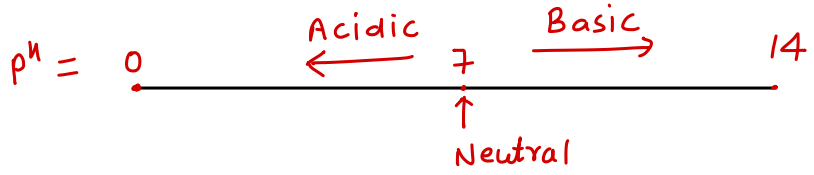
$[OH^-] > \sqrt{K_w}$, $[H^+] < \sqrt{K_w}$

or

$pOH < \frac{1}{2} pK_w$, $pH > \frac{1}{2} pK_w$

} → basic soln

at 25°C, $pH > 7$, $pOH < 7$



Q. write the nature of following soln :—

(i) $pH = 5$ — Acidic

(ii) $pOH = 3$ — Basic

(iii) $pOH = 6$ at 90°C ($K_w = 10^{-12}$) — Neutral

(iv) $pH = 8$ — Basic

(v) $pOH = 6.5$ at 85°C ($K_w = 10^{-13}$) — Neutral

(vi) $pH = 7$ at 90°C — Basic

(vii) $[H^+] = 10^{-3}$ M — Acidic

(viii) $[OH^-] = 10^{-6}$ M at 90°C — Neutral

Common ion effect ⟶ Ionisation of weak electrolyte is suppressed in the presence of common ion.

$$\underset{(WE)}{AB_{(aq)}} \rightleftharpoons A^+_{(aq)} + B^-_{(aq)}$$

$$\underset{(SE)}{AC_{(aq)}} \longrightarrow A^+_{(aq)} + C^-_{(aq)}$$

If AB is ionised in the presence of AC then

$[A^+] \uparrow \Rightarrow$ eq. Rx^n of AB proceeds in Backward dir^n

$\Rightarrow$ Degree of ionisation of AB $\downarrow$

$\alpha > \alpha'$

α ↓ Degree of Ionisation in the absence of common ion

α' → Degree of ionisation in the presence of common ion

Calculation of pH for strong acids or strong bases ⟶

(i) 3×10^{-2} M $HCl_{(aq)}$

$$HCl \longrightarrow H^+ + Cl^-$$

	HCl	H^+	Cl^-
$t=0$	3×10^{-2} M	0	0
end	0	3×10^{-2} M	3×10^{-2} M

$$[H^+]_{Total} = (3\times10^{-2}) + \cancel{10^{-7}} \simeq 3\times10^{-2}\ M$$

$$pH = -\log(3\times10^{-2}) = 2 - \log 3$$

$$= 1.52$$

(ii) 2×10^{-4} M H_2SO_4 (aq)

$$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$$

$$4\times10^{-4}\ M$$

$$[H^+]_{Total} = (4\times10^{-4}) + \cancel{10^{-7}} \simeq 4\times10^{-4}$$

$$pH = 4 - \log 4 = 3.4$$

(iii) 6×10^{-3} M $NaOH_{(aq)}$

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

$$6\times10^{-3}\ M$$

$$[OH^-]_{total} = (6\times10^{-3}) + \cancel{10^{-7}}$$

$$\simeq 6\times10^{-3}$$

$$pOH = 3 - \log 6$$

$= 2.22$

$pH = 14 - 2.22 = 11.78$

(iv) 7×10^{-2} M $Ba(OH)_2$ (aq)

$Ba(OH)_2 \longrightarrow Ba^{2+} + 2OH^-$

14×10^{-2} M

$[OH^-]_{total} = (14 \times 10^{-2}) + 10^{-7}$

$\simeq 14 \times 10^{-2}$

$pOH = 2 - \log 14 = 0.85$

$pH = 14 - 0.85$

$= 13.15$

(v) 10^{-8} M HCl (aq)

$HCl \longrightarrow H^+ + Cl^-$

10^{-8} M $\quad 10^{-8}$

$[H^+]_{total} = 10^{-8} + 10^{-7}$

$= 1.1 \times 10^{-7}$

$pH = 7 - \log(1.1) = 6.96$ (Approximate answer)

Considering the common ion effect →

$$H_2O \rightleftharpoons \underset{x+10^{-8}}{H^+} + \underset{x}{OH^-}$$

$$HCl \longrightarrow \underset{10^{-8}+x}{H^+} + Cl^-$$

$$K_w = [H^+] \times [OH^-] = (x + 10^{-8})(x)$$

$$10^{-14} = (x + 10^{-8})\,x$$

$$x^2 + 10^{-8}x - 10^{-14} = 0$$

$$x = \frac{-10^{-8} + \sqrt{10^{-16} + (4 \times 10^{-14})}}{2}$$

$$= \frac{(2 \times 10^{-7}) - 10^{-8}}{2} = 0.95 \times 10^{-7}$$

$$[H^+]_{total} = 10^{-8} + x = 1.05 \times 10^{-7}\ M$$

$$pH = 7 - \log(1.05) = 6.98 \text{ (Exact answer)}$$

(vi) 10^{-7} M $NaOH_{(aq)}$

$$NaOH \longrightarrow Na^+ + \underset{10^{-7}\ M}{OH^-}$$

$$[OH^-]_{total} = 10^{-7} + 10^{-7} = 2 \times 10^{-7}$$

$$pOH = 7 - \log 2 = 6.7$$

$$pH = 7.3 \quad \text{(Approximate answer)}$$

Considering common Ion effect —

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$x \qquad x + 10^{-7}$$

$$x(x + 10^{-7}) = 10^{-14}$$

$$x^2 + 10^{-7}x - 10^{-14} = 0$$

$$x = \frac{-10^{-7} + \sqrt{10^{-14} + (4 \times 10^{-14})}}{2}$$

$$= 0.62 \times 10^{-7}$$

$$[OH^-] = 1.62 \times 10^{-7}$$

$$pOH = 7 - \log(1.62)$$

$$= 7 - 0.21 = 6.79$$

$$pH = 14 - 6.79$$

$$= 7.21 \quad \text{(Exact answer)}$$

(vii) 10^{-12} M NaOH (aq)

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

10^{-12} M

$$[OH^-]_{total} = 10^{-12} + 10^{-7} \simeq 10^{-7} \text{ M}$$

$$pOH \simeq 7$$

$$pH \simeq 7$$

(viii) 2×10^{-3} M HNO_3 (aq)

$$HNO_3 \longrightarrow H^+ + NO_3^-$$

$$[H^+]_{Total} = (2 \times 10^{-3}) + 10^{-7}$$

$$\simeq 2 \times 10^{-3} \text{ M}$$

$$pH = 3 - \log 2$$

$$= 3 - 0.3 = 2.7$$

Calculation of pH for a mix. of 2 or more strong acids or 2 or more strong bases →

For mix. of strong acids → $[H^+]_f = \dfrac{[H^+]_1 V_1 + [H^+]_2 V_2}{V_1 + V_2}$

For mix. of strong bases →

$$[OH^-]_f = \frac{[OH^-]_1 V_1 + [OH^-]_2 V_2}{V_1 + V_2}$$

Q. Calculate the pH of mix. obtained by mixing equal volumes of pH = 2 and pH = 4 (strong acids) ?

Soln →

$$[H^+]_f = \frac{(H^+)_1 V_1 + [H^+]_2 V_2}{V_1 + V_2}$$

$$= \frac{(10^{-2} \times V) + (10^{-4} \times V)}{2V}$$

$$= \frac{10^{-2} + 10^{-4}}{2} \simeq 5 \times 10^{-3}$$

$$pH = 3 - \log 5 = 2.3$$

Q. Calculate the pH of a mix. obtained by mixing soln of equal vol. of $pH = 9$ and $pH = 12$?

Soln →

$$[OH^-]_f = \frac{[OH^-]_1 V_1 + [OH^-]_2 V_2}{V_1 + V_2}$$

$$= \frac{(10^{-5} V) + (10^{-2} V)}{2V}$$

$$= \frac{\cancel{10^{-5}} + 10^{-2}}{2} = 5 \times 10^{-3}$$

$$pOH = 3 - \log 5 = 2.3$$

$$pH = 11.7$$

Q. Calculate the pH of a mix. obtained by mixing 0.02 M, 200ml $Ba(OH)_2$ soln and 0.03 M, 200ml NaOH soln.

Soln →

$$[OH^-]_f = \frac{(0.04 \times 200) + (0.03 \times 200)}{400}$$

$$= \frac{14}{400} = \frac{7}{2} \times 10^{-2}$$

$$pOH = 2 - \log 7 + \log 2$$

$$= 2 - 0.85 + 0.3 = 1.45$$

$$pH = 14 - 1.45 = 12.55$$

calculation of pH of a mix. of strong acid and strong base ⟶

Acid : $[H^+] \cdot V_{acid}$ or $N_{acid} \cdot V_{acid}$

Base : $[OH^-] \cdot V_{base}$ or $N_{base} \cdot V_{base}$

Find nature of resulting soln.

$[H^+] \cdot V_{acid} = [OH^-] \cdot V_{base} \Rightarrow$ Neutral soln

$\Rightarrow pH = 7$ at $25^\circ C$

$[H^+] \cdot V_{acid} > [OH^-] \cdot V_{base} \Rightarrow$ Acidic soln

$$\Rightarrow [H^+]_f = \frac{[H^+] \cdot V_{acid} - [OH^-] \cdot V_{base}}{V_{acid} + V_{base}}$$

$[H^+] \cdot V_{acid} < [OH^-] \cdot V_{base} \Rightarrow$ basic soln

$$\Rightarrow [OH^-]_f = \frac{[OH^-] \cdot V_{base} - [H^+] \cdot V_{acid}}{V_{acid} + V_{base}}$$

Q. Calculate pH of mix. obtained by mixing 200 ml soln of $pH = 3$ and 400 ml soln of $pH = 11$.

Soln Acid : $[H^+] \cdot V_{acid} = 10^{-3} \times 200$

Base : $[OH^-] \cdot V_{base} = 10^{-3} \times 400$

$\Rightarrow$ Resulting soln is basic.

$$[OH^-]_f = \frac{(400 \times 10^{-3}) - (200 \times 10^{-3})}{200 + 400}$$

$$= \frac{1}{3} \times 10^{-3}$$

$$pOH = 3 - \log\left(\frac{1}{3}\right) = 3 + \log 3$$

$$= 3.48 \Rightarrow pH = 10.52$$

Q. Calculate pH of a mix. obtained by mixing 0.02 N, 400 ml KOH soln and 0.02 N, 500 ml H_2SO_4 soln.

Acid : $N_a V_a = 0.02 \times 500 = 10$

Base : $N_b V_b = 0.02 \times 400 = 8$

$\Rightarrow$ Resulting soln is acidic

$$[H^+]_f = \frac{10 - 8}{500 + 400} = \frac{2}{900}$$

$$= \frac{2}{9} \times 10^{-2}$$

$$pH = 2 - \log 2 + \log 9$$

$$= 2 - 0.3 + 0.96$$

$$= 2.66$$

Calculation of pH of diluted soln of strong acid or strong base $\longrightarrow$

$$N_1 V_1 = N_2 V_2$$

For strong acid, Normality = molarity of H^+ ion

For strong base, Normality = Molarity of OH^- ion.

12. 50 mL of H_2O is added to 50 mL of 1×10^{-3} M barium hydroxide solution. What is the pH of the resulting solution?

(A) 3.0 **(B)** 3.3 **(C)** 11.0 **(D)** 11.7

Soln →

$$N_1V_1 = N_2V_2$$

$$(2 \times 10^{-3}) \times 50 = N_2 \times 100$$

$$N_2 = [OH^-] = 10^{-3} \text{ M}$$

$$pOH = 3$$

$$pH = 11$$

11. 10^{-6}M NaOH is diluted 100 times. The pH of the diluted base is :

(A) between 7 and 8 **(B)** between 5 and 6

(C) between 6 and 7 **(D)** between 10 and 11

Soln →

$$N_1V_1 = N_2V_2$$

$$(10^{-6} \times V) = N_2 \times (100V)$$

$$N_2 = 10^{-8} = [OH^-]_{new} \text{ from NaOH}$$

$$[OH^-]_{total} = 10^{-8} + 10^{-7}$$

$$pOH = 6.96 \text{ (Approximate)}$$

$$6.98 \text{ (Exact)}$$

$$pH = 14 - 6.98 = 7.02$$

Homework

DTS-1-11
Q. 2,5,6,9-14,18-20,61-69,71-74,77-79,83-85,88,93,95, 118-120,122,126

JEE MAIN archive
Q.2,6,8,11,12,16,22,26,33,37,45

JEE ADVANCED ARCHIVE
Q.2,3,9,10,18,19,35,58