ARJUNA

JEE AIR 2024

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Physical Chemistry

Ionic Equilibrium

Lecture No. - 08

By- Dr. Gopal Chaturvedi Sir
(GC Sir)

Topics to be Covered

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- Topic: Titration
- Topic: Indicator Theory
- Topic: Solubility (S)
- Topic: Solubility product (K_{SP})

Recap of Previous Lecture

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Topic Buffer Action

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Dilution of Buffer solution :-

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Addition of $H_2O(\ell)$

$CH_3COONa\ (aq)$; C_1

$CH_3COOH\ (aq)$; C_2

After dilution.

$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

$C_2' - x'$ $\quad C_1' + x' \quad x'$

Before dilution ; $K_a = \dfrac{(C_1 + x)x}{(C_2 - x)}$; $x = [H^+]$

After dilution ; C_1' & C_2' $K_a = \dfrac{(C_1' + x')x'}{(C_2' - x')}$; $x' = [H^+]_{new}$

(i). Addition of $H_2O(\ell)$ in small amount ; no appreciable change in pH

(ii). Addition of $H_2O(\ell)$ in large amount ; pH of buffer solution $\rightarrow 7$ at 25°C

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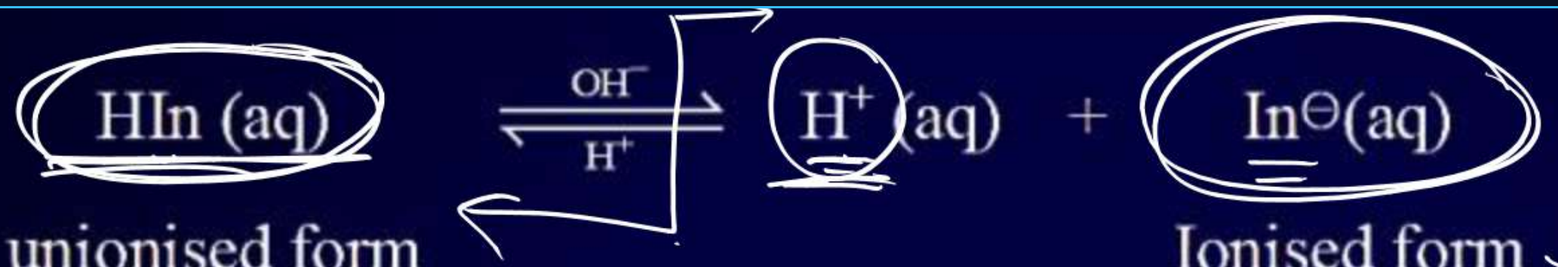
In general indicators are either weak organic acids or weak organic bases having different coloured characteristics in ionised and unionised form.

General acidic indicator ; HIn



unionised form

or

Acidic form

(colour I)

Ionised form

or

Ionic form

(Colour II)

$$K_{HIn} \text{ or } K_{In} = \frac{[H^+]_{sol}[In^-]}{[HIn]}$$

$$[H^+]_{sol} = K_{In}\left\{\frac{[HIn]}{[In^-]}\right\}$$

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$$\boxed{pH = pK_{In} + \log\frac{[In^-]}{[HIn]}}$$

$$\%\ \text{ionised form of indicator} = \frac{[In^-]}{[HIn]+[In^-]} \times 100 = \frac{[In^-]/[HIn]}{1+\frac{[In^-]}{[HIn]}} \times 100$$

$$\%\ \text{unionised form of indicator} = \frac{[HIn]}{[HIn]+[In^-]} \times 100$$

Titration

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This is an experimental technique by which we can determine amount of unknown conc^{n} solution with the help of reaction between different nature of substance.

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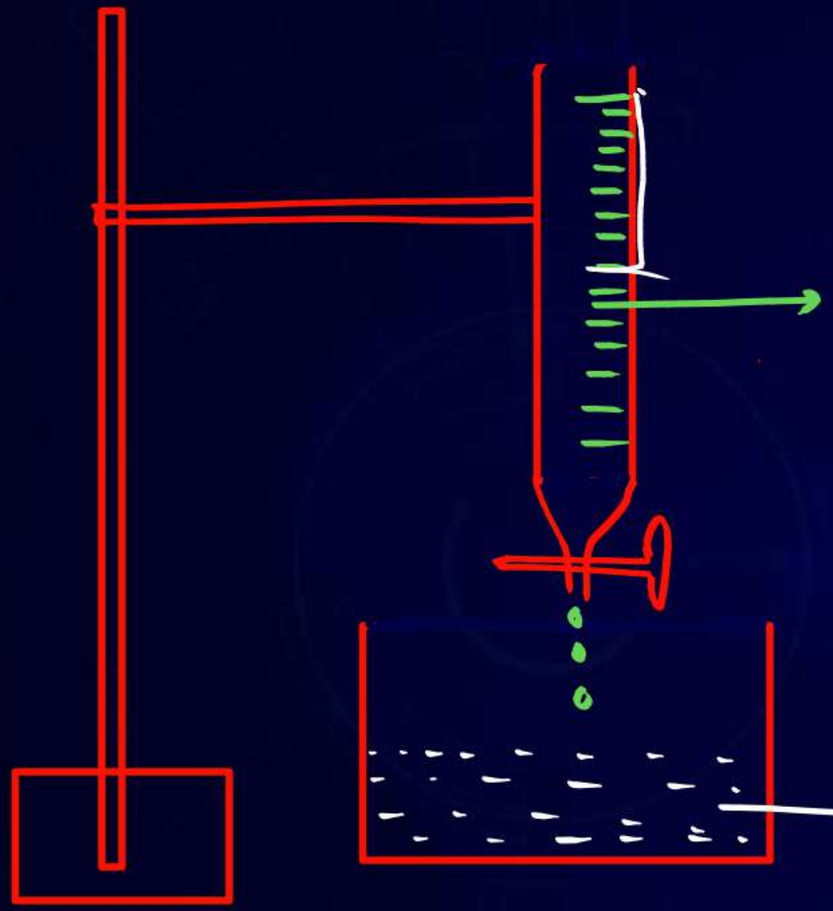

Standard Solution (Titrant)

[known Conc^n Solution]

M_2 e.g. Acid HCl(aq)

Analyte [Unknown Conc^n Solution]

V_1 ml (Given) e.g. NaOH(aq)

M_1 (Unknown)

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Given.

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

M_2	V_1 ml
V_2 ml	M_1
(Used)	(Unknown)

When $M_1V_1 = M_2V_2$ ⇒ Equivalent point or neutralisation point.

$NaCl(aq)$ Soln.

$$M_1 = \frac{M_2V_2}{V_1}$$

$$\text{Acid (aq.)} + \text{Base (aq.)} \longrightarrow \text{Salt (aq.)} + H_2O\ (\ell)$$

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NaOH base

M_2 , V_2

CH_3COOH(acid)

M_1, V_1

At equivalent point in acid-base neutralisation

No. of equivalent of Acid = No. of equivalent of base

$$1 \times \boxed{M_1V_1 = M_2V_2} \times 1$$

Indicator change its colour in certain pH range, this pH range is called colour transition range.

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$$\frac{[In^-]}{[HIn]} \simeq \frac{1}{10} \text{ to } \frac{10}{1}$$

$$\boxed{pH = pKIn \pm 1}$$

$$(pK_{In} - 1) \longleftrightarrow (pK_{Zn} + 1)$$

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Lower pH

Higher pH

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General basic indicator : InOH

$$\underset{\text{unionised form}}{InOH(aq)} \rightleftharpoons \underset{\text{Ionised form}}{In^{+}(aq)} + OH^{-}(aq)$$

or

basic form

(colour-I)

or

acidic form

(colour-II)

Methyl Orange : Basic Indicator

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$$\underset{\text{Yellow}}{MeOH(aq)} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} \underset{\text{Red}}{Me^+(aq)} + OH^-(aq)$$

, CTR 3.1 ⟷ 4.4

⇒ If pH of solution ≥ 4.4 ; then solution has yellow colour.

⇒ ✓ If pH of solution ≤ 3.1 ; then solution has (red) colour

⇒ In between 3.1 to 4.4 ; indicator change its colour.

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Phenophthalein :- Acidic indicator

$$HPh(aq) \rightleftharpoons H^+(aq) + Ph^-(aq)$$

unionised form or acidic form (colour less)

Ionised form or basic form (Pink)

CTR

(8.2 → 10)

⇒ If pH of solution ≥ 10 ; then solution has pink colour.

⇒ If pH of solution ≤ 8.2 ; then solution is colourless.

⇒ In between 8.2 to 10 ; indicator change its colour.

Eg:

Titration of SA with SB

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Q. If HCl(aq) is titrated against 0.1M NaOH(aq) solution. (50ml)

Used Volume of NaOH

(1) 0 ml

(2) 49 ml

(3) 50 ml

(4) 51 ml

Calculate the pH of Soln.

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(1) Resulting soln.

HCl(aq)
50ml
0.1M

$P^H = -\log 10^{-1} = 1$

(2) $HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$

mmoles 5 4.9

Resulting Solution HCl(aq) & NaCl(aq)

$(HCl(aq)) = \frac{(5-4.9)}{99} = \frac{0.1}{99}$;

$P^H = -\log\left(\frac{0.1}{99}\right) \approx 3$

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(3) $HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$

mmoles (5) (5)

$NaCl(aq) + H_2O(l)$ $\longrightarrow$ $P^H = \frac{1}{2} P^{K_w} = 7$ at 25°

Neutralisation point.

(4) $HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$

mmole	5	5.1	—	—
After reaⁿ mmole	—	(5.1 − 5) = 0.1	5	5

Resulting soln $NaOH(aq) + NaCl(aq)$ ~ $[NaOH(aq)] = \frac{0.1}{101} \simeq 10^{-3}$

$p^{OH} \simeq 3$, $p^H = 11$ at 25°C

Titration of WA against SB

If $CH_3COOH(aq)$ is titrated against 0.1M NaOH(aq) solution.
(50ml, 0.1M)

Used volume of 0.1M NaOH(aq) are

(1) 0 ml
(2) 25 ml
(3) 49 ml
(4) 50 ml
(5) 51 ml

$K_a = 1.8 \times 10^{-5}$
(CH_3COOH)

Calculate p^H of resulting solution.

Sol:

1. Resulting Solution

$CH_3COOH(aq)$ Soln
50 ml
0.1 M

W. Acid Soln

$[H^+] = \sqrt{K_a \times C}$

$P^H = \frac{1}{2}(P^{K_a} - \log C)$

$= \frac{1}{2}(4.74 + 1) = 2.87$

$P^{K_a} = -\log(1.8 \times 10^{-5})$

$= 4.74$

2. $CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa(aq) + H_2O(l)$

	CH_3COOH	$NaOH$	CH_3COONa	H_2O
mmoles	5	2.5	—	—
After reaction mmoles	2.5	—	2.5	

$CH_3COOH(aq), CH_3COONa(aq)$

Acid ← → Basic

$P^H = P^{K_a} = 4.74$

Max. Buffer Capacity ⑤ = ⑨

3. $CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa(aq) + H_2O(l)$

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m moles	5	4.9		
m moles	0.1	—	4.9	4.9

Resulting Solution $CH_3COOH(aq)$, $CH_3COONa(aq)$

$$pH = 4.74 + \log\left(\frac{4.9}{0.1}\right) = 4.74 + 2\log 7$$

$$= 6.43$$

$\log 7 \rightarrow 0.8451$

4. $CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa(aq) + H_2O(l)$

m mole	5	5	—	—
m mole	—	—	5	5

$$CH_3COONa(aq) + H_2O(l)$$

Basic

$$[CH_3COONa] = \frac{5}{100} = 0.05$$

$$pH = pK_w - pOH, \quad pH = \frac{1}{2}pK_w + \frac{1}{2}(pK_a + \log C) = 7 + \frac{1}{2}[4.74 + \log(0.05)]$$

$$\simeq 8.71$$

5. $CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COONa(aq) + H_2O(\ell)$

m mole	5	5·1		
m mole	—	(5·1 − 5) = 0·1	5	

$NaOH(aq)$, $CH_3COONa(aq)$, $H_2O(\ell)$

$[NaOH] = \frac{0.1}{101} = C_1$ ← $\frac{5}{101} = C_2$

Hydrolysis of CH_3COO^- in pr. of b

SB

$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$

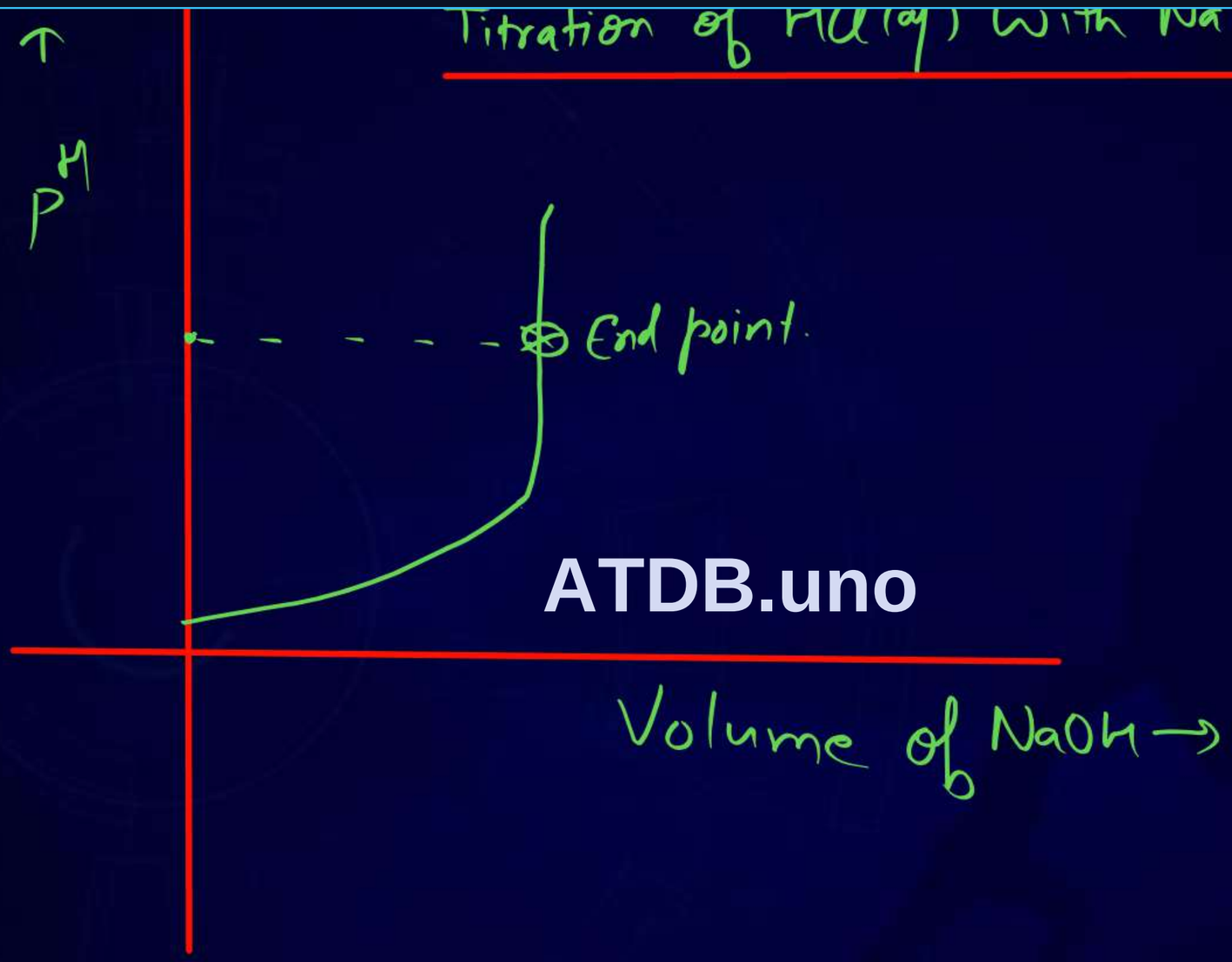
$CH_3COO^-(aq) + H_2O \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$

$C_2 - x$ | x | $(x + C_1)$

$[OH^-]_T = [OH^-]_{\text{from } NaOH} + x \simeq C_1$

$[OH^-] = 10^{-3}$

$pH = 11$



Question

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#Q. (a) Determine the pH of a 0.2 M solution of pyridine C_5H_5N. $K_b = 1.5 \times 10^{-9}$

(b) Predict the effect of addition of pyridinium ion $C_5H_5NH^+$ on the position of the equilibrium. Will the pH be raised or lowered?

(c) Calculate the pH of 1.0 L of 0.10 M pyridine solution to which 0.3 mol of pyridinium chlorides $C_5H_5NH^+$ Cl, has been added, assuming no change in volume.

HW

Ans. (a) pH = 9.239 (b) lowered (c) pH = 4.699

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Question

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#Q. Calculate the pH of a solution which result from the mixing of 50.0 ml of 0.3 M HCl with 50.0 ml of 0.4 M NH_3. [K_b (NH_3) = 1.8×10^{-5}]

HW

Ans. 8.7782

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Question

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#Q. Calculate the pH of a solution made mixing 50.0 ml of 0.2 M NH_4Cl & 75.0 ml of 0.1 M NaOH. [K_b (NH_3) = 1.8×10^{-5}]

HW

Ans. 9.7324

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Question

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#Q. A buffer solution was prepared by dissolving 0.02 mol propionic acid & 0.015 mol sodium propionate enough water to make 1.00 L of solution (K_a for propionic acid is 1.34×10^{-5})

(a) What is the pH of the buffer?

(b) What would be the pH if 1.0×10^{-5} mol HCl were added per 10 ml of the buffer?

(c) What would be the pH if 1.0×10^{-5} mol NaOH were added per 10 ml of the buffer.

HW

Ans. (a) 4.7525 (b) 4.697, (c) 4.798

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Question

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#Q. A solution was made up to be 0.01 M in chloroacetic acid, $ClCH_2COOH$ and also 0.002 M in sodium chloroacetate $ClCH_2COONa$. What is $[H^+]$ in the solution? $K_a = 1.5 \times 10^{-3}$.

HW

Ans. $[H^+] = 2.5 \times 10^{-3}$

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Question

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#Q. For the indicator thymol blue, pH is 2.0 when half the indicator is in unionized form. Find the % of indicator in unionized from in the solution with $[H^+] = 4 \times 10^{-3}$ M.

HW

Ans. $[Hl_n] = 28.57\ \%$

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Question

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#Q. Bromophenol blue is an indicator with a K_a value of 6×10^{-5}. What % of this indicator is in its basic form at a pH of 5?

HW

Ans. 85.71%

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Question

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#Q. An acid base indicator has a K_a of 3×10^{-5}. The acid from of the indicator is red & the basic form is blue. By how much must the pH change in order to change the indicator form 75% red to 75% blue?

HW

Ans. $\Delta pH = 0.954$

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Question

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#Q. Calculate the hydronium ion concentration and pH at the equivalence point in the reaction of 22.0 mL of 0.10 M acetic acid, CH_3COOH, with 22.0 mL of 0.10 M NaOH.

HW

Ans. 8.71

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Question

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#Q. Calculate the hydronium ion concentration and the pH at the equivalence point in a titration of 50.0 mL of 0.40 M NH_3 with 0.40 M HCl.

HW

Ans. 4.98

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