Part I

Solution..

Titration of formic Acid with NaOH.

Volume of Formic Acid = 100mL.

$[HCOOH] = 0.50 M$.

pka of $HCOOH = 3.75$.

$ka = 10^{-3.75}$

$ka = 1.778 \times 10^{-4}$.

① Initial pH.

$$HCOOH \rightleftharpoons H^+ + HCOO^-$$

I	0.50	0	0
C	$-0.50 \times \alpha$	$+0.50\alpha$	$+0.50\alpha$
E	$0.50 - 0.50\alpha$	0.50α	0.50α

where, α = degree of dissociation

α = degree of Ionization.

$$ka = \frac{[H^+][HCOO^-]}{[HCOOH]}$$

$$Ka = \frac{(0.50\alpha)(0.50\alpha)}{0.50 - 0.50\alpha} = \frac{(0.50\alpha)^2}{(0.50)(1-\alpha)}$$

$$178 \times 10^{-4} = \frac{(0.50\alpha)^2}{(1-\alpha)}$$

α is very small.

$$1.778 \times 10^{-4} = \frac{0.50\alpha^2}{1}$$

$$\alpha^2 = 3.556 \times 10^{-4}$$

$$\alpha = 0.018857$$

now, $[H^+] = 0.50\alpha$

$[H^+] = (0.50 \times 0.018857)$

$[H^+] = 0.0094286 M$.

Now, $pH = -\log[H^+] = -\log[0.0094286]$

$pH = 2.0255$

$pH = 2.02$

Initial $pH = \underline{\underline{2.02}}$.

② Percent of ionization

$$= \left(\frac{0.018857}{1} \times 100\%\right).$$

$$= 1.8857.$$

$$= \underline{\underline{1.886\%}}$$

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③. Addition of 10ML, NaOH.

$[NaOH] = 1.0M$

moles of NaOH added $= \left(\frac{1.0M \times 10mL}{1000}\right) = 0.01$ moles.

Reaction

$$HCOOH + NaOH \longrightarrow HCOO^- Na^+ + H_2O.$$

moles of $HCOO^-$ formed = 0.01 moles

Initial moles of HCOOH = molarity × volume (L).

$$= \left(\frac{0.50M \times 100}{1000}\right) = 0.05$$

Final moles of HCOOH $= (0.05 - 0.01) = 0.04$ moles.

$HCOOH/HCOO^-$ makes an acidic buffer solution.

$$pH = pka + \log \frac{[HCOO^-]}{[HCOOH]}$$

$$pH = 3.75 + \log \frac{[0.01]}{[0.04]}$$

$$pH = 3.75 + \log (0.25)$$

$$pH = 3.75 - 0.602$$

$$pH = 3.15.$$

④. 25Ml NaOH added.

moles of NaOH $= \left(\frac{1.0M \times 25mL}{1000}\right) = 0.025$ moles

moles of $HCOO^-$ formed $= 0.025$ moles.

remaining moles of HCOOH $= (0.05 \text{ moles} - 0.025 \text{ moles})$.
$= 0.025$ moles

$[HCOOH] = [HCOO^-]$

$$pH = pka + \log \frac{[HCOO^-]}{[HCOOH]}$$

$$pH = pka + Log \frac{[0.025]}{[0.025]}$$

$pH = Pka + 0 = 3.75$

$pH = 3.75$

⑤ At equivalence point volume required

moles of Formic Acid $= \left(\frac{0.50M \times 100mL}{1000}\right)$
0.05 moles

moles of NaOH = moles of Formic Acid
= 0.05 moles.

∴ volume of NaOH at equivalence point.
$= \left(\frac{0.05 \text{ moles}}{1.0M} \times 1000\right)$

$= \underline{\underline{50\text{ml}}}$

6. At equivalence point there is $HCOO^-$

Total volume $= (100 + 50)\ mL$

$= 150\ ml$

$$HCOO^- + H_2O \rightleftharpoons HCOOH + OH^-$$

$$[HCOO^-] = \left(\frac{0.05 \text{ moles}}{150} \times 1000\right)$$

$$= \underline{\underline{0.333\ M.}}$$

I	0.333	0	0
C	$-x$	$+x$	$+x$
E	$0.333 - x$	x	x

$$Kb = \frac{[HCOOH][OH^-]}{[HCOO^-]}$$

$$\frac{Kw}{Ka} = \frac{x \cdot x}{0.333 - x}$$

$$\frac{Kw}{Ka} = \frac{x^2}{0.333}$$

$$x^2 = 0.333 \times \frac{Kw}{Ka}$$

$$x^2 = \left(0.333 \times \frac{1.0 \times 10^{-14}}{1.778 \times 10^{-4}}\right)$$

$$x^2 = 1.8797 \times 10^{-11}$$

$$x = 4.3298 \times 10^{-6}$$

$$[OH^-] = x = 4.3298 \times 10^{-6} M$$

$$pOH = -\log[OH^-] = -\log[4.3298 \times 10^{-6}]$$

$pOH = 5.36$ at equivalence point.

⑦ pH at equivalence point

$$pH = 14 - pOH$$
$$= 14 - 5.36$$
$$= \underline{\underline{8.64}}$$

⑧ After 100ml addition of NaOH

50mL is equivalence point.

So extra 50mL NaOH is added after end point.

$$\text{extra moles of NaOH} = \left(\frac{50mL \times 1.0M}{1000}\right)$$
$$= \underline{\underline{0.05 moles}}.$$

$$\text{total volume} = 100 + 100 = 200mL$$

$$[OH^-] \text{ final} = \left(\frac{0.050 moles}{200} \times 1000\right)$$
$$= 0.\underline{\underline{25}}M.$$

$$[H^+] = \frac{kw}{[OH^-]} = \frac{1.0 \times 10^{-14}}{[0.25]}$$

$$[H^+] = 4 \times 10^{-14}$$

$$pH = -\log[H^+]$$
$$= -\log[4 \times 10^{-14})$$

$$pH = 13.40$$

$$pH \doteq 13.40$$

⑨ Molarity $= \left(\dfrac{\text{moles} \times 1000}{\text{volume}}\right)$

moles = 0.05 moles of HCl.

volume = 100 ML

$$= \left(\frac{0.05\,\text{moles} \times 1000}{100}\right)$$

$$= \underline{\underline{0.5\,M}}.$$

Percentage of dissociation of formic Acid.

$$= \left(\frac{0.5}{1.0}\right) \times 100\%$$

$$= \underline{\underline{50\%}}.$$

Part II.

Solution.

①. Reaction for solubility of $Ca(OH)_2$.

$$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$$

②. Molar solubility of $Ca(OH)_2$.

$$Ksp[Ca^{2+}][OH^-]^2 = (s)(2s)^2 = 4s^3$$

$$4s^3 = 4.68\times10^{-6} \qquad s = \frac{\sqrt[3]{4.68\times10^{-6}}}{4}$$

$$\underline{\underline{s = 1.05\times10^{-2}}}\,M.$$

③. Concentration of $OH^- = 2s = 2(1.05\times10^{-2}M)$

$$= \underline{\underline{2.10\times10^{-2}M}}$$

④. $pH = 14 - pOH$

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

$$pH = 14 - [-\log[2.10\times10^{-2}M]]$$

$$= (14 - 1.677)$$

$$= \underline{\underline{12.32}}.$$

⑤. a. Decreasing pH → Right

decreasing pH means reducing OH^- concentration

b. Add $CaCl_2$ → Left

(increasing Ca^{2+} conc. would shift the equilibrium to the left.

c. Decreasing temparature → Left.

(reaction is exothermic).

d. Add NaBr → Right

(Ca^{2+} would get consumed).