1) Calculate the pH of a

   a) 0.220 M aqueous solution of chloroacetic acid. ($K_a = 1.4 \times 10^{-3}$) (Ans: 1-76)

$$HA \rightleftharpoons H^{\oplus} + A^-$$

$0.220 - x \qquad +x \qquad +x$

$$\sqrt{1.4 \times 10^{-3} \times 0.22} = x$$

$$= 0.01755$$

$$\boxed{pH = 1.76}$$

   b) 0.550 M solution of formic acid. ($K_a = 1.8 \times 10^{-4}$) (Ans: 2.00)

$$\sqrt{1.8 \times 10^{-4} \times 0.55} = x$$

$$9.95 \times 10^{-3} = x$$

$$\boxed{pH = 2.00}$$

2) Formic acid, which is a component of insect venom, has a $K_a = 1.8 \times 10^{-4}$. What is the $[H_3O^+]$ in a solution that is initially 0.10 *M* formic acid, HCOOH? (Ans: 4.2×10^{-3} M)

$$HA \rightleftharpoons H^{\oplus} + A^{\ominus}$$

0.1M.

$$\sqrt{1.8 \times 10^{-4} \times .1} = \boxed{4.2 \times 10^{-3}\ M}$$

3) What is the $[H_3O^+]$ of a 0.250 HPr (propionic acid)? (K_a HPr= 1.3×10^{-5}) (Ans: 5.70×10^{-3} M)

$$\sqrt{\cancel{1}.3 \times 10^{-5} \times 0.25} = \boxed{1.81 \times 10^{-3} M}$$

4) Butyric acid is responsible for the odor in rancid butter. ~~What the~~ A solution of 0.25 M butyric acid has a pH of 2.71. What is the K_a for the acid? (Ans: 1.53×10^{-5})

$$HA \rightleftharpoons A^{\ominus} + H^{\oplus}$$

0.25M

1.95×10^{-3}

$$K_a = \frac{(1.95 \times 10^{-3})^2}{(0.25 - 1.95 \times 10^{-3})} = \frac{3.803 \times 10^{-6}}{0.2481} = \boxed{1.53 \times 10^{-5}}$$

5) What is the K_a of a 0.150 M phenylacetic acid (HPAc) with a pH of 2.63? (Ans: 3.66 × 10^{-5})

$$HA \rightleftharpoons A^{\ominus} + H^{\oplus}$$

0.15

2.344×10^{-3}

$$K_a = \frac{(2.344 \times 10^{-3})^2}{0.15 - 2.344 \times 10^{-3}} = \frac{5.495 \times 10^{-6}}{0.147675} = \boxed{3.72 \times 10^{-5}}$$

note: $\frac{5.49 \times 10^{-6}}{0.15} = 3.66 \times 10^{-5}$

6) What is the pH of a 0.200 M solution of NH_4Cl? (K_b NH_3 = 1.8 × 10^{-5}) (Ans: 4.98)

$$K_a = 1.0 \times 10^{-14} / 1.8 \times 10^{-5} = 5.56 \times 10^{-10}$$

$$NH_4Cl \xrightarrow{+H_2O} H_3O^{\oplus} + NH_3$$

0.2M $\quad +x \quad +x$

$$5.56 \times 10^{-10} = \frac{x^2}{0.2 - x} ; \quad x = \sqrt{5.56 \times 10^{-10} \times 0.2}$$

$$= 1.054 \times 10^{-5} M$$

$$\boxed{pH = 4.98}$$

*7) Piperidine $C_5H_{11}N$ ($K_b = 1.29 \times 10^{-3}$) is a colorless liquid with a smell of pepper. What is the pH of a 0.0250 M piperidine? (Ans: ~~11.8)~~

$$C_5H_{11}N \rightleftharpoons C_5H_{11}N^{\oplus} + OH^{\ominus}$$

$0.025-x \qquad x \qquad x$

$\boxed{\frac{M}{Kb} = \frac{0.025}{1.29\times10^{-3}} < 100}$

have to use quadratic eqn.

$1.29\times10^{-3} = \frac{x^2}{0.025-x}$; $x^2 + 1.29\times10^{-3}x - 3.23\times10^{-6} = 0.$

$$x = \frac{-1.29\times10^{-3} +/- \sqrt{(1.29\times10^{-3})^2 - 4(1)(-3.23\times10^{-6})}}{2}$$

$x = 1.26\times10^{-3} \longrightarrow$ find pOH $= 2.9$.

OR $=$ $-$ value x. $\quad$ pH $= 14 - 2.9 = \boxed{11.1}$.

*8) Hydrazoic acid HN_3 has a ($K_a = 1.91 \times 10^{-5}$). What molarity of HN_3 is required to produce an aqueous solution with pH = 3.10? (Ans: ~~1.5 × 10^-5~~ M)

pH = 3.10 $\rightarrow$ antilog 7.94×10^{-4} M.

$HN_3 + H_2O \longrightarrow N_3^{\ominus} + H_3O^{\oplus}$.

? M $\qquad 7.94\times10^{-4}$. $\quad 7.94\times10^{-4}$

$$ka = 1.91\times10^{-5} = \frac{(7.94\times10^{-4})^2}{[M]}.$$

$$M = \frac{(7.94\times10^{-4})^2}{1.91\times10^{-5}} = \boxed{0.033M}.$$

9) Codeine, a commonly prescribed painkiller, is a weak base. In a saturated solution of codeine, 0.0278 M the solution has a pH of 9.80. What is the K_b of codeine? (Ans: 1.43×10^{-7})

$$C_{18}H_{21}NO_3 + H_2O \rightleftharpoons [C_{18}H_{21}NHO_3]^+ + OH-$$

pOH = 14 − 9.80 = 4.2 $\longrightarrow$ take antilog. 6.31×10^{-5} M

cod. + $H_2O \rightleftharpoons$ Hcod.$^{\oplus}$ + $OH^{\ominus}$

0.0278M. $\qquad 6.31\times10^{-5} \quad 6.31\times10^{-5}$

$$K_b = \frac{(6.31\times10^{-5})^2}{0.0278} = \boxed{1.43\times10^{-7}}.$$

11) Dimethylamine (Me_2NH) has a K_b of 5.9 x 10^{-4}. What is the pH of a 1.50 M solution of Me_2NH? (Ans: 12.5)

$$Me_2NH + H_2O \rightleftharpoons Me_2NH_2^{\oplus} + OH^{\ominus}.$$

$$1.5 - x \qquad x \qquad x.$$

$$\sqrt{5.9\times10^{-4} \times 1.5} = x. = 3.0\times10^{-2}\,M = [OH^{\ominus}]$$

$$H_3O^{\oplus} = \frac{1\times10^{-14}}{3\times10^{-2}} = 3.3\times10^{-13}\,M$$

log $\rightarrow$ $\boxed{pH = 12.48}$

12) Farmers who raise cotton once used arsenic acid, H_3AsO_4, as a defoliant at harvest time. Arsenic acid is a polyprotic acid with $K_1 = 2.5 \times 10^{-4}$, $K_2 = 5.6 \times 10^{-8}$, and $K_3 = 3 \times 10^{-13}$. What is the pH of a 0.500 *M* solution of arsenic acid? (Ans: 1.96)

(1) $H_3AsO_4 \rightleftharpoons H_2AsO_4^{\ominus} + H^{\oplus}$

$0.5M - x \qquad +x \qquad +x.$

$$\sqrt{(2.5\times10^{-4} \times 0.5)} = x = 0.0112M$$

(2) $H_2AsO_4^{\ominus} \rightleftharpoons HAsO_4^{2-} + H^{\oplus}.$

$0.0112 - x. \qquad +x \qquad +x$

$$\sqrt{5.6\times10^{-8} \times 0.0112} = x = 2.5\times10^{-5}\,M$$

(3) will be very small since ka = 10^{-13}.

total $[H_3O^{\oplus}] = 0.112 + 2.5\times10^{-5} = 0.0112 5M$

$\boxed{pH = 1.95}$

13)Classify the following as acidic, basic or neutral salts:

a) LiCl b) KNO_3 c) NH_4Cl d) Na_3PO_4

neutral neutral acidic basic

14)Which of the following will give an acidic or basic solution in water?

a) CH_3CH_2COOK b) $Mg(NO_3)_2$ c) $HCOONH_4$ d) $NaNO_3$

basic acidic

15)Which of the following solutions and substances will suppress the ionization of formic acid, HCOOH?

a) NaCl b) KOH(aq) ✓ c) $HClO_4$ d) Na_2CO_3 ✓

16)For a 0.080 M NaOCl a) write the equation for hydrolysis; b) determine the equilibrium constant for this equation; and c) calculate the pH. K_a HOCl: 2.98×10^{-8}. (Ans: 3.4×10^{-7}; 10.2)

a) $NaOCl \rightarrow Na^+ + OCl^{\ominus} + H_2O \rightleftharpoons HOCl + OH^{\ominus}$

b) $K_b = 1 \times 10^{-14} / 2.98 \times 10^{-8} = 3.4 \times 10^{-7}$

c) $\sqrt{3.4 \times 10^{-7} \times 0.08} = 1.65 \times 10^{-4} = [OH^{\ominus}]$

$pOH = 3.78$

$\boxed{pH = 10.22}$

17)What is the pH of 0.450 M NaAc (sodium acetate)? ($K_a = 1.8 \times 10^{-5}$) (Ans: 9.20)

$NaAc + H_2O \rightleftharpoons AcH + OH^{\ominus}$

0.45M, $-x$ $+x$ $+x$

$\frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = \frac{x^2}{0.45 - x}$

$x = \sqrt{5.56 \times 10^{-10} \times 0.45} = 1.581 \times 10^{-5} = [OH^{\ominus}]$

$pOH = 4.8$

$\boxed{pH = 9.2}$

18)Calculate the pH of a solution that is 0.132 M in diethylamine $(CH_3CH_2)_2NH$ and 0.145 M in diethylammonium chloride $(CH_3CH_2)_2NH_2Cl$. (K_b $(CH_3CH_2)_2NH = 6.9 \times 10^{-4}$) (Ans: 10.9)

$(CH_3CH_2)_2NH \rightleftharpoons (CH_3CH_2)_2NH_2Cl + OH^{\ominus}$

0.132 M   0.145 M   acidic salt

$-x$ $+x$ $+x$

$K_b = 6.9 \times 10^{-4} = \dfrac{(0.145+x)(x)}{(0.132-x)}$ +/- x very small

$x = \dfrac{6.9 \times 10^{-4} \times 0.132}{.145} = 6.28 \times 10^{-4} = [OH^{\ominus}]$

pOH = 3.2

$\boxed{pH = 10.8}$

(Look up the K_a and K_b from data tables of your textbook in case it is not provided here.)

19) Which of the following solutions can be buffers?

KCl/HCl	$KHSO_4/H_2SO_4$	KNO_2/HNO_2
no	no	yes

20) Calculate the pH of the following buffers:

a) 0.15 M NH_3/0.35 M NH_4Cl. ($K_b = 1.8 \times 10^{-5}$) (Ans: 8.89)

$$K_a = 1\times10^{-14} / 1.8\times10^{-5} = 5.56\times10^{-10}$$

$$pK_a = 9.26.$$

$$pH = 9.26 + \log\frac{0.15}{0.35} = \boxed{8.89}$$

b) 0.10 M Na_2HPO_4/0.15M KH_2PO_4. ($K_a = 6.3 \times 10^{-8}$). (Ans: 7.03)

$$pH = 7.2 + \log\frac{0.1}{0.15} = \boxed{7.02}$$

21) The pH of a sodium acetate/acetic acid buffer is 4.50. Calculate the ratio of $[CH_3COO^-]$/$[CH_3COOH]$ needed to make the buffer. ($K_a = 1.76 \times 10^{-5}$) (Ans: 0.58)

$$pH = pK_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$4.5 = 4.74 + \log\frac{[CH_3COO^\ominus]}{[CH_3COOH]}$$

$$-0.24 =$$

$$\text{antilog } 0.58 = \frac{[CH_3COO^\ominus]}{[CH_3COOH]}$$

$pH = pKa + \log\frac{[B]}{[A]}$

22)Calculate a) the pH of a 1.00 L of a buffer 1.00 M CH_3COONa/1.00 M CH_3COOH before and after the addition of b) 0.080 mol NaOH and c) 0.12 mol HCl. (Assume there is no change in volume) ($K_a = 1.76 \times 10^{-5}$) (Ans: a) 4.75; b) 4.82; c) 4.64)

a) $pH = 4.75 + \log\frac{1}{1} = 4.75.$

b). $CH_3COOH + OH^{\ominus} \rightleftharpoons CH_3COO^{\ominus} + H_2O$

NaOH

$1.00 - 0.08 = 0.92$ $\quad 0.08 - 0.08 \quad$ $1.00 + 0.08 = 1.08$

$pH = 4.75 + \log\left(\frac{1.08}{0.92}\right)$

$= \boxed{4.82}$

c). $CH_3COO^{\ominus} + H^{\oplus} \rightleftharpoons CH_3COOH.$

HCl.

$1.00 - 0.12 = 0.88$ $\quad 0.12 - 0.12 \quad$ $1.00 + 0.12 = 1.12$

$pH = 4.75 + \log\left(\frac{0.88}{1.12}\right).$

$\boxed{4.64}$

23)Calculate the a) pH of a 1.000 L of a buffer 0.2450 M CH_3NH_2 and 0.1860 M CH_3NH_3Cl. What is the pH of the buffer after the addition of b) 30.00 mL of 0.7500 M NaOH and c) 20.00 mL of 0.8500 M HCl. ($K_b = 4.2 \times 10^{-4}$) (Ans: a) 10.72; b) 10.81; c) 10.65)

$Ka = 1.0\times10^{-14}/4.2\times10^{-4} = 2.38\times10^{-11} \xrightarrow{\text{take log}} pka = 10.6$

a) $pH = 10.6 + \underbrace{\log\frac{0.245}{0.186}}_{0.1196} = \boxed{10.72}.$

b). $0.03L \times 0.75M = 0.0225\,mol\ NaOH.$

Base $= 0.2450 + 0.0225 = 0.2675$

Acid $= 0.1860 - 0.0225 = 0.1635$

$pH = 10.6 + \underbrace{\log\frac{0.2675}{0.1635}}_{0.2138}$

$= \boxed{10.81}$

c) $0.02L \times 0.85M = 0.017\,mol\ HCl$

Base $= 0.2450 - 0.017 = 0.228$

Acid $= 0.1860 + 0.017 = 0.203$

$pH = 10.6 + \underbrace{\log\frac{0.228}{0.203}}_{0.05}$

$= \boxed{10.65}$

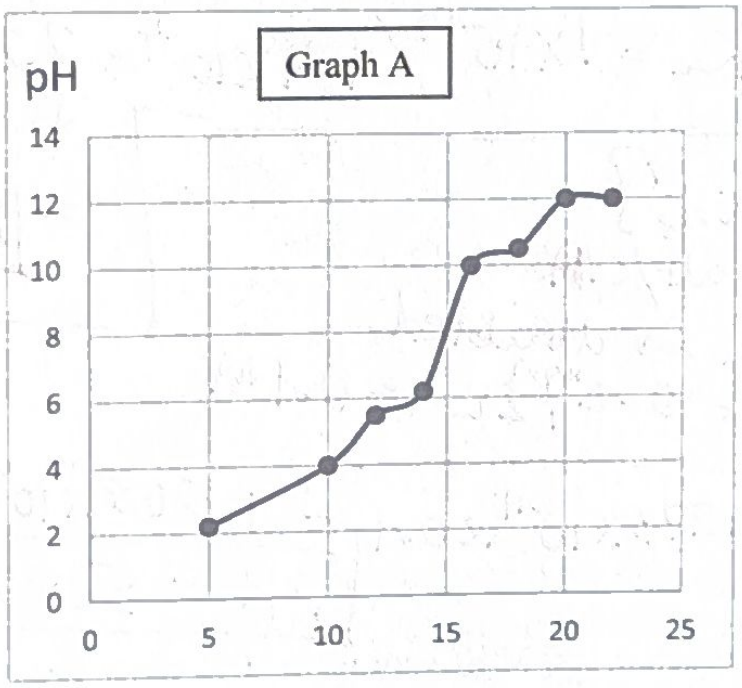
24) In a titration experiment 12.5 mL of 0.500 M H_2SO_4 neutralizes 50.0 mL of NaOH. What is the concentration of the NaOH solution? (Ans: 0.25M)

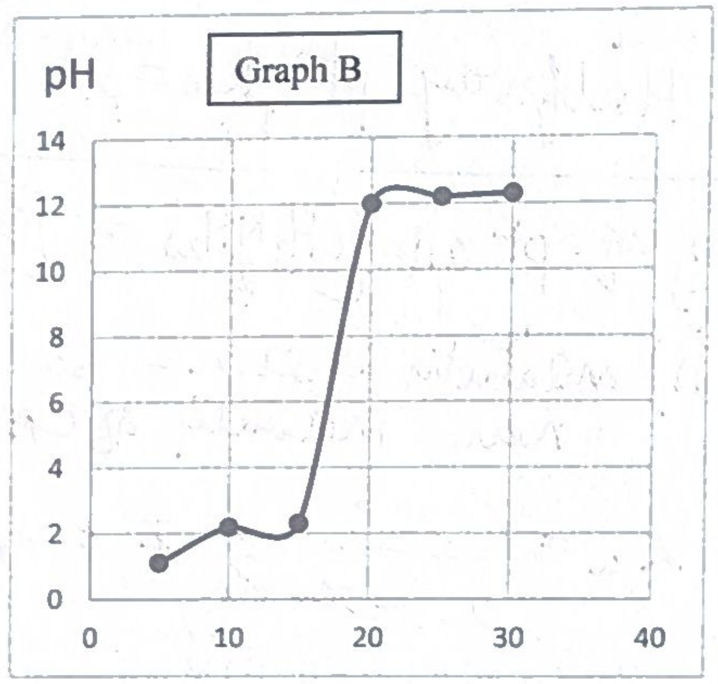
$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + H_2O$

$$\frac{12.5\text{mL} \times 0.5\text{M}}{1\text{ mol}} = \frac{M_b \times 50\text{mL}}{2}$$

$$\boxed{M_b = 0.25\text{M}}$$

25) Answer the following questions for the graphs below.





a) What kind of titration does graph A represent? Weak/strong acid/base? What is the pH at equivalence point?
b) What kind of titration does graph B represent? Weak/strong acid/base? What is the pH at equivalence point?
c) Compare the two graphs and write a sentence of two explaining how you can use titration curves to determine type of acid base titrations,

a) weak acid + strong base. pH ≃ 8.

b) strong acid + strong base pH ≃ 7

c) eq. pt for SA + SB is steep since pH changes drastically with even one drop of strong base (in this case).

26) Calculate the pH when 15.50 mL of 0.550 M NaOH has been added to 45.00 mL of 0.7500 M CH_3COOH in an acid base titration. (K_a = 1.8 x 10^{-5}) (Ans: 5.08)

$CH_3COOH + OH^{-} \rightleftharpoons CH_3COO^{-} + H_3O^{+}$

(0.045×0.75) mol $\quad (0.0155 \times 0.55)$ mol

0.03375 $- 8.525 \times 10^{-3}$ $\quad + 8.525 \times 10^{-3}$

mol NaOH = 15.5×10^{-3} L $\times$ 0.55 M = 8.525×10^{-3} mol

$K_a = \frac{[CB][H_3O^+]}{[A]}$; $[H_3O^+] = ka \times \frac{[A]}{[CB]} = 1.85 \times 10^{-5} \times \frac{0.025225}{8.525 \times 10^{-3}}$

$= 5.47 \times 10^{-5}$ $\boxed{pH = 4.26}$

27) Calculate the pH at halfway point and equivalence point for the titration of 0.20 M HCl and 0.20 M (CH_3NH_2) (Where volume is not given, assume it is1L). (K_b = 4.4 x 10^{-4}) (Ans:10.6; 5.32)

a) Halfway pt pka = pH $\quad K_a = 1 \times 10^{-14} / 4.4 \times 10^{-4} = 2.273 \times 10^{-11}$ → log $= \boxed{10.6}$

b) i) eq. pt all $[CH_3NH_2]$ (B) = $[CH_3NH_3^+]$ salt/CA.

ii) molarity is same so vol is doubled.

new Molarity of CA = 0.2 mol / 2L = 0.1 M

$K_a = \frac{x^2}{0.1 - x}$; $x = \sqrt{2.273 \times 10^{-11} \times 0.1} = 1.508 \times 10^{-6}$

$\boxed{pH = 5.82}$

28) A 10.0 mL solution of 0.300 M NH_3 is titrated with 0.100 M HCl solution. Calculate the pH after the addition of a) 0.0 mL, b) 10.0 mL and c) 30.0 mL HCl solution. (K_b = 1.8 x 10^{-5}) (Ans: a) 11.36, b) 9.55, c) 5.19)

a) $NH_3 + H_2O \rightleftharpoons NH_4^{+} + OH^{-}$

0.3 M $\quad x \quad x$

$K_b = \frac{x^2}{0.3 - x}$; $\sqrt{1.8 \times 10^{-5} \times 0.3} = x = 2.32 \times 10^{-3}$ → log is 2.6

pH = 14 − 2.6 = $\boxed{11.36}$

b) 10 mL HCl ; 0.01L × 0.1 M = 0.001 mol HCl. $\quad$ (0.01L × 0.3M)

NH_4^{+} = 0.001 mol ; NH_3 remaining = 0.003 mol − 0.001 mol = 0.002 mol.

$K_a = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$

$H_3O^{+} = K_a \frac{[acid]}{[base]} = 5.56 \times 10^{-10} \times \frac{0.001 mol}{0.002 mol} = 2.78 \times 10^{-10}$ → log $\boxed{9.55}$

c) 30 mL HCl is eq. pt. (mols of acid base are equal)

mols of salt = 0.003 mol ÷ total vol (0.04L) = 0.075 M salt

$K_a = \frac{x^2}{0.075 - x}$; $x = \sqrt{0.075 \times 5.56 \times 10^{-10}} = 6.46 \times 10^{-6}$ → log $\boxed{5.19}$

29) A 25.0 mL of 0.100 M CH_3COOH is titrated with 0.200 M KOH solution. Calculate the pH when the following volumes of KOH has been added: a) 0.00 mL, b) 5.0 mL, c) at halfway point and d) 12.5 mL of the KOH. ($K_a = 1.76 \times 10^{-5}$) (Ans: a) 2.88, b) 4.58, c) 4.75; d) 8.78)

$CH_3COOH + KOH \rightleftharpoons CH_3COO^{\ominus} + H_2O$

a) @ ØmL KOH $x = \sqrt{1.76 \times 10^{-5} \times 0.1} = 1.33 \times 10^{-3} \xrightarrow{\log} \boxed{2.88}$

b) $0.025L \times 0.1M = 2.5 \times 10^{-3}$ mol acid ; $0.005 \times 0.2 = 1 \times 10^{-3}$ mol base

Acid remaining $= 2.5 \times 10^{-3} - 1 \times 10^{-3} = 1.5 \times 10^{-3}$.

CB formed $= 1 \times 10^{-3}$

using Hendersen eqn $pH = \underbrace{-\log 1.76 \times 10^{-5}}_{(4.75)} + \log \frac{1 \times 10^{-3}}{1.5 \times 10^{-3}} = \boxed{4.57}$

c) @ halfway $pH = pKa$ $\boxed{pH = 4.75}$.

d) mol acid = mol base = neutralization. CB formed $= 2.5 \times 10^{-3}$ mol.

$[CB] = 2.5 \times 10^{-3}$ mol $/ 0.0375L = 0.0667 M$

$K_b = 1 \times 10^{-14} / 1.76 \times 10^{-5} = 5.68 \times 10^{-10}$ || $x = \sqrt{5.68 \times 10^{-10} \times 0.0667} = 6.16 \times 10^{-6} \xrightarrow{\log}$

$pOH = 5.21$ $\boxed{pH = 8.78}$

30)Calculate the pH when 40.00 mL of 0.100 M propanoic acid is titrated with the following volumes of 0.100 M NaOH: a) 0.00 mL; b) 30.00 mL and c) 40.00 mL.($K_a = 1.3 \times 10^{-5}$) *(Hint: calculation of a) is initial pH and c) is equivalent point)* (Ans: a) 2.94; b) 5.36; c) 8.79)

$A + B \rightarrow CB + H_2O$.

a) at Ø mL $x = \sqrt{1.3 \times 10^{-5} \times 0.1} = 1.14 \times 10^{-3} \xrightarrow{\log} \boxed{2.94}$.

b) $0.04L \times 0.1M = 4 \times 10^{-3}$ mol Acid ; $0.03L \times 0.1M = 3 \times 10^{-3}$ mol Base

Acid remaining $= 4 \times 10^{-3} - 3 \times 10^{-3} = 1 \times 10^{-3}$ mol

CB formed $= 3 \times 10^{-3}$ mol.

$pH = -\log 1.3 \times 10^{-5} + \log \frac{3 \times 10^{-3}}{1 \times 10^{-3}} = \boxed{5.36}$.

c) pKa = pH @ eq. pt. $\boxed{4.89}$