ALMUSTAQBAL UNIVERSITY COLLEGE

College of Engineering and Engineering Techniques

Biomedical Engineering Department
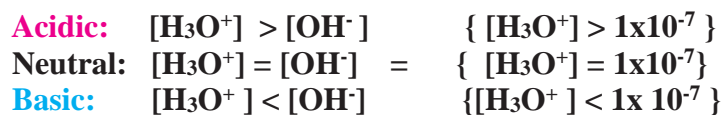
Stage   : Second year students

Subject : Chemistry 1 - Lecture 8

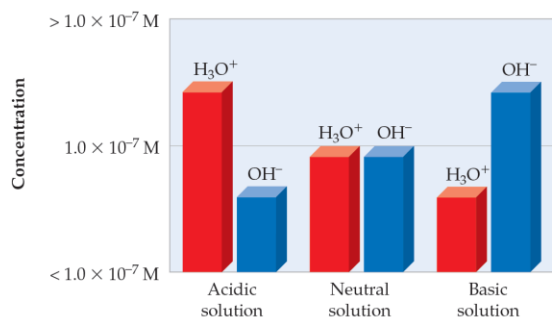**Lecturer: Assistant professor   Dr. SADIQ . J. BAQIR**

Dissociation equilibria for weak acids and bases (K_a & K_b)

Acidic, Neutral, and Basic aqueous solutions can be distinguished by the relative values of the H_3O^+ and OH^- concentrations:

**Acidic:** $[H_3O^+] > [OH^-]$ { $[H_3O^+] > 1x10^{-7}$ }
Neutral: $[H_3O^+] = [OH^-]$ =   { $[H_3O^+] = 1x10^{-7}$}
Basic: $[H_3O^+] < [OH^-]$ {$[H_3O^+] < 1x 10^{-7}$ }

as shown in figure.

Weak acids
Are acids that dissociate partially in water. So when they are dissolved in water, partial dissociation occurs. for example in acetic acid solution (weak acid), most of the acid remains un dissociated, with only a small fraction dissociated and present as (H_3O^+) in solution.

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$$
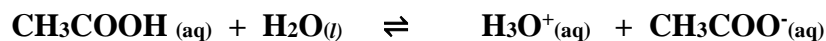
The extent of dissociation is given by the equilibrium constant:

$$K = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH][H_2O]}$$

$$K[H_2O] = K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

As $[H_3O^+] = [CH_3COO^-]$ from above equation then

$$K_a = \frac{[H_3O^+]^2}{[CH_3COOH]}$$

$$[H_3O^+] = \sqrt{K_a[CH_3COOH]} = \sqrt{K_a C}$$

K_a is an equilibrium constant and is called acid dissociation constant

*The value of K_a provides information about the relative strength of the weak acid,

The smaller k_a corresponding to a weaker acid.

On the opposite, small pk_a values characterize stronger acids

Table : The K_a and pK_a values for a number of common weak acids

Compound (weak acid)	K_a	pK_a
Hydrocyanic acid (HCN)	4.93×10^{-10}	9.31 **weakest acid**
Acetic acid (CH_3COOH)	1.77×10^{-5}	4.75
Benzoic acid (C_6H_5COOH)	6.46×10^{-5}	4.19
Formic acid (HCOOH)	1.77×10^{-4}	3.75
Salicylic acid(HOC_6H_4COOH)	1.05×10^{-3}	2.98
Chloroacetic acid($ClCH_2CO_2H$)	1.4×10^{-3}	2.85 **strongest acid**

Conversions

1. **To convert K_a to pK_a**
   $$pK_a = -\log K_a$$

Example:

Convert ($K_a = 4.93 \times 10^{-10}$) to pK_a

$pK_a = -\log 4.93 \times 10^{-10} = 9.31$

2. **To convert pK_a to K_a**

   $$K_a = 10^{-pK_a}$$

Example:

convert $pK_a = 4.75$ to K_a

$K_a = 10^{-4.75} = 1.77 \times 10^{-5}$

Example:

Arrange the following weak acids : acetic acid ($pK_a=4.75$) , formic acid ($pK_a=3.75$), and Chloroacetic acid ($K_a=1.4 \times 10^{-3}$) in the order of increasing their acid strength.

Solution:

We have to convert all to Ka or all to pKa which is easier and compare :

Method 1: (converting all to pKa)

$$pK_a = -\log K_a$$

For Chloroacetic acid ($ka=1.4 \times 10^{-3}$) then

$pKa = -\log (1.4 \times 10^{-3}) = 2.85$

Then

Acid	pKa
Chloroacetic acid	2.85 (**the strongest acid**)
formic acid	3.75
acetic acid	4.75 (**the weakest acid**)

As small pk_a values characterize stronger acids then Chloroacetic acid is **the strongest acid** and acetic acid is **the weakest acid** .

Method 2:   (converting all to Ka)

$K_a = 10^{-pKa}$

For acetic acid $pK_a = 4.75$ then $Ka = 10^{-4.75} = 1.77 \times 10^{-5}$

For formic acid $pK_a = 3.75$ then $Ka = 10^{-3.75} = 1.77 \times 10^{-4}$

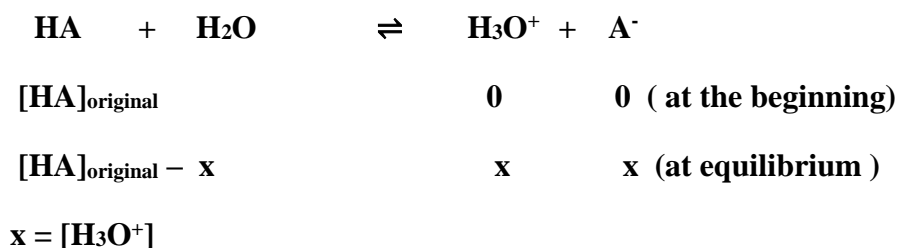| Acid	Ka
acetic acid	1.77×10^{-5} (**the weakest acid**)
formic acid	1.77×10^{-4}
Chloroacetic acid	1.4×10^{-3} (**the strongest acid**)

As the smaller k_a corresponding to a weaker acid. Then

acetic acid is **the weakest acid** and Chloroacetic acid is **the strongest acid.**

Exercise *(Home work)* :

 Arrange the following weak acids : Oxalic acid ($pK_a = 1.23$) , Lactic acid ($pK_a = 3.08$) , Citric acid ($Ka = 7.41 \times 10^{-4}$) and Ascorbic acid ($Ka = 7.94 \times 10^{-5}$) in the order of decreasing their acid strength .

Calculations of [H_3O^+] concentration for weak acid [HA]:

$$HA \quad + \quad H_2O \quad\quad \rightleftharpoons \quad\quad H_3O^+ \; + \; A^-$$

$[HA]_{original}$ 0   0 (at the beginning)

$[HA]_{original} - x$ x   x (at equilibrium)

$x = [H_3O^+]$

$$[H_3O^+] = \sqrt{Ka\ C}$$

Example : Calculate [H_3O^+] concentration of 0.12 M aqueous solution of Nitrous acid HNO_2, (Ka= $5.1x10^{-4}$) .

$$HNO_2 \quad + \quad H_2O \qquad \rightleftharpoons \qquad H_3O^+ + NO_2^-$$

$$[H_3O^+] = \sqrt{Ka\ C}$$

$$[H_3O^+] = \sqrt{5.1x10^{-4}\ x\ 0.12}$$

$$[H_3O^+] = \sqrt{6.12\ x\ 10^{-5}} = 7.82\ x\ 10^{-3}$$

$$pH = -\log(7.82\ x\ 10^{-3}) = 2.11$$

Concentration before dissociation		Equilibrium concentrations after dissociation		

Strong acid — HA — ~100% dissociation — H_3O^+ — A^- — HA — The extent of dissociation is nearly 100% for a **strong acid**.

Weak acid — HA — Partial dissociation — HA — H_3O^+ — A^- — The extent of dissociation is considerably less than 100% for a **weak acid**.

Very weak acid — HA — ~0% dissociation — HA — H_3O^+ — A^- — The extent of dissociation is nearly 0% for a **very weak acid**.

Weak bases

Are bases that partially dissociate in water and are characterized by base dissociation constant (K_b).

$$B \quad + \quad H_2O \qquad \rightleftharpoons \qquad BH^+ \quad + \quad OH^-$$
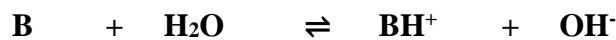
w.base   conjugate acid

$$K_b = \frac{[OH^-][BH+]}{[B]}$$

The value of (K_b) provides information about the relative strength of the weak base.

The smaller K_b corresponding to a weaker base.

On the opposite, small pK_b values characterize stronger base.

Table : The K_b and pK_b values for a number of common weak bases.

Compound(weak Base)	K_b	pK_b
Acetamide (CH_3CONH_2)	2.5×10^{-13}	12.60 **weakest Base**
Glycine(H_2NCH_2COOH)	2.24×10^{-12}	11.65
Aniline $C_6H_5NH_2$	7.4×10^{-10}	9.13
Pyridine C_5H_5N	1.7×10^{-9}	8.77
morphine	$7.5 \times 10{-7}$	6.12
Codeine($C_{18}H_{21}NO_3$)	$1.6 \times 10{-6}$	5.79
Ephedrine($C_{10}H_{15}ON$)	$1.3x10{-4}$	3.88
Methylamine(CH_3NH_2)	4.38×10^{-4}	3.36
Dimethylamine($CH_3)_2NH$	5.4×10^{-4}	3.26 **strongest Base**

Conversions:

1. To convert K_b to pK_b

   $pK_b = -\log K_b$

Example: Convert ($K_b = 2.54 \times 10^{-13}$) to pK_b

$pK_b = -\log 2.5x10^{-13} = 12.60$

2. To convert pK_b to K_b

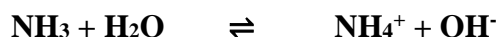 $K_b = 10^{-pK_b}$

Example: Convert $pK_b = 4.75$ to K_b

$K_b = 10^{-4.75} = 1.7 \times 10^{-5}$

Exercise (Home work) **: Arrange the following weak bases Glycine ($pK_b=11.65$) ,
Ephedrine ($pK_b=3.88$) , Pyridine($K_b=1.7 \times 10^{-9}$) and Dimethylamine ($K_b=5.4 \times 10^{-4}$) in
the order of decreasing their base strength.**

Calculations of [OH $^-$] concentration for weak bases:

For   weak base :

$NH_3 + H_2O \qquad \rightleftharpoons \qquad NH_4^+ + OH^-$

$C_b \qquad\qquad\qquad\qquad 0 \quad\; 0 \qquad$ (at the beginning)

$C_b- x \qquad\qquad\qquad\quad x \quad\; x \qquad$ (at equilibrium)

$x = [OH^-]$

$[OH^-] = \sqrt{K_b C_b}$

Example :

 Calculate $[H_3O^+]$ concentration of 0.2M aqueous NH_3 solution, $K_b= 1.8 \times 10^{-5}$.

$NH_3 \quad + \quad H_2O \rightleftharpoons \quad NH_4^+ + OH^-$
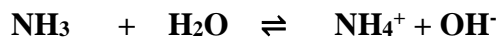
$[OH^-] = \sqrt{K_b C_b}$

$[OH^-] = \sqrt{1.8 x 10^{-5} x 0.2} \quad = \sqrt{3.6\ x\ 10^{-6}}$

$[OH^-] = 1.89 \times 10^{-3}$ $[H_3O^+] = \dfrac{Kw}{[OH-]} \qquad = \dfrac{10^{-14}}{1.89\ x 10^{-3}}$
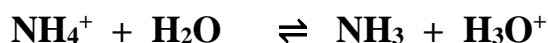
$[H_3O^+] = 5.29 \times 10^{-12}$

$pH = -\log (5.29 \times 10^{-12}) = 11.27$

Relationship between dissociation constants for conjugate acid-base pair :

$NH_3 + H_2O \qquad \rightleftharpoons NH_4^+ + OH^-$

$K_b \quad = \quad \dfrac{[NH4+][OH-\ ]}{[NH3]} \qquad\qquad$ ----------------- **(1)**

$NH_4^+ + H_2O \qquad \rightleftharpoons NH_3 + H_3O^+$
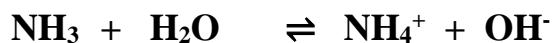
$$K_a = \frac{[NH3][H3O+]}{[NH4+]} \quad\quad \text{------------- (2)}$$

Multiplication of equation (1) with (2) gives :

$$K_b \text{ x } K_a = \frac{[NH4+][OH-\ ]}{[NH3]} \text{ x } \frac{[NH3][H3O+]}{[NH4+]}$$

$$K_a \text{ x } K_b = [\ H_3O^+\ ]\ [\ OH^-\ ]$$

but $[\ H_3O^+\ ]\ [\ OH^-\ ] = K_w$

Therefore , K_a x $K_b = K_w$

Exercise :

 Prove that for the weak acid CH₃COOH and its conjugate base CH₃COO⁻ then (K_a x K_b = K_w).

Hint: CH₃COOH₍aq₎ + H₂O₍l₎ ⇌ H₃O⁺₍aq₎+ CH₃COO⁻₍aq₎ [w.acid (K_a)]

CH₃COO⁻ ₍aq₎ + H₂O₍l₎ ⇌ H₃O⁺₍aq₎+ CH₃COOH₍aq₎ [conjugate base (K_b)]

Calculations of [H₃O⁺] , pH , [OH⁻] and pOH for strong Acids and BasesA
solution is acidic if $[H_3O^+] > [OH^-]$. and is basic if $[H_3O^+] < [OH^-]$.

Strong acids are acids that completely dissociate in water.

Strong acids, such as HNO₃, almost completely dissociated

$$HNO_3\ (aq) + \quad H_2O\ (l) \quad \rightarrow \quad\quad H_3O^+(aq) \quad + \ NO_3^-(aq)$$

    0.1 M   0.1 M
The hydronium ion [H₃O⁺]   is the acidic species in solution, and its concentration determines the acidity of the resulting solution

 pH of a strong acids:
 When a solution of 0.1 M HNO₃ dissolves in water it dissociates completely to its ions (i.e : 0.1M [H₃O⁺]) .

 $[H_3O^+] = C$ where C is the initial concentration of the strong acid

Example :
Calculate the pH of a 0.1 M solution of HCl.
HCl(aq) + H₂O(l) → H₃O⁺(aq) + Cl⁻(aq)
0.1 M   0.1 M
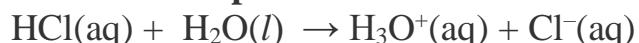
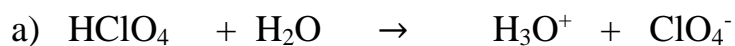$[H_3O^+] = C =$ The original concentration of the strong acid $[HCl] = 0.1$ M

$pH = - \log [H_3O^+] = - \log (0.1) = 1$

Example:

Calculate the pH of the following strong acid solutions:

(a) 1.3×10^{-2} M $HClO_4$, (b) 1.3×10^{-3} M HCl, (c) 1.3×10^{-4} M HNO_3 .

solution:

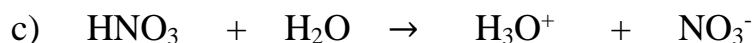a) $HClO_4$ + H_2O → H_3O^+ + ClO_4^-

   1.3×10^{-2} M 1.3×10^{-2} M

  $pH = - \log [H_3O^+] = - \log 1.3 \times 10^{-2} = 1.89$

(b) HCl + H_2O → H_3O^+ + Cl^-

   1.3×10^{-3} M 1.3×10^{-3} M

$pH = - \log [H_3O^+] = - \log 1.3 \times 10^{-3} = 2.89$

c) HNO_3 + H_2O → H_3O^+ + NO_3^-

   1.3×10^{-4} M 1.3×10^{-4} M

$pH = - \log [H_3O^+] = - \log [1.3 \times 10^{-4}] = 3.89$

Example:

Calculate the pOH and pH of the following strong base solutions:

(a) 0.05 M NaOH,   (b) 0.05 M $Ca(OH)_2$,   (c) 0.05 M $La(OH)_3$.

solution:

a) NaOH → Na^+ + OH^-

0.05 M   0.05 M

$pOH = - \log [OH^-] = - \log 5 \times 10^{-2} = 1.3$

As pH +pOH = 14

pH = 14 − 1.3 = 12.7

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

  0.05 M 2(0.05) = 0.1 M

pOH = − log [OH^-] = − log 0.1 = 1.0

pH = 14 − 1.0 = 13.0

 c) $La(OH)_3$ $\rightarrow$ La^{3+} + 3 OH^-
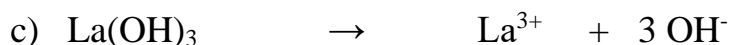
   0.05 M 3(0.05) = 0.15 M

 pOH = − log [OH^-] = − log 0.15 = 0.82

 pH = 14 − 0.82 = 13.18

Example:

 Calculate the hydrogen ion concentration [H_3O^+] for the solutions with the following pH values: (a) 0.2 (b) 3.47 (c) 8.60 .

solution:

pH = − log [H_3O^+]

log[H_3O^+] = − pH

[H_3O^+] = 10^{-PH}

 (a) [H_3O^+] = 10^{-PH} = $10^{-0.2}$ = 6.3×10^{-1} M .

 (b) [H_3O^+] = 10^{-PH} = $10^{-3.47}$ = 3.4×10^{-4} M .

 (c) [H_3O^+] = 10^{-PH} = $10^{-8.6}$ = 2.5×10^{-9} M .

Changing the pH by 1 unit changes [H_3O^+] by a factor of 10.

e.g: When the pH changes from 3 to 4, [H_3O^+] changes from 10^{-3} to 10^{-4} M.

e.g: For pH = 3 [H_3O^+] = 10^{-3} for pH=4 [H_3O^+] =10^{-4}
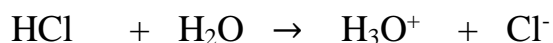
$$\frac{10^{-3}}{10^{-4}} = 10$$

Example :

Calculate the pH of a solution obtained by mixing the following volumes of the two solutions of the strong acid HCl :

a) 100 mL of (pH= 2)

b) 500 mL of (pH= 4) .

solution:

HCl   + H_2O → H_3O^+ + Cl^-

$[H_3O^+] = 10^{-PH}$

$[H_3O^+]_a = 10^{-2}$ M the concentration of the pH =2 acid

$[H_3O^+]_b = 10^{-4}$ M the concentration of the pH =4 acid

No. of moles of $[H_3O^+]_{total}$ = No. of moles of $[H_3O^+]_a$ + No. of moles of $[H_3O^+]_b$

No. of moles = Molarity (M) x Volume (liter)

V_a(liter) = $\frac{100\ (mL)}{1000}$ = 0.1 L V_b(liter) = $\frac{500\ (mL)}{1000}$ = 0.5 L

No. of moles of $[H_3O^+]_a = 10^{-2}$ M x 0.1 liter $=10^{-3}$ mole

No. of moles of $[H_3O^+]_b = 10^{-4}$ M x 0.5 liter = 5 x 10^{-5} mole

No. of moles of $[H_3O^+]_{total} = 5$ x $10^{-5} + 10^{-3} = 1.05$ x 10^{-3} moles

Molarity of the resulting solution = $\frac{No.of\ moles\ of\ [H_3O^+]_{total}}{(V_a+V_b)liter}$

Molarity of the resulting solution = $\frac{1.05\ x10^{-3}\ mole}{(0.1+0.5)liter}$ = 1.75 x 10^{-3} M

$[H_3O^+]_{total} = $ 1.75 x 10^{-3} M

pH = -log (1.75 x 10^{-3} M) = 2.75

Exercise 1: Calculate the pH of the acidic solution obtained by mixing 100 mL of (pH= 2) of HCl with 400 mL of (pH= 3) of HNO_3.

Exercise 2: Calculate the pH of the basic solution obtained by mixing 200 mL of (pH= 10) of KOH with 300 mL of (pH= 8) of NaOH.

Example :

Calculate the pH of a solution obtained by mixing 50 mL of the strong acid HCl solution (pH= 3.0) with 10 mL of the strong base KOH solution (pH= 12.0) .

Answer:

$[H_3O^+] = 10^{-PH}$

$[H_3O^+]$ for HCl solution $= 1.0 \times 10^{-3}$ M .

$[H_3O^+]$ for KOH solution $= 1.0 \times 10^{-12}$ M .

As $[OH^-] = \dfrac{K_w}{[H_3O^+]}$ then

$[OH^-]$ for KOH solution $= \dfrac{1.0x10^{-14}}{1.0x10^{-12}} = 1.0x10^{-2}$ M

m mole HCl = Molarity x volume(mL)

m mole HCl $= 1.0 \times 10^{-3}$ M x 50 mL $= 0.05$ mmol

m mole KOH $= 1.0 \times 10^{-2}$ M x 10mL $= 0.1$ mmol

| | HCl | + | KOH | → | KCl | + | H_2O |

HCl   +   KOH   →   KCl   + H_2O
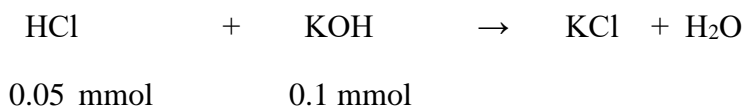
0.05 mmol   0.1 mmol

Excess of KOH = mmole KOH – mmole HCl

Excess of KOH = (0.1 – 0.05)mmol = 0.05 mmole

$[OH^-] = \dfrac{0.05\ mmol}{(50+10)mL} = 8.33$ x10^{-4}M

pOH = - log [OH^-] = - log (8.33 $\times 10^{-4}$) = 3.08

pH = 14 − 3.08 = 10.92

Exercise: Calculate the pH of the solution obtained by mixing 10 mL of 0.20 M H_2SO_4 and 20 mL of 0.30 M NaOH .
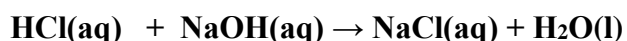
VOLUMETRIC (Titration) CALCULATIONS

No. of moles A = molarity A(mol / L) x volume(L)

No. of mmoles A = molarity A(mmol /mL) x volume(mL)

Example 1:

Calculate the molar concentration of 100 mL of NaOH solution titrated to the end point with 75.8 mL of a 0.1 M standard solution of HCl.

HCl(aq) + NaOH(aq) → NaCl(aq) + H_2O(l)

$n_a = 1$ $n_b = 1$ (stiochiometric mole ratios of acid and base)

No. of moles = Molarity (M) x volume (L)

No. of mmoles = Molarity (M) x volume (mL)

$$** \quad \frac{M_a\, V_a}{n_a} = \frac{M_b\, V_b}{n_b}$$

M_a = molarity of the acid   , V_a = volume of the acid   , n_a= No. of moles (acid)
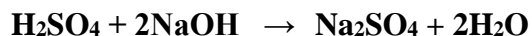
M_b = molarity of the base   , V_b = volume of the base , n_b= No. of moles (base)

$$\frac{75.8\ x\ 0.10}{1} = \frac{M_b\ x\ 100}{1}$$

$$M_b = \frac{75.8\ x\ 0.10}{100} = 0.0758\ M$$

Example 2:

20 mL of H_2SO_4 (98 g/mole) was neutralized with 25mL of 0.1M sodium hydroxide solution. The equation of reaction is

H_2SO_4 + 2NaOH → Na_2SO_4 + $2H_2O$

Calculate (i) conc. of acid in M (ii) acid content of the solution in grams.

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Solution:

$$\frac{M_a\, V_a}{n_a} = \frac{M_b\, V_b}{n_b}$$

$$\frac{M_a x\, 20.0}{1} = \frac{0.10\, x\, 25}{2}$$

Concentration of H₂SO₄ (Mₐ) = $\frac{1\, x\, 0.10\, x\, 25}{2\, x\, 20}$ **= 0.0625 M**

ii) mass of the acid in the solution(g)

mass (g) = Molarity(M) x Volume (L) x Molar mass

mass (g) = 0.0625 x (20x10⁻³) L x 98 = 0.1225 g

Example 3:

50 mL portion of HCl solution required 29.71 mL of (0.019M) Ba(OH)₂ to reach an end point with bromocresol green indicator , Calculate the molarity of HCl .

Solution:

Ba(OH)₂ + 2HCl → BaCl₂ + 2H₂O
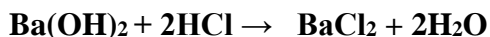
1mole   2 mole   1mole

$$\frac{M_a\, V_a}{n_a} = \frac{M_b\, V_b}{n_b}$$

$$\frac{M_{Ba(OH)2}\, x\, V_{Ba(OH)2}}{1} = \frac{M_{HCl}\, x V_{HCl}}{2}$$

$$M_{HCl} = \frac{2[M_{Ba(OH)2}\, x\, V_{Ba(OH)2\,]}}{V_{HCl}}$$

$$M_{HCl} = \frac{2[0.019 x\, 29.71]}{50} = 0.023\ M$$