

Equilibrium constant

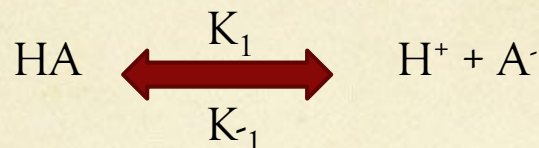
# Equilibrium constant

- Many reactions that occur in nature are reversible and do not proceed to completion.
- They come to an equilibrium where the net velocity = 0
- The velocity of forward reaction is equal to the reverse reaction.
- The position of equilibrium is described by equilibrium constant,  $K_{eq}$ .



# Equilibrium constant cont'ed

- Example: dissociation of a weak acid:



The forward velocity, is proportional to the [HA]

$$V_f \propto [\text{HA}]$$

$$V_f = k_1 [\text{HA}]$$

$K_1$  is proportional to the constant rate

$$V_r \propto [\text{H}^+] \text{ and } V_r \propto [\text{A}^-]$$

$$V_r \propto [\text{H}^+][\text{A}^-]$$


$$V_r = k_{-1} [\text{H}^+][\text{A}^-]$$

# Equilibrium constant cont'ed

At equilibrium:  $V_f = V_r$

Or  $k_1 [\text{HA}] = k_{-1} [\text{H}^+][\text{A}^-]$

$$\frac{k_1}{k_{-1}} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

  $K_{\text{eq}} = \frac{k_1}{k_{-1}}$

$$K_{\text{eq}} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$





# Acids and Bases

# Acids and Bases

- *Acid*: is a substance that can donate protons (hydrogen ions).
- *Base*: is a substance that can accept protons.
- Bronsted concept:





# Ionization of strong acids and bases

- A strong acid is a substance that ionizes 100% in aqueous solutions.



- A strong base is a substance that ionizes totally in solution to produce  $\text{OH}^-$  ions.



# Ionization of Water



$$K_{\text{eq}} = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

- Water is amphoteric it can accept and donate protons.
- In pure water 1 mole of  $[\text{H}^+]$  produces 1 mole of  $[\text{OH}^-]$ , ie.  $[\text{H}^+] = [\text{OH}^-]$
- The pH of water = 7
- Then:  $[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ M}$



# Ionization of Water cont'ed

- Thus the molarity of water:

$$M = \frac{\text{no. of moles}}{\text{volume of solution in L}}$$

In 1 liter of water = 1000g of water

$$\text{Mwt H}_2\text{O} = 18$$

No. of moles  $1000 / 18 = 55.6$  moles

$$M = 55.6 / 1 = 55.6 \text{ M}$$

Since part of water molecules is ionized

The actual conc. of the water is =  $55.6 \cdot 10^{-7}$

# Ionization of Water cont'ed

- The  $10^{-7}$  is very small it can be neglected
- Since the concentration of the water is constant thus  $K_{\text{eq}}$  of water can be written as follows:

$$K_{\text{eq}} = [\text{H}^+] [\text{OH}^-]$$

$$K_{\text{w}} = [\text{H}^+] [\text{OH}^-]$$

$$K_{\text{w}} = 10^{-7} \times 10^{-7}$$

$$K_{\text{w}} = 10^{-14}$$

$$\text{p}K_{\text{w}} = -\log 10^{-14}$$

$$\text{p}K_{\text{w}} = 14$$



# Ionization of weak acids

- Weak acids have a weak affinity towards their proton



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

The concentration of water is not considered since it is a constant

# Ionization of weak acids cont'ed



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

- Since weak acids ionize partially only thus their  $K_a$  value will always be less than one because the concentration of  $[\text{HA}]$  is always higher than the concentration of both  $[\text{H}^+]$  and  $[\text{A}^-]$

**Between weak acids the higher the  $K_a$  the stronger the acid.**



# Ionization of Weak Bases

- Weak bases have a weak affinity towards their proton.



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$$

# pH

- Although the concentration of both  $\text{OH}^-$  and  $\text{H}^+$  are very effective in reactions, it's usually the concentration of the  $[\text{H}^+]$  ions in solutions that is measured.
- The concentration of  $[\text{H}^+]$  ions in solutions is usually very low; thus it's expressed as pH.



# pH and pOH

- By definition pH is the negative logarithm of hydrogen ion activity.
- Similarly pOH is the negative logarithm of the hydroxyl ion activity.

pH:

$$\text{pH} = -\log a_{\text{H}^+}$$

pOH:

$$\text{pOH} = -\log a_{\text{OH}^-}$$

- In dilute solutions of acids and bases and in pure water, **the activities of  $H^+$  and  $OH^-$  may be considered to be the same as their concentrations.**

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

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

To calculate pH or pOH of **strong** acids or bases

- In all aqueous solutions the equilibrium for the ionization of water must be satisfied, that is,  $[H^+][OH^-] = K_w = 10^{-14}$ . Thus, if  $[H^+]$  is known, we can easily calculate  $[OH^-]$ .



Furthermore, we can derive the following relationship between pH and pOH:

Taking the logarithm:

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

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

$$-\log [H^+] = \text{pH} \quad \left| \quad -\log[OH^-] = \text{pOH} \quad \right| \quad -\log K_w = \text{p}K_w$$

$$\text{pH} + \text{pOH} = \text{p}K_w$$

$$K_w = 10^{-14}$$

$$\text{p}K_w = -\log 10^{-14} = +14$$

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

# pH of Solutions of Weak Acids

- The dissociation of a **weak monoprotic acid**, HA, yields, H<sup>+</sup> and A<sup>-</sup> in equal concentration.
- If K<sub>a</sub> and the initial concentration of HA are known, H<sup>+</sup> can be calculated easily:

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+]^2}{[HA]}$$

$$[H^+]^2 = K_a [HA]$$

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

$$\text{Log}[H^+] = \frac{1}{2} \text{Log } K_a [HA]$$



# pH of Solutions of Weak Acids Cont'ed

Multiply by -1

$$-\text{Log}[\text{H}^+] = \frac{1}{2} (-\text{Log } K_a - \text{Log} [\text{HA}])$$

$$\text{pH} = \frac{1}{2} (\text{p}K_a + \text{p} [\text{HA}])$$

→ To calculate pH of weak acids

○ A similar relationship can be derived for weak bases:

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

$$\text{pOH} = \frac{1}{2} (\text{p}K_b + \text{p} [\text{A}^-])$$

# Example 1

What are the:

1.  $\text{H}^+$  ion concentration.
2. pH.
3.  $\text{OH}^-$  ion concentration.
4. pOH.

of a 0.001 M solution of HCl?



# Answer

A. HCl is a strong inorganic acid; it is 100% ionized in dilute solution. So when 0.001 mole of HCl is introduced into a litre of H<sub>2</sub>O, it immediately dissociates into 0.001 M H<sup>+</sup> and 0.001 M Cl<sup>-</sup>. The ionization of water is neglected.

B.  $\text{pH} = -\log[\text{H}^+]$

$$= -\log 10^{-3}$$

$$= -(-3) = +3$$

$$C. [H^+][OH^-] = K_w \longrightarrow [OH^-] = K_w / [H^+]$$

$$[OH^-] = (1 \times 10^{-14}) / (1 \times 10^{-3})$$

$$[OH^-] = 1 \times 10^{-11}$$

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

$$= -\log(10^{-11})$$

$$= -(-11)$$

$$pOH = 11$$

OR:



$$pH + pOH = 14$$

$$pOH = 14 - pH$$

$$pOH = 14 - 3 = 11$$



# Example 2

○ What are the:

A.  $[\text{H}^+]$ .

B.  $[\text{OH}^-]$ .

C. pH.

D. pOH.

Of a 0.002 M solution of  $\text{HNO}_3$  ?

# Answer

A.  $\text{HNO}_3$  is a strong inorganic acid.

$$[\text{H}^+] = 0.002 \text{ M} = 2 \times 10^{-3} \text{ M}$$

B.  $[\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$

$$[\text{OH}^-] = (1 \times 10^{-14}) / (2 \times 10^{-3}) = 0.5 \times 10^{-11}$$

$$[\text{OH}^-] = 5 \times 10^{-12} \text{ M}$$

C.  $\text{pH} = \log 1/[\text{H}^+]$

$$= \log 0.5 \times 10^3$$

$$= \log 5 \times 10^2 = 0.699 + 2$$

$$\text{pH} = 2.699$$

D.  $\text{pH} + \text{pOH} = 14$

$$\text{pOH} = 14.000 - 2.699 = 11.301$$



# Example 3

- What is the concentration of  $\text{HNO}_3$  in a solution that has a pH of 3.4?

$$[\text{H}^+] = \text{antilog } -\text{pH}$$

$$= 10^{-\text{pH}}$$

$$= 10^{-3.4}$$

$$[\text{H}^+] = 3.98 \times 10^{-4}$$

# Example 4


- How many: (a)  $\text{H}^+$  ions , (b)  $\text{OH}^-$  ions present in 250 ml of a solution of a pH 3?

$$\text{pH} = 3$$

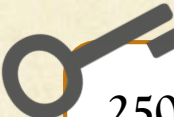
$$[\text{H}^+] = 10^{-3} \text{ M (g/L)}$$

$$1 \text{ g/L} = 6.023 \times 10^{23} \text{ ion/L}$$

$$10^{-3} \text{ g/L} = ? \text{ ion/L}$$


$$\frac{6.023 \times 10^{20}}{4}$$

$$= 1.506 \times 10^{20} \text{ ion/250 ml}$$



250 ml is  $1/4^{\text{th}}$  1000ml  
(1L)



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

$$3 + \text{pOH} = 14$$

$$\text{pOH} = 14 - 3 = 11$$

$$[\text{OH}^-] = 10^{-11}$$

$$1 \text{ g/L} = 6.023 \times 10^{23} \text{ ion/L}$$

$$10^{-11} \text{ g/L} = ? \text{ ion/L}$$

$$\begin{array}{c} \longrightarrow \frac{6.023 \times 10^{12}}{4} \end{array}$$

$$= 1.506 \times 10^{12} \text{ ion/250 ml}$$

# Neutralization of strong acids and bases

To answer any question related to neutralization , follow the steps below:

1-Know that to neutralize an acid or a base and form salt +water (pH=7) :

no. of moles /equivalents of  $H^+$  = no. of moles /equivalents of  $OH^-$

2- Choose either moles /equivalents depending on the (n) if it is for both acid and base:

- same  $\rightarrow$  then moles
- Different  $\rightarrow$  then equivalents

3- finally, calculate according to what is ordered in the Q.



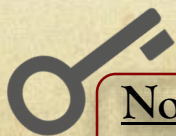
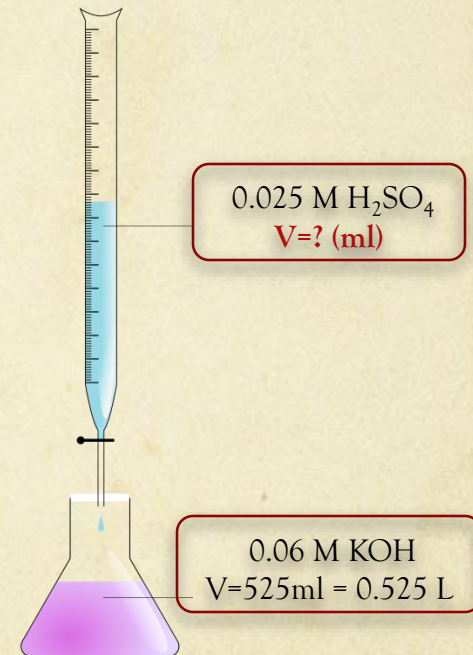
# Example 1

- 1- How many ml of 0.025 M  $\text{H}_2\text{SO}_4$  are required to neutralize exactly 525 ml of 0.06 M KOH?
- 2- What is the pH of the neutralized solution?

No. of equivalents of  $\text{H}^+$  required = no. of equivalents of  $\text{OH}^-$  present

$$V \text{ (in L)}_{\text{acid}} \times N_{\text{acid}} = \text{no. of equivalents}$$

$$V \text{ (in L)}_{\text{acid}} \times N_{\text{acid}} = V \text{ (in L)}_{\text{base}} \times N_{\text{base}}$$



**Note :** No of equivalents is calculated instead of moles , since  $\text{H}_2\text{SO}_4$  release 2  $\text{H}^+$  and KOH release 1  $\text{OH}^-$  (i.e. different (n) number)

# Cont'ed

$$N_{\text{acid}} = M \times n = 0.025 \text{ M} \times 2 = 0.05 \text{ N}$$

$$N_{\text{base}} = M \times n = 0.06 \text{ M} \times 1 = 0.06 \text{ N}$$

$$V (\text{in L})_{\text{acid}} \times 0.05 = 0.525 \times 0.06$$

$$V (\text{in L})_{\text{acid}} = (0.525 \times 0.06) / 0.05$$

$$= 0.63 \text{ L} = 630 \text{ ml}$$

- The neutralized solution contains only  $\text{K}_2\text{SO}_4$  “a salt” of a strong acid and strong base has no effect on pH

$$\text{pH} = 7$$



# Example 2

- How many ml of 0.05 N HCl are required to neutralize exactly 8g of NaOH?

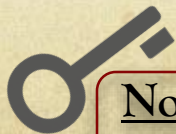
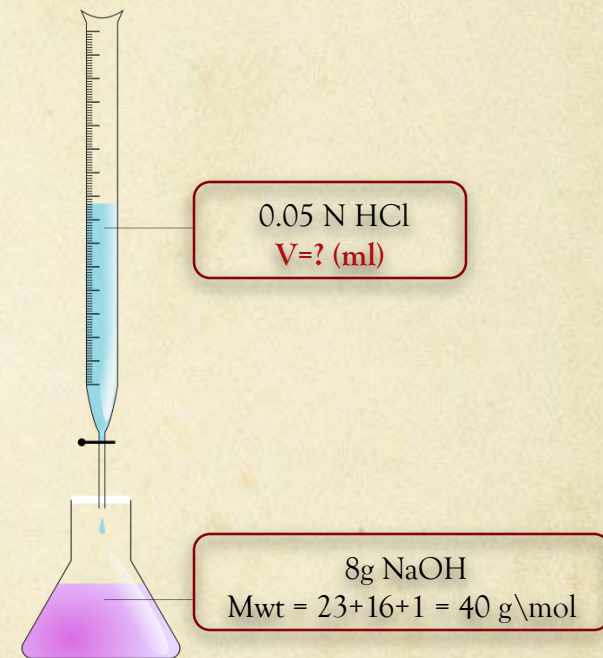
At the equivalent point:

The no. of moles  $H^+$  added = no. of moles  $OH^-$  present

$V \text{ (in L)}_{\text{acid}} \times M_{\text{acid}} = \text{no. of moles of } H^+ \text{ added}$

$M = N/n \rightarrow 0.05/1 = 0.05M$

$\text{wt}_{\text{NaOH}} / \text{Mwt}_{\text{NaOH}} = \text{no. of moles of } OH^- \text{ present}$



**Note :** No of moles is calculated, since HCl release 1  $H^+$  and NaOH release 1  $OH^-$  (i.e. same (n) number)

# Cont'ed

$$V \text{ (in L)}_{\text{HCl}} \times N_{\text{HCl}} = \text{wt}_{\text{NaOH}} / \text{Mwt}_{\text{NaOH}}$$

$$V \text{ (in L)}_{\text{HCl}} \times 0.05 = 8 / 40$$

$$V \text{ (in L)}_{\text{HCl}} = 0.2 / 0.05 = 4 \text{ L or } 4000 \text{ ml}$$



# Relationship between $K_a$ and $K_b$ for weak acids and bases

- Weak acids (HA) dissociates in water:



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

- If we start with conjugated base  $\text{A}^-$  and dissolve it water, it ionizes as a typical base:



$$K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

$$[\text{H}^+] = \frac{[\text{HA}] K_a}{[\text{A}^-]}$$

$$[\text{OH}^-] = \frac{[\text{A}^-] K_b}{[\text{HA}]}$$

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

$$\frac{\cancel{[\text{HA}]} K_a}{\cancel{[\text{A}^-]}} \times \frac{\cancel{[\text{A}^-]} K_b}{\cancel{[\text{HA}]}} = K_w$$

$$K_a \times K_b = K_w$$

$$\text{Log } K_a + \text{Log } K_b = \text{Log } K_w$$

$$-\text{Log } K_a - \text{Log } K_b = -\text{Log } K_w$$

$$\text{p}K_a + \text{p}K_b = \text{p}K_w$$

$$14 = \text{p}K_w$$

$$\text{p}K_a + \text{p}K_b = 14$$

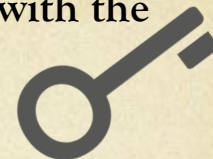


# Example

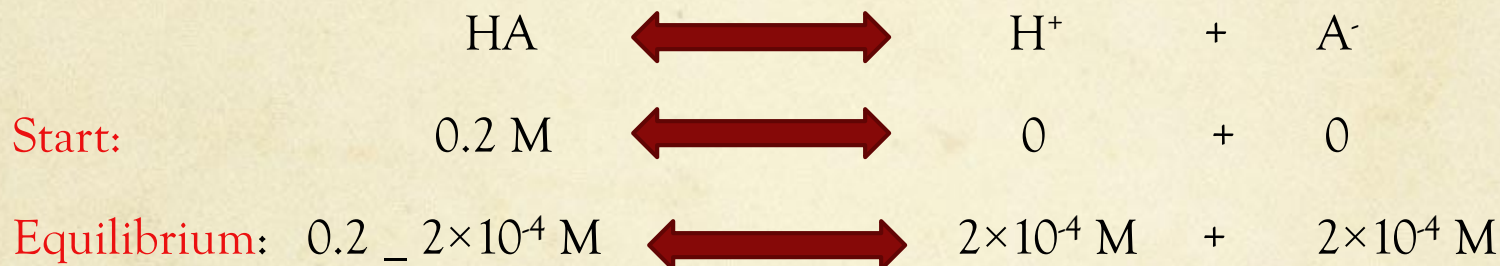
- A weak acid HA, is 0.1% ionized (dissociated) in a 0.2 M solution.
  - a) What is the equilibrium constant of the acid  $K_a$ ?
  - b) What is the pH of the solution?
  - c) How much weaker is the active acidity of the HA solution compared to a 0.2 M solution of HCl?
  - d) How many ml of 0.1 N KOH would be required to neutralize completely 500 ml of 0.2 M HA solution?

# Answer

A) First, calculate the dissociation fraction by multiplying the starting conc (0.2M) with the dissociation% to find the conc. of both ions at equilibrium.



The dissociation fraction =  $(0.1/100) \times 0.2 = 2 \times 10^{-4} \text{ M}$



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(2 \times 10^{-4}) \times (2 \times 10^{-4})}{0.2 - 2 \times 10^{-4}}$$

When the amount of HA that has dissociated is small, 10% or less the  $K_a$  is simplified by ignoring the subtraction from [HA]



$$K_a = ((2 \times 10^{-4}) \times (2 \times 10^{-4})) / 0.2$$

$$K_a = 4 \times 10^{-8} / 2 \times 10^{-1}$$

$$K_a = 2 \times 10^{-7}$$

B)  $\text{pH} = -\text{Log} [\text{H}^+]$

$$\text{pH} = -\text{Log} 2 \times 10^{-4}$$

$$\text{pH} = 3.7$$

C) A 0.2 M HCl would be 100% ionized and yields 0.2 M  $\text{H}^+$

$$\text{pH} = -\text{Log} [\text{H}^+]$$

$$\text{pH} = -\text{Log} 0.2$$

$$\text{pH} = 0.7$$

The weak acid is 3 pH units less than HCl but this is a log scale, actually HA is 1000 times weaker than HCL

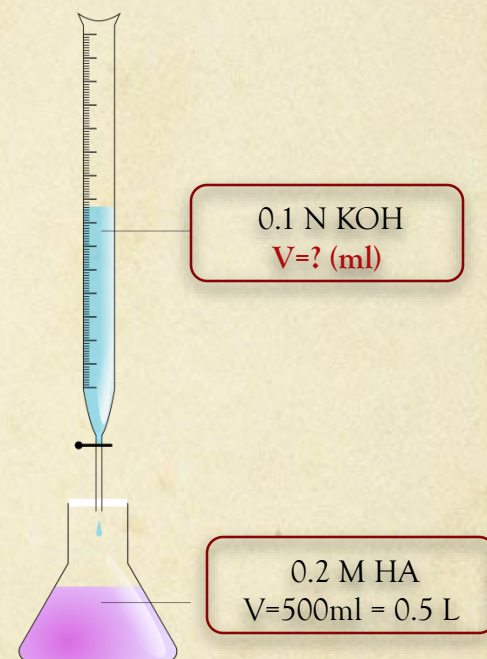
D) No. of moles of  $\text{OH}^-$  required = no. of moles of  $\text{H}^+$  present

$$V \text{ (in L)}_{\text{base}} \times M_{\text{base}} = V \text{ (in L)}_{\text{acid}} \times M_{\text{acid}}$$

$$N_{\text{base}} = M_{\text{base}} \quad (n=1)$$

$$V \text{ (in L)}_{\text{base}} \times 0.1 = 0.5 \times 0.2$$

$$V_{\text{base}} = 0.1 / 0.1 = 1 \text{ liter} = 1000\text{ml}$$



**Note :** No of moles is calculated, since HA release 1  $\text{H}^+$  and KOH release 1  $\text{OH}^-$  (i.e. same (n) number)