

Hydrolysis: CATION & ANION REACTIONS

1)

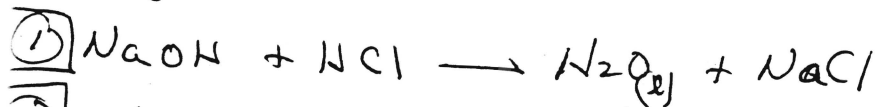
EQUATION WITH TWO (2) EQUILIBRIA

① BETWEEN H_2O & ITS IONS

② BETWEEN ION OF WEAK ACIDS (BASES)

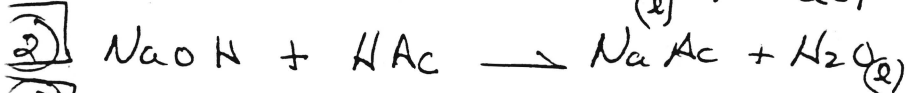
THE EXTENT DEPENDS ON STRENGTH OF THE ACID AND ITS CONJUGATE BASE (RE: BRONSTED LOWRY)

Examples:

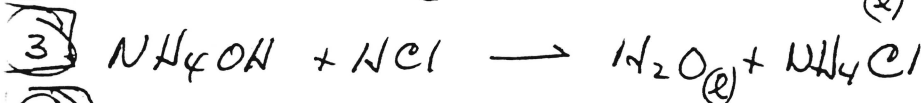


AT END POINT

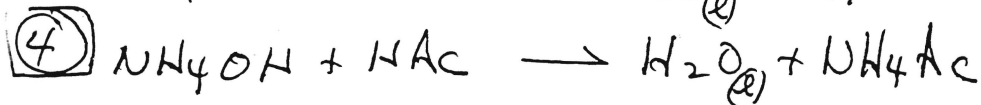
$pH = 7$



$pH \approx 7 (> 7)$



$pH \approx 7 (< 7)$



see explanation

Examples:

① A STRONG ACID - STRONG BASE REACTION — NO INTERACTION OF IONS WITH H_2O .

② A WEAK ACID

SINCE EQUATION ② goes to completion due to WEAK ELECTROLYTE (H_2O) THEN IONS ARE Na^+ AND Ac^- AND SINCE Na^+ APPARENTLY DID NOT REACT WITH WATER IN EQUATION ①

WE CAN ASSUME IT DOES NOT REACT WITH THIS ARGUMENT ALSO.



AND THE HYDROLYSIS CONSTANT K_h IS

① $K_h = \frac{[HAc][OH^-]}{[Ac^-]} = \frac{x^2}{c-x} \leftarrow \text{small} \quad (c = \text{SOME CONCENTRATION})$

SINCE K_w HAS BEEN DEFINED AS

② $K_w = [H^+][OH^-]$ THEN THIS REACTION WRITTEN IN TERMS OF $[OH^-]$ IS,

③ $[OH^-] = \frac{K_w}{[H^+]}$ SUBSTITUTING INTO EQUATION ① GIVES

④ $K_h = \frac{[HAC] K_w}{[Ac^-][H^+]}$ AND, OBVIOUSLY, $\frac{[HAC]}{[Ac^-][H^+]} = \frac{1}{K_a}$

and EQUATION ④ IS

⑤ $K_h = \frac{K_w}{K_a}$ FOR WEAK ACID REACTIONS

IN OUR EXAMPLE: $Ac^-(aq) + H_2O(l) \rightleftharpoons HAC + OH^-$, THE K_h

IS $K_h = \frac{K_w}{K_a} = \frac{[HAC][OH^-]}{[Ac^-]}$ AND CLEARLY ONLY $[OH^-]$ MUST BE FOUND.

EXAMPLE ③ A WEAK BASE

SINCE EQUATION ③ GOES TO COMPLETION (SAME ARGUMENT) AS ② THE IONS ARE $NH_4^+ + Cl^-$ (Cl^- SAME ARGUMENT)

THEN: $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$

AND THE HYDROLYSIS CONSTANT, K_h IS

① $K_h = \frac{[NH_3][H^+]}{[NH_4^+]}$ ($[H^+] = [H_3O^+]$)

AND SINCE K_w HAS BEEN DEFINED AS 3

② $K_w = [H^+][OH^-]$ AND THIS REACTION WRITTEN IN TERM OF $[H^+]$ IS,

③ $[H^+] = \frac{K_w}{[OH^-]}$ SUBSTITUTING INTO EQUATION ② GIVES

④ $K_h = \frac{[NH_3] K_w}{[NH_4^+][OH^-]}$ AND, OBVIOUSLY, $\frac{[NH_3]}{[NH_4^+][OH^-]} = \frac{1}{K_b}$

AND EQUATION ④ IS

⑤ $K_h = \frac{K_w}{K_b}$ FOR WEAK BASE REACTIONS.

IN OUR EXAMPLE: $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$

THE K_h IS $K_h = \frac{K_w}{K_b} = \frac{[NH_3][H^+]}{[NH_4^+]}$ AND CLEARLY ONLY

$[H^+]$ MUST BE FOUND

SOME K_b 's FOR BASES

$$NH_4OH = 1.79 \times 10^{-5}$$

$$Ba(OH)_2 = 5.0 \times 10^{-11}$$

$$Cu(OH)_2 = 4.0 \times 10^{-2}$$

$$Pb(OH)_2 = 9.6 \times 10^{-4}$$

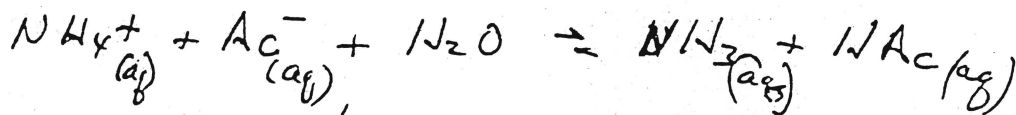
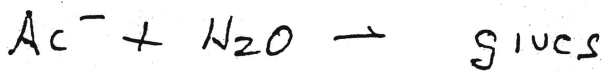
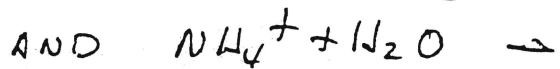
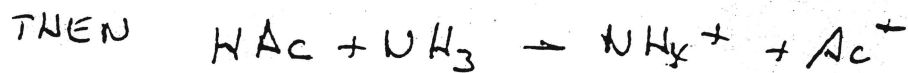
$$AgOH = 1.01 \times 10^{-4}$$

$$Zn(OH)_2 = 4.4 \times 10^{-5}$$

QUESTION (4) WEAK ACID AND WEAK BASE

4

IONS ARE $\text{NH}_4^+ + \text{Ac}^-$ HOWEVER $\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{NH}_3$



AND THE HYDROLYSIS CONSTANT K_h IS

$$K_h = \frac{[\text{NH}_3][\text{HAc}]}{[\text{NH}_4^+][\text{Ac}^-]} \left[\text{multiply } \times \frac{K_w}{K_w} \text{ or } \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}^+][\text{OH}^-]} \right]$$

Sectioning we have

$$K_h = \frac{[\text{NH}_3]}{[\text{NH}_4^+][\text{OH}^-]} \left(\frac{1}{K_b} \right) \frac{[\text{HAc}]}{[\text{Ac}^-][\text{H}^+]} \left(\frac{1}{K_a} \right) [\text{H}^+][\text{OH}^-] = K_w$$

then Equation (2) becomes

$$K_h = \frac{K_w}{K_a K_b} ; \text{ However, we can further}$$

simplify this if we assume $[\text{NH}_3][\text{HAc}] = [\text{NH}_4^+][\text{Ac}^-]$
(from Equation above) Then

$$K_h = \frac{K_w}{K_a K_b} = \frac{[\text{NH}_3][\text{HAc}]}{[\text{NH}_4^+][\text{Ac}^-]} \text{ and}$$

$$\frac{K_w}{K_a K_b} = \frac{[\text{HAc}]^2}{[\text{concentration}]^2} \text{ or } \frac{[\text{HA}]^2}{c^2}$$

THEN EQUATION (5) REWRITTEN IN TERMS OF HAc IS (6)

$$\text{HAc} = c \sqrt{\frac{K_w}{K_a K_b}} \quad \text{AND OBVIOUSLY } \text{HAc ALSO} = \frac{[\text{H}^+][\text{Ac}^-]}{K_a}$$

EQUATION (6) THEN IS WRITTEN

$$(7) \quad \frac{[\text{H}^+][\text{Ac}^-]}{K_a} = c \sqrt{\frac{K_w}{K_a K_b}} \quad \text{AND } [\text{Ac}^-] = c \quad \text{OBVIOUSLY}$$

$$(8) \quad \frac{[\text{H}^+][c]}{K_a} = c \sqrt{\frac{K_w}{K_a K_b}} \quad \text{AND } \div \text{ BY } \frac{1}{c} \text{ GIVES}$$

$$(9) \quad \frac{[\text{H}^+]}{K_a} = \sqrt{\frac{K_w}{K_a K_b}} \quad \text{AND } (9) \text{ IS WRITTEN AS}$$

$$(10) \quad [\text{H}^+] = K_a \sqrt{\frac{K_w}{K_a K_b}} \quad \text{AND } \left(\frac{K_a}{\sqrt{K_a}} = \sqrt{K_a} \right) \text{ CLEARLY}$$

$$(11) \quad [\text{H}^+] = \sqrt{\frac{K_w K_a}{K_b}}, \quad \text{IT; HOWEVER,}$$

BECOMES OBVIOUS TO THE OBSERVER THEN THAT IN A WEAK ACID-BASE SYSTEM LIKE EXAMPLE (4) THE $[\text{H}^+]$ IS INDEPENDENT OF THE CONCENTRATION OF THE SOLUTIONS INVOLVED IN THIS TYPE OF REACTIONS

Buffer Solutions

Common ion to control acidity

Ex 1 1M HAc $\text{pH} = 2.4$

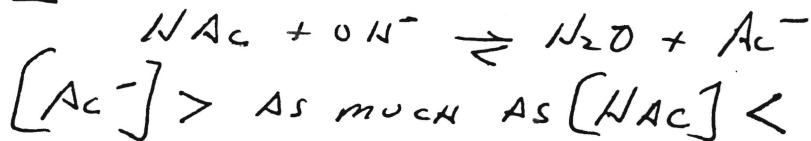
Ex 2. add 1 mole NaAc to 1M HAc $\text{pH} = 4.8$

Ex 3 calc pH of sol'n containing 5.7% NaAc / 0.1M HAc

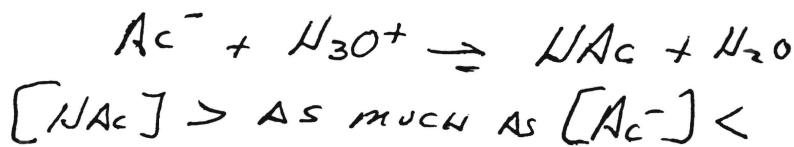
To a sol'n containing - WEAK ACID & SOME SALT OF THE ACID
WEAK BASE & SOME SALT OF THE BASE

CAN ADD STRONG ACID OR BASE

STRONG BASE to HAc & NaAc



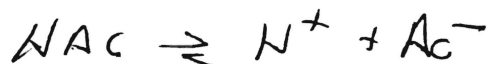
STRONG ACID



CHANGE IN RATIO $\frac{[\text{Ac}^-]}{[\text{HAc}]}$

Example: if 2ml of 1.0M sol'n of HCl is ADDED to 100ml of a solution that is 0.2M NaAc & 0.2M HAc, WHAT ΔpH will occur (Assume 100ml Vol)

① find pH of sol'n



$$K_a = \frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}]}$$

$$[\text{HAc}] = 0.2 \text{ M}$$
$$[\text{Ac}^-] = 0.2 \text{ M}$$

Then $1.8 \times 10^{-5} = \frac{[\text{H}^+][0.2]}{[0.2]} = 1.8 \times 10^{-5}$

$\text{pH} = 4.74$ (INITIAL)

② Find pH when Acid is Added

Find $[Ac^-]$ in 100ml that is changed to HAc

[Assume HCl converts = quantity of Ac^-]

$$M_A V_A = M_{Ac^-} V_{Ac^-}$$

$$1 \times 2ml = 0.2 V$$

$$V = 10ml$$

Then 10ml of Ac^- converted to HAc i.e. $1/10$ th amount

$$\text{Now } Ac^- \text{ left} = 0.2 \times 9/10 = 0.18M$$

$$\text{HAc increased} = 0.2 \times 1/10 = 0.22M$$

SUBSTITUTE INTO EQ

$$K_a = \frac{[H^+][Ac^-]}{[HAc]}$$

$$1.8 \times 10^{-5} = \frac{[H^+][0.18]}{[0.22]}$$

$$[H^+] = \frac{1.8 \times 10^{-5} \times 0.22}{0.18} = 2.2 \times 10^{-5}$$

$$pH = 4.66$$

$$\text{Then } \Delta pH = 4.74 - 4.66 = 0.08 \text{ pH units}$$

AND ADDITION OF APPRECIABLE AMOUNT OF STRONG ACID ONLY CHANGES pH SMALL AMOUNT.

ANOTHER EXAMPLE

ASSUME 1L OF ACID pH 4.85 (NOT BUFFERED)

ADD 1ml 1M HCl

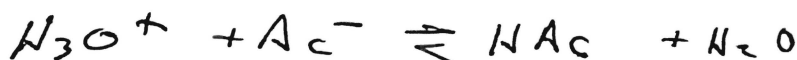
$$\text{pH} = 4.85 \quad [\text{H}^+] = 1.41 \times 10^{-5} \quad \text{ADD } .001 \text{ M HCl}$$

Then .001 M H^+

$$\text{ORIGINAL } 1.41 \times 10^{-5} + .001 = 1.014 \times 10^{-3}$$

$$\text{pH} = 2.99 \quad (\text{ALMOST } 2 \text{ UNITS OF pH (200X)})$$

HOWEVER LOOK AT 4% HAc & .5% NaAc

ALL ACID REACTS WITH $[\text{Ac}^-]$ 

$$K = \frac{[\text{HAc}]}{[\text{H}^+][\text{Ac}^-]} = \frac{\text{Reverse}}{K_a} = \frac{1}{K_a} = \frac{1}{1.8 \times 10^{-5}} = 5.7 \times 10^4$$

LARGE K. THEN H^+ TO HAcTHEN $[\text{H}^+] = .001 \text{ M}$ TO HAc NOW .401 M

$$\text{DECREASE } [\text{Ac}^-] = .500 - .001 = .499$$

$$\text{H}^+ = \frac{0.401}{0.499} \times 1.8 \times 10^{-5} = 1.415 \times 10^{-5}$$

$$\text{pH} = 5 - 0.151 = 4.849$$

ONLY .001 pH UNIT Δ RATHER THAN 2 UNITS