General & Organic Chemistry

Lecture 9

L9: Acids & Bases

12/NOV/2024

General & Organic Chemistry , ,Ch14 , Acids & Bases

* Models of Acids & Bases :

Arrhenius : Acids produce H^+ ions in solution
Bases produce OH^- ions in solution

but this definition was NOT enough
bc we have some bases & acids that could be assigned without having to have an aqueous solution

So the modified definition was according to bronsted - Lowry : where
Acids are Proton (H^+) $\boxed{\text{donors}}$
Bases are Proton (H^+) $\boxed{\text{acceptors}}$

ex: $\underset{\substack{\text{Acid} \\ \text{(donor of } H^+\text{)}}}{HCl} + \underset{\substack{\text{base} \\ \text{(Acceptor of } H^+\text{)}}}{H_2O} \rightleftharpoons Cl^- + H_3O^+$

Acid in water

(HA)

The general reaction for an acid is represented by:

Conjugate pair

Conjugate pair

$$\underset{\text{Acid}}{HA} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{Conjugate Acid}}{H_3O^+} + \underset{\text{Conjugate base}}{A^-}$$

→ this reaction is in equilibrium so the acid used is a <u>weak</u> acid. if it was strong... the reaction would go in one direction

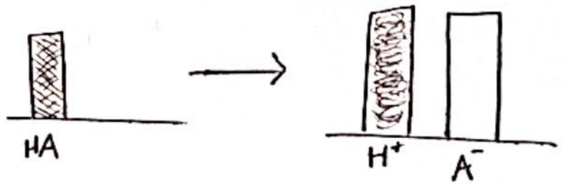
Conjugate base: it is all that is remaining of the acid after losing its Proton

Conjugate acid: formed when the Proton is transferred to the base

Strong Acid:

- Dissociate <u>Completely</u>
- ionization equilibrium will lie to the right (more <u>Products</u>)
- it yields and Produces a weak conjugate base
- <u>High Ka</u>

strong:



we notice there is nothing left of the original acid (HA)

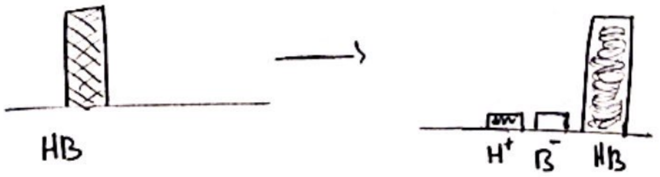
* bc the conj base is weak (very weak) it can't react back to make the acid again with the conj acid that is also <u>weak</u>

The strength of acid depends on the <u>Ka</u>. The higher the Ka the stronger the acid (means more dissociation)

weak Acid:

- <u>Partially</u> dissoiates
- ionization equilibrium Lies to the left (more <u>reactants</u>)
- it yields and Produces a strong base (the weaker the acid the stronger the conjugate base)
- <u>Low Ka</u>

weak:



* bc the conj base and acids are strong here (stronger than the acid and reacted base) they react forming the original acid back again over & over

still big amounts of acid <u>undissociated</u>

✱ Various ways to describe acid strength:

Property	strong acid	weak acid
Ka value	high Ka value	low Ka value
Position of (ionization) equilibrium	far to the <u>right</u>	far to the <u>left</u>
Equilibrium $[H^+]$ compared with the original concentration of HA	$[H^+] \approx [HA]$	$[H^+] \ll [HA]$
strength of conj base compared with that of water	A^- much <u>weaker</u> than H_2O	A^- much <u>stronger</u> than H_2O

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water as an <u>acid</u> & a <u>base</u>

- water is <u>amphoteric</u>
  - ↳ behaves as <u>either</u> acid or base depended on <u>what it reacts with</u>
    - ex: if reacted with an acid it will act as a base and if reacted with a base it reacts as an acid

at 25°c:

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

$$H_2O + H_2O \rightleftharpoons OH^- + H_3O^+$$

$$\frac{K'}{1} = \frac{[OH^-][H_3O^+]}{[H_2O]}$$

↳ constant bc liquid

① $K'[H_2O] = K_w = [OH^-][H_3O^+]$

↳ this is considered as constant value bc the number of moles in 1 dm³ of water present is always the same bc the concentrations of $[OH^-]$ & $[H_3O^+]$ are effectively very small compared to it that we don't count them ②

③ also a constant value

and No matter what the solution contains, the product of $[H^+]$ & $[OH^-]$ must always equal <u>1.0×10^{-14}</u> at 25°c

④ and constant × constant = constant

K_a $[H_2O]$ $[H^+][OH^-]$

⑤ K' only changes with <u>temperature</u> and at 25°c or 298 K

$K_w = 1 \times 10^{-14} = [OH^-][H_3O^+]$

* There are three Possible situations for Solutions:

* $[H^+] = [OH^-]$; neutral Solution
* $[H^+] > [OH^-]$; Acidic Solution
* $[H^+] < [OH^-]$; Basic Solution

Concept check:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

the equilibrium constant expression:

$$K = \frac{[H_3O^+][A^-]}{[HA]}$$

- if the equilibrium lies to the right, the value for Ka is Large (Ka > 1)

- if to the left, Ka is Small (Ka < 1)

* in the above reaction ($HA_{(aq)} + H_2O_{(L)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$)
  - if water was a better base than (A^-) that mens that H_2O is strong compared to it therefore dissociate more giving more Products than staying as reactants and that A^- is too weak to re-react again with H_3O^+ to make water and HA again
    - this also means that (HA) is a strong acid in comparison bc it gave a weak conj base
    - this also means that the value of Ka for HA is greater than 1

Concept Check :

Considering a reaction :

1.0 M solution of HCl

also use the earlier HA reaction

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

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

order the following from Strongest to weakest (bases)

- we know that HCl is a very strong acid (high Ka) so it will Produce a very very weak base

therefore H_2O is stronger than Cl^-

- and from the second reaction since its a weak acid reacting, it will produce a stronger base to be able to form again therefore A^- should be stronger than H_2O

So : $H_2O > Cl^-$

$A^- > H_2O$ $\Longrightarrow$ $A^- > H_2O > Cl^-$

Concept check : Considering the solution of NaA where A^- is the anion of the weak acid HA

$$\overset{\text{spectator ion}}{\underset{\text{base}}{NaA}} + \underset{\text{acid}}{H_2O} \rightleftharpoons AH^+ + NaOH$$

⇓ Could be written as :

$$\underset{\text{strong conj base}}{A^-} + H_2O \rightleftharpoons OH^- + \underset{\text{weak acid}}{HA}$$

~~so the equilibrium will lie to the right bc A⁻ being strong means its dissociates [illegible]~~

- while yes you might think that bc A^- is a strong base in comparisen bc it came from a weak acid that would mean it dissociates more therefore you think the equilibrium is to the right, but when looked at, NaOH or OH^- is an extrenly strong bases therefore it force the reaction with HA even if it was a weak acid and equilibrim lies to the left

and the value of $K_b < 1$

then is more reactants

and still A^- is a weak base compared to OH^-

Concept check:

Acetic acid ($HC_2H_3O_2$) & HCN Are both weak acids and acetic acid is stronger than HCN

if $HC_2H_3O_2 > HCN$

this means $C_2H_3O_2^- < CN^-$

organise the bases

H_2O
Cl^-
CN^-
$C_2H_3O_2^-$
weakest to strongest

and from the reaction:

$$HCl + H_2O \longrightarrow Cl^- + H_3O^+$$

Cl^- is very very weak
$H_2O > Cl^-$ as a base

So: $Cl^- < H_2O < C_2H_3O_2^- < CN^-$

Concept check:

Discuss whether the value of K for the reaction is: >1 or <1 or =1

$$HCN_{(aq)} + F^-_{(aq)} \rightleftarrows CN^-_{(aq)} + HF_{(aq)}$$

$Ka_{HCN} = 6.2 \times 10^{-10}$
$Ka_{HF} = 7.2 \times 10^{-4}$

from what we know, the higher the Ka, the stronger the acid is

and $Ka_{HCN} < K_{a\,HF}$

therefore $HCN < HF$

and $CN^- > F^-$

bc the stronger the acid the weaker the conj base is

this all mens that bc HCN is weaker than HF it dissociates less and HF dissociates more therefore there is more reactants then Products

so the K value would be $\underline{<1}$

which is: [illegible]

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to find the K values:

$$\left(HCN + F^- \rightleftharpoons CN^- + HF \right)$$

first we Put the Ka's and each acids reaction

$K_a HCN = 6.2 \times 10^{-10}$ $HCN + H_2O \rightleftharpoons CN^- + H_3O^+$

$K_a HF = 7.2 \times 10^{-7}$ $HF + H_2O \rightleftharpoons F^- + H_3O^+$

to write the overall reaction (the one in the beginning) which is $\underline{HCN} + F^- \rightleftharpoons CN^- + \underline{HF}$

we have HCN on this side so we write its reaction

here we have the HF on the opposite side so we need to flip its reaction

$$HCN + \cancel{H_2O} \rightleftharpoons CN^- + \cancel{H_3O^+}$$

$$F^- + \cancel{H_3O^+} \rightleftharpoons HF + \cancel{H_2O}$$

$$HCN + F^- \rightleftharpoons CN^- + HF$$

and when we flip a reaction that means its Ka value is $\frac{1}{K_a}$

so $K_a = \frac{1}{K_{a\,HF}}$

and the K value is $\frac{K_{a\,HCN}}{K_a HF}$

So $\frac{6.2 \times 10^{-10}}{7.2 \times 10^{-4}} = 8.6 \times 10^{-7}$

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or we can simply Put the concentration in relation to Ka

$$K_a HCN = \frac{[CN^-][H_3O^+]}{[HCN]}$$

$$K_a HF = \frac{[F^-][H_3O^+]}{[HF]}$$

$$K = \frac{[CN^-][HF]}{[HCN][F^-]}$$ but the H_3O^+ is missing so $\times \frac{H_3O^+}{H_3O^+}$

$\Rightarrow$ ★

★ $\Rightarrow K = \underbrace{\frac{[CN^-][H_3O^+]}{[HCN]}}_{K_a HCN} \underbrace{\frac{[HF]}{[HF][H_3O^+]}}_{\frac{1}{K_{a\,HF}}}$

so $\frac{K_a HCN}{K_a HF} = 8.6 \times 10^{-7}$

The pH scale

another way to express acid strength

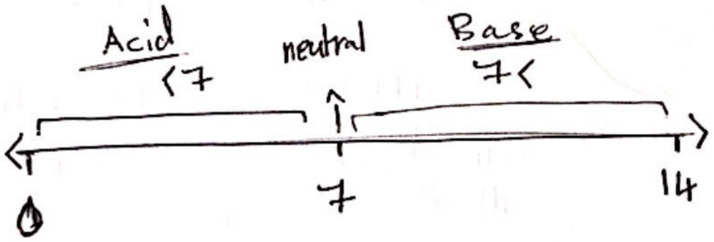
$pH = -\log[H^+]$

it changes by 1 for every Power of 10 change in $[H^+]$

pH decreases as $[H^+]$ increases

(a rule of sigfigs: the number of decimal places in the log is equal to number of sigfigs in the original number)

pH Range:



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the pH of a solution is 5.85 what is the $[H^+]$

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

$5.85 = -\log[H^+]$

$[H^+] = 10^{-5.85} = 1.4 \times 10^{-6}\ M$

pH & pOH

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

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

$pK_w = pH + pOH = 14.00$

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* Thinking about Acid-Base Problems:

- what are the major species in solution
  - Acids?
  - Bases?
  - Conjugates?
- what is the dominant reaction that will take place
  - is it an equilibrium reaction or a reaction that will go essentially to completion
    - Strong Acid/Base?
    - Weak Acid/Base?
  - react all major species until you are left with an equilibrium reaction

Solve for pH if needed

Concept check:

Considering (aq) solution of 2.0×10^{-3} M HCl

- what are the major species in solution? $HCl + H_2O \rightleftarrows Cl^- + H_3O^+$

H_2O, Cl^-, H_3O^+ bc the HCl dissociates completely so none is left

what is the pH??

$$\underset{\text{b4 dissociation}}{[HCl]} = \underset{\text{after dissociation}}{[Cl^-] = [H_3O^+]}$$

so $[H_3O^+]$ or $[H^+] = 2.0 \times 10^{-3}$ M

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

$= 3 - \log(2.0) = 2.70$

Concept check :

Calculate the pH of a 1.5×10^{-11} M Solution of HCl

* for this question, if solved directly, we find that the value of pH will be 10.82 but it doesn't really make any sense since we added a Strong Acid (HCl) and such pH of 10.82 is Basic

this mens that the H^+ concentration coming from the acid is much smaller than it for the water bc the $[H^+]$ of water is 10^{-7} mening 10 thousand times more than 1.5×10^{-11} almost so it can be neglected bc it's such a small value

and for that we take the $[H^+]$ of water as an answer
so pH = 7.00

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but for example if we added a 10^{-8} M solution of HCl it is still smaller of that of water of $[H^+]$ but it cannot be nglected be the diffrence is only a 10 times diffrence unlike the past concept check of 10000 times the diffrence and here we would have to add the $[H^+]$ of water and $[H^+]$ of the acid and calculate the pH and you will find a small yet not neglectable diffrence

Concept check :

Calculate the pH of a 1.5×10^{-2} Solution of $\boxed{HNO_3}$ → strong acid

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

$pH = -\log[1.5 \times 10^{-2}]$

$pH = 1.82$

$HNO_3 \xrightarrow{H_2O} NO_3^- + H^+$

- why is this reaction NOT likely to happen?

$NO_2^- + H_2O \leftrightharpoons HNO_3 + OH^-$

bc HNO_3 is a strong acid (high Ka) so it completely dissociates

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Solving weak acid equilibrium Problems

1- List the major species in the Solutions

2- Choost the species that can produce H^+ & write a balanced equation for it

3- using the values of the equilibrium Constants for the reactions you have written, decide which equilibrium will dominate in Producing H^+

4- write the equilibrium expression for the dominant equilibrium

5- list the initial [ ]'s of species in dominant equili..m

6- define $\underline{x}$, the change needed to achieve equili...m

7- write equil-m [ ]'s in terms of X

8- substitute the equilibrim [ ]'s into the equil-m expression

9- Solve using the easy way assuming $[HA] - X \simeq [HA]$

10- use the 5% rule (don't actually use)

11- Calculate $[H^+]$ & pH

Consider a 0.80 M aqueous Solution of the weak acid HCN
$K_{a_{HCN}} = 6.2 \times 10^{-10}$

- what are the major species in Solution?

$H_2O + HCN \rightleftharpoons CN^- + H_3O^+$

Major species are: H_2O, HCN only
bc its Ka is very low therefore only a small Portion of it is dissociated therefore no Products almost in Comparison to HCN so H^+ & CN^- aren't major Species

and considering:

$HCN + H_2O \rightleftharpoons CN^- + H_3O^+$
$K_a = 6.2 \times 10^{-10}$

&

$H_2O + H_2O \rightleftharpoons OH^- + H_3O^+$
$K_w = 1 \times 10^{-14}$

the HCN reaction is the one Controling the pH bc it contributes more $[H^+]$ than water does

Exercise:

Calculate the pH of a 0.50M aq Solution of the weak acid $\boxed{HF}$

$K_a = 7.2 \times 10^{-4}$

$$H_2O + HF \rightleftharpoons F^- + H_3O^+$$

init: 0.50M 0 0

eq: $\underbrace{0.50-x}_{\simeq 0.50 \text{ approximately}}$ x x

$[F^-] = [H_3O^+]$

$$K_a HF = \frac{[F^-][H_3O^+]}{[HF]}$$

$$7.2\times10^{-4} = \frac{F^{-}\ x^2}{0.50}$$

$$x^2 = 3.6 \times 10^{-4}$$

$$x = 0.018\ M = [F^-] = [H_3O^+]$$

$$pH = -\log(0.018) = 1.72$$

★ Percent Dissociation (ionization)
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$$\text{Percent dissociation} = \frac{\text{amount dissociated (mol/L)}}{\text{Initial concentration (mol/L)}} \times 100\%$$

- for a given weak acid, the Percent dissociation increases as the acid becomes more dilute

thats because having a dilute acid, that means that in its initial concentration, its molecules & particles are more apart off each other so they are surrounded (each of them) by the most number of slovent molecules so dissociates more

ex: Just like Putting a drop of oil in a large tank of water, although oil doesn't dissolve in water this drop will dissolve bc its out numbred and forced to do so

Exercise:

A Solution of 8.00 M Formic acid ($HCHO_2$) is $\underbrace{0.47\%\ \text{ionized in water}}$ → very small value (evidence of weak acid)

Calculate Ka of $HCHO_2$

$$\text{Percent dissolved} = \frac{\text{amnt dis}}{\text{Initial conc}} \times 100\%$$

$$0.\cancel{47}\ \cancel{\%} = \frac{x}{8.00} \times 100\cancel{\%}$$

$$\boxed{x = 0.0376\ M}$$

$$HCHO_2 + H_2O \rightleftharpoons CHO_2^- + H_3O^+$$

	$HCHO_2$	CHO_2^-	H_3O^+
init	8	0	0
equil	$8-x$ ≈ 8	x	x

$$K_a = \frac{[CHO_2^-][H_3O^+]}{[HCHO_2]}$$

$$K_a = \frac{x^2}{[HCHO_2]} = \frac{1.413 \times 10^{-3}}{8.00} = 1.76 \times 10^{-4} = K_a$$

$$\boxed{= 1.8 \times 10^{-4}}$$

pH = 1.42