

الخمعن يعرد (H⁺) خند فومانه القاعدة تور (اكت) = =

فغوم ارمنیوس محدود النقریف

O Arrhenius Theory

- Arrhenius defined an acid as a <u>substance</u> that liberates hydrogen ions, H⁺ and a base as a <u>substance</u> that supplies hydroxyl ions, OH⁻ on dissociation.
- However; Arrhenius definition could not explain the basic behavior of many compounds that do not contain hydroxyl ions, OH- (e.g.NH₃) ما بعدر يفسر اون المركبات المركبات

THE NH3 + HCI - NH4++ CI

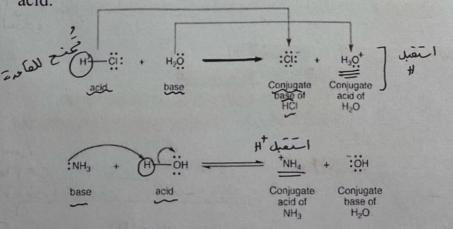
• Therefore; the Brönsted-Lowry theory is more useful than the Arrhenius theory for the representation of ionization in both aqueous and non-aqueous systems.

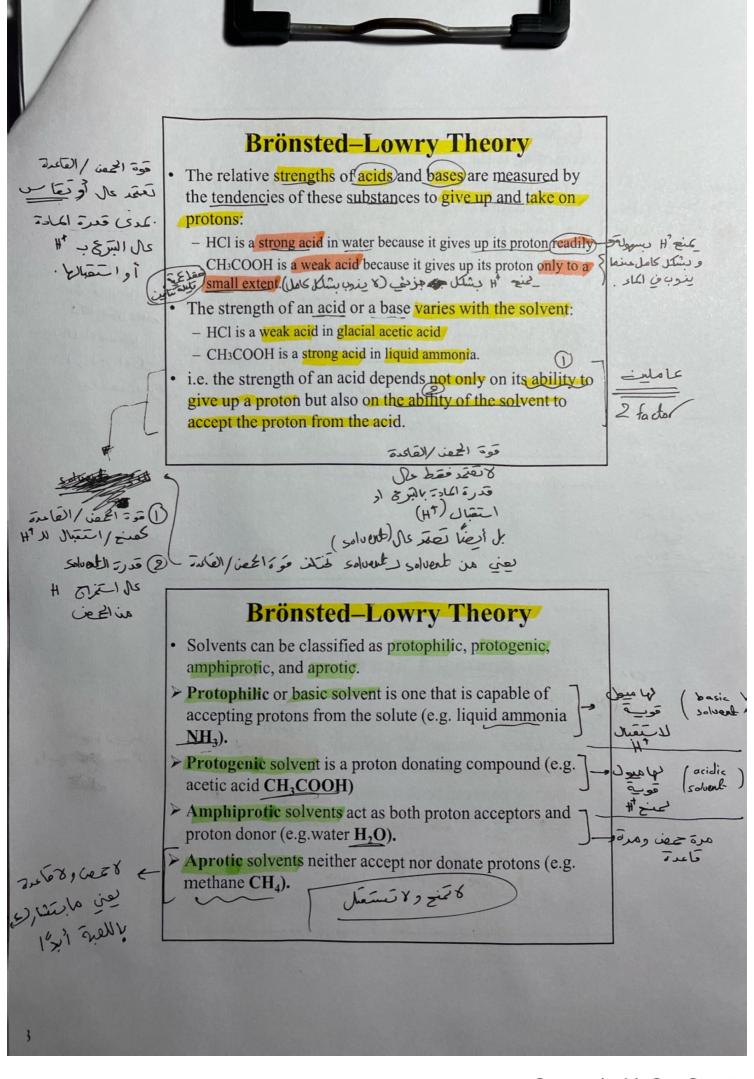
non aqueous

الحين يصنع/يترع 14 (H)

Brönsted-Lowry Theory

• According to the Brönsted-Lowry theory, an acid is a substance that is capable of donating a proton, and a base is a substance that is capable of accepting a proton from an acid.







(3)

3 Lewis Electronic Theory

According to the Lewis theory:

اغمى (جرند/ ايعن) يعبل زوج من (ع) الما القاعدة تقدم زوج من (ع)

- An acid is a molecule or an ion that accepts an electron pair to form a covalent bond.
- A base is a substance that provides the pair of unshared electrons to coordinate with an acid.
- Certain compounds such as BF₃ are considered acids even when they are not proton donors (do not contain hydrogen).

• Other compounds such as ethers and NH₃ are considered bases even when they do not accept proton.

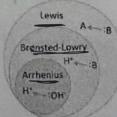
الماعدد + H عق بقرع منه، و الكامويمبر عفد لا اه استعبل الزواج الماكلترون

بنعبره عدده حت لوها عدده القدرة يستعلوا لل بس بتبرعوا بالديكرونان في المرتبطة ويكونوا روابط تساهمة

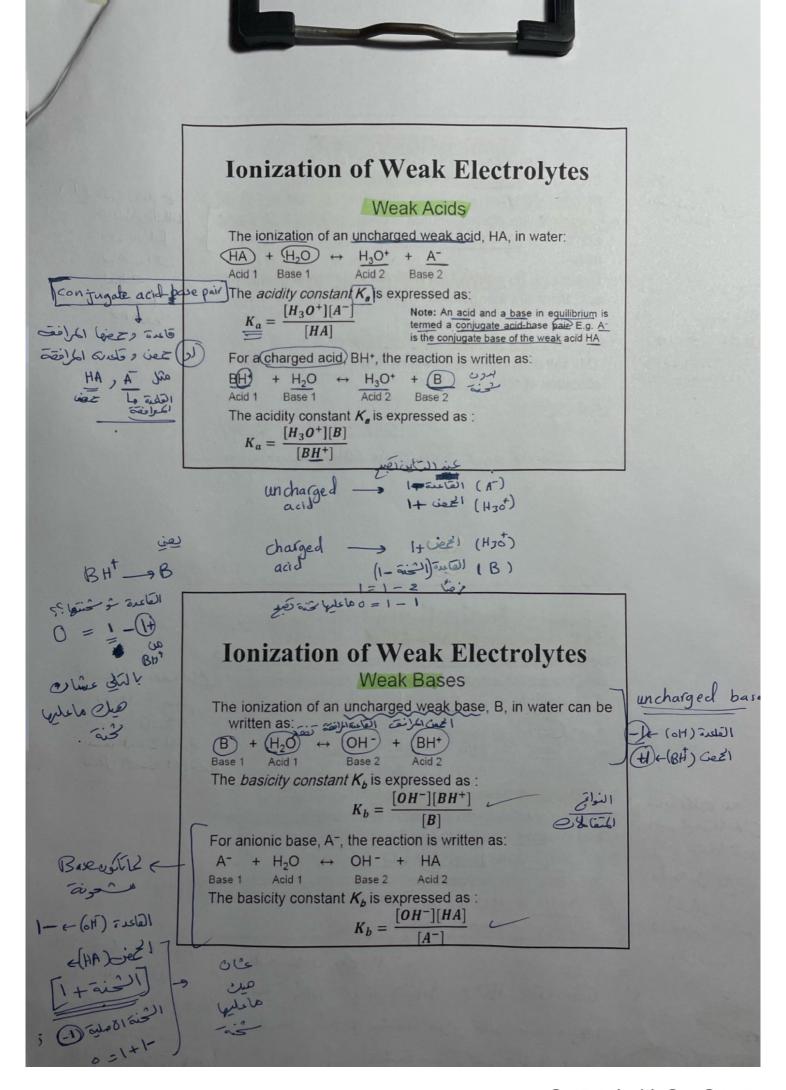
Lewis Electronic Theory

- The Lewis systems is probably too broad for convenient application to ordinary acid-base reactions.
- These reactions can be described as a form of electron sharing rather than as acid-base reactions.

Arrhanux Bronsted < Lewis



مفهوم لويس



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Lonization of salts

- Salts are the non-water product of an acid base neutralization.
- Drug salts are often used due to their complete ionization, and thus better aqueous solubility than weak acids and bases.
- Depending on the strength of the acid and base that form the salt, there are four possible types:

1.Salt of strong acid and a strong base (e.g. NaCl)

- This salt dissociates to give ions that practically do not consume or release protons.
- E.g. NaCl Na++ Cl-Salt (Practically neither Acid) or (Base)

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(4) EL, 5 / Balks عال التأن الكامل نعزز ذوبانيا ر الوائل الذلك [isu ~ 18cer

Ionization of salts 2. Salt of weak acid and strong base (e.g. NaOAc) This salt dissociates into ions; from which one acts as a base كاليتفكك هاد النوكم and consumes a proton to give its conjugate weak acid: Na+ + OAc-) مذالاملاح ينكم NaOAc The to since Base1 (Salt) تستفاعل مع الهله $OAc^- + H_2O \leftrightarrow (HOAc) + (OH^-)$ لتعلى الحيما المراضة Acid1 Acid2 Base2 Base1 3. Salt of weak base and strong acid (e.g. NH₄CI) This salt dissociates into ions; from which one acts as a n acid and releases a proton to give its conjugate weak base: → \NH4+ /27+ \ CI-NH₄CI

كالتفكل هاد النوع مذالاملاح vez vice fine وسفاعل مع الم افقة

Acid1 $NH4^{+} + H_{2}O \leftrightarrow (NH_{3}) + H3O^{+}$ Base1 Base2

Salt

NaOA do vien

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لازيا هستقة من

هارح تتفاعل مع حما

Ionization of salts

4. Salt of weak acid and weak base (e.g. NH4OAc)

This salt dissociates into ions from which one acts as an acid and the other as a base.

E.g.
$$NH_4OAc \rightarrow NH_4^+ + OAc^-$$
Salt $Acid 1$ Base 1

$$NH_4^+ + H_2O \leftrightarrow NH_3 + H_3O^+$$
Acid 1 Base 1 Base 2 Acid 2

$$AcO^- + H_2O \leftrightarrow AcOH + OH^-$$
Base 1 Acid 1 Acid 2 Base 2

کایتغکان هوه رح یطینی حمن رماعد مادة عما مدادة مرافق

Ionization of Polyprotic Electrolytes

Polyprotic acids can lose more than one H+ ion. (Htio) (افقال المرابعة عنوان المرابعة المرابعة عنوان المرابعة المرابعة

E.g. Diprotic acids, such as H₂SO₄ and H₂CO₃ which release 2 protons, and Triprotic acids, such as H₃PO₄ which releases β protons

Consider the ionization of the weak diprotic acid, H₂CO₃ that dissociates in two steps:

$$H_2CO_3 + H_2O \leftrightarrow H_3O^+ + H_2O_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2^-}$$

Two acidity constants is used to describe the two equilibrium:

$$\underbrace{K_{a1}} = \underbrace{[H_3O^+][HCO_3^-]}_{[H_2CO_3]}, \quad \underbrace{K_{a2}} = \underbrace{[H_3O^+][CO_3^{2^-}]}_{[HCO_3^-]}$$

 ${\sf K_{a1}}$ is larger than ${\sf K_{a2}}$ because the polyprotic acid lose its first proton more easily than the second (and third) proton.

فقدان [†] الاول دان کموت اسهل من فقدان [†] الثانی

Ionization of Polyprotic Electrolytes

Polyprotic bases can accept more than one H⁺ ion.

E.g. Diprotic bases, such as CO32- which accepts 2 protons, and Triprotic bases, such as PO43- accepts 3 protons.

Consider the ionization of the weak diprotic base, CO32 that consumes protons in two steps:

$$CO_3^{2-}$$
 + $H_2O \leftrightarrow OH^-$ + HCO_3^{4-} -2+1=-
 HCO_3^{1-} + $H_2O \leftrightarrow OH^-$ + H_2CO_3 -1+1= C

Two basicity constants is used to describe the two equilibrium:

$$K_{b1} = \frac{[OH^-][HCO_3^-]}{[CO_3^{2-}]}, \qquad K_{b2} = \frac{[OH^-][H_2CO_3]}{[HCO_3^-]}$$

K_{b1} is larger than (K_{b2}) because the polyprotic base consumes its first proton more easily than the second (and third) proton.

لا نه م اكتساب البروتون الاول يكون المهل هي البروتون الثاني.

Ionization of Water

المان المنابع المنابع المنابع المنابع Water ionizes slightly to yield hydrogen and hydroxyl ions by reacting with another molecule of water (autoprotolytic reaction):

H2O + H2O ↔ OH + H3O+

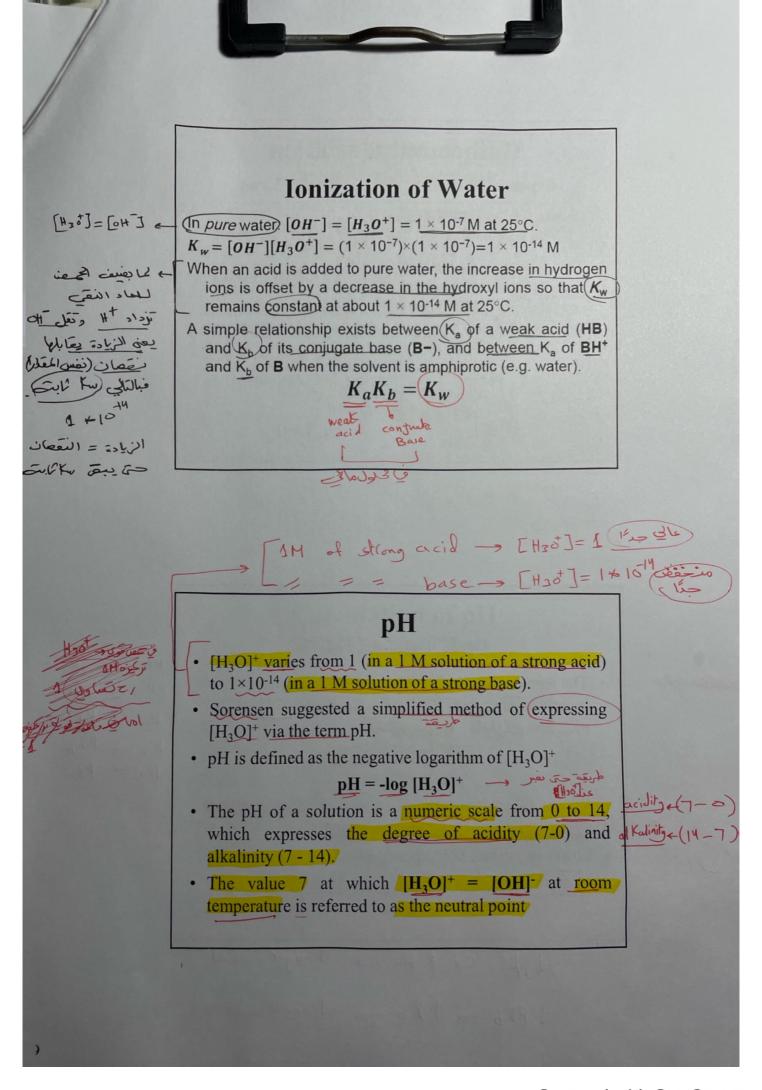
The equilibrium constant is expressed as:

$$K = \frac{[OH^-][H_3O^+]}{[H_2O]^2} \implies K[H_2O]^2 = [OH^-][H_3O^+]$$

[H2O] 2 is considered as a constant and is combined with K to give a new constant, Kw, known as the autoprotolysis constant, or the ion product of water:

$$K_{W} = [OH^{-}][H_{3}O^{+}]$$

 $4 + 10^{-19} = [OH^{-}] + [H_{3}O^{+}]$





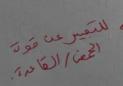
Mathematical revision

Exponential Laws	Logarithm Laws
$\underline{x}^a \cdot \underline{x}^b = x^{a+b}$	$\log(ab) = \log(a) + \log(b)$
$\frac{x^a}{x^b} = x^{a-b}$	$\log\left(\frac{a}{b}\right) = \log(a) - \log(b)$
$(x^a)^b = x^{ab}$	$\log(a^b) = b \cdot \log(a)$
$x^{-a} = \frac{1}{x^a}$	$\log_{x}\left(\frac{1}{x^{a}}\right) = -a$
$x^{0} = 1$	$\log_x 1 = 0$

pK and pOH

The term "p" is also used to express the negative logarithm of each of [OH⁻], K_a, K_b, K_w as pOH, pK_a, pK_b, and pK_w

- pk_a and pK_b values provide a means of comparing the strengths of weak acid and weak bases:
- Lower pk_a values correspond to stronger acids
- Lower pK_b values correspond to stronger Bases



Strong Acids and Bases

• A strong acid, HA, ionizes completely to H₃O⁺ and A⁻. Therefore $[H_3O^+] = [HA]$ and pH is calculated as:

· While a strong base, B ionizes completely to BH+ and OH-. Therefore [OH-] = [B] and pOH is calculated as:

Since pH = pKw - pOH

Then: pH = pKw - (-log[B]) or:

$$pH = pKw + log [B]$$

base acid

Calculation of pH

Weak Acids and Bases

A weak acid, HA, ionizes partially H₃O⁺ and A⁻:

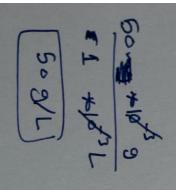
$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$
 Since $[A^-] = [H_3O^+]$

Then
$$\underline{K_a} = \frac{[H_3 O^+]^2}{[HA]}$$

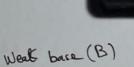
$$[H_3O^+]^2 = K_a [HA] \implies [H_3O^+] = (K_a [HA])^{1/2}$$

$$[H_3O^+]^2 = K_a [HA] \Rightarrow [H_3O^+] = (K_a [HA])^{1/2}$$

$$pH = \frac{1}{2}(pK_a - \log[HA])$$



Example Calculate the pH of a 50 mg mL-1 solution of ascorbic acid (MW 176.1, pK_a 4.17) $pH = \frac{1}{2} \frac{bab}{(4.17 - \log 0.284)}$ $pH = \frac{1}{2}(4.17 + 0.574) = (2.36)$ $\underline{pH} = \frac{1}{2} (pKa - \log[HA]) \rightarrow$ M = 50 / 176.1 = 0.284 mol/L Convert concentration to M (or mol/L) C = 50 mg/mL = 50 g/LCalculation of pH Weak Acids and Bases الفه القائض الله القائض



$$P(OH) = \frac{+1}{2} P_b - \frac{1}{2} log [B]$$

$$PH = \frac{1}{2} (PK\omega - PK\alpha) - \frac{1}{2} \log [B]$$

$$PH = \frac{1}{2} (PK\omega + PK\alpha + \frac{1}{2} \log [B])$$

$$PH = \frac{1}{2} (PK\omega + PK\alpha + \log [B])$$

Slide

Weak Acids and Bases

Example

Calculate the pH of a saturated solution of codeine monohydrate (MW 317.4, pKa 8.2, solubility at room temperature is 1 g in 120 mL

Convert concentration to mol/L

$$C = 1 g / 120 mL = 8.33 g/L$$

$$M = 8.33/317.4 = 0.0263 \text{ mol/L}$$

$$pH = \frac{1}{2}(pK_{w} + pKa + \log[B])$$

$$pH = \frac{1}{2}(14 + 8.2 + \log 0.0263)$$

$$pH = \frac{1}{2}(14 + 8.2 - 1.58) = 10.31$$

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Calculation of pH

Salts of Strong Acid and Strong Base

• The salt of strong acid and strong base (e.g. NaCl) dissociates in water into Na⁺ and Cl⁻.

NaCl $\rightarrow (Na^+) + (Cl^-) \rightarrow H_2O_{2a}$

- Neither Na⁺ nor Cl⁻ ions are capable of consuming or releasing protons from /to water (they are neither acids nor bases)
- Therefore these ions have no effect on pH. The pH of the solution remains the same as that of pure water, 7.

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Salts of Weak Acid and Strong Base

The salt of weak acid and strong base (e.g. Sodium acetate, AcONa (designated as S)) dissociates into Na⁺ and AcO⁻.

AcONa → AcO- + Na+

AcO- acts as a base and consumes one proton to form AcOH

AcO+ H2O (AcOH+ OH-

The pH is calculated in the same way as in weak base:

$$\underline{pH} = \frac{1}{2}(\underline{pK_{w} + pKa + \log[AcO^{-}]})$$

Since $[AcO^-] = [S]$

Then

$$\underline{pH} = \frac{1}{2}(\underline{pK_w} + \underline{pKa} + \underline{\log[S]})$$

Note: the pH is always > 7

للنه * تأثيرالقامدة

Calculation of pH

Salts of Weak Base and Strong Acid

The salt of weak base and strong acid (e.g. ammonium chloride, NH₄Cl (designated as S)) dissociates into NH₄⁺ and Cl⁻.

NH₄CI → CI⁻ + NH₄+

NH₄⁺ acts as an acid and releases one proton to form NH₃

NH₄+ + H₂O ↔ NH₃+ H₃O+

The pH is calculated in the same way as in weak acid:

$$pH = \frac{1}{2}(pK_a - \log[NH_4^+])$$

Since $[NH_4^+] = [S]$

Then $pH = \frac{1}{2}(pKa - log[S])$

Note: the pH is always < 7

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Salts of Weak Acid and Weak Base

The salt of weak acid and weak base (e.g. ammonium acetate, AcONH₄) dissociates into NH₄+ and AcO-.

AcONH₄ → AcO⁻ + NH₄+

NH₄+ acts as an acid and releases one proton to form NH₃, while AcO acts as a base and consumes one proton to form AcOH

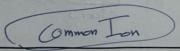
 $NH_4^+ + H_2O \leftrightarrow NH_3 + H_3O^+$

AcO+ H2O ↔ AcOH + OH-

The pH can be calculated by:

 $pH = \frac{1}{2}(pK_w + pKa - pK_b)$

Note: the pH does not depend on the concentration of the salt, but rather depends on the strength of the weak acid and weak base



Calculation of pH

Weak Acids and their Salts

When a weak acid and a salt of that acid exist in solution (e.g., acetic acid and sodium acetate), both compound dissociate to give the conjugate base of that acid (in this case OAc-).

OAc in this case is called a common ion.

Most OAc will come from the salt NaOAc, therefore;

[OAc⁻] = [NaOAc] (designated as [S])

The pH is calculated by the following equation:

$$\underline{pH} = \underline{pKa} + log \frac{[S]}{[HA]}$$
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The solution above is considered a buffer solution, and the equation above is named Henderson-Hasselbalch equation for buffers of weak acids.

وولا بنعانه وعلاما خيمة و معاناند يزدا و الايون المشترك و ترداد الم يعني (تقل الحوض) و ترز الا المحال الله بنستفد على (١١٠٠ بقدر الدكام من تابن المحين) حرة تنظم الم المحلول (دلانه بقدر الدكام من تابن المحين)

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Weak Acids and their Salts

Example

What is the pH of a solution containing acetic acid 0.3 M and sodium acetate 0.05 M? (Ka for acetic acid = 1.75 ×10-5)

$$pK_{a} = -\log K_{a}$$

$$pK_{a} = -\log 1.75 \times 10^{-5} = 4.76$$

$$pH = pKa + \log \frac{[S]}{[HA]}$$

$$pH = 4.76 + \log \frac{0.05}{0.3} \neq 3.98$$

على المنتول بكون عاد ا من الملح ف تؤكيز الليون المشترك من الحمن نفيه كيمل و رح نعوم [الايود المشتران] مذالكم

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[iez] = [dbl] = [dbl] NAJ=[CT]=[Wac1]

Calculation of pH

Weak Bases and their Salts

When a weak base and a salt of that base exist in solution (e.g., NH3 and NH4CI), both compound dissociate to give the conjugate acid of that base (in this case NH₄+).

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

 $NH_4CI \rightarrow NH_4^+ + CI^-$

NH₄+ in this case is called a *common ion*.

Most NH₄+ will come from the salt NH₄CI, therefore;

 $[NH_4^+] = [NH_4CI]$ (designated as [S])

The pH is calculated by the following equation:

 $\underline{pH} = \underline{pKa} + log(B)$

The solution above is considered a buffer solution, and the equation above is named Henderson-Hasselbalch equation for buffers of weak bases.

لذلك تركيز

Weak Bases and their Salts

Example

What is the pH of a solution containing ephedrine 0.1 M and ephedrine HCI (0.01 M)? (K_b for ephedrine = 2.3×10^{-5})

$$pK_b = -\log K_a$$

$$pK_b = -\log 2.3 \times 10^{-5} = 4.64$$

$$pK_a = pKw - pKb$$

$$pK_a = 14 - 4.64 = 9.36$$

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

$$pH = 9.36 + \log \frac{0.1}{0.01} = 10.36$$

CS. 16 PH = 10.36

Calculation of pH

Diprotic Acids and Bases

For weak diprotic acid, the [H₃0 +] mostly comes from the first step of dissociation. Therefore; The second step is ignored during calculation of pH:

$$\underline{pH} = \frac{1}{2}(\underline{pKa} - \underline{\log[HA]})$$

pH is calculated the same way as with monoprotic weak acid

For weak diprotic base, the [OH] mostly comes from the first step of reaction. Therefore; The second step is ignored during calculation of pH:

$$pH = rac{1}{2}(pK_{
m w} + pKa + \log[B])$$
 pH is calculated the same way as with monoprotic weak base

pH is calculated the same way

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