Acids, Bases and buffers

Acids - base Theories

1- Arrhenius Theory (1884)

Acid is any substance that ionized in water (partially or completely) to give hydrogen ions

Base is any substance that ionized in water to give hydroxyl ions

According to this definition, HCl is an acid NaOH is a base as shown below:

$HCl \longrightarrow H^+ + Cl^-$

$NaOH \longrightarrow Na^+ + OH^-$

Acid chemically reacts with a base as follow:

$HCl + NaOH \longrightarrow Na^+ + Cl^- + H_2O$

2- Brønsted-Lowry Theory (1923)

Acid: is any substance that can donate a proton.

Base: is any substance that can accept a proton.

3- Lewis Theory (1923)

Acids: is a substance which can accept an electron pair by combining with a second substance with al unshared pair of electrons.

A base Is a substance which shares it unshared electron - pair during chemical reaction

$BCl_3 + :NH_3 \longrightarrow Cl_3B:NH_3$

$NH_4^+ = H^+ + NH_3$

H_2O: conjugated acid for OH^-

NH_3: is conjugated base for (NH_4^+)

or NH_4^+ = is conjugated acid for (NH_3) base

Acid- Base strength: When acid or base is dissolved in water it will dissociate or ionize. The degree of ionization depends on the strength of the acid

A strong electrolyte is completely dissociated

A weak electrolyte is partially dissociated

Weak acid has a relatively small dissociation constant (Ka) where's strong acid has a large dissociation constant.

The strength of an acid depends on its type and is not related to the concentration.

(e.g.): HCI strong acid regardless of whether its concentration. 1M or 10^{-4} M

Strong base: is a base with relatively large K_b

Weak base: is a base with relatively small K_b

Acid bases equilibria in water

$Kw = [H^+][OH^-] = 1.0 \times 10^{-14}$ (ionization content of water)

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

$[H^+] = [OH^-] = 1.0 \times 10^{-7}$

Conc. of $[H^+]$ in a solution is often expressed as the pH of the solution which is the negative of the logarithm of $[H^+]$

$pH = -\log[H^+]$ $\quad$ $pOH = -\log[OH^-]$

$pKw = pH + pOH = 14$

H.W. : Calculate the pH of 2×10^{-3} M of hydrochloric acid solution?

In order to determine the pH of weak (partially ionized), strong (completely ionized) acids or bases and salts, different calculations must be followed as shown in the

1- Strong acid / base

Since the strong electrolyte is completely dissociated for that the concentration of $[H^+]$/ $[OH^-]$ is equal of the initial concentration.

Exp: What is the pH of a 0.010 M HCl solution?

Since HCl is a strong acid, the hydronium ion concentration will be equal to the HCl concentration:

$[H_3O^+] = 0.010$ M

The pH can be found by taking the negative log of the hydronium ion concentration:

$pH = -\log[H_3O^+] = -\log(0.010) = 2.00$

2- Weak acid / base

It's important to realize that a weak acid is not the same thing as a dilute solution of a strong acid. Whereas a strong acid is 100% dissociated in aqueous solution, a weak acid is only partially dissociated. It might therefore happen that the concentration from complete dissociation of a dilute strong acid is the same as that from partial dissociation of a more concentrated weak acid.

Equilibrium exists between the weak acid, water, H_3O^+, and the anion of the weak acid. The equilibrium lies to the left hand side of the equation, indicating that not much H_3O^+ is being produced. The fact that very little H_3O^+ is being produced is the definition of a weak acid.

The K_a for a weak acid is small, usually a number less than 1.

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

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

Note that water has been omitted from the equilibrium equation because its concentration in dilute solutions is essentially the same as that in pure water and pure liquids are always omitted from equilibrium equations

Exp: The initial concentration of HNO_2 is 0.45 M, $K_a = 4.5 \times 10^{-4}$.

$$HNO_{2(aq)} + H_2O(l) \leftrightarrows NO_2^-{}_{(aq)} + H_3O^+{}_{(aq)}$$

Init	0.45	0	0
Change	-x	+x	+x
Equal.	0.45 – x	x	x

$$K_a = \frac{[NO_2^-][H_3O^+]}{[HNO_2]} = \frac{(x)(x)}{0.45 - x} = 4.5 \times 10^{-4}$$

Simplifies to: since $K_a * 100 \leq C_i$

$$X = [NO_2] = [H^+] = \sqrt{K_a\ C_i} = \sqrt{4.5x10^{-4}} x\ 0.45 = 0.014$$

$$[HNO_2] = 0.45\text{-}0.014 = 0.436\ M$$

$$[OH^-] = \frac{K_w}{[H^+]} \frac{1x10^{-14}}{0.014} = 7.1x10^{-13}$$

H.W: **Codeine ($C_{18}H_{21}NO_3$), a drug used in painkillers and cough medicines, is a naturally occurring amine that has kb =1.6×10^{-6}. Calculate the pH and the concentrations of all species present in a 0.0012 M solution of codeine.**

3- *pH of Salt*

Salts such as NaCl that are derived from a strong base (NaOH) and a strong acid (HCl) yield neutral solutions because neither the cation nor the anion reacts appreciably with water to produce or ions. As the conjugate base of a strong acid, has no tendency to make the solution basic by picking up a proton from water. As the cation of a strong base, the hydrated ion has only a negligible tendency to make the solution acidic by transferring a proton to a solvent water molecule.

The following ions do not react appreciably with water to produce either H_3O^+ or OH^- ions:

- Cations from strong bases: Alkali metal cations of group 1A: Li^{+}, Na^{+}, K^{+}

Alkaline earth cations of group 2A: Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2} except for Be^{+2}

- Anions from strong monoprotic acids: Cl^{-}, Br^{-}, I^{-}, NO_3^{-}, and ClO_3^{-}

Salts that contain only these ions give neutral solutions in pure water (pH= 7).

Salts such as NH_4Cl that are derived from a weak base (NH_3) and a strong acid (HCl) produce acidic solutions. In such a case, the anion is neither an acid nor a base, but the cation is a weak acid

$$NH4^{+}_{(aq)} + H_2O_{(l)} \longleftrightarrow H_3O^{+}_{(aq)} + NH_{3(aq)}$$

Finally, salt such as $(NH_4)_2CO_3$ in which both the cation and the anion can undergo proton-transfer reactions. Because is a weak acid and is a weak base, the pH of an $(NH_4)_2CO_3$ *solution* depends on the relative acid strength of the cation and base strength of the anion:

We can distinguish three possible cases:

- $k_a > k_b$ If k_a for the cation is greater than k_b for the anion, the solution will contain an excess of H_3O^{+} ions (pH< 7).
- $k_a < k_b$ If k_a for the cation is less than k_b for the anion, the solution will contain an excess of OH^{-} ions (pH> 7).
- $k_a = k_b$ If k_a for the cation and k_b for the anion are comparable, the solution will contain approximately equal concentrations of H_3O^{+} and OH^{-} ions (pH=7).

- Calculate the pH of a 0.10 M solution of $AlCl_3$; k_a for $Al(H_2O)_6^{+3}$, is 1.4×10^{-5}.

- Calculate the pH of a 0.10 M solution of NaCN; k_a for HCN is 4.9×10^{-10}

- *Calculate the pH of* 0.20 M $NaNO_2$; k_a for HNO_2 is 4.6×10^{-4}.

- Calculate k_a for the cation and k_b for the anion in an aqueous NH_4CN solution. Is the solution acidic, basic, or neutral?

4- Solution and indicators for acid/base reaction (titration)

Neutralization titrations depend on a chemical reaction between the analyte and a standard reagent. The point of chemical equivalence is indicated by a chemical indicator or an instrumental method.

- ***Standard solution***

  A primary standard is a chemical or reagent which has certain properties such as: 1- High purity (e.g.99.9%by weight)

2- Atmospheric stability

3- Absent of hydrate water

4- Modest cost

5- Reasonable solubility in the titration medium

6- Reasonable large molar mass.

- ***Acid/Base Indicators***

An acid / base indicator is a weak organic acid or weak organic base who's undissociated from differs in color from its conjugate base or its conjugate acid form.

$$HIn + H_2O \longleftrightarrow In + H_3O^+$$

$$In + H_2O \longleftrightarrow InH^+ + OH^-$$

$$K_a = \frac{[H_3O^+][In^-]}{HIn} \quad , \quad H_3O^+ = K_a \frac{[HIn]}{[In^-]}$$

Water superheated under pressure to 200 °C and 750 atm has Kw= 1.5×10^{-11} What is $[H_3O^+]$ and $[OH^-]$ at 200 °C? Is the water acidic, basic, or neutral?

Water at 500 °C and 250 atm is a supercritical fluid. Under these conditions, Kw is approximately 1.7×10^{-19} Estimate $[H_3O^+]$ and $[OH^-]$ at 500 °C. Is the water acidic, basic, or neutral?

Calculate the pH to the correct number of significant figures for solutions of Question 1?

Calculate the concentration to the correct number of $[H_3O^+]$, $[OH^-]$ significant figures for solutions with the following pH values: 4.1 10.82 , 0.00 , 14.25 , 5.238, -1.0, 9, 14.25 -0.3, 10.75

A solution of NaOH has a pH of 10.50. How many grams of CaO should be dissolved in sufficient water to make 1.00 L of a solution having the same pH?

A solution of KOH has a pH of 10.00. How many grams of SrO should be dissolved in sufficient water to make 2.00 L of a solution having the same pH?

8- Calculate the pH of solutions prepared by:

Dissolving 4.8 g of lithium hydroxide in water to give 250 mL of solution

Dissolving 0.93 g of hydrogen chloride in water to give 0.40 L of solution

Diluting 50.0 mL of 0.10 M HCl to a volume of 1.00 L

(d) Mixing 100.0 mL of HCl and 400.0 mL of $HClO_4$ (Assume that volumes are additive.)

9- Calculate the pH of solutions prepared by:

Acid-base Theories

1. نظرية ارهينيوس: المادة التي تتأين بالماء لتعطي ايونات هيدروجين تدعى الحامض

المادة التي تتأين بالماء لتعطي ايونات الهيدروكسيل تدعى القاعدة

$HCl \rightarrow H^+ + Cl^-$ acid

$NaOH \rightarrow Na^+ + OH^-$ base

$HCl + NaOH \rightarrow NaCl + H_2O$

حامض قاعدة ملح ماء

2. نظرية برونشتد لوري

الحامض: هي المادة التي تمنح بروتون donate Proton

القاعدة: " " تستقبل البروتون accept Proton

3. نظرية لويس:

الحامض: هي المادة التي تستقبل الكترون باتحادها مع مادة ثانية تحتوي على زوج الكتروني

القاعدة: هي المادة التي تشارك بزوجها الالكتروني خلال اتحادها الكيميائي.

$BCl_3 + :NH_3 \rightarrow Cl_3B:NH_3$

Acid-Base strength

عند اذابة حامض او قاعدة في الماء فانها ستتفكك او تتأين

درجة التأين تعتمد على قوة الحامض

* الالكتروليت القوي يتفكك كلياً
* الالكتروليت الضعيف تتفكك جزئياً

* الحامض الضعيف قيمة K_a له تكون قليلة - لا يعني الحامض القوي قيمة ثابت التفكك له عالية
مثال عن الحامض القوي HCl

* القاعدة القوية لها عالية K_b والقاعدة الضعيفة K_b واطئة

$$K_w = [H]^+[OH^-] = 1 * 10^{-14}$$ (ثابت تفكك الماء)

$$[H^+][OH^-] = 1 * 10^{-14} \Rightarrow [H^+] = [OH^-] = 1 \times 10^{-7}$$

$$pH = -\log[H]^+ \qquad pOH = -\log[OH^-]$$

$$pK_w = pH + pOH = 14$$

Strong acid / base

الالكتروليت القوي تتفكك كليا اذن تراكيز H^+ ، OH^- تساوي في التركيز الابتدائي

$$HCl \longrightarrow H^+ + Cl^-$$

0.1 0

0.1

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

When $HCl = 0.1\ M \Longrightarrow [H^+] = 0.1\ M$ also

لانه يتفكك كليا

$$PH = -\log[H^+] = -\log(0.1) = 2.0$$

Weak acid / base

اما الالكتروليت الضعيف فانه يتفكك جزئيا

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

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

حالة التوازن للحامض الضعيف والماء

تكون قيمة K_a واطئة وغالبا تكون اقل من 1

The Initial conc $HNO_2 = 0.45\ M$, $K_a = 4.5 \times 10^{-4}$

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

	HNO_2	NO_2^-	H_3O^+
Init	0.45	0	0
	$0.45 - x$	$+x$	$+x$

$$K_a = \frac{[NO_2^-][H_3O^+]}{[HNO_2]} = \frac{(x)(x)}{0.45 - x} = 4.5 \times 10^{-4}$$

pH of salt

Strong acid weak base

* اذا كان ملح مشتق من حامض قوي وقاعدة ضعيفة

$$[H^+] = \sqrt{\frac{[K_w][salt]}{K_b}}$$ نطبق القانون

* اذا كان الملح مشتق من حامض ضعيف وقاعدة قوية

strong base and weak acid

نستخدم القانون

$$[H^+] = \sqrt{\frac{K_w \cdot K_a}{[salt]}}$$

Standard Solution

1. نقاوة عالية 2. مستقرة في الجو
3. خالي من جزيئات الماء (غير متميع)
4. كلفة واطئة 5. سهل الذوبان 6. وزن عالي

الدلائل Indicators :- هي مواد عضوية (حامضية او قاعدية) لها الوان معينة في المحاليل

Q1 Calculate PH for a 0.5 liter Solution Containing 3.25 gm of Potassium cyanide (KCN), Know that $K_a(HCN) = 4.9 * 10^{-10}$, $Mwt(KCN) = 65$ g/mol.

Sol:

$$M_{KCN} = \frac{wt}{Mwt} * \frac{1000}{V(ml)} \Rightarrow \frac{3.25}{65} * \frac{1000}{500} = 0.1\,M$$

$$[H^+] = \sqrt{\frac{K_w * K_a}{[Salt]}} \longrightarrow \sqrt{\frac{10^{-14} * 4.9*10^{-10}}{0.1}} \Rightarrow [H^+] = 7*10^{-12}\,M$$

$$PH = -\log[H^+] = 11.2.$$

Q2 Calulate $[OH^-]$ for a 0.5 liter Solution Containg (5.35) gm of NH_4Cl Ammonium chloride, Know that $K_b(NH_3) = 2*10^{-5}$, $Mwt(NH_4Cl) = 53.5$ g/mol.

Solu

$$M = \frac{wt}{Mwt} * \frac{1000}{V(ml)} \Longrightarrow \frac{5.35}{53.5} * \frac{1000}{500}$$

$$M = 0.2$$

$$[H] = \sqrt{\frac{K_w[Salt]}{[K_b]}} \Rightarrow \sqrt{\frac{0.2*10^{-14}}{2*10^{-5}}} \Rightarrow [H] = \sqrt{10^{-10}}\,M$$

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{10^{-5}} = 10^{-9}\,M$$

Examples for -pH-

Ex. 1

Calculate number of moles for (salts) required to solve in 100 ml of distilled water to prepare a solution with pH = [9]

Know that K_a for the weak acid is $= 1 * 10^{-5}$

Solu

$$[H^+] = \sqrt{\frac{K_w * K_a}{[salt]}}$$

$$10^{-9} = \sqrt{\frac{10^{-14} * 10^{-5}}{[salt]}} = 1 * 10^{-1} \Leftarrow$$ تركيز الملح

$$M = \frac{wt}{Mwt} * \frac{1000}{V(ml)} \Rightarrow M = \text{no. of moles} * \frac{1000}{V}$$

$$\text{no. of mole} = 1 * 10^{-2} \text{ mole} \Leftarrow 10^{-1} = \text{no. of mole} * \frac{1000}{100}$$

Ex 3

calculate PH of a 0.1M Solution of NaCN

Know that $K_{a\,[HCN]} = 4.9 * 10^{-10}$

$$[H^+] = \sqrt{\frac{K_w * K_a}{[Salt]}}$$

$$[H^+] = \sqrt{\frac{1*10^{-14} * 4.9*10^{-10}}{0.1}} \Rightarrow [H^+] = 7*10^{-12}\ M$$

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

$$= 11.2 = PH$$