#### 8.4.0 IONIZATION CONSTANTS OF ACIDS (Ka)

Acids and bases when dissolved in water may or may not be completely dissociated. Many acids are weak electrolytes and they ionize to an extent which is much less than 100%. The value of Ka called the dissociation constant of acid, is the quantitative measure of the strength of the acid. Suppose we have an acid HA dissolved in water, in a reversible manner

HA + H O 2 ฀H O + A3 + -

Kc for the reversible reaction will be written as follows.

[H O ][A3 + - ]

K =c [HA][H O2 ]

At the equilibrium stage, the concentration of water is almost the same as at the initial stages because it has been taken in large excess. A reasonable approximation, therefore, is to take the concentration of water to be efectively constant and take it on the left-hand side with Kc.

[H O ][A3 + - ]

K [H O] =c 2

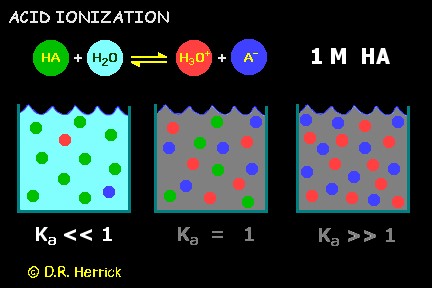
[HA]

Let K [H O] = Kc 2 a

Ka is another constant

Hence K =a [H O ][A3 + - ]

[HA]



*Animation 8.10: IONIZATION CONSTANTS OF ACIDS (K*

*a*

*)*

*Source & Credit :*

[*eechem*](http://eechem3.net/pquiz/223pq3.htm)

[*3*](http://eechem3.net/pquiz/223pq3.htm)

This equation can be used to calculate Ka for any acid solution if we know the pH or [H+] of that solution and the initial concentration of acid [HA] dissolved. This can also be used to calculate the equilibrium concentration of H3O+ and A- produced if we know the initial concentration of acid HA and its Ka value.

When K < 10a -3acid is weak

K = 1 to 10a -3 acid is moderately strong

K > 1a  acid is strong

The values of Ka for some acids are given in the Table (8.7)

**Table (8.7) Dissociation constants of some acids at 250C and their relative strength**

|  |  |  |  |
| --- | --- | --- | --- |
| Acid | Dissociation | Ka | Relative strength |
| HCl | HCl ฀ H + Cl+ - | very large(10 )+7 | Very strong |
| HNO3 | HNO 3 ฀ H + NO+ 3− | very large(10 )+3 | Very strong |
| H2SO4 | H SO 2 4 ฀ H + HSO+ 4− | Large(10 )+2 | Very strong |
| HSO-4 | HSO-4 ฀H + SO+ 42- | 1.3x10-4 | Strong |
| HF | HF ฀ H + F+ - | 6.7x10-5 | Weak |
| CH3COOH | CH COOH 3 ฀H + CH COOH+ 3 - | 1.85x10-5 | Weak |
| H2CO3 | H CO2 3 ฀H + HCO+ 3- | 4.4x10-7 | Weak |
| H2S | H S 2 ฀ H + HS+ - | 1.0x10-7 | Weak |
| NH4+ | NH4 ฀H + NH+ 3 | 5.7x10-10 | Weak |
| HCO3- | HCO3- ฀H + CO+ 32- | 4.7x10-11 | Weak |
| H2O | H O 2 ฀ H + OH+ - | 1.8x10-16 | Very weak |

**Percentage of Ionization of Acids**

We can calculate the percentage ionization of weak acid and the formula is as follows:

Amount of acid ionized

%ionization= x 100

Amount of acid initially available

The percentage ionization of weak acids depend upon the extent of dilution of their aqueous solutions. Table (8.8) shows the change in percentage ionization of acetic acid at diferent concentrations. Lesser the molarity, diluted the solution, greater the chances for electrolyte to be dissociated. When 0.1 mole of CH3COOH is dissolved in 1000cm3 of solution, then 1.33 molecules are dissociated out of 100, and 13.3 out of 1000. When the 0.001 moles are dispersed per dm3 of solution then 12.6 molecules of CH3COOH get dissociated out of 100. Remember that Ka remains the same at all dilutions at a constant temperature.

[**Table (8.8) Percentage ionization and ionization constants of acetic acid at 250C**](http://www.sabaq.pk/)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Molarity | % Ionized | [[H3O+](http://www.sabaq.pk/)] | [C[H3COOH]](http://www.sabaq.pk/) | [Ka](http://www.sabaq.pk/) |
| [0.10000](http://www.sabaq.pk/)  [0.0500 0.0100 0.0050](http://www.sabaq.pk/)  [0.0010](http://www.sabaq.pk/) | [1.33 1.89 4.17](http://www.sabaq.pk/)  [5.86](http://www.sabaq.pk/)  [12.60](http://www.sabaq.pk/) | [0.001330 0.000945 0.000417 0.000293](http://www.sabaq.pk/)  [0.000126](http://www.sabaq.pk/) | [0.098670 0.049060 0.009583 0.004707](http://www.sabaq.pk/)  [0.000874](http://www.sabaq.pk/) | [1.79x10-5 1.82x10-5 1.81x10-5 1.81x10-5](http://www.sabaq.pk/)  [1.72x10-5](http://www.sabaq.pk/) |

[**Example 4:**](http://www.sabaq.pk/)

What is the percentage ionization of acetic acid in a solution in which 0.1 moles of it has been [dissolved per dm3 of the solution.](http://www.sabaq.pk/)

[**Solution:**](http://www.sabaq.pk/)

[O](http://www.sabaq.pk/) [O](http://www.sabaq.pk/)

|  |  |
| --- | --- |
| [฀](http://www.sabaq.pk/) [฀](http://www.sabaq.pk/)  CH -C-O-H [3](http://www.sabaq.pk/)[฀](http://www.sabaq.pk/) CH -C-O +[3](http://www.sabaq.pk/)[-](http://www.sabaq.pk/)[H+](http://www.sabaq.pk/) | [K = 1.85x1a](http://www.sabaq.pk/)[0-5](http://www.sabaq.pk/) |
| Initial conc. 0.10 moles 0 moles 0 moles [Change in concentration due to ionization](http://www.sabaq.pk/) | [t = 0 sec.](http://www.sabaq.pk/) |
| (0.1=x) moles [฀](http://www.sabaq.pk/) xmoles + xmole[s](http://www.sabaq.pk/)  [Concentration at equilibrium](http://www.sabaq.pk/) | [t=equilibrium](http://www.sabaq.pk/) |
| (0.1-x) [≈](http://www.sabaq.pk/) 0.10 [฀](http://www.sabaq.pk/) xmoles + xmole[s](http://www.sabaq.pk/) | [t=equilibrium](http://www.sabaq.pk/) |

[(0.1 - x) is approximately 0.1, because the value of x is very small as compared to 0.1. The reason is that CH3COOH is a much weak electrolyte.](http://www.sabaq.pk/)

[CH COO ][H[3](http://www.sabaq.pk/)[-](http://www.sabaq.pk/)[+](http://www.sabaq.pk/)] x.[x](http://www.sabaq.pk/) K = [a](http://www.sabaq.pk/) =

[CH COOH[3](http://www.sabaq.pk/)] 0.[1](http://www.sabaq.pk/)

Putting the value of Ka

-5 x2

1.85x10 =

0.1

or x =0.1x1.8x10 =1.8x102 -5 -6

Taking square root on both sides

x = 0.1 x 1.8 x 10-5 = 1.8x10-6

In other words [H+] = 1.3 x 10-3 mole dm-3 (amount of acid ionized)

concentration of ionized acid

%ionization= x 100

original concentration

1.3x10 x100-3

%ionization= = 1.3 Answer

0.1

Hence, out of 1000 molecules of acetic acid only 13 are dissociated into ions, when 0.1 molar solution is prepared. In other words when 6 g of CH3COOH i.e 0.1 moles is dissolved in 1000 cm3 of solution only 13 molecules ionize out of energy 1000 CH3COOH molecules.

This is known as Ostwald’s dilution law, that dilution increases the degree of dissociations.

#### 8.5.0 IONIZATION CONSTANT OF BASES (Kb)

Unlike, strong bases weak Bronsted bases which are proton acceptors, usually consist of molecules or ions. They react with water, remove a proton from it, and generate OH- ions. Take the examples of NH3 and CO32-.

NH (aq) + H O( )  ฀ NH +(aq) + OH (aq- )

3 2 4

CO 2-(aq) + H O( )  ฀ HCO 1-(aq) + OH (aq- )

3 2 3

NH3 and C032- have acted as bases in above reactions. They have diferent abilities to accept protons from water molecules. We compare these abilities of bases by knowing the equilibrium constant Kb, which is called base ionization constant of a base.

Let the base is represented by B. Then

B(aq) + H O( )  ฀ BH (aq) + OH (aq)+ -

2

[BH ][OH+ -] K = c

[B][H O2 ]

Since, the concentration of H2O constant, being in large excess

|  |  |  |
| --- | --- | --- |
| So, |  | [BH ][OH+ -]  K [H O]= c 2  [B] |
| Put |  | K [H O] =Kc 2 b |
| Hence |  | [BH ][OH+ -]  K = b  [B] |

Kb value of a base is the quantitative measurement of strength of a base Smaller the Kb value, weaker the base. Table (8.9) gives the Kb values for some bases.

##### Table (8.9) Kb of some important bases

|  |  |  |  |
| --- | --- | --- | --- |
| Base | Dissociation | Kb | Relative strength |
| NaOH | NaOH ฀Na + OH+ - | Very high | Very strong |
| KOH | KOH ฀K + OH+ - | Very high | Very strong |
| Ca(OH)2 | Ca(OH)2 ฀Ca2+ + 2OH | High | Very strong |
| NH OH4 | NH OH4 ฀NH4+ + OH- | 1.81x10-5 | Weak |
| CH NH3 2  (Mathyl amine) | CH NH + H O3 2 2 ฀CH NH3 3+ + OH- | 4.38x10-4 | Weak |
| C H NH6 5 2  (Aniline) | C H NH + H O6 5 2 2 ฀C H NH6 5 3+ + OH- | 4.7x10-10 | Very weak |

**pKa and pKb**

Table (8.7) and (8.9), we conclude that the values of Ka and Kb for weak acids and bases are small numbers usually expressed in exponential form. It is convenient to convert them into whole numbers by taking their negative log. Thus we obtain pKa and pKb values of acids and bases.

pK = -logKa  a

pK = -logKb  b

Larger the pKa, weaker is the acid and vice versa. Similarly, larger the pKb, weaker is the base. If the diference of pKa values of the two acids is one, then acid with smaller pKa is ten times stronger than the other. If the diference is two, then one is hundred times stronger than the other.

#### 8.6.0 LOWRY BRONSTED ACID AND BASE CONCEPT

According to this concept, acids are those species which donate the proton or have a tendency to donate and bases are those species which accept the proton or have a tendency to accept the proton.

Whenever, a weak acid or a weak base is dissolved in water, the conjugate acid base pair is produced. There is a close relationship between Ka of the acid, Kb of the conjugate base and Kw of water. Let us have an acid HA, and it gives protons to water in a reversible manner. H3O+ gives proton to A- and is an acid, but A- accepts H+ from H3O+ and act as a conjugate base of HA.

HA + H O 2 ฀H O + A3 +  acid base conjugate acid conjugate base

of H2O of HA

Now,

[H O ][A3 + - ] [H ][A+ - ]

K = c  or K = a

[H O][HA2 ] [HA]

In case A- is dissolved in water, the equation for hydrolysis of conjugate base A- will be,

A + H O - ฀ HA + OH-

2

base acid acid base So, its

K =b [HA][OH- - ]

[A ]

Let us multiply two expressions for Ka and Kb

[H ][A+ 1- ] [OH ][HA- ]

K xK = a b [HA] x [A1- ]

Or K xK = [H ][OH ]a b + -

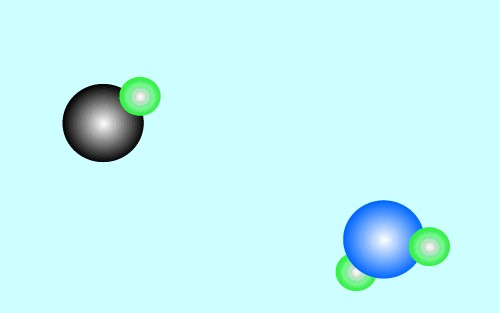
Or

a

b

w

KxK = K



*Animation 8.11: Lowry Bronsted*

*Source & Credit :*

[*dynamicscienc*](http://www.dynamicscience.com.au/tester/solutions1/chemistry/acidity%20constants/animatedconjugates.gif)

[*e*](http://www.dynamicscience.com.au/tester/solutions1/chemistry/acidity%20constants/animatedconjugates.gif)

This equation is useful in the sense that if we know Ka of the acid, we can calculate Kb for the conjugate base and vice versa. The value of Kw is a constant at a given temperature. i.e 10-14 at

25c°

Let us take the log of above equation

log(K xK ) = log(K )a b w

or logK + logK = logKa b w

Multiply both sides by ‘-1’

|  |  |
| --- | --- |
|  | -logK - logK = -logKa b w |
| Since | pK = -logK and pK = - logKa a b b |
| or | pK + pK = pKa b w |

Since pKw=14, at 250C hence pKa and pKb of conjugate acid base pair has a very simple relation with each other.

pK + pK = 14 at 25 Ca b o

This equation proves the following facts.

1. Conjugate base of a very weak acid is relatively very strong base.
2. Conjugate acid of a very strong base is relatively very weak acid.

So Ka ∝ 1

Kb

We can calculate the pKb of CH3COO-, if we know pKa of CH3COOH. Similarly, if we know pKb of NH3, we can calculate pKa of NH4+ .

### 8.7 COMMON ION EFFECT

The suppression of ionization of a weak electrolyte by adding a common ion from outside is called common ion efect.

We are familiar with puriication of sodium chloride by passing hydrogen chloride gas through saturated brine. Sodium chloride is fully ionized in the solution. Equilibrium constant expression for this process can be written as follows:

NaCl(s) ฀Na (aq) + Cl (aq)+ -

[Na ][Cl+ - ]

K = c [NaCl]

HCl also ionizes in solution

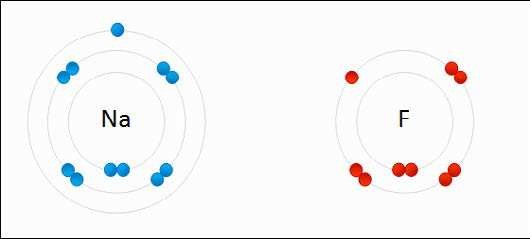
HCl ฀H (aq) + Cl (aq)+ -

On passing HCl gas, concentration of Cl- ions is increased, therefore NaCl crystallizes out of the solution to maintain the constant value of the equilibrium constant.

This type of efect is called the common ion efect. The addition of a common ion to the solution of a less soluble electrolyte suppresses its ionization and the concentration of unionized species increases, which may come out as a precipitate.

+ −

Na (aq) + Cl (aq) ฀NaCl(s)



*Animation 8.12: COMMON ION*

*Source & Credit :*

[*boundles*](https://www.boundless.com/chemistry/textbooks/boundless-chemistry-textbook/atoms-molecules-and-ions-2/chemical-formulas-37/formulas-of-ionic-compounds-211-3607/)

[*s*](https://www.boundless.com/chemistry/textbooks/boundless-chemistry-textbook/atoms-molecules-and-ions-2/chemical-formulas-37/formulas-of-ionic-compounds-211-3607/)

**More Examples of Common Ion Effect**

1. The solubility of a less soluble salts KClO3 in water is suppressed by the addition of a more soluble salt KCl by common ion efect. K+ is a common ion. The ionization of KClO3 is suppressed and it settles down as precipitate.

KClO (s)3 ฀K (aq) + ClO (aq)+ -3

KCl ฀ K (aq) + Cl (aq)+ -

1. Similarly, the dissociation of a weak acid H2S in water can be suppressed by the addition of stronger acid HCl. H+ is a common ion. H2S becomes less dissociated in acidic solution. In this way low concentration of S-2 ion is developed.

H S 2 ฀ 2H (aq) + S (aq+ 2- )

This low concentration of S-2 ions helps to do the precipitation of radicals of second group basic radicals during salt analysis.

HCl(aq) ฀ H (aq) + Cl (aq)+ -

1. An addition of NH4Cl in NH4OH solution suppresses the concentration of OH- (aq) due to the presence of a large excess of NH4+ from NH4Cl. Actually, NH4Cl is a strong electrolyte. The combination of these two substances is used as a group reagent in third group basic radicals

NH Cl(aq) ฀ NH +(aq) + Cl (aq- )

4 4

NH OH(aq) 4 ฀ NH4+(aq) + OH (aq- )

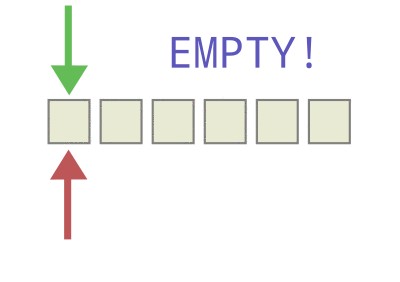
1. Common ion efect inds extensive applications in the qualitative analysis and the preparation of bufers.

#### 8.8.0 BUFFER SOLUTIONS

Those solutions, which resist the change in their pH when a small amount of an acid or a base is added to them, are called bufer solutions. They have a speciic constant value of pH and their pH values do not change on dilution and on keeping for a long time. Bufer solutions are mostly prepared by mixing two substances.

1. By mixing a weak acid and a salt of it with a strong base. Such solutions give acidic bufers with pH less than 7. Mixture of acetic acid and sodium acetate is one of the best examples of such a bufer.
2. By mixing a weak base and a salt of it with a strong acid. Such solutions will give basic bufers with pH more than 7. Mixture of NH4OH and NH4Cl is one of the best examples of such a basic bufer.
3. **Why Do We Need Buffer Solution?**

It is a common experience that the pH of the human blood is maintained at pH 7.35, if it goes to 7.00 or 8.00, a person may die.



*Animation 8.13: BUFFER*

*Source & Credit :*

[*hackada*](http://hackaday.com/2015/10/29/embed-with-elliot-going-round-with-circular-buffers/)

[*y*](http://hackaday.com/2015/10/29/embed-with-elliot-going-round-with-circular-buffers/)

Sometimes one wants to study a reaction under conditions that would sufer any associated change in the pH of the reaction mixture. So, by suitable choice of the solutes, a chemist can ensure that a solution will not experience more than a very small change in pH, even if a small amount of a strong acid or a strong base is added. Bufers are important in many areas of chemistry and allied sciences like molecular biology, microbiology, cell biology, soil sciences, nutrition and the clinical analysis.

Bufer is not a new concept at this stage of our discussion, it is just the application of common ion efect.

1. **How Do the Buffers Act?**

Let us take the example of an acidic bufer consisting of CH3COOH and CH3COONa. Common ion efect helps us to understand how the bufer will work. CH3COOH, being a weak electrolyte undergoes very little dissociation. When CH3COONa, which is a strong electrolyte, is added to CH3COOH solution, then the dissociation of CH3COOH is suppressed, due to common ion efect of

CH3COO- .

CH COOH(aq)+H O( )  ฀ CH COO (aq) + H O (aq)- +

3 2 3 3

CH COONa(aq) ฀ CH COO (aq) + Na (aq)- +

3 3

If one goes on adding CH3COONa in CH3COOH solution, then the added concentrations of CH3COO- decrease the dissociation of CH3COOH and the pH of solution increases. The table (8.10) tells us how the pH value of a mixture of two compounds is maintained. Greater the concentration of acetic acid as compared to CH3COONa, lesser is the pH of solution.

##### Table (8.10) Effect of addition of acetate ions on the pH of acetic acid solution

|  |  |  |  |
| --- | --- | --- | --- |
| [CH3COOH] (mole dm-3) | [CH3COO-]  (mole dm-3) | % Dissociation | pH |
| 0.10 0.10 0.10  0.10 | 0.00 0.05 0.10  0.15 | 1.3  0.036 0.018  0.012 | 2.89 4.44 4.74  4.92 |

Actually a bufer mentioned above is a large reservoir of CH3COOH and CH3COO- components. When an acid or H3O+ ions are added to this bufer, they will react with CH3COO- to give back acetic acid and hence the pH of the solution will almost remain unchanged. The reason is that CH3COOH being a week acid will prefer to remain undissociated. Similarly, the pufer solution consisting of NH4Cl and NH4OH, can resist the change of pH and pOH, when acid or base is added from outside. When a base or OH- ions are added in it, they will react with H3O+ to give back H2O and the pH of the solution again will remain almost unchanged.

**Calculating the pH of a Buffer**

Let us try to learn, how a bufer of deinite pH can be prepared. Consider a weak acid HA and its salt NaA with a strong base say NaOH. The reversible reactions for dissociation of HA are as follows:

HA

฀ H + A+ -

NaA ฀ Na +A+ -

The dissociation constant of a weak acid HA is given by:

[H ][A+ - ]

K =a

[HA]

Rearranging the equation,

+ K [HA]a -

[H ] =

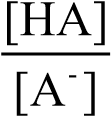
[A ]

The concentration of A in the reaction mixture is predominantly being supplied by NaA which is a stro ger electrolyte than HA, and the ionization of HA is being suppressed by common ion efect (A- is the common ion in this bufer solution). Taking log of this equation.

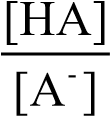
+ K [HA]a

log[H ] =log -

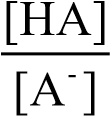
[A ]

log[H ] =log(K ) + log+ a 

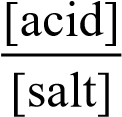
Multiplying with (-1) on both sides

-log[H ] =-log(K ) - log+ a 

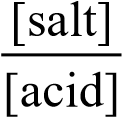
Since - -log[H ] =pH and -log(K ) =pK+ a a

So, pH =pK - loga 

[A-] refers to the concentration of the salt. Actually, maximum possible concentrate of A- is given by NaA, being a strong electrolyte

pH =pK - loga 

Interchanging the numerator and denominator the sign of log changes

or pH =pK + loga 

This relationship is called Henderson’s equation. This equation shows that two factors evidently govern the pH of a bufer solution. First is the pKa of the acid used and second is the ratio of the concentrations of the salt and the acid. The best bufer is prepared by taking equal concentration of salt and acid.

So, pH is controlled by pKa of the acid. For example, for acetic acid sodium acetate bufer, if

[CH COOH3 ] = [CH COONa3 ]

then pH =pK + loga [CH COONa3 ]

[CH COOH3 ]

pH =pK + log(1)a

so pH =pK + 0 = pKa a

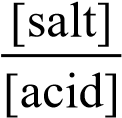
pH = 4.74.

It means that the pH of this bufer is just equal to the pK of the acid. Similarly for formic acid sodium formate bufer, if

[HCOOH] = [HCOONa] then pH =pK + 0 = pKa a

so pH = 3.78.

To prepare a bufer of deinite pH, we need a suitable acid for that purpose. We can also manage the bufer of our own required pH by suitably selecting the concentration ratio of the salt and the acid. If [CH3COOH] is 0.1 mole dm and that of [CH3COONa] is 1.0 mole dm-3 then

pH= 4.74 + log 

1.0

pH= 4.74 + log = 4.74 + log10

##### 0.1

Since log10 =1

pH = 4.74 + 1 = 5.74

pH = 5.74

Similarly, if [CH3COOH] is 1.0 mole dm-3 and [CH3COONa] is 0.1 moles dm-3 , then

0.1 pH= 4.74 + log

1

pH= 4.74 + log =4.74+log10-1

pH = 4.74 - 1 = 3.74

or pH = 3.74

Anyhow, the above mentioned combination can be used to prepare bufers from 3.74 to 5.74. The bufer beyond this range will not be good bufers and will have small bufer capacities. Just like acidic bufers, the basic bufer have their own Henderson equation. For this purpose, let us use the mixture of NH4OH and NH4Cl. NH4OH is a solution of NH3 in water and it can be represented as follows:

NA (aq) + H O( )  ฀ NH +(aq) + OH (aq- )

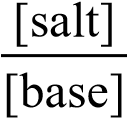
3 2 4

[NH4+ ][OH-1]

K = b

[NH3]

Taking the log, multiplying with negative sign and rearranging, we get

pOH = pK + logb 

Using this relationship, we can prepare a basic bufer of the required pOH or pH by suitably selecting a base and adj usting the ratio of [salt] / [base].

**Example :**

Calculate the pH of a bufer solution in which 0.11 molar CH3COONa and 0.09 molar acetic acid solutions are present. K for CH COOH is 1.85 x 10-5

a 3

**Solution:**  0.11M CH COONa solution means that 0.11 moles are dissolved in 1 dm3 of solution.

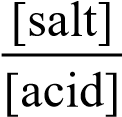
3

[CH COONa] =0.11M3

[CH COOH] =0.09M3

K of CH COOH =1.85x10a 3 -5

pK = -log(1.8x10 ) -5 = 4.74

pH = pK + loga 

0.11

pH = pK + loga

0.09

pH = 4.74 + 0.087 = 4.83 Answer

Since, the concentration of CH3COONa is more than that of CH3COOH, so pH of bufer is greater than 4.74. In other words, the solution has developed the properties of a base, because CH COONa has Na+ ion which is from a strong base.

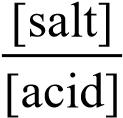
3

**8.8.1 Buffer Capacity**

The bufer capacity of a solution is the capability of a bufer to resist the change of pH. It can be measured quantitatively that how much extra acid or base, the solution can absorb before the bufer is essentially destroyed. Bufer capacity of a bufer solution is determined by the sizes of actual molarities of its components. So,a chemist must decide before making the bufer solution, what outer limits of change in its pH can be tolerated.

Let us do some calculations to check the efectiveness of a bufer system. Consider, that we have a bufer having 0.11 molar CH3COONa and 0.09 molar acetic acid. Its pH will be 4.83. Let us add 0.01 moles of NaOH in one dm3 of the bufer solution (remember that addition of 0.01 moles NaOH per dm3 of solution will change the pH from 7.00 to 12.00 in pure water).

Since NaOH is a strong base and it is 100% dissociated, it generates 0.01 moles OH-. Out of 0.09 mole of CH3COOH, 0.01 mole will react with OH- and 0.08 moles of CH3COOH is left behind in one dm3 of solution. This neutralization of course makes the identical change in the amount of CH3COONa and its concentration will increase from 0.11 mole to 0.12 mole.

Henderson equation is, pH = pK + loga 

Putting the new concentrations of salt and acid after addition of NaOH.

pH = 4.74+ log 0.12

0.08

pH = 4.74+ log(1.5)

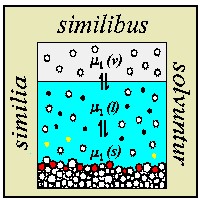
pH = 4.74+ 0.176

pH = 4.92 Answer

It means that there is a very small change in pH from 4.83 to 4.92, that is only a diference of 0.1. So we reach the conclusion that a bufer does not hold the pH exactly constant. But it does a very good job in limiting the change in pH to a very small amount.

#### 8.9.0 EQUILIBRIA OF SLIGHTLY SOLUBLE IONIC COMPOUNDS (SOLUBILITY PRODUCT)

When a soluble ionic compound is dissolved in water, like NaCl, it dissociates completely into ions. But for slightly soluble salts the dissociation is not complete at equilibrium stage. For example, when PbCl2 is shaken with water the solution contains Pb2+, Cl- and undissociated PbCl2. It means that equilibrium exists between solid solute, PbCl2 and the dissolved ions, Pb2+ and Cl-.



*Animation 8.14: SOLUBILITY*

*Source & Credit :*

[*iupa*](http://old.iupac.org/divisions/V/502/homepage/welcome.html)

[*c*](http://old.iupac.org/divisions/V/502/homepage/welcome.html)

PbCl (s) ฀PbCl (aq) ฀Pb2+(aq) + 2Cl (aq- )

2 2

According to law of mass action K =c [Pb2+(aq) ][Cl-(aq) ]2

[PbCl2 ]

Lead sulphate is a well known sparingly soluble compound and it dissociates to a very small extent like PbCl2.

PbSO (s)4 ฀PbSO (aq)4 ฀Pb2+(aq) + SO42-(aq)

Law of mass action applied to the dissociation of PbSO4 gives equilibrium constant Kc

[Pb2+ ][SO42−]

K =c

[PbSO4 ]

Being a sparingly soluble salt the concentration of lead sulphate (PbSO4) almost remains constant. Bring [PbSO4] on L.H.S. with Kc

K [PbSO ] = [Pbc 4 2+ ][SO42-]

if K [PbSO ] = Kc 4 sp

then K =[Pb (aq)][SOsp 2+ 42-(aq)]= 1.6x10 at 25 C-8 o

Ksp is called the solubility product of PbSO4. It is the product of molar solubilities of two ions at equilibrium stage.

Similarly,for PbCl K =[Pb (aq)][Cl (aq)]2 sp 2+ - 2

Ksp is usually a very small quantity at room temperature. The value of Ksp is temperature dependent. For a general, sparingly soluble substance, AxBy.

A Bx y ฀xA+y +yB-x

K =[Asp +y ] +[B ]x -x y

So, the solubility product is the product of the concentrations of ions raised to an exponent equal to the co-eicient of the balanced equation. The value of Ksp is a measure of how far to the right dissolution proceeds at equilibrium i.e. saturation. The following Table (8.10) shows us the Ksp values of slightly soluble ionic compounds.

Smaller the value of Ksp, lesser the capability to be dissociated.

**Table (8.10) Ksp values for some ionic compounds (compounds are arranged alphabetically).**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Salt | Ion Product | Ksp | Salt | Ion Product | Ksp |
| AgBr | [Ag ][Br+ −] | 5.0x10-13 | CuS | [Cu2+][S2−] | 8x10-34 |
| Ag CO2 3 | [Ag ] [CO+ 2 32−] | 8.1x10-12 | FeS | [Fe2+][S2−] | 6.3x10-18 |
| AgCl | [Ag ][Cl+ −] | 1.8x10-10 | Fe S2 3 | [Fe ][S3+ 2−]3 | 1.4x10-85 |
| Agl | [Ag ][I+ −] | 8.3x10-17 | Fe(OH)3 | [Fe ][OH3+ −]3 | 1.6x10-39 |
| Ag S2 | [Ag ] [S+ 2 2−] | 8x10-48 | HgS | [Hg2+][S2−] | 2x10-50 |
| Al(OH)3 | [Al3+][OH−]3 | 3x10-34 | MgCO3 | [Mg2+][CO32−] | 3.5x10-8 |
| BaCO3 | [Ba2+][CO32−] | 2x10-9 | Mg(OH)2 | [Mg2+][OH−]2 | 6.3x10-10 |
| BaSO4 | [Ba2+][SO42−] | 1.1x10-10 | MnS | [Mn2+][S2−] | 3x10-11 |
| CdS | [Cd2+][S2−] | 8.0x10-27 | PbCl2 | [Pb2+][Cl−]2 | 1.6x10-5 |
| CaCO3 | [Ca2+][CO32−] | 3.3x10-9 | PbCrO4 | [Pb2+][CrO42−] | 2.3x10-13 |
| CaF2 | [Ca2+][F−]2 | 3.2x10-11 | PbSO4 | [Pb2+][SO42−] | 1.6x10-8 |
| Ca(OH)2 | [Ca2+][OH−]2 | 6.5x10-6 | PbS | [Pb2+][S2−] | 8.0x10-28 |

**8.9.1 Applications of solubility product**

**(a) Determination of Ksp, from solubility**

From the solubility of the compounds, we can calculate Ksp of the salt. The solubility for most of the compounds are given in terms of the grams of the solute per 100 g of water. Since the quantity of solute is very very small, so 100 g of water solution is considered to be 100 ml of solution. The reason is that the density of water is very close to unity. Hence, we get the concentration in moles dm-3. The number of moles of solute dm-3 of the solution is calculated by dividing the mass of solute by its molar mass. Then by using the balanced equation, we ind the molarity of each ion and then ind Ksp.

**Example 6 :**

The solubility of PbF2 at 250C is 0.64 gdm-3. Calculate Ksp of PbF2.

**Solution:**

First of all convert the concentration from g dm 1 to moles dm 3;

Mass of PbF dessolved dm = 0.64g2 -3

Molecular mass of PbF = 245.2g mol2 -1

Number of moles of PbF = 2 0.64gdm-3-1 =2.6x10-3

245.2gmol

The balanced equation for dissociation of PbF2 is,

PbF (s)2 ฀Pb2+(aq) + 2F (aq1- )

2.6x10-3M 0 + 0 t = 0 sec

"zero" moles 2.6x10-3moles + 2x2.6x10 moles-3 t=equilibrium

The expression of Ksp is

K = [Pbsp 2+ ][F- 2]

Putting values of concentration

|  |
| --- |
| -8 |

K = 2.6x10 x(2x2.6x10 ) = 7.0x10 Answersp -3 -3 2

**(b) Determination of Solubility from Ksp**

For this purpose we need the formula of the compound and Ksp value. Then the unknown molar solubility S is calculated and the concentration of the ions are determined. Table (8 .11 ) shows the relationship between the Ksp values and the solubility of some sparingly soluble compounds.

**Table (8.11) Relationship between Ksp and the solubility of some compounds.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Formula | No. of ions | Cation  Anion | Ksp | Solubility gdm-3 |
| MgCO3 | 2 | 1/1 | 3.61x10-8 | 1.9x10-4 |
| PbSO4 | 2 | 1/1 | 1.69x10-8 | 1.3x10-4 |
| BaCrO4 | 2 | 1/1 | 1.96x10-10 | 1.4x10-5 |
| Ca(OH)2 | 3 | 1/ 2 | 6.5x10-6 | 1.175x10-2 |
| BaF2 | 3 | 1/ 2 | 1.35x10-5 | 7.2x10-3 |
| CaF2 | 3 | 1/ 2 | 3.2x10-11 | 2.0x10-4 |
| Ag CrO2 4 | 3 | 2 /1 | 2.6x10-12 | 8.7x10-5 |

**Example 7 :**

Ca(OH)2 is a sparingly soluble compound. Its solubility product is 6.5x10-6 Calculate the solubility of Ca(OH)2.

**Solution:**

Let the solubility is represented by S in terms of moles dm-3.

The balanced equation is

Ca(OH) ฀Ca2+(aq) + 2OH (aq- )

2

Ca(OH)2 ฀ 0 + 0 Initial stage

Ca(OH)2 ฀ S + 2S Equilibrium stage

The K =6.5x10sp -6

The concentration of OH- is double than the concentration of Ca2+, so

K = [Casp 2+ ][OH ] = S x (2S- 2 )2

4S = 6.5 x 3 10-6

So, S=  6.5x10-6 1/3 = (1.625x10 )-6 1/3

 4 

S= (1.625)1/3 x10-2

S= 1.175 x10-2

Hence, at equilibrium stage 1.175 x 10-2 moles dm-3 of Ca2+ and 2x1.175 x 10-2 = 2.75 x 10-2 moles dm-3 OH- are present in the solution. In this way, we have calculated the individual concentrations of Ca2+ and OH- ion from the solubility product of Ca(OH)2.

**Effect of Common Ion on Solubility**

The presence of a common ion decreases the solubility of a slightly soluble ionic compound. In order to explain it, consider a saturated solution of PbCrO4, which is a sparingly soluble ionic salt.

PbCrO (aq)4 ฀Pb (aq) + CrO2+ 42-(aq)

Now add Na2CrO4 which is a soluble salt. CrO42- is the common ion. It combines with Pb2+ to form more insoluble PbCrO4. So equilibrium is shifted to the left to keep Ksp constant.

### KEY POINTS

1. There versible chemical reactions can achieve a state in which the forward and the reverse processes are occurring at the same rate. This state is called state of chemical equilibrium. The concentrations of reactants and products are called equilibrium concentrations and the mixture is called equilibrium mixture.
2. Law of mass action provides the relationship among the concentrations of reactants and products of a system at equilibrium stage.The ratio of concentrations of the products to the concentrations of reactants is called equilibrium constant. The equilibrium constants are expressed as Kc, Kp, Kn and Kx.
3. The value of equilibrium constant can predict the direction and extent of a chemical reaction.
4. The efect of change of concentration, temperature, pressure or catalyst in a reaction can be s adied witii the help of Le-Chatelier’s principle. Increasing concentrations of reactants or decreasing concentrations of products or heating of the endothermic reactions shifts the reaction to the forward direction. The change of temperature disturbs the equilibrium position and the equilibrium constant of reaction. A catalyst decreases the time to reach the equilibrium and does not alter the equilibrium position and equilibrium constant under the given conditions.
5. Water is a very weak electrolyte and ionizes to a slight degree. The extent of this a autoionization is expressed by ionic product of water called Kw, having a value 10-14 at 250C. The addition of an acid or a base changes the [H+] and [OH-], but the ionic product remains the same at 250C.
6. The concentration of H+ is expressed in terms of pH and that of [OH-] in terms of pOH. Neutral water has a pH = 7 and pOH= 7.The value of pKw is 14 at 250C.
7. According to Lowry-Bronsted concept of an acid and a base the conjugate base of a strong acid is always weak. So pKa + pKb = pKw Where pKa and pKb are the parameters to measure the strengths of acids and bases.
8. Those solutions which resist the change of pH are called bufer solutions. Bufer solutions of pH below 7 are prepared by mixing a weak acid and salt of it with a strong base while basic bufers can be prepared by combining a weak base and salt of it with a strong acid. Hendersen’s equation guides us quantitatively to have the bufer solutions of good bufer capacity and to select the pair of compounds for this purpose.
9. The solubility of sparingly soluble substances are calculated from the solubility product data. This data provides us the information about the selective precipitation and fractional precipitation.
10. Common ion efect operates best in bufer solutions, and puriication of certain substances. It is one of the best applications of Le-Chatelier’s principle.

### EXERCISE

Q1. Multiple choice questions

i) For which system does the equilibrium constant, Kc has units of (concentration)’?

1. N +3H2 2 ฀2NH3
2. H +I2 2 ฀2HI
3. 2NO2 ฀N O2 4
4. 2HF ฀H +F2 2 ii) Which statement about the following equilibrium is correct

2SO (g) + O (g2 2 ) ฀2SO (g) 3 Ä H= -188.3kJ mol -1

1. The value of Kp falls with a rise in temperature
2. The value of Kp falls with increasing pressure
3. Adding V2O5 catalyst increase the equilibrium yield of sulphur trioxide (d) The value of Kp is equal to Kc.
4. The pH of 10-3 mol dm-3 of an aqueous solution of H2SO4 is
   1. 3.0 (b) 2.7 (c) 2.0 (d) 1.5
5. The solubility product of AgCl is 2.0 x 10-10 mol2 dm-6. The maximum concentration of Ag+ ions in the solution is
   1. 2.0 x 10-10 mol dm-3  (b) 1.41 x 10-5 mol dm-3

(c) 1.0 x 10-10 mol dm-3 (d) 4.0 x 10-20 mol dm-3

1. An excess of aqueous silver nitrate is added to aqueous barium chloride and precipitate is removed by iltration. What are the main ions in the iltrate?
   1. Ag+ and NO3- only (b) Ag+ and Ba2+ and NO3-

(c) Ba2+ and NO3- only (d) Ba2+ and NO3- and Cl-

Q2. Fill in the blanks

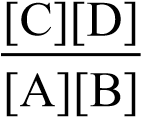
i) Law of mass action states that th e\_\_\_\_\_\_\_\_\_\_ at which a reaction proceeds, is directly proportional to the product of the active masses of the \_\_\_\_\_\_\_\_\_\_. ii) In an exothermic reversible reaction,\_\_\_\_\_\_\_ temperature will shift the equilibrium towards the forward direction. iii) The equilibrium constant for the reaction 2O3 ฀3O2 is 1055 at 250C, it tells that ozone is\_\_\_\_\_\_\_\_\_\_ at room temperature.

1. In a gas phase reaction, if the number of moles of reactants are equal to the number of moles of the products, Kc of the reaction is\_\_\_\_\_\_\_\_\_\_ to the Kp.
2. Bufer solution is prepared by mixing together a weak base and its salt with or a weak acid and its salt with\_\_\_\_\_\_\_\_\_\_.

Q3. Label the sentences as True or False.

i) When a reversible reaction attains equilibrium both reactants and products are present in a reaction mixture. ii) The Kc of the reaction

A + B ฀C + D is given by

K =c 

therefore it is assumed that

[A] = [B] = [C] = [D]

1. A catalyst is a substance which increases the speed of the reaction and consequently increases the yield of the product.
2. Ionic product Kw of pure water at 250C is 10-14 mol2 dm-6 and is represented by an expression Kw

= [H+][OH-] = 10-14 mol2 dm-6

1. AgCl is a sparingly soluble ionic solid in water. Its solution produces excess of Ag+ and Cl- ions. Q4 (a) Explain the term s” reversible reaction” and “state of equilibrium”.
   1. Deine and explain the Law of mass action and derive the expression for the equilibrium constant(Kc).
   2. Write equilibrium constant expression for the following reactions
      1. Sn+2(aq)+2Fe (aq3+ ) ฀Sn4+ (aq)+2Fe2+ (aq)
      2. Ag (aq)+Fe+ 2+ (aq) ฀Fe (aq)+Ag(s)3+
      3. N (g)+O (g)2 2 ฀2NO(g)
      4. 4NH (g)+5O (g3 2 ) ฀4NO(g)+6H O(g2 )
      5. PCl (g)5 ฀PCl (g)+Cl (g)3 2

Q5 (a) Reversible reactions attain the position of equilibrium which is dynamic in nature and not static. Explain it.

(b) Why do the rates of forward reactions slow down when a reversible reaction approaches the equilibrium stage?

Q6 When a graph is plotted between time on x-axis and the concentrations of reactants and products on y-axis for a reversible reaction, the curves become parallel to time axis at a certain stage.

* 1. At what stage the curves become parallel ?
  2. Before the curves become parallel, the steapness of curves falls! Give reasons.
  3. The rate of decrease of concentrations of any of the reactants and rate of increase of concentrations of any of the products may or may not be equal, for various types of reactions, before the equilibrium time. Explain it.

Q7 (a) Write down the relationship of diferent types of equilibrium constants i.e. Kc and Kp for the following general reaction.

aA + bB ฀cC + dD

(b) Decide the comparative magnitudes of Kc and Kp for the following reversible reactions.

i) Ammonia synthesis ii) Dissociation of PCl5

Q8 (a) Write down Kc for the following reversible reactions. Suppose that the volume of reaction mixture in all the cases is ‘V’ dm3 at equilibrium stage.

i) CH COOH + CH CH OH3 3 2 ฀CH COOC H + H O3 2 5 2 ii) H + I2 2 ฀2HI iii) 2HI ฀H + I2 2 iv) PCl5 ฀PCl + Cl3 2

v) N + 3H2 2 ฀2NH3

(b) How do you explain that some of the reactions mentioned above are afected by change of volume at equilibrium stage.

Q9 Explain the following two applications of equilibrium constant. Give examples

i) Direction of reaction ii) Extent of reaction

Q10 Explain the following with reasons.

* 1. The change of volume disturbs the equilibrium position for some of the gaseous phase reactions but not the equilibrium constant.
  2. The change of temperature disturbs both the equilibrium position and the equilibrium constant of a reaction.
  3. The solubility of glucose in water is increased by increasing the temperature.

Q11 (a) What is an ionic product of water? How does this value vary with the change in temperature? Is it true that its value increase 75 times when the temperature of water is increased form 00C to 100 0C.

* 1. What is the justiication for the increase of ionic product with temperature?
  2. How would you prove that at 250C, 1dm3 of water contains 10-7 moles of H3O+ and10-7 moles of OH

Q12 (a)Deine pH and pOH. How are they related with pKw.

* + 1. What happens to the acidic and basic properties of aqueous solutions when pH varies from zero to 14?
    2. Is it true that the sum of pKa and pKb is always equal to 14 at all temperatures for any acid? If not why?

Q13 (a) What is Lowry Bronsted idea of acids and bases? Explain conjugate acid and bases.

(b) Acetic acid dissolves in water and gives proton to water, but when dissolved in H2SO4, it accepts protons. Discuss the role of acetic acid in both cases.

Q14 In the equilibrium

|  |  |
| --- | --- |
| PCl (g) ฀PCl (g) + Cl (g)  5 3 2  What is the efect on | ∆H=+90kJ mol-1 |
| (a) the position of equilibrium | (b) equilibrium constant? if |
| i) temperature is increased | ii) volume of the container is decreased |
| iii) catalyst is added Explain your answer. | iv) chlorine is added |

Q15. Synthesis of ammonia by Haber’s process is an exothermic reaction.

N (g) + 3H (g)2 2 ฀2NH (g) Ä H = -92.46 kJ3

* + 1. What should be the possible efect of change of temperature at equilibrium stage?
    2. How does the change of pressure or volume shifts the equilibrium position of this reaction ?
    3. What is the role of the catalyst in this reaction?
    4. What happens to equilibrium position of this reaction if NH3 is removed from the reaction vessel from time to time?

Q16 Sulphuric acid is the king of chemicals. It is produced by the burning of SO2 to SO3 through an exothermic reversible process.

* + 1. Write the balanced reversible reaction.
    2. What is the efect of pressure change on this reaction?
    3. Reaction is exothermic but still the temperature of 400-5000C is required to increase the yield of SO3. Give reasons.

Q17 (a) What are bufer solutions? Why do we need them in daily life?

* + 1. How does the mixture of sodium acetate and acetic acid give us the acidic bufer?
    2. Explain that a mixture of NH4OH and NH4Cl gives us the basic bufer.
    3. How do you justify that the greater quantity of CH3COONa in acetic acid decreases the dissociating power of acetic acid and so the pH increases. (e) Explain the term bufer capacity.

Q18 (a) What is the solubility product? Derive the solubility product expression for sparingly soluble compounds, AgCl, Ag2CrO4 and PbCl2.

* + 1. How do you determine the solubility product of a substance when its solubility is provided in grams/100 g of water?
    2. How do you calculate the solubility of a substance from the value of solubility product?Q19 Kc value for the following reaction is 0.016 at 5200C

2HI(g) ฀H (g) + I (g)2 2

Equilibrium mixture contains [HI] = 0.08 M, [H2] = 0.01M, [I2] = 0.01M. To this mixture more HI is added so that its new concentration is 0.096M. What will be the concentration of [HI], [H2] and [I2] when equilibrium is re-established.

(Ans: 0.0926 mole, 0.01168 mole, 0.01168 mole)

Q20 The equilibrium constant for the reaction between acetic acid and ethyl alcohol is 4.0. A mixture of 3moles of acetic acid and one mole of C2H5OH is allowed to come to equilibrium. Calculate the amount of ethyl acetate at equilibrium stage in number of moles and grams. Also calculate the masses of reactants left behind.

(Ans: 79.5g,126g,4.6g) Q21 Study the equilibrium

H O(g)+CO(g)2 ฀H (g)+CO (g)2 2

1. Write an expression of Kp
2. When 1.00 mole of steam and 1.00 mole of carbon monoxide are allowed to reach equilibrium, 33.3 % of the equilibrium mixture is hydrogen. Calculate the value of Kp. State the units of Kp.

( Ans: 4, K, has no unit)

Q22 Calculate the pH of

1. 10-4 mole dm-3 of HCl (Ans: 4)
2. 10-4 mole dm-3 of Ba(OH)2 (Ans: 10.3)
3. 1.0 mole dm-3 of H2X, which is only 50% dissociated. (Ans: zero) (d) 1.0 mole dm-3 of NH4OH which is 1% dissociated. (Ans: 12)

Q23

1. Benzoic acid, C6H5COOH, is a weak mono-basic acid (Ka= 6.4 x 10-5 mol dm-3). What is the pH of a solution containing 7.2 g of sodium benzoate in one dm3 of 0.02 mole dm-3 benzoic acid. (Ans: 4.59)
2. A bufer solution has been prepared by mixing 0.2 M CH3COONa and 0.5 M CH3COOH in 1 dm3 of solution. Calculate the pH of solution. pKa of acid = 4.74 at 250C. How the values of pH will change by adding 0.1 mole of NaOH and 0.1 mole of HCl separately.

(Ans: 4.34, 4.62, 3.96)

Q24 The solubility of CaF, in water at 25°C is found to be 2.05 x 10 1 mol dm f. What is the value of

Ksp at this temperature.

(Ans: 3.446 x 10-11)

Q25 The solubility product of Ag2CrO4 is 2.6 x 10-2 at 250C. Calculate the solubility of the compound.

(Ans: 0.1866 mol dm-3)