

Buffer capacity and buffer
index;
Electrolyte Equilibrium And pH
Indicators

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Buffer capacity and buffer index

- The buffering capacity of milk products is an important physico-chemical characteristic that corresponds to the ability of the product to be acidified or alkalized.
- The parameters of this value depend on several compositional factors including small constituents (inorganic phosphate, citrate, organic acids) and milk proteins (caseins and whey proteins).
- Natural and induced variations in the composition of milk affect this physico-chemical parameter.
- Thus, some processing treatments and physico-chemical changes, such as heat treatment, membrane separation technology, high-pressure treatment and salt addition, results in a buffering capacity specific to the transformed product (heated milk, retentate, fermented milk)

BUFFERING CAPACITY

- In milk, aggregation or dispersion of protein micelles and fat globules is dependent up on its buffering capacity, pH, acidity and electrical conductivity.
- Determination of these properties and range of variation will help in assessing the technological properties of milk.
- Stability of milk suspension is mainly controlled by the acid base equilibrium in milk.
- Substances which liberate protons (acid) and of those that combine with them (Bases) are responsible for maintaining this stability of milk constituents.
- The ionized and ionizable constituents of milk are in a state of rather delicate physical balance. The treatments such as heating or changing in milk compositional qualities alter the state of dispersion of proteins and salts which is reflected in protons.

- Buffers resist changes in pH.
- The Buffering Capacity increases as the molar concentration (molarity) of the buffer salt/acid solution increases.
- The closer the buffered pH is to the pKa, the greater the Buffering Capacity.
- Buffering Capacity is expressed as the molarity of Sodium Hydroxide required to increase pH by 1.0 unit / litre of solution.

$$\beta = dn/dpH$$

Where,

n is number of equivalents of added strong base.

Note that addition of dn moles of acid will change pH by exactly the same value but in opposite direction.

BUFFER INDEX

- This can be defined as the differential ratio of the increase in the amount of strong acid or strong base added, to pH variation.
- The buffer capacity is used in the quantitative chemical analysis and the buffer index in studying biological systems.

Buffering Groups In Milk

Group	Concentration (mM)	pK _a value
Protein-Bound residues		
Aspartic acid	19	4.1
Glutamic acid	50	4.6
Histadine	6	6.5
Tyrosine	12	9.7
Lysine	20	10.5
Ester-phosphate	7	2.6
N-Acetyl Neuraminic Acid	0.5	5
Terminal group	1.5	3.7,7.9
Salts		
Phosphate	21	3.,5.8,6.6
Citrate	9	3.,4.1,4.8
Phosphate ester	2.5	1.7,5.9
Carbonate	2	6.4,10.1
Various carboxylic acids	2	4.8
Various amines	1.5	7.6
Lactic acid	50-120	3.95

- The ionizable groups of the proteins, the phosphates, and the citrates mainly determine the acidity and the buffering capacity of milk.
- There will be variation in the titration curves due to the considerable variation in the concentration of these substances.
- Some of the ionizable groups in a protein may even be unavailable for titration, as they are buried in the hydrophobic interior of the molecules.
- Ionizable groups of the whey proteins and casein molecules. are not exposed
- The presence of Ca^{2+} ions strongly modifies the ionization of di and triprotic acids such as phosphoric acid and citric acids they will behave as if they are titrated by $\text{Ca}(\text{OH})_2$ instead of NaOH or HCl .

- Lowering of the pH of milk will make calcium phosphate soluble because it is not soluble in normal pH of milk whereas colloidal phosphate will increase when the pH is increased.
- The Magnesium citrate and protein affect the composition and quantity of colloidal phosphate. Consequently the buffering index of various groups is not strictly additive.

Electrolyte Equilibrium And pH Indicators

- Electrolytes when added to water will dissociate into charged particles and can pass electric current while nonelectrolytes although dissolve in water but cannot pass electric current.
- The number of dissociated and undissociated ions attain equilibrium which is necessary for the stability of the solution.

DISSOCIATION OF IONS IN SOLUTIONS

- Some of the compounds like sodium chloride (NaCl), hydrochloric acid (HCl), acetic acid (CH₃COOH) etc dissolve in water by dissociating into ions.
- To begin this process the ions require some energy which they obtain by the process known as **hydration**.

HYDRATION

This is a process in which opposite charges attract one another.

In the present example,

The partial positive charge on the hydrogen molecule of H_2O is attracted to the anion and the partial negative charge on oxygen is attracted to cations.

In this way during hydration each ion is surrounded by a group of opposite charges thereby lowering the overall energy of the solution.

It may be mentioned that these substances in their pure state are not separated ions, are electrically neutral and do not conduct electricity

CONDUCTIVITY

- The molecular compounds such as pure acetic acid do not conduct electricity. Under the influence of water and during the process of hydration these compounds can be broken down into ionic species due to which the solution conducts electricity.
- Ionic compounds are also poor conductors of electricity when not in solution.

REVERSIBLE REACTIONS AND EQUILIBRIUM

- Hydration is an example of a reversible reaction. Most chemical reactions are the equilibrium of the hydration process is largely influenced by the type of electrolyte i.e, strong or weak electrolyte.
- Weak electrolytes upon introduction into water begin to dissociate into ions but most of the particles remain in molecular form. But the tendency of the particles in the molecular form to dissociate is same as those molecules that have already dissociated into ions.
- What could be the reason for these molecules to continue to exist in their undissociated form?

- In fact, these molecules have also been dissociated but they immediately get associated into their molecular form. In this way, the total number of ions and molecules stays the same while each is constantly becoming the other.
- In the case of strong electrolytes the molecules dissociate to a great extent than weak electrolytes and the equilibrium shifts to one side of the reaction where there are more ions and no molecular particles are found in the solution.
- The situation or the stage in which the number of ion pairs and molecular particles stay the same is called Equilibrium.
- Equilibrium should not be thought of as the end of a reaction but rather a stage or point at which no net change occurs.

KINDS OF EQUILIBRIUM

- Many kinds of equilibrium could be observed in solutions

1. Physical equilibrium can be reached between a solid salt and a saturated solution of that salt



Physical equilibrium between liquid water and gaseous water in a closed container



Physical equilibrium can be reached between molecular particles and ions in solution



Chemical equilibrium can be reached between reactants and products



NON EQUILIBRIUM SYSTEMS

- Some reactions have an end point and due to the formation of precipitate.
- These reactions are not considered equilibrium because a product formed by this reaction does not become available to react in the reverse direction, a precipitate is insoluble and will not react with ions in solution a gas escapes to the atmosphere and is no longer even physically present to react.

Le CHÂTELIER'S PRINCIPLE

- Reversible reactions will reach equilibrium which is a point at which no net reaction is occurring or the reaction is progressing backward at the same time it is progressing forward. if it is left undisturbed. It is possible to disturb this equilibrium causing the reaction to progress more in one direction than another until a new equilibrium is reached. There are many conditions which will disturb this equilibrium which are
- Change in temperature i.e., any addition or subtraction of energy from the system
- A change in pressure
- The removal or addition of a product or reactant

As mentioned by Le Chatelier “any change in one of the variables that determines the state of system in equilibrium causes a shift in the position of equilibrium in the direction that tends to counteract the change in the variable under consideration

pH INDICATORS

- A pH indicator is a chemical compound that is added in small amounts to a solution so that the pH (acidity or alkalinity) of the solution can be determined easily.
- A pH indicator is a chemical detector for protons (H^+). Normally, the indicator causes the colour of the solution to change depending on the pH, of the solution.
- pH indicators themselves are frequently weak acids or bases. When introduced into a solution, they may bind H^+ (Hydrogen ion) or OH^- (hydroxide) ions.
- The different electronic configuration of the bound indicator causes indicator's colour to change.

- Since determination of colour change is subjective in nature the results obtained by using pH indicators are most likely approximate and not precise. However, for applications requiring precise measurement of pH, a pH meter is frequently used.
- pH indicators are frequently employed in titrations in analytic chemistry and biology experiments to determine the extent and magnitude of a chemical reaction.
- Indicators usually exhibit intermediate colour at pH values inside the listed transition range. For example, phenol red exhibits an orange colour between pH 6.6 and pH 8.0. The transition range may shift slightly depending on the concentration of indicator in solution and on the temperature at which it is used.

Common Laboratory pH Indicators

Indicator	Colour at low pH	Transition pH range (approximate)	Colour at high pH
Methyl violet	blue-violet	0.0-1.6	yellow
Thymolblue(first transition)	Red	1.2-2.8	yellow
Methyl yellow	Red	2.9-4.0	yellow
Bromophenol blue	yellow	3.0-4.6	violet
Congo red	Blue	3.0-5.2	red
Methyl orange	Red	3.1-4.4	yellow
Litmus	Red	• 4.5-8.3	blue
Bromocresol purple	yellow	5.2-6.8	violet
Bromothymol blue	yellow	6.0-7.6	blue
Phenol red	yellow	6.6-8.0	red
Thymol blue (second transition)	yellow	8.0-9.6	blue
Phenolphthalein	colorless	8.2-10.0	pink
Thymolphthalein	colorless	9.4-10.6	blue
Alizarin Yellow R	yellow	10.1-12.0	red
Indigo carmine	blue •	11.4-13.0	yellow

- Universal Indicator is a blend or mixture of different indicators that exhibits several smooth colour changes over wide range of pH values.
- Anthocyanins are a class of compounds that occur in many different plants; they appear red in acidic solutions and blue in bases.
- Extracting anthocyanins from red cabbage leaves to form a crude acid-base indicator is a popular introductory chemistry demonstration.