UNIT 10 THERMAL PROCESSING OF MILK

Structure

10.0 OBJECTIVES

After reading this unit, we shall be able to:

- name various heating processes used in dairy industry.
- explain effect of heat on milk.
- define freezing of milk.
- enumerate important enzymes and their role in processing of milk

10.1 INTRODUCTION

The main purpose of application of heat is preservation of milk and milk products. In some cases controlling microbial contamination is the primary criteria. In products like dried milk main purpose is to preserve the product from chemical deterioration apart from microbial spoilage. The purpose of heat is to meet public health requirements such as pasteurization and sterilization, to remove water, to destroy enzymes, to facilitate mixing and blending processes, such as in ice cream mix, processed cheese and cultured dairy products and to impart desirable properties such as development of flavours.

10.2 HEAT PROCESSING OF MILK

There are several processes in which the main purpose of heat application is to make milk safe for human consumption and increase its keeping quality. Common process in which heat is applied are as follows:

i) **Pasteurization:** The main aim of pasteurization of milk is to kill all pathogenic microoganism and make it safe for human consumption. Pasteurization of milk is done either by High temperature short time (HTST) or Low temperature long time (LTLT) process. In Holder process milk is heated for not less than 30 minutes at 63^0C while in HTST pasteurization heating not less than 71.7^0C for 15 seconds is used. Pasteurization of milk is done to meet the public health requirement. Pasteurization leads to the destruction of pathogenic bacteria, e.g. Mycobacterium tuberculosis and most of the non-pathogenic organisms and the enzymes present in milk. Both in Holder and HTST process alkaline phosphatase activity is taken as an index of destruction of Mycobacterium tuberculosis.

ii) **Sterilization**: The purpose of heat sterilization is to destroy all micro-organisms and their spores in milk. Sterilization is primarily employed for the preparation of sterilized milk. In the preparation of evaporated milk sterilization at temperature of 116^{0}C for 15 minutes is employed. Sterilized milk can be stored at room temperature for longer period.

ii) **Forewarming or Preheating:** Forewarming or preheating is applied for the manufacture of condensed or evaporated milk and dried milk. Temperatures between 88^{0}C to 100^{0}C are employed for forewarning. Present trend is to heat milk above 100^{0}C to give maximum heat stability.

iv) **Condensing:** In condensing heating is carried out under vacuum to remove water. In a single effect vacuum evaporator the temperature ranges between 43 to 55^0 C. With the widespread use of multiple effect evaporators for condensing milk, it is not possible to specify precisely the degree of heat treatment which may be subjected in condensing operation.

v) **Drying**: The purpose of drying is to completely remove water with minimum physico-chemical changes in the dried product. The temperature employed in spray drying process ranges between 71 to 177^{0}C in terms of air inlet temperatures. The precise temperature conditions vary with the particular drying equipment.

vi) **UHT Process:** In the ultra high temperature process for preparing UHT milk, the milk is heated at a high temperature of 135^{0}C – 150^{0}C with holding time of few (1 to 8) seconds. This is a microbially safe milk. UHT milk can be stored at room temperature for further use

vi) **Homogenization:** Homogenization is carried out to break down the fat globules into a smaller size, resulting in stable state of dispersion. Though homogenization can be carried out without heating but heating is generally required for proper and satisfactory homogenization. Before homogenization heating facilitates melting of fat and inactivation of the enzyme like lipase. If heating is not done it leads to the development of hydrolytic rancidity with the liberation of lower chain fatty acids. Heating destroys lipase and thus prevents lypolysis. Non-heating and homogenization will result in fast lypolysis by lipase resulting in rancid flavour by liberation of lower chain fatty acids from the glycerides. It is desirable to heat the milk before homogenization. Other due to heating and homogenization there are other physico-chemical changes which occur in milk. These include easy digestibility of milk, soft curd formation and tasteful products. However, homogenization results in difficulty in cream separation. Homogenization is primarily employed in the preparation of flavoured milk, ice cream mix and evaporated milk.

10.3 EFFECT OF HEAT ON MILK

I) **Effect on salt system:** The heat-induced changes in the milk salt system can be covered under three cateogories:

- Readily reversible shift in salt balance by changes in temperature
- Irreversible shift in salt balance.

Variations in temperature and concentration adversely affect salt balance. Calcium phosphate is less soluble at high temperature than at low temperature. Thus, the concentration of soluble calcium and phosphate is decreased during heating. Dissolved or soluble calcium and phosphate during heating is transferred to the colloidal state. This transfer action occurs on the colloidal micelles of caseinate phosphate. This transfer of soluble calcium and phosphate causes extensive changes in the structure of the micelles produced by heat treatment. Dissolved calcium and phosphate tend to revert to the original system but it is not completely transferred to the original structure after heat treatment. At the same time aggregation of the caseinate-phosphate micelles may occur (reversibly or irreversibly).

II) **Effect on Acidity:** During heat treatment CO_2 is removed from the milk system. This causes a decerase in acidity of milk. The effect is through the release of H^+ions. This process is affected by the insolubilization of calcium and phosphate.

$$3Ca^{++} + 2HPO_4^- \rightarrow Ca_3(PO_4)_2 + 2H^+$$

On the basis of available data, heat treatment lead to an increase in the dissolved citrate in milk.

III) **Effect on the milk proteins:** The heat-induced changes in milk are of great practical importance to the dairy industry. During denaturation the original three-dimensional structure changes. Denaturation consists of non-proteolytic changes in the structure of protein. Amongst the heat induced changes caused by denaturation of whey proteins are:

- Development of cooked flavour
- Development of anti-oxygenic properties
- Impairment of clotting properties
- Imparting of soft curd characteristic to milk
- Prevention of age-thicking in evaporated milk
- Improvement in the baking quality for non-fat dry milk in the bakery industry

These changes are related to whey proteins. The whey proteins are present to the extent of 0.6 to 0.7% in milk. Beta-lactoglobulin is the major whey protein of milk accounting for 50 percent of the total whey proteins. The observed changes in milk are: release of H_2S production, of cooked flavour, development of anti-oxygenic properties and lowering of curd tension. All these changes are related to whey proteins.

a) **Heat denaturation of whey proteins:** Heat denaturation of whey proteins occur between 68^0C to 80^0C. Heat denaturation starts from 68^0C onwards when milk is heated for 30 minutes or 71^0C for 15 minutes. The denaturation of whey proteins occurs at a higher temperature than pasteurization. The order of denaturation of whey proteins are immunoglobulin, blood serum albumin, beta-lactoglobulin while alpha-lactalbumin is the most heat resistant whey protein.

b) **Changes associated with whey protein denaturation:** Above 75^0C –SH groups are released from whey protein, which are highly reducing in nature. These groups are susceptible for oxidation. The activation of-SH groups accompanies by an important phenomenon of anti -oxygenic property of heat-induced changes in whey protein. Sulphahydryal (-SH) groups are powerful reducing agent. The ability of these groups to bind oxygen results in anti-oxygenic property. As a result it lowers the oxidation-reduction potential of milk, which shows the activation of these groups. Formation and activation of -SH also results in the liberation of volatile sulphides. These volatiles also include H_2S. The release of H_2S is one of the most important component responsible for cooked flavour of milk. Cysteine amino acid containing maximum number of -SH group is responsible for producing H_2S. Whey proteins are a rich source of cysteine and are a main cause of cooked flavour. Beta-lactoglobulin is very rich in -SH group.

Another important change resulting, as a function of heat denaturation of whey proteins is the soft curd forming property of milk. It is accompanied by two important changes in curd. These are the development of a soft curd characteristic in the curd and partial loss of clotting property in cheese manufacture. These are related to changes in the flocculation of serum protein particles. The impairment of milk clotting property seems to be due to interaction of casein with whey protein (beta-lactoglobulin). The denatured whey proteins bind with casein and thus affect its clotting property.

Milk contains a factor, which affect the loaf volume of bread when milk is added during bread making. As a result volume of bread is depressed and slackens dough is produced. This defect can be overcome by heating milk. This is supported by the role of added skim milk powder to dough during bread making, which contain heat denatured whey proteins. Heat denaturation of whey proteins in skim milk powder is thus used as an index of baking quality.

There is loss of creaming property and increase in whitening of milk due to denauration of whey protein. Loss of creaming property has been attributed to the interactions between whey proteins notably immunoglobulins which interact with proteins of fat globules. This interaction affect the creaming ability. Cream layer formed in such milk is shallow and indistinct from normal milk. Reflectance or improvement in whitening has been attributed to a heat denatured state of milk proteins just before browning. At this stage flocculation of whey protein occur, along with aggregation of casein and conversion of soluble calcium to insoluble salt.

c) **Destabilization of caseinate system:** Caseinate-phosphate particles in milk exist in a precarious equilibrium with soluble Ca^{++} and Mg^{++}, dissolved salts and whey proteins. Slight changes occurring as a result of heating or changes in ionic environment through pH will alter this equilibrium. Casein binds Ca^{++} and Mg^{++} ions very strongly. Casein is stabilized in the system by charge it carries. Heating causes pH changes which affect this process. The caseinate particles are very sensitive to changes in pH. Casein start precipitating below pH 6.0 and micelles precipitation starts at pH 5.2 to 5.3 where they still contain Ca^{++} and Mg^{++} attached to them. The manufacture of cottage cheese is based on the phenomenon of caseinate system by heat and acidity. During this process the destabilization of the caseinate particles leads to the formations of a smooth gel occupying the entire volume originally occupied by the milk. In this system a three-dimensional type network is formed that entraps the liquid along with gel structure formation or a network and a semi-solid system is formed. On applying heat to this system at cooking stage of the process, the caseinate particles become more closely knit together, water is expelled, and the clot shrinks. A desirable product is obtained by judicious use of pH and proper heat treatment.

The calcium caseinate phosphate micelles are readily precipitable by addition of various salts such as ammonium sulphate and urea. Heating hastens the process. This is the basis of producing various fractions of casein. The effects of heat and divalent cations are important from the view point of rennet action and heat. In this phenomenon ionic concentration and heat play an important role in the stability of casein micelles. Phosphate and citrate ordinarily exert an opposite effect over Ca^{++} and Mg^{++} because they form undissociated complexes with Ca^{++} and Mg^{++}.

Some milk apparently are stabilized by added calcium and destabilized by ions such as phosphate and citrate that sequester calcium. Observations of this type are the basis of the well-known salt balance theory first suggested by Sommer and Hart (1926). This theory holds that optimum stability depends on a certain ratio of calcium and magnesium ions to those of phosphate and citrate. The concept has been of great practical utility in developing practical procedures for controlling the stability of evaporated milk during heat sterilization. In practice evaporated milk to be sterilized is treated, as a series of samples on a pilot scale with graded level of phosphate or Ca the later being rarely if ever necessary. The samples are then sterilized and after cooling the minimum level of added salt that imparted satisfactory stability is noted and used to stabilize the lot of milk to be sterilized.

IV. **Forewarming process and heat stability:** Before sterilization in the preparation of evaporated milk forewarming of milk provides heat stability to milk. Generally, heating milk at 95^0C for 10 minutes provide heat stability to milk. It has been shown that a high temperature short time process of heat treatment provides a better heat stability. However, it may be stated that this phenomenon of heat stability is complex and depends upon other factors such as quality of milk, storage temperature of milk, etc.

V. **Browning of milk:** Browning reactions in milk and milk products are the manifestation of heat induced processing of milk. Browning reaction occur due to changes related with pH, storage conditions, moisture content, relative humidity and temperature of processing and storage of milk and milk products. Browning reaction is absent in pasteurized milk but is evident in highly heated sterilized milk on storage. Browning reaction occurs in two forms on heating. The two types of browning in relation to heating are (a) amino sugar or Maillard browning and (b) non-amino browning or caramelization.

a) **Amino Sugar or Maillard browning:** Two components are responsible for this browning reaction. They are milk protein particularly casein and lactose present in milk and milk products. Phosphate salts and whey proteins make minor contribution in browning reaction. Browning reaction is complex. The reaction occurs between aldehyde groups (-CHO) of sugars and amino groups (-NH_2) of amino acids. They together start the browning reaction which ultimately lead to the formation of brown pigment melanoidin.

CHO l H–C–OH l	+	H_2N – R	D	RNH l H–C–OH l
Sugar (Lactose) with aldehyde group		Amino group of amino acid of the protein		Complex ultimately leading to the formation of melanoidin

b) **Caramelization or non-amino browning:** Caramelization or browning may be defined as the heat decomposition of sugar as a function of pH and buffers in the absence of amino compounds. It requires a relatively high order of heat energy. On the other hand, Maillard type browning requires a relatively low order of energy for its initiation and exhibit autocatalytic qualities once it has started. Caramelization is desirable in milk based products such as caramelized flavour which is desirable and liked.

c) **Changes related to browning:** Along with browning many complex reactions also occur with the formation of various compounds. In addition, fluorescent and reducing substances, various sugar fragments and flavour compounds are formed. Many of these are detected before browning starts. These changes have great practical utility. Notable amongst these is the development of flavour especially caramelized flavour. Following changes related to browning can occur:

- **Compound formation:** A large number of lactose degradation compounds are formed. These include furfuryl alcohol, furfuryl aldehyde, maltol, acetol, acetaldehyde, acetic, formic and pyruvic acid, NH_3, H_2S and CO_2
- **Reducing substances:** Heated and dried milk contain's a complex reducing system involving –SH compounds, ascorbic acid and substances associated with browning reaction. Heating concentrated milk for a similar period has a significant effect on browning reaction.

d) **Factors affecting browning of milk:** The principle factors responsible for browning in milk are:

i) **pH:** A pH above 6.8 favours browning reaction. This defect is predominant in evaporated milk where pH of milk plays an important role. Due to variations in pH and protein concentration in different milks browning is affected due to these variations. This is due to release of protons during heating. As the pH is raised above pH 6.6 browning reaction occurs at a faster rate.

ii) **Storage and temperature:** Higher temperature and prolonged storage period favours browning. These changes are favoured in the presence of increased humidity and moisture. Colour intensity increases with storage time and is highest at a storage temperature of 40^0C.

iii) **Total solids concentration:** During concentration of milk total solids concentration increases. As the total solids concentration in milk increases the browning reaction also gains momentum. Lactose plays a major part of total solids concentration along with casein. The interaction results in increased browning.

iv) **Heat treatment:** Heating milk as a pre-heat treatment between 85-100^0C for 30 minutes or more favours browning. It is one of the most important factors of browning. Reducing the heating time such as with HTST process will reduce the browning of milk products.

v) **Oxygen:** Oxygen favours browning as it reacts with –SH groups released during heating. Presence of oxygen destroys these reducing groups. Problem can be reduced by replacing O_2 with N_2 while storing heated and dried milk products.

e) **Prevention of Browning:** Browning can be prevented to a great extent by storing milk and milk products at low temperatures and short period of storage. In dried products moisture should be below 5%. Also N_2 packing helps in reducing browning due to replacement of oxygen. Strong and long duration heating should be avoided.

10.4 FREEZE PROCESSING OF MILK

Freezing has been suggested as a means for tansporting frozen concentrated milk. This is to co-ordinate supply to those areas, which are not adequately covered to supply liquid milk. The objective of freezing is to prepare frozen concentrated milk to replace liquid milk supply to distant areas, which are not well connected.

Freezing of milk and its effect on milk system: To manufacture frozen milk, the milk is first concentrated and then frozen stored. During frozen storage of milk and its subsequent thawing very fine milk particles called flocculates are formed. Initially flocculates are readily dispersible but prolonged storage period makes them difficult to disperse.

Effect of freezing on lactose and caseinate system: Lactose is the first component of milk which is affected during frozen storage. Frozen storage results in crystallization of lactose especially at very low temperatures. Lactose is present in milk in a highly supersaturated state which readily crystallize on storage. Lactose binds calcium from milk but calcium is released on crystallization. In the dissolved state lactose binds calcium but releases calcium upon crystallization. No change in protein denaturation occurs on storage even though flocculation occurs. The reason for destabilization is calcium. It has been seen that frozen stored casein remains unchanged in terms of solubility. Casein isolated from frozen stored milk has the same sensitivity to calcium precipitation as casein isolated from fresh milk. Although casein flocculates on frozen storage but protein seems to be unchanged.

Check Your Progress 1

1. Define denaturation of protein. Name some of the major proteins affected by denaturation.

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2. What is the reason for development of cooked flavour during heating?

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3. Name the agents of browning reaction.

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4. Discuss the role of ions during heating.

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5. How lactose affect frozen storage of milk?

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10.5 ENZYMES IN RELATION TO PROCESSING

Enzymes are organic catalytst, which are found in plant and animal cells. The enzymes bring about metabolic reactions but they don't undergo any chemical change. They are colloidal and proteinous in nature and are classified as per the reaction performed e.g., lipase, the fat splitting enzyme. The activity is affected by pH, heat, light etc. Enzyme in milk gain entry via udder or externally.

Milk enzymes are technologically important. They are related with flavour (e.g., lipase). Study and knowledge of these enzymes is essential to understand their role.

Functions of enzymes

The following functions are related to enzymes.

- Oxidising enzymes (e.g., peroxidase)
- Lipolytic enzyme hydrolyzing fat (e.g., lipase)
- Decomposing H_2O_2 (e.g., catalase)
- Decomposes phosphorous esters.(e.g., phosphatase)
- Lactose hydrolyzing enzyme (e.g., lactase)
- Reductase as reducing enzyme (e.g., MBR test)
- Proteolytic enzymes hydrolyzing protein (e.g., protease)
- Hydrolysing aldehyde (e.g., xanthine oxidase)

Peroxidase, lipase, catalase, reductase, phosphatase, xanthine oxidase, lactase are all present in freshly drawn milk. Other enzymes enter via bacterial contamination.

i) **Peroxidase:** Peroxidase is present in milk as lactoperoxidase enzyme. The enzyme is destroyed between 70-80^{0}C. Lactoperoxidase enzyme act on H_2O_2 in the presence of thiocyanate ions, forming hypothiocyanate ions ($OSCN^-$) are lethal to microbes. This enzyme has been used in milk to improve shelf life during transportation of milk from distant places to milk plant. The enzyme is also used as an index of detecting proper heating of milk as it is destroyed at 70^{0}C, especially for detecting high temperature heat treatment of milk.

ii) **Phosphatase:** Phosphatase catalyse the hydrolysis of phosphate esters. Alkaline phosphatase is the most important milk enzyme. It is destroyed by pasteurization of milk. At the temperature of pasteurization of milk tubercle bacili bacteria present in milk are also destroyed. The inactivation of this enzyme is thus taken as the process of destruction of TB organisms. Under health consideration pasteurization of milk is mandatory in various countries. Phosphatase test has been developed to ascertain if the milk has been properly pasteurized. So as to ensure the destruction of Micobacterium tuberculosis which is destroyed at a temperature wherein alkaline phosphatase is inactivated.

iii) **Lipases:** Lipases hydrolyse milk fat into corresponding fatty acids and glycerol. In milk they are linked with hydrolytic rancidity of milk fat releasing butyric acid. Excessive presence of butyric acid in milk causes rancid flavour defect. This defect may also be present in butter. They are destroyed at 63^{0}C when heated for 20 minutes.

iv) **Proteases:** Proteins are hydrolysed by proteases to simple compounds such as proteose, peptone, amino acid and other compounds. They are inactivated in the presence of salt or preservative. Proteases are destroyed by heating milk between 70-80^{0}C. Proteolytic enzymes have been employed externally for preparing different varieties of cheese. These enzymes primarily hydrolyze casein.

Catalase →

v) **Reductase:** Reductase are enzymes of bacterial origin. These enzymes are capable of reducing certain dyes to their colourless leuco-compounds. It has been shown that generally speaking the reduction time at 38^0 C is approximately proportional to the number of bacteria.. They are used as measure of microbial population and determine the extent of contamination of milk by bacteria. This is possible through methylene blue reduction test (MBRT). The blue dye is reduced to a colourless compound in the presence of reductase. The earlier the dye lost its blue colour greater is the contamination.

vi) **Catalase:** Catalase catalyses the decomposes hydrogen peroxide as per the following reaction

$2H_2O_2 \qquad 2H_2O+O_2$

Catalase content varies in milk from different animals and within the same species. It is also affected by feed given to the animal. Catalase content is high in colostrum, mastitis milk and milk contaminated with mastitis or colostrum milk or bacterial contamination. It tends to parallel leucocyte count. It increases with multiplication of bacteria in milk. It is destroyed when milk is heated to about 65^{0}C or over.

vii) **Xanthine oxidase:** A variety of substances are oxidized by this enzyme including xanthine, hypoxanthine, aldehyde, oxypurines, etc. Thus in the presence of O_2 and an aldehyde following reaction takes place:

$$RCHO + H_2O + O_2 \xrightarrow{\text{Xanthine oxidase}} RCOOH + H_2O_2$$

Xanthine oxidase is a prominent enzyme of milk and was discovered as early as 1902.

Xanthine oxidase content varies from cow to cow and increases with stage of lactation. It is associated with fat globules. It can be isolated from cream or buttermilk. The following table gives the data for inactivation of the enzymes in milk.

Table 10.1: Inactivation temperature of enzymes

S.No.	Enzymes	Inactivation temperature (^{0}C)
1.	Lipase	80^{0C} (weakend at 60^0C)
2	Peroxidase	72^{0C} (for 30 minutes)
3	Reductase	Above 80^{0C}
4	Catalase	65 to 70^{0C}(for 30 minutes)
5	Phosphatase	62.5^{0C} (for 20 minutes)
6	Lactase	75 to 80^{0C}

Check Your Progress 2

1. What are enzymes?

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2. Name some of the enzymes present in milk.

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3. Name the enzyme responsible for hydrolytic rancidity and cause for rancid flavour.

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10.6 LET US SUM UP

Thermal processing of milk is an important aspect. The milk industry will come to a standstill if heat is not applied. This is because milk is a highly perishable commodity. Also heat is necessary to evaporate water to prepare dried milk and related products. Preservation of milk and milk products is the primary objective of heat.

Heat treatment consists of several processes such as pasteurization, sterilization, forewarming, condensing, drying and UHT processing. Heat treatment causes changes in milk in terms of denaturation of proteins including whey proteins, altering of salt balance, browning reaction, caramelization, development of flavour and compounds formed from lactose. Heating also results in changes in various other properties including development of cooked flavour, anti-oxygenic property, clotting and soft curd characteristics and baking quality of milk.

Freezing of milk results in lactose crystallization, Ca^{++} binding and flocculation of milk particles. Various enzymes are present in milk. They have been involved in processing of milk such as pasteurization e.g., phosphatase and lactopeoxidase, catalase as index of mastitis or leucocytes, lactoperoxide system for milk preservation.

10.7 KEY WORDS

Enzyme : Organic proteinous catalyst involved in metabolic raction

Pasteurization : A process of heating milk to kill pathogenic organisms

Amino group : A group present in amino acid

Denaturation : A process by which structure is changed e.g.,enzyme or protein

Cations : Positively charged ions e.g., Ca^{++}

Anions : Negatively charged ions e.g., Cl^{-}

Melanoidin : A brown coloured pigment

Reducing sugar : Sugar with free aldehyde or ketonic group

10.8 SOME USEFUL BOOKS

Jenness, R and Patton, S. (1959). Principles of Dairy Chemistry, John Wiley and Sons. Inc. New York

Webb, H.H., Johnson, A. and Alford, J.A. (1978). Fundamentals of Dairy Chemistry. The AVI Pub, Co. Inc. West Port, Connecticut.

Ling, E.R. (1956). A Textbook of Dairy Chemistry, Vol. 1& 2, Chapman and Hall, London, UK

10.9 ANSWER TO CHECK YOUR PROGRESS

Your answers should include following points

Check Your Progress 1

1) i. Denaturation may be defined as the change in the original native three-dimensional structure of protein. It consists of non-proteolytic structural changes of protein. The major proteins responsible for denaturation are whey proteins such as immunoglobulin, beta – lactoglobulin, alpha – lactalbumin and serum albumin.

2) i. The reason for cooked flavour development in milk is release of H_2S. It is liberated from sulphur containing amino acid cysteine.

3) i. The two reactants of browning reaction are – CHO or aldehyde group of reducing sugar lactose and $-NH_2$ or amino group of basic amino acids such as lysine.

4) i. Frozen storage results in crystallization of lactose at low temperature. Lactose binds to Ca^{++} and release calcium upon crystallization

Check Your Progress 2

1) i. Enzymes are organic catalysts which are found in plant and animal cells. The enzymes bring about metabolic changes but they do not undergo any chemical change.

2) i. The enzymes present in milk are -

- Peroxidase
- Lipase
- Phosphatase
- Lactase
- Reductase
- Protease
- Xanthine oxidase

3) i. Lipase is responsible for hydrolytic rancidity in milk by releasing butyric acid from milk fat.