

Freezing preservation of fish, Physical, chemical and thermodynamic properties of refrigerants

Chapter 1: Principle of freezing

Heat Units

3.1.1. Specific heat

Specific heat is the quantity of heat that must be supplied or removed from a gram of substance to bring about change in temp of 1°C. It is expressed in terms of kilojoules (KJ) or kcal in applied science.

Heat capacity/specific heat of fish depends on its chemical composition; that is the content of water, fat and minerals. It is the total heat capacity of individual components which is given by the following formula.

$$C_f = C_w \times W + L + C_m \times m$$

Where,

C_f = heat capacity of fish (kcal/kg)

C_w = specific heat of water (kcal/kg)

C_L = specific heat of fat/lipid (kg)

C_m = specific heat of minerals (kg)

W, L and M are contents of water, lipid and mineral in Kgs in a kg of fish.

Example : Specific heat of fish also depends on temperature. There is no applicable change in specific heat. When fish is cooled from 30°C to 0°C (prior to freezing) and in this range of temperature, specific heat of major components of fish are given as follows.

Water - 4.18 KJ/kg°C or 1 kcal/kg °C

Fat - 2.075 KJ/kg°C or 0.5 kcal/kg °C

Dry matter other than fat - 1.505 KJ/ kg °C or 0.36 Kcal/ kg °C (i.e., protein + minerals)

Based on these values specific heat of various fishes were calculated and found to be between **0.74 to 0.91 Kcal / kg °C between 30 to 0°C**. As fish gets cooled further its specific heat goes on decreasing. Chilled fish has sp. heat of 0.845 kcal/ kg °C which gets reduced to 0.440 kcal/ kg °C, when the same fish is frozen. This indicates less quantity of heat is required to change the temperature by 1°C in frozen fish when compared to unfrozen fish. This difference is large especially when all the water in the fish is frozen (i.e., to below -8°C).

3.1.2. Thermal conductivity

In an unevenly heat body, where there is always a difference in temperature, there is always a flow of heat from warmer to colder layers. This type of heat exchange depends on direct heat transfer between adjoining particles and this continues until the temperature of body is uniform. **The rate of heat transfer depends on the co-efficient of thermal conductivity of the substance which is defined as thermal conductivity of medium in which a unit of heat (calorie) flows through a unit surface area of unit thickness at a temperature gradient of 1 unit.** Consequently expresses the amount of heat (calories) passing through a unit area of flat surface having unit thickness at a temp difference of 1 unit in unit time. The units of thermal conductivity are erg/cm. sec. °C or cal/cm sec, °C or kcal/m. Lr. °C.

When fish is heated or cooled, the rate of conduction of heat within the fish or rate of removal of heat depends on the co-efficient of thermal conductivity. It depends on chemical composition of fish, physical structure, specific gravity, specific heat and temperature of fish. The thermal conductivity in fish is important it determines the chilling, freezing and thawing process in it. Effect of temperature on the co-efficient of their mass conductivity can be illustrated by the following table.

Temp °C	Co-efficient of thermal conductivity
+30 °C	0.4 kcal/m.hr. °C
0 °C	0.401-405 kcal/m.hr. °C
-1 °C	0.522 kcal/m.hr. °C
-2 °C	0.638 kcal/m.hr. °C
-4.5 °C	0.94 kcal/m.hr. °C
-30 °C	1.5 kcal/m.hr. °C

Co-efficient of thermal conductivity in fish can be theoretically calculated if its water and dry matter, content is known . If = $l_o \times XW + l_n \times N$

If = coefficient of thermal conductivity of fish

lo = coefficient of thermal conductivity of water in fish

ln = coefficient of thermal conductivity of dry matter in fish (0.22 kcal/m.hr. °C)

W and N are respective water and dry matter %age in fish.

Co-efficient of thermal conductivity of ice is 2.07 kcal/m.hr. °C which is almost 4 times that of water (0.52 kcal/m.hr. °C). Hence heat transfer in frozen fish is faster than unfrozen chilled fish.

3.1.4 Latent heat

It is the quantity of heat required to change the state or condition or phase under which a substance exists without change in temp. Eg. a definite quantity of heat must be transferred to ice at 0°C to change it to water at the same temperature. This definite quantity of heat is known as latent heat of fusion of water/ice.

Latent Heat of fusion of ice/water = 79.7 cal/g or 80 cal/g

It is also expressed in terms of BTU/lb

1 BTU/lb = 0.5556 kcal/kg or/k cal/kg = 1.80 BTU/lb

Latent heat of fusion of any food can be calculated if its water content is known.

Latent heat = 80X% water in food

100

Latent heat of fusion of some food stuffs.

Food Product	Latent Heat of fusion	
	BTU/lb	kcal/kg
Eggs	100	55.56
Fish	101	56
Green peas	106	58.88
Milk	124	68.85
Oyster meat	125	69.44
Pork	86	47.77
Water	144	80

3.1.5 Principles of freezing

It is a common fact that the foods with high moisture content rapidly deteriorate in quality. During freezing, the water in the food is separated out from other food components, and is frozen. Thus, a food is protected, preserved from deteriorating influences such as temperature and water. The lower temperature slows down the rate of chemical reaction and water is also removed from the sphere of activity. The water is reabsorbed by the food components upon thawing and food is restored to its original quality. However, when a food is frozen, ie. When the water undergoes transition from liquid to solid state and also in subsequent thawing ie., when there is transition from solid to liquid state, there is a damaging effect on food. The texture and the structure of the food may be affected to such an extent that it may become irreversible and upon thawing the food will not be restored to its original condition.

Fresh fish flesh normally contains 60-80% water and the freezing process converts most of this water into ice. At normal atmospheric pressure, pure water will change from liquid to solid (ice) at 0°C, i.e., it will freeze. The water in fish flesh contains salts and chemicals, which have the effect of lowering the temperature at which the water begins to freeze. The water in fish flesh begins to freeze at about -1°C and as the temperature drops below -1°C, more water is frozen out and the concentration of salts in the remaining water rises, so that its freezing point is lowered further. At -5°C, it would appear that all the water is frozen, but over 20% of the water in fish muscle is still unfrozen. **Even at -30°C, approximately 10% of the water remains unfrozen.**The above defined heat units are applied here.

In order to change the physical state of a substance from a liquid to a solid, energy or latent heat has to be removed from the substance. In order **to lower the temperature of 1g of water by 1°C, at temperatures above 0°C, 1 calorie of heat must be removed** this is known as the "specific heat". However, **to change water at 0°C to ice at 0°C, 80 calories must be removed for each g of water.** In other words, the specific heat of liquid water is 1 and the latent heat of changing liquid water to ice is 80. The specific heat of ice at temperatures

below 0°C is 0.5, which means that to lower the temperature of ice by 1°C, 0.5 calories of heat needs to be removed. For all practical purposes, it is assumed that fish have the same values for specific heat and latent heat as water. All this means that, if heat is removed from fish at a constant rate, there will be a period during the fish freezing, where the temperature of fish will not drop. This period lasts until approximately 75% of the water is frozen, when the temperature begins to drop again. There are three stages to freezing fish (fig.1). During stage 1, the temperature falls fairly rapidly to just below 0°C (and it is called as initial falling rate period), during stage 2, the temperature remains fairly constant at about -1°C as the bulk of the water (three quarters of the water) in the fish freezes (this stage is known as the 'thermal arrest' period) and during stage 3 (final falling rate period), the temperature again drops and most of the remaining water becomes frozen. The temperature at -1.1°C, freezing begins, and -5°C, about 80% of water is frozen, this range is termed as '**Critical range**'. The ideal thermal arrest is only 30min. Freezing is complete only when the equilibrium temperature reaches -18°C (ie. the process should not be regarded as complete unless and until the product temperature has reached -18°C at the thermal centre after thermal stabilization). It also shows that even at temperatures as low as -30°C, a portion of water in the fish muscle still remains in the unfrozen state.

Under ideal conditions, **fish should be frozen to -30°C in 2 hours.**

Using simple mathematics, the amount of energy required to freeze fish can be calculated.

Suppose, if 1 kg fish at 25°C is to be frozen at -30°C. During stage 1, one calorie of energy has to be extracted for each gram material for each drop of 1°C. In an example, the temperature of 1000g of fish will be lowered from 25°C to -1°C, ie., by 26°C. The energy required will be equal to 1000 x 26 x the specific heat of water (1) = 26000 calories or 26 kilocalories (kcal).

During stage 2, 80 calories of energy needs to be extracted for each gram material frozen. In the example, 1000g of fish are to be frozen. The energy required will be equal to 1000 x the latent heat for freezing water (80), which equals 80,000 calories or 80kcal.

During stage3, 0.5 calories of energy needs to be extracted for each g material for each 1°C drop in temperature. In the example, the temperature of 1000g of fish will be lowered from -1 to -30°C, ie., by 29°C. The energy required will be equal to 1000 x 29 x the specific heat of ice (0.5) = 14500 calories = 14.5 kcal.

To summaries:

Stage 1,	1000 x 26 x 1	=	26 kcal
Stage 2,	1000 x 80	=	80 kcal
Stage 3,	1000 x 29 x 0.5	=	14.5 kcal

Adding these three figures gives 120.5 kcal, ie., to freeze 1kg of fish from 25°C to -30°C, 120.5 kcal of energy is required.

From the above example, it is apparent that more than 50% of the energy extraction during freezing of fish is taking place in stage 2. The thermal arrest period, where little or no drop in temperature is occurring, and this period is a critical one, if a good frozen product is to be produced. Ideally, fish should pass through the thermal arrest period as quickly as possible, due to the following reasons:

1. It is postulated that slow freezing produces large ice crystals in the cells of the fish, which can be larger than the cells themselves and so break the cell walls. But it is not so, because it is evident that the walls of fish muscle cells are sufficiently elastic to accommodate the larger ice crystals without excessive damage. Also, most of the water in fish muscle is bound to the protein in the form of a gel and little fluid would be lost.
2. As the water begins to freeze in the flesh, the concentration of salts and chemicals in the remaining water rises. This high concentration of salts and enzymes can cause accelerated autolysis and denaturation of protein during slow freezing, This result in an inferior quality product and it is mainly due to denaturation of the protein. Changes take place in some fractions of the protein as a result of freezing and since the proteins are altered from their "native" state they may be said to be "denatured", hence the term "protein denaturation".
3. At temperature around 0°C, certain types of bacteria are still active and bacterial spoilage can still occur.
4. Textural changes occur in fish, which have been frozen slowly, caused by the presence of large ice crystals and denaturation of protein during the accelerated autolysis. In addition, a phenomenon known as 'thaw drip' occurs, when slowly frozen fish are thawed. On thawing, the water which was originally bound within the cells are released and considerable loss in weight can occur.

However, from a textural point of view, it is unlikely that a highly trained taste panel could detect the difference between fish frozen in 1 hour and those frozen in 8 hours, Freezing times of 24 hours or more will almost certainly result in an inferior product and very long freezing times can result in bacterial spoilage making the fish unfit for consumption.

Chapter 2: Physical, chemical and thermodynamic properties of refrigerants

3.2.1. Refrigerant

It is any substance that absorb heat through expansion or vaporization and loses it through condensation

in a refrigeration system. It is otherwise called as working fluid in a refrigeration system

Desirable properties of an ideal Refrigerant

1. Low boiling point
2. High critical temperature
3. High latent heat of vaporization
4. Low specific volume of vapour
5. Non-corrosive to metal
6. Non-flammable and non-explosive
7. Non – toxic
8. Low cost
9. Easy to liquefy at moderate pressure and temperature
10. Easy of locating leaks
11. Mixes well with oil

A refrigerant is chosen which has larger advantages and less disadvantages.

3.2.2. Thermodynamic properties

1. Boiling temperature

Should be low at atmospheric pressure. If it is high, compressor should be operated at high vacuum, reduces capacity and increase the cost of the system.

e.g.

Refrigerant	Boiling temperature (°C)
R-12 (CCl ₂ F ₂)	- 29
R-717 (NH ₄)	-33.3
R.744 (CO ₂)	-73.6
R-764 (SO ₂)	-10

2. Freezing temperature:

Should be below the operating temperature of evaporator. Freezing temperature of most of refrigerants are below -35°C

Refrigerant	Boiling temperature (°C)
R-12	- 157.5
R-717	-35
R.744	- 56.7
R-764	- 75.6

3. Evaporator and condenser pressure

Both the evaporating and condensing pressure should be +ve (*i.e.* above atmospheric pressure). The + ve pressure are necessary to prevent leakage of air, moisture into the refrigeration systems. It also permits easier detection of leaks.

Critical temperature & pressure:

It is the highest temperature at which refrigerant can be condensed to liquid, regardless of high pressure.

Refrigerant	Critical temperature (°C)	Critical pressure (bar)
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R-12	112	41.2
R-717	133	113.86
R.744	31	73.8
R-764	157	78.7

Coefficient of performance and power requirements

For an ideal refrigerant operating between -15°C evaporator temperature and 30°C condenser temperature. The theoretical coefficient of performance for the reversed cycle is 5.74.

Refrigerant	Coefficient of performance	Power HP/TR
R-12	4.70	1.00
R-11	5.09	0.93
R-717	4.76	0.99
R.744	2.56	1.84
R-764	4.87	0.97

3.2.3. Latent heat of vaporization

A refrigerant should have a high latent heat of vapour at the evaporator temperature. It results in high refrigerating effect per kg of refrigerant and which reduces the mass of refrigerant to be circulated per ton of refrigerants.

Refrigerant	Latent heat of vapour at 15°C (Kcal/kg)
R-12 (CCl_2F_2)	37.97
R-717 (NH_4)	314.42
R.744 (CO_2)	65.44
R-764 (SO_2)	94.27

Specific volume

It indicates the theoretical displacement of the compressor (i.e volume of suction vapour to compressor).

3.2.4 Physical properties of refrigerants

Stability and inertness

An ideal refrigerant should not decompose at any temperature normally encountered in the refrigerating system. This is due to the reaction with metal. To avoid this, a refrigerant should be inert with respect to all material used in refrigerated system.

Corrosive property

Freon groups are non-corrosive with all metals. NH_4 is used only with steel and Sn. SO_2 is non-corrosive to all metals in the absence of water because it reacts with water and forms sulphuric acid.

Viscosity:

The refrigerant in the liquid and vapour states should have low viscosity because the heat transfer through condenser and evaporator is improved at low viscosities.

Thermal conductivity

The refrigerant in the liquid and vapour states should have high thermal conductivity. This is required in finding the heat transfer coefficient in evaporator and condensers.

Leakage tendency:

It should be low and the leakage of refrigerant should be easily detected by its pungent odour and also by using burning sulphur candle which forms white fumes of ammonium sulphate in the presence of ammonia.

Cost

It is not so important for small refrigerant units but it is very much important in high capacity refrigerant system like industry and commercial. Ammonia is the cheapest one. So it is widely used in large industrial plant such as cold storage and ice plants. R-22 is costlier than R-12. The cost of loss due to leakage is also important.