IMPACT: International Journal of Research in Applied, Natural and Social Sciences (IMPACT: IJRANSS)
ISSN (P): 2347-4580; ISSN (E): 2321-8851
Vol. 6, Issue 9, Sep 2018, 93-110

DEMONSTRATION OF SUPERCOOLING AND MODELING THE FREEZING TIME OF FOOD PRODUCTS BY THERMOFRIDGE PUMP

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Received: **23 Aug 2018** **Accepted:** **31 Aug 2018** **Published:** **30 Sep 2018**

ABSTRACT

In this article we were able to highlight the super cooling during the freezing of water and model the duration of freezing of different food products from their temperature of entry to their temperature of end of freezing. The numerical model thus obtained makes it possible, knowing the mass and the water content of the product to be frozen, to predict the time necessary for the total and thorough freezing of the product. The results obtained by the numerical model thus presented corroborate well with those obtained experimentally, which comforts us in our numerical approach with regard to cold rooms of small dimensions.

KEYWORDS: *Thermofridge Pump, Freezing, Water Content, Modeling*

INTRODUCTION

The use of energy in all these forms must respond to factors that make it possible to obtain maximum efficiency; this explains the interest we devote to this study. In the context of this article, we are interested in the thermofridge pump. With this machine, we were able to freeze water, meat and dry food products. The glass transition temperatures Tg measured for beef and fish are respectively -13.2°C and -15°C, but different glass transition temperatures have been measured for beef (Tg = -12°C). C) by Lebenswittel et al, a value much superior to the previous data cited by these same authors (-60°C and -40°C) or those reported by Torregianni et al (-80°C and -35°C). Values of -20°C and -13.5°C have also been proposed for pork and turkey meat by Claude Genot. And finally, we modeled the freezing time of food products knowing their water content in line with the equations given by meat specialists.

MATERIALS AND METHODS

For the conduct of our experiments, we worked with the following equipment:

- A thermofridge pump designed and produced in situ,
- A scale of precision 1/100,
- A 12-probe temperature display,
- A graduated burette.

Figure 1: **Thermo Fridge Pump**

Figure 2: **12-Probe Temperature Display**

Figure 3: Scale of Precision 1/100

Figure 4: Graduated Burette

Experimental conduct consists of freezing different bodies of water, 2 cm thick beef, 2 cm thick fish and drying thiacry and banana. The refrigerant that allowed us to conduct our experiments is R12, the gross volume of the freezer being 190 l. For freezers in general, their freezing capacity down to -18°C per 24 h and per 100l of gross volume is between 3.5 l and 4l of water, ie a mass of 7 kg of food [1].

RESULTS AND DISCUSSIONS

Freezing Water

The results obtained allowed us to draw the different curves illustrating the temperature decrease during the freezing of the water materialized in Figure 5 below.

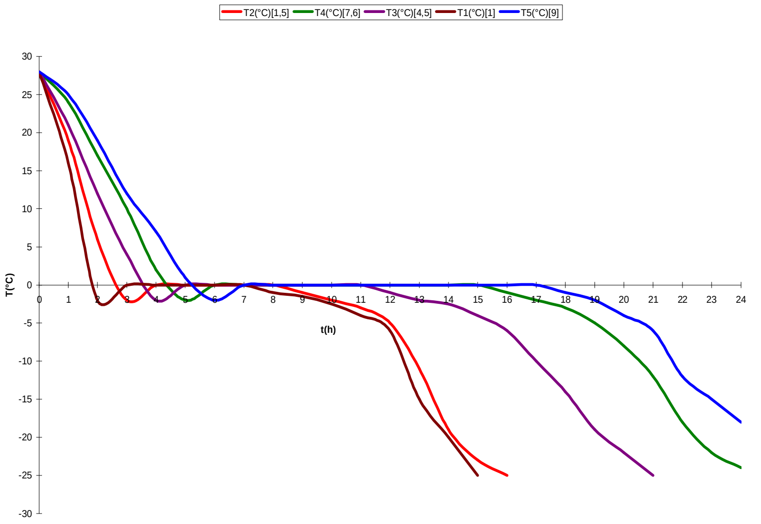

Figure 5: Evolution of the Water Température for Different Masses with Freon 12

The evidence of the supercooling of the water during its change of state was observed during the experiments. The appearance of the first ice crystals is at a temperature of -2°C as confirmed by the experiment of solidification of pure water led by B. Rouède Missy College La Rochelle [2].

Figure 5 illustrates the supercooling observed during the change of state of liquid water in ice. We can notice :

- a cooling of the water in the liquid phase and obtaining supercooling;

- when the supercooling stops, ice needles appear. The temperature rises almost instantly to zero and stays there for the duration of the water-ice transition. Since ice has a low thermal conductivity, its progression, initially rapid, becomes slower as it approaches the center;

- we can observe the birth of gas bubbles in the vicinity of the ice: it is the dissolved air gases whose concentration increases to the threshold of saturation;

- the last amounts of liquid water having disappeared and all that remains is ice. Then the temperature starts to decrease very quickly. The experiment is stopped as soon as we reach the minimum temperature allowed by the freezer.

By plotting the cooling and freezing curves and taking into account the slopes, we were able to write the modeling equation for the operation of the conservation and freezer appliances in the form:

$$\mathbf{t = 0{,}078m^{0,3728}(T_{p0}-T_C) + 0{,}0652m^3 - 0{,}8373m^2 + 3{,}7837m + 1{,}9885} \quad (1)$$

Note: m represents the total mass of water in kg contained in the products to be frozen from their introduction temperature to their end-of-freezing temperature TC.

Table 1 presents the theoretical results and the expérimental results obtained.

Table 1: Comparative Theoretical and Experimental Results

Mass (kg)	t (h)$_{th}$	t (h)$_{exp}$
1	7,1	7
1,5	8,4	9
4,5	11,7	12
7,6	15,5	16
9	20,5	18

The comparison of the experimental results with those obtained by the theory makes it possible to affirm that the modeling equation thus defined corroborates well with the values obtained experimentally.

Freezing of Beef

The results obtained during the freezing of the meat are represented in figure 6.

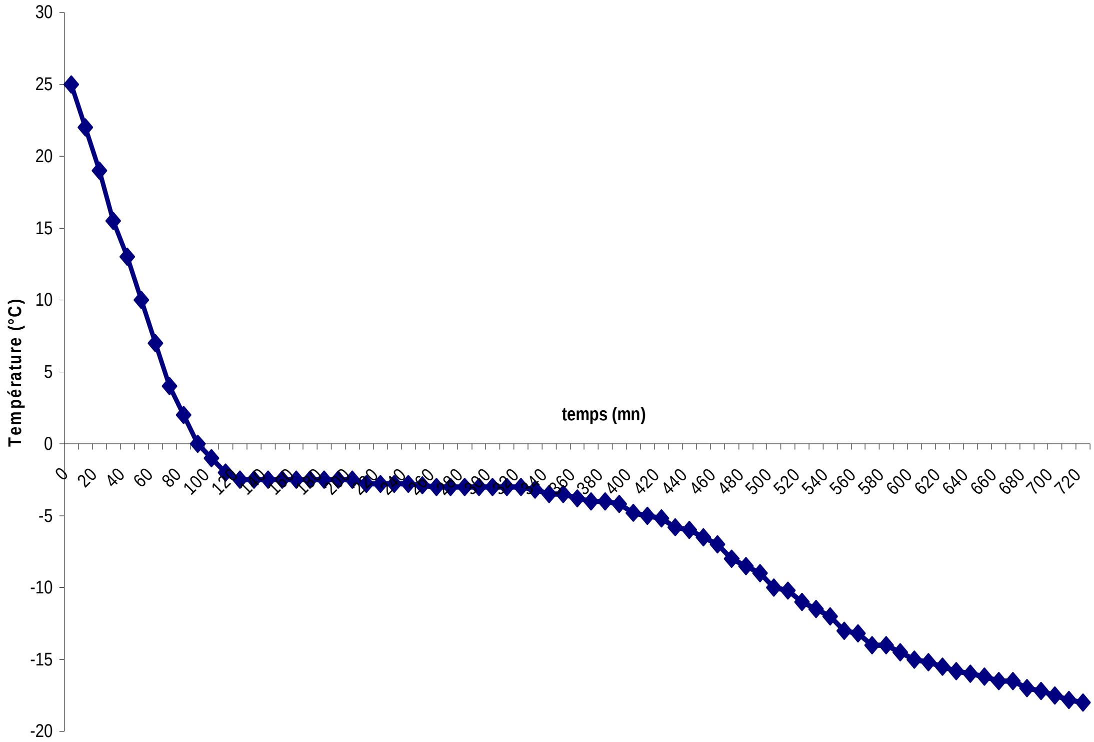

Figure 6: Variation of the Temperature as a Function of Time during the Freezing of the Beef

The appearance of the meat refrigeration phase is not linear and is limited to - 2,5°C. The starting freezing temperature noted is - 2.5°C and the phase change plateau varies over time by the values of - 2.8°C, - 3°C, - 3.8°C up to at - 4.8°C. From - 5°C, the curve weakly decreases to -7°C and this decrease is more pronounced in the range [- 7°C, - 14°C]. Below - 14°C, the curve returns to a slower slope until the final temperature reached by the machine. c- Freezing fish. The results obtained during the freezing of the fish allowed us to draw figure 7.

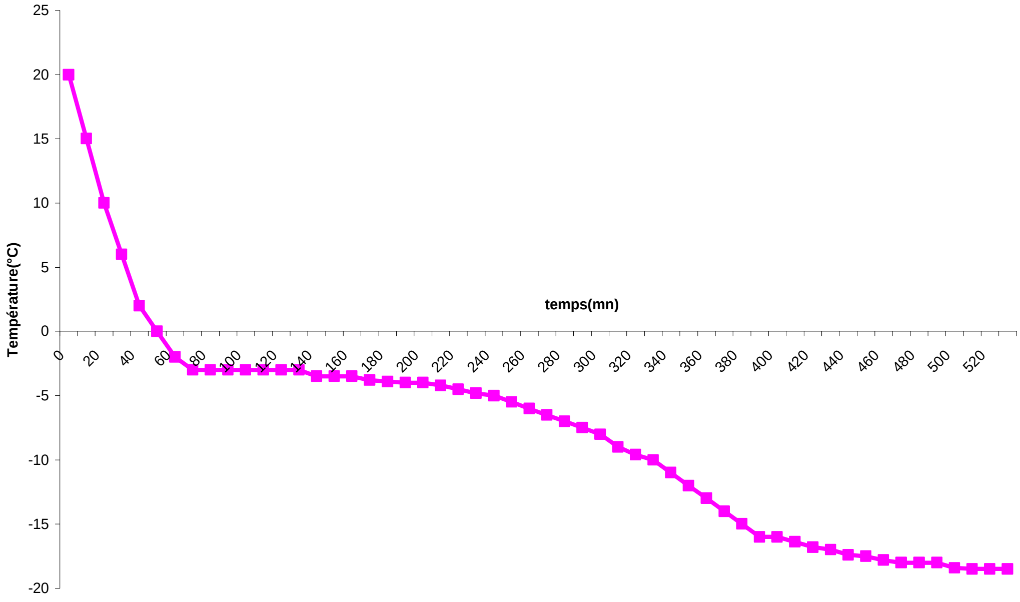

Figure 7: Variation of the Temperature as a Function of Time during the Freezing of the Fish

The appearance of the fish refrigeration phase is not linear and is limited to a value of -3°C.

The starting freezing temperature noted is - 3°C and the phase change plateau varies over time through the values of -3°C, -3.5°C, -3.8°C up to at -5°C. From -5.5°C, the curve decreases slightly to -8 ° C and this decrease is more pronounced in the range [-9°C, -15°C]. Below - 16°C, the curve returns to a slower slope until the final temperature reached by our device.

Finally, the analysis of the curve showing the temperature decrease during the freezing of fish and beef presents three phases as shown in figure 8 below:

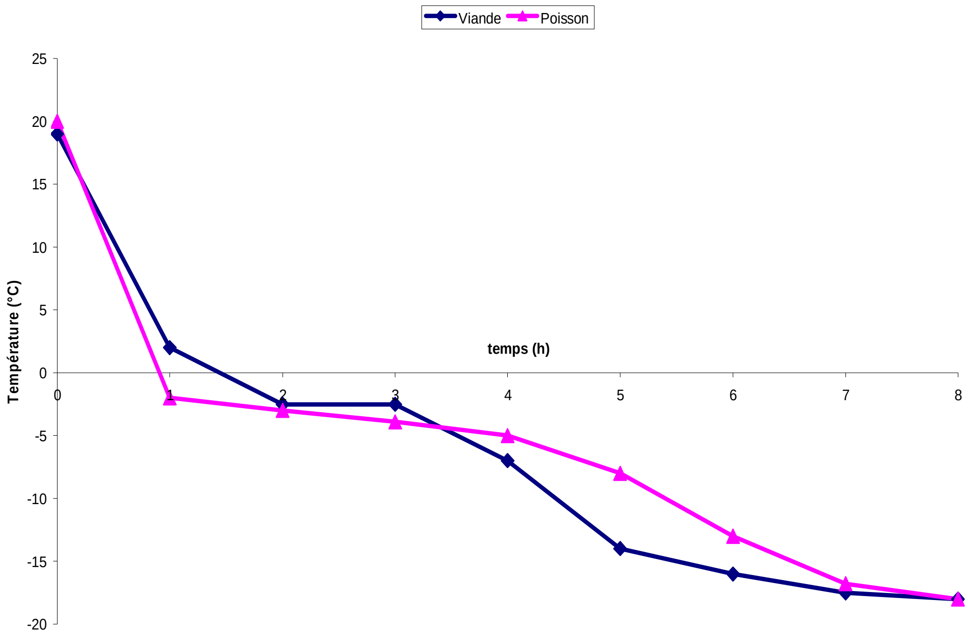

Figure 8: Comparative Evolution of the Evolution of Temperature during the Freezing of Fish and Beef

Freezing allows, even more than refrigeration, to slow the microbiological and biochemical alterations developing in the meat after the death of the animal. Practiced under good conditions, it stops the natural evolution of the product and keeps it "frozen" in the state reached just before freezing and until it thaws. The weather is somehow "suspended" for the few weeks, months or years of frozen storage. However, precautions must be taken concerning freezing: - freeze only healthy products, - keep them only in an environment where the temperature is less than or equal to -18°C, - respect the cold chain during all the storage time of the products. There are three phases in the process: - pre-cooling, where the temperature drops without changing state, - the freezing zone, with a starting freezing temperature, towards -1 / -1.5°C for the meat and a progressive slowdown of the lowering of the temperature down to -7 / -10°C: it s' acts of the maximum phase of crystallization, - the subcooling zone, where the temperature lowers again more quickly, most of the freezing water is frozen to the storage temperature.

The Freezing Stage is Characterized by:

- the initial freezing (or melting) temperature or cryoscopic temperature (Tc). The biological tissue behaves as a first approximation as a dilute solution, and Tc decreases when the concentration of solute increases. In meat, Tc is close to -1.5°C [3]. The temperature at which the first nuclei begin to form, or freezing point, is less than Tc, which characterizes the phenomenon of supercooling or subcooling. This initial reduction in temperature results from the activation energy of the nucleation.

As far as meat is concerned, there are freezing temperatures of between -1°C and -3°C [3].

Once nucleation has begun, the system yields more latent heat than is strictly necessary for crystal growth, and the temperature rises rapidly to Tc. Subsequently, if the thermal regime is sufficient, the temperature gradually decreases to be at most equal to Tc, which gradually decreases due to the cryoconcentration of solutes [3].

The nucleation rate is the number of nuclei formed per unit of time. It is higher when the cooling is fast:

for each degree of subcooling, the nucleation rate is multiplied by 10;

- The growth rate of the crystals is largely controlled by the heat flux removed from the crystallization zone, but also by the cryocentricity of intra and extracellular fluids during freezing, which progressively slows down growth [3].

During freezing, the mass enthalpy drops sharply; then it continues to decrease gradually during the cooling phase as shown in Figure 9 below:

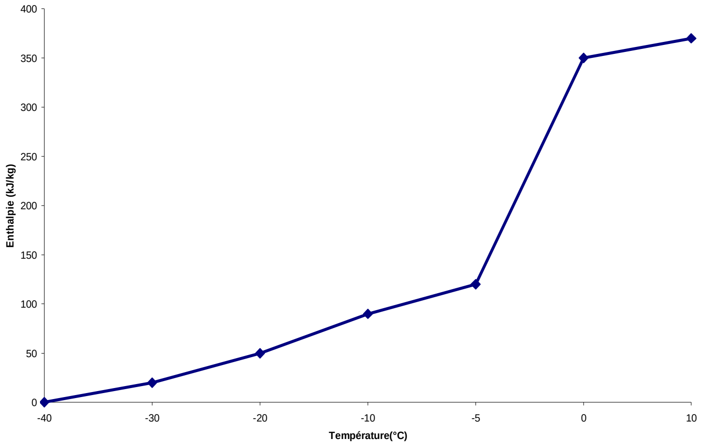

Figure 9: Mass Enthalpy of Beef as a Function of Temperature

Values were calculated by setting an enthalpy of 0 kJ / kg at -40°C

This reduction conditions the design calculations of the freezers.

The density of the product also decreases during freezing corresponding to the increase in volume which is of the order of 6% at the end of freezing. The thermal conductivity of the product increases because that of ice is four times higher than that of water. The thermal conductivity of adipose tissue is lower than that of muscle tissue and, in the latter, it is slightly higher if the heat flow is parallel to the direction of the muscle fibers than if it is perpendicular [4].

As in all products being frozen, the proportion of frozen water increases as the temperature decreases.

Thus at -7°C water in the form of ice represents 80% of the total water of the product. When the temperature reaches -20°C, almost 90% of the water is in the solid state, this percentage not noticeably increasing for a lower temperature. At very low temperatures, there is either formation of a eutectic or transition to the vitreous state. The fraction of unfrozen water thus decreases during freezing to a limit value, as well as the water activity and the crystallization temperature (Tc), while the concentration of solutes increases.

The formation of a eutectic during freezing is unlikely [5]. The conditions could be met in case of slow freezing, viscosity of the weak liquid phase and solutes in high concentration. The glass transition temperatures Tg measured for beef and fish are respectively -13.2°C and -15°C, but different glass transition températures have been measured for beef (Tg = -12°C)[6], a value much higher than the previous data cited by these authors (-60°C and -40°C) or those reported by Torregianni et al (-80°C and -35°C) [7]. Values of -20°C and -13.5°C have also been proposed for pork and turkey meat [3].

However, speed and duration of freezing depend on the total amount of heat to be extracted, the initial temperature and the final temperature, the characteristics of the product such as its composition, its total mass, its dimensions (in particular thickness) and its structure, of the presence of a package and its nature and finally the cooling process. Concerning this last point, in the case of processes based on a superficial heat exchange, are particularly important: the difference between the final temperature of the product and that of the freezing medium (air, cryogenic fluid, metal plates);

the coefficient of heat transfer between the product and the freezing medium. This coefficient depends in particular on the speed of circulation of the cryogenic fluid and the quality of the contact between product and freezing plates [7].

Thus, we present in the table below the freezing capacity of the machine in 24 hours up to the temperature of -18°C for different food products.

Table 2: Freezing Capacity for Different Food Products

Commodity	Water content (%) [8]	Mass (kg)
Meat	75	12
Fish	75	12
Ripe mango	83	10,84
Ripe banana	77	11,7
Raw potato	78	11,5
Carrot raw	89	10,1
Watermelon	94	9,6
Whole cow's milk	85	10,6
Cow's milk butter	21	42,8
Non-alcoholic beverages	87	10,3
Chicken	72	12,5
Okra, fresh fruit	89	10,1

The results obtained led us to the simulation equations of the operating time of domestic refrigeration and freezing appliances. Such an equation allows us by knowing the mass of products introduced as well as their water content to make a forecast of the operating time necessary to obtain the desired temperature.

Since the characteristic curve of the pre-freezing of the water is linear, we have plotted the different curves for certain water masses represented by figure 10.

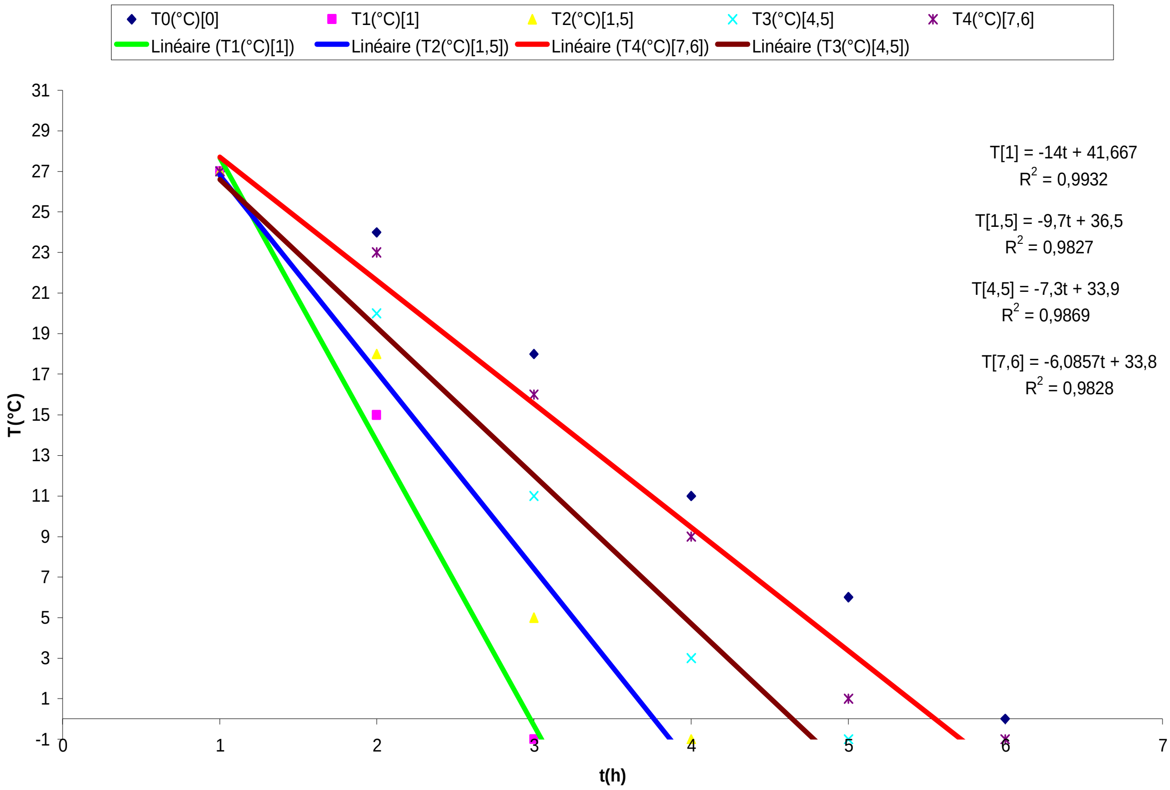

Figure 10: Evolution of the Refrigeration Temperature as a Function of Time

The curves thus obtained are of the form: $T = at + b$ (2)

The correlation coefficients displayed are satisfactory because they are very close to 1 (0.98); This allows us to confirm the findings set out above.

Thus, the different slopes obtained enabled us to represent in figure 11 the characteristic curve of the evolution of the slope as a function of the mass of water.

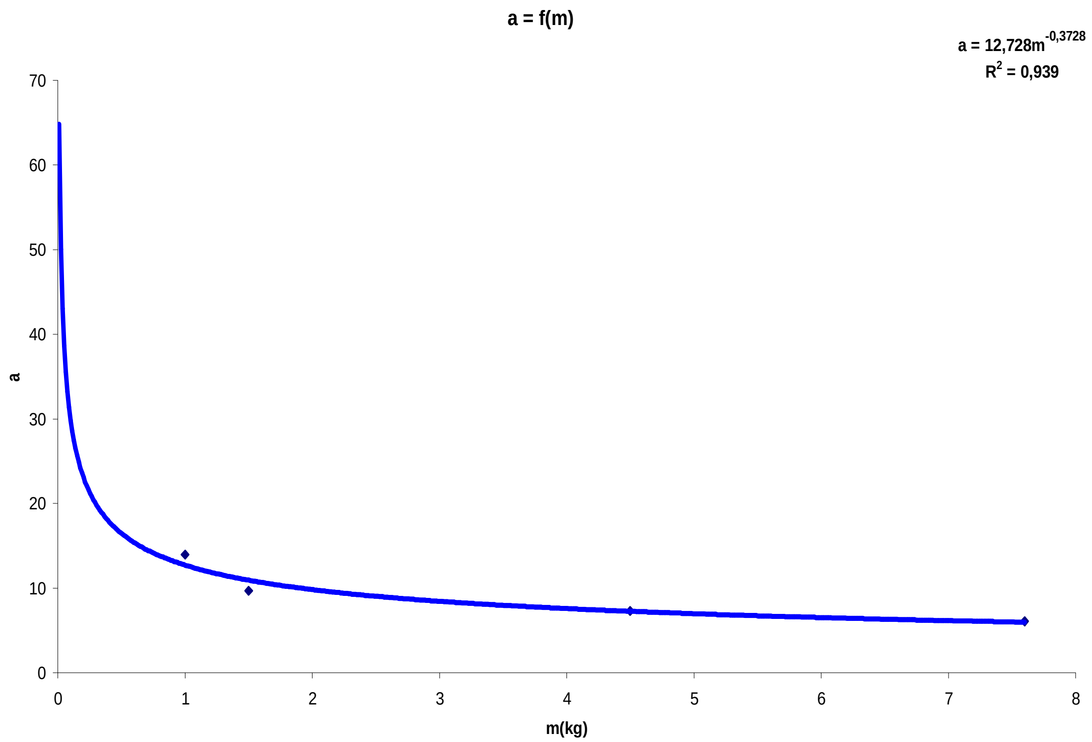

Figure 11: Evolution of the Slope According to the Mass

The trend curve thus obtained has a correlation coefficient of 0.94, a value slightly different from 1.

Finally, we can write the modeling equation for the pre-freezing of water in the form:

$$t = \frac{1}{a}\left(T_{p0} - T\right) \tag{3}$$

with: $a = 12{,}728m^{-0{,}3728}$

$$t = 0{,}078m^{0{,}3728}\left(T_{p0} - T\right) \tag{4}$$

t in hours; T (°C) is the final temperature for product refrigeration, Tp0 (°C) is the initial product temperature and m is the water mass in kg.

In the case of freezing, T (°C) represents the freezing temperature of the product Tc.

Figure 12 shows the freezing time of the water as a function of the body of water. The trend line reveals a correlation coefficient of 1.

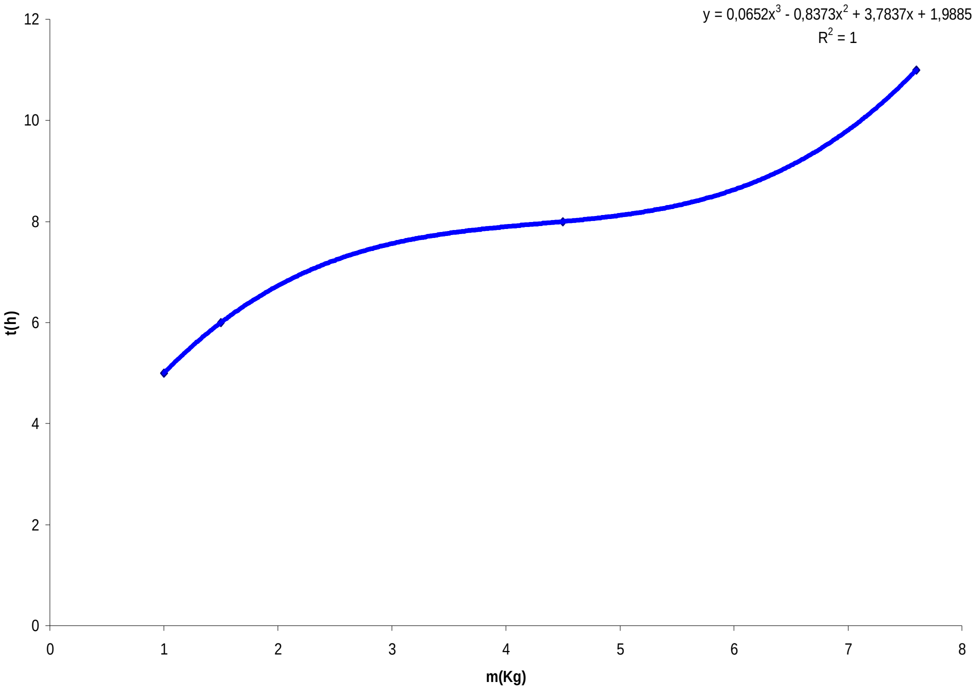

Figure 12: Evolution of Freezing Time as a Function of Mass

The equation,

$$t = 0{,}0652m^3 - 0{,}8373m^2 + 3{,}7837m + 1{,}9885 \qquad (5)$$

Determined with a correlation coefficient of 1 allows the modeling of the freezing time of the products in the vicinity of their freezing point (# 0) thus defined corroborates with that given by some specialists of the cold as far as the freezing of the meat of which the water composition reaches 75% [8]. And finally, the sub-cooling zone or cooling zone after freezing does not have a linear appearance but polynomial, we have shown in figure 13 the trend curves relative to water bodies.

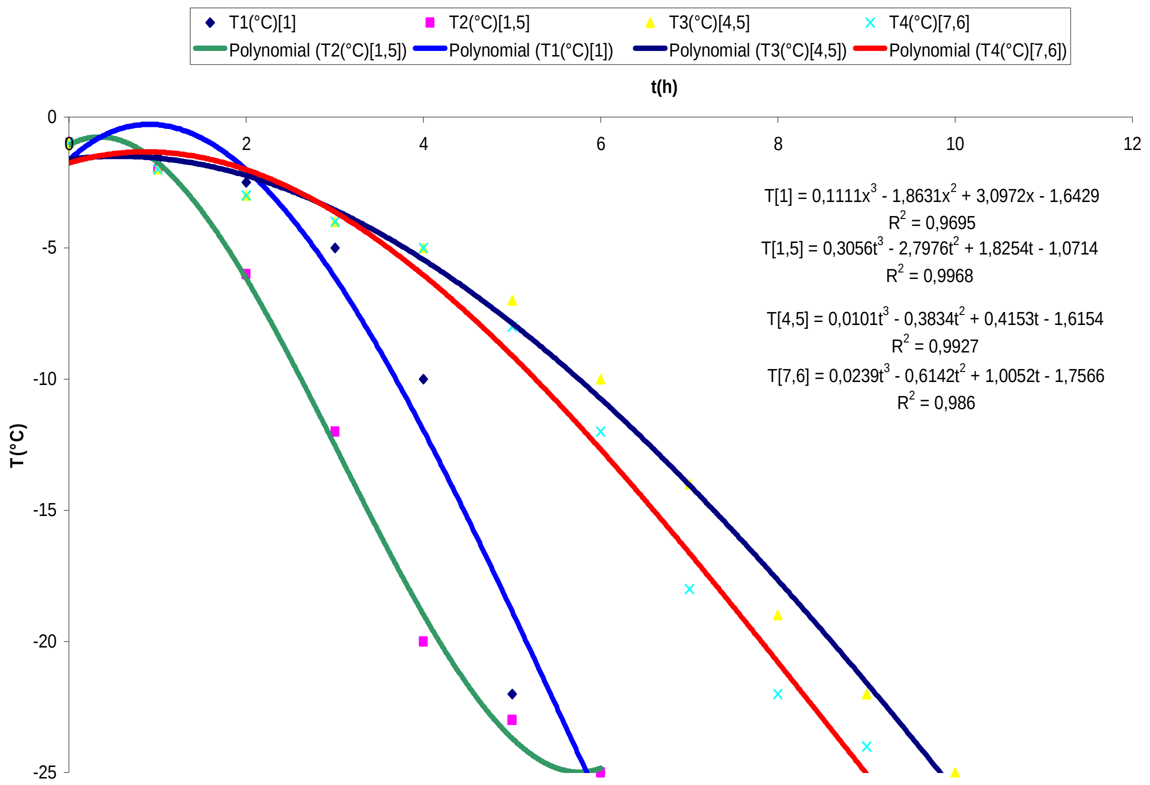

Figure 13: Evolution of the Freezing Temperature of Water as a Function of Time

Thus, the desired freezing temperature is a function of time according to the polynomial law: (6) The coefficients A, B, C and D are constants which depend on the body of water. They are determined experimentally. - T: final temperature of the frozen product in °C, - t: time to time necessary to reach the final freezing temperature of the product from its freezing temperature. This allows us to describe the modeling equation for the operation of household appliances for preservation and freezing in the form: (7) Note: m represents the total mass of water in kg contained in the products to be frozen from their introduction temperature to their end-of-freezing temperature TC. Table 3 presents the theoretical results and the experimental results obtained.

Table 3: Comparison of Theoretical and Experimental Results

Mass (kg)	t $(h)_{th}$	t $(h)_{exp}$
1	7,1	7
1,5	8,4	9
4,5	11,7	12
7,6	15,5	16
9	20,5	18

The comparison of the experimental results with those obtained by the theory makes it possible to affirm that the modeling equation thus defined corroborates well with the values obtained experimentally. **Validation of the numerical model:** Several equations have been put forward on the freezing time of food products. Of these, we selected Planck and meat specialists.

- **1.** Planck equation [5]: $t = \frac{\Delta h * \rho}{\Delta \theta} * \frac{1}{N} * D * \left(\frac{4D}{\lambda} + \frac{1}{\alpha} \right)$ (8)

Δh : quantity of heat to extract from the product between the freezing temperature Tc and the temperature at the end of freezing,

ρ : density of the product in kg/m^3 ,

$\Delta \theta$: temperature difference between the product and the medium,

D : thickness of the product to be frozen in m,

λ : coefficient of thermal conductivity of the product,

α : superficial coefficient of exchange between the product and the medium,

N : coefficient that depends on the shape of the product:

- plate: N = 2,

- cylinder: N = 4,

-sphere: N = 6,

t : freezing time expressed in seconds.

- **2.** Equation of meat specialists [5]: $\begin{cases} t(jours) = \frac{2D}{|T_i|} \\ t(jours) = \frac{1{,}5D}{|T_i|} \end{cases}$ (9)

t : freezing time in days,

D : thickness of the piece to be frozen in cm,

Ti : temperature of the freezing medium.

The classic Planck formula for calculating the freezing time for foodstuffs can lead to serious errors because of the simplifying assumptions that it assumes: zero heat capacity of the frozen part, initial temperature of the product equal to the temperature of the product. beginning freezing, etc. The analysis in figure 14 shows that the freezing time of the fish at heart to - 4°C is 3.3h. This value corresponds to that given by the numerical model which predicts this duration of freezing for the same mass of water.

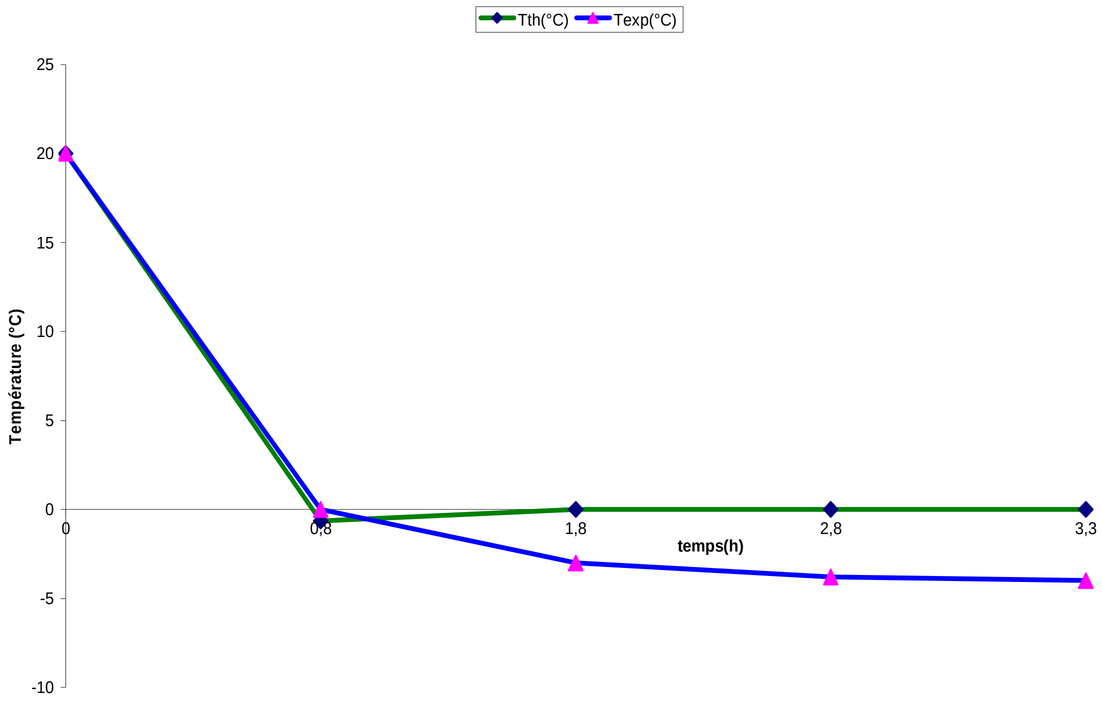

Figure 14: Comparative Evolution of Temperature as a Function of Time for Fish: Numerical and Experimental Model

In the same way, the analysis of Figure 15 shows that the freezing time of meat at heart to - 2.8°C is 4h. This value corresponds to that given by the numerical model which predicts this duration of freezing for the same mass of water.

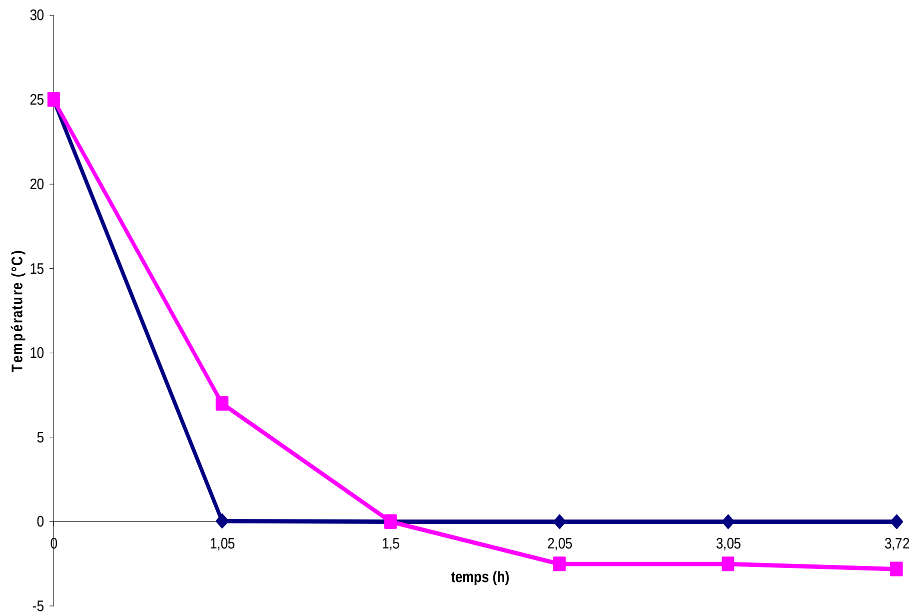

Figure 15: Comparative Evolution of Temperature as a Function of Time for Meat: Numerical and Experimental model

By comparing the theoretical and experimental results, we note a strong correlation of the data that can lead to a satisfactory conclusion of the use of the numerical model thus proposed. Tables 4 and 5 give the freezing times for the different equations proposed.

Table 4: Freezing time by different methods for fish

	Planck	Specialists	Digital Method	Experimental Method
Freezing temperature (°C)	-	-	0	- 4
Duration of freezing (h)	6,8	3,2	3,3	3,3

Table 5: Freezing Time by Different Methods for Beef

	Planck	Specialists	Digital Method	Experimental Method
Freezing temperature (°C)	-	-	0	- 2,8
Duration of freezing (h)	7,1	3,2	3,72	3,72

The results thus obtained corroborate well with those already advanced by other authors. As the starting freezing temperature for beef was -1.7°C, we were able to freeze it up to a core temperature of -8.8°C for a freezing time of 4 hours. numerical equation thus proposed.

The Planck equation gives a freezing time of 7.1 h corresponding to a core temperature of - 5.2°C which is outside the freezing range. This temperature (-5.2°C) is in the refrigeration stage after freezing when it is known that this equation only takes into account the latent heat of freezing of the products. It is this noted difference in temperature that explains the high freezing time. Thus the Planck equation is only interested in the freezing phase only and not the pre-cooling and cooling after freezing of the product.

For fish, the core freezing temperature reached is - 4°C corresponding to a freezing time of 3.3 h given by the numerical model. The Planck equation gives a freezing time of 6.8 h; this time corresponds to the core freezing temperature of the product of - 16.4°C very far from the starting freezing temperature which is - 3°C.

Thus, the numerical model thus developed not only makes it possible to predict the duration of freezing but it also informs us on the temperature of freezing at heart reached. This model takes into account the initial temperature of the products to be frozen but also its mass (mass of water contained in the products) contrary to the Planck equation mentioned above.

The equation that has been proposed by the meat specialists does not take into account the mass of the product but rather its thickness and does not tell us about the freezing temperature reached.

Thus, the Planck equations and meat specialists have limitations on their use. However, they tell us about the freezing time and not the freezing temperature of the product. These equations are only used for atmospheres maintained at a constant temperature, contrary to the numerical model proposed, which shows a decrease in temperature from the initial temperature of the cold room environment (motor stopped).

CONCLUSIONS

In this article, we have highlighted the supercooling of water during its solidification. We have been able to model the freezing time of food products that know their water content. The experimental results thus obtained corroborate those obtained theoretically. And lastly, we were able to use the heat released in the condenser to dry food products. A new design of household appliances such as freezers and refrigerators incorporating a dryer compartment is strongly recommended because it would not only dry food products but also reduce the size of the condenser and the refrigerant charge.

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