

# THERMOPHYSICAL PROPERTIES OF FOODS

## 1. Introduction

Some of the thermophysical properties we will be using and dealing are the following along with their units in SI:

Specific heat,  $c \left( \frac{J}{kg \ K} \right)$

Latent heat,  $L$  or  $h_{fg} \left( \frac{J}{kg} \right)$

Enthalpy,  $h \left( \frac{J}{kg} \right)$

Density,  $\rho \left( \frac{kg}{m^3} \right)$

Porosity,  $\varepsilon$  (dimensionless)

Thermal conductivity,  $\lambda \left( \frac{W}{mK} \right)$

Thermal diffusivity,  $\alpha \left( \frac{m^2}{s} \right)$

Specific heat, latent heat, enthalpy and thermal conductivity are proper thermal properties. Density and thermal diffusivity are thermophysical properties; density, together with specific heat and thermal conductivity, make up thermal diffusivity ( $\alpha = \lambda / \rho c$ ).

Porosity is also a thermophysical property in the present context because the density and thermal conductivity, and thus the thermal diffusivity, of a porous food depend upon it.

Specific heat, latent heat, enthalpy, thermal conductivity and thermal diffusivity are all properties of state. The last two are properties of related to heat transfer as well.

### 1.1. The importance of thermophysical properties in food engineering

The most basic phenomena in food processing are the three fundamental transfer processes:

- Heat transfer
- Momentum transfer
- Mass transfer

Heat transfer, in particular, is a very common unit operation or unit process (as well as being a fundamental transfer process).

The transfer of heat **into** a food or food system (to heat it) is used to accomplish objectives such as:

- Thawing/melting
- Evaporation
- Distillation
- Drying
- Blanching, pasteurizing, sterilizing

The transfer of heat **out of** a food or food system (to cool it) is used to accomplish one of the following:

- Cooling after heat treatment (e.g. after pasteurization) to minimize heat damage
- Chilling
- Freezing

Heating **or** cooling is used

- To bring the temperature to an optimum value for a particular operation such as centrifugal separation or homogenization.
- To control the temperature to a desired value (e.g. the optimum temperature for the fermentation of milk to make yogurt).

A food engineer who has to design, optimize or control a heating or cooling operation needs to be able to find out the answers to two questions.

## **(1) HOW MUCH?**

**HOW MUCH** energy must be expended (in terms of fuel consumption) to effect the desired temperature change?

In **heating**, chemical energy in fuel (gas, coal, etc.) is converted (often via electrical energy) to heat energy, which is then transferred to the food.

In **cooling**, energy from the fuel (after transformation into electrical energy) is used to drive a refrigeration system which removes heat from the food.

Some fuel is consumed at power stations, and the energy transported to food processing plants in the form of electricity. Some fuel (gas, coal) and some by-products

(e.g. bagasse in sugar cane processing) are burnt by processing companies on site to raise steam for process heating and produce power.

## (2) HOW FAST?

There are two important considerations here:

- **Time is money.** The faster a given type of heat exchange equipment can transfer heat (for a given food throughput, e.g. in  $kg/h$ , a given temperature change in the food and for a given temperature driving force for heat transfer) the cheaper the equipment will be in terms of both capital and operating costs. A more efficient piece of heat exchange equipment can be smaller; this makes it cheaper to buy (i.e. lower capital cost) and cheaper to run in terms of heat losses, necessary floor space, etc (i.e. lower operating costs).
- **Speed means better quality.** Generally, the faster a food can be heated or cooled the less will be the effect on its quality of the heating or cooling operation, i.e., the faster the better.

The food scientist or engineer must therefore be able to calculate

### HOW MUCH?

and

### HOW FAST?

The person who is able to calculate accurate answers to these questions will be able to

- Maximize plant throughput;
- maximize overall energy efficiency; and
- minimize food product quality degradation during processing.

### *The HOW MUCH? Thermophysical properties*

**HOW MUCH?** Depends on the **enthalpy change** required to bring about a rise (heating) or a fall (cooling) in temperature, hence the importance of **enthalpy** and the related properties **specific heat** and **latent heat**. Knowledge of these is essential also in calculating energy balances.

### *The HOW FAST? Thermophysical properties*

We can introduce some thermophysical properties by means of the equation for one-dimensional steady state heat flux:

$$q = -\frac{\lambda}{c\rho} \frac{d(c\rho\theta)}{dx} = -\alpha \frac{d(c\rho\theta)}{dx} \quad \left( \frac{W}{m^2} \right) \quad (1)$$

Equation (1) is a form of Fourier's law of heat conduction. If the density  $\rho$  and the heat capacity  $c$  are constants, Eq.(1) simplifies to the Fourier Heat Conduction equation discussed when we review basic principles of Heat Transfer and given as:

$$q = -\frac{\lambda}{c\rho} \frac{d(c\rho\theta)}{dx} = -\lambda \frac{d\theta}{dx} \quad \left( \frac{W}{m^2} \right) \quad (1a)$$

where  $\lambda$  is the thermal conductivity of the material with units  $\frac{W}{m K}$ . In the basic heat transfer notes we used  $k$  as the symbol for thermal conductivity. In the general case, heat conduction is in three dimensions under unsteady state conditions; a more general form of Fourier's equation is needed to deal with this, but the proportionality constant is still the thermal diffusivity  $\alpha$ .

As equation (1) and its more general form are **rate** equations, the importance of specific heat, density, thermal diffusivity (and porosity) is obvious.

## 1.2 Thermophysical properties data for foods

Where does food engineer or the food scientist find the numerical data on food thermophysical properties necessary for carrying out accurate **HOW MUCH?** and **HOW FAST?** calculations?

- Data can be **looked up** in the food literature (handbooks, textbooks, journals, etc.).
- Thermophysical properties can be directly **measured** experimentally.
- Values of thermophysical properties can be **predicted** using appropriate equations.

Looked-up data, even if it can be found, can be very unreliable. To be of any use, it must be data for the particular food, food composition, temperature, etc. involved in the **HOW MUCH?** or **HOW FAST?** problem at hand.

The accurate measurement of thermophysical properties, while perfectly feasible, is a specialist task, and is time-consuming and expensive. Sometimes it is not a reasonable option for the technologist or engineer employed in the food industry.

The mathematical prediction of thermophysical properties is perhaps a more realistic option for those working in the industry or needing quick information concerning thermophysical properties. Thus, prediction of thermophysical properties is a viable option to which any food engineer or food scientist could resort if that is needed. The

remainder of these notes deals with how to predict the thermophysical properties of a food from knowledge of

- the food's chemical composition,
- the food's structure (in some cases,
- the thermophysical properties of the major components of food, and
- temperature

The composition of foods is covered in Section 2, and the thermophysical properties of food components in Section 3.

The concepts of temperature and heat are briefly reviewed in Section 4.

Then, the prediction of thermophysical properties, starting with the **HOW MUCH?** question, is covered in detail.

### 1.3. Thermophysical properties of packaging materials

They are extremely important to estimate heat transfer operations though packaged foods. They will not be covered in this course as it may require a complete course to deal with the whole subject. Abundant information on packaging material properties are provided by suppliers of these materials.

## 2. THE COMPOSITION OF FOODS

The proximate compositions of a range of foods are shown in Table 1. A *proximate* analysis of a food is one in which the proportions of the major components only are measured; a food contains thousands of individual chemical compounds, but most of these account for only a very small proportion of the mass of the food, and are not measured in a proximate analysis. Thus the figures in each row of Table 1 add up to *approximately* 100%).

Fiber (indigestible carbohydrate, e.g. cellulose) is differentiated from available (digestible) carbohydrate (sugars and starches) because of its nutritional significance, and because – important in the present context – its thermophysical properties are somewhat different from those of available carbohydrates (see Tables 2 and 3).

*Ash* means the mineral content of the food. It is, literally, the ash (incombustible material) left when a sample of food is deliberately burnt to drive off all the organic (combustible) components.

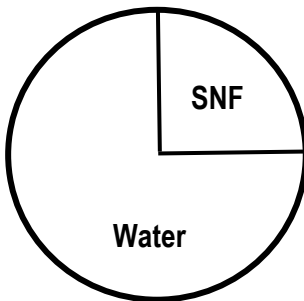
The protein, available carbohydrate, fiber and ash together make up the **solids-not fat (SNF)** content of the food; the SNF content includes everything except fat and water.

From the point of view of using food composition data in the prediction of food thermophysical properties, it is necessary to divide foods into non-fatty and fatty foods. In addition and because during freezing the amount of water in a food is largely reduced

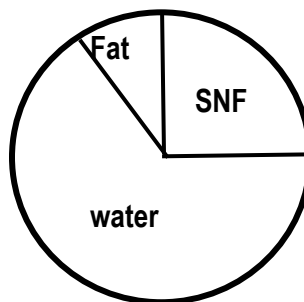
by the formation of ice, we will have to consider two temperature ranges (see Fig. 6): above freezing (i.e., above the initial freezing point) and below freezing (i.e., below the initial freezing point). An equation to calculate the initial freezing point was derived in a previous course (ABE 202) and will be reviewed in a thermodynamics review.

Non-fatty foods are defined here as food containing  $< 2\%$  fat, and fatty foods as those containing  $\geq 2\%$  fat. The gross compositions of non-fatty and fatty foods in terms of SNF, fat (if  $\geq 2\%$ ) and water are highlighted in Table 1.

At temperatures above freezing, the mass compositions of non-fatty and fatty food may be represented as in Figs. 1 and 2.

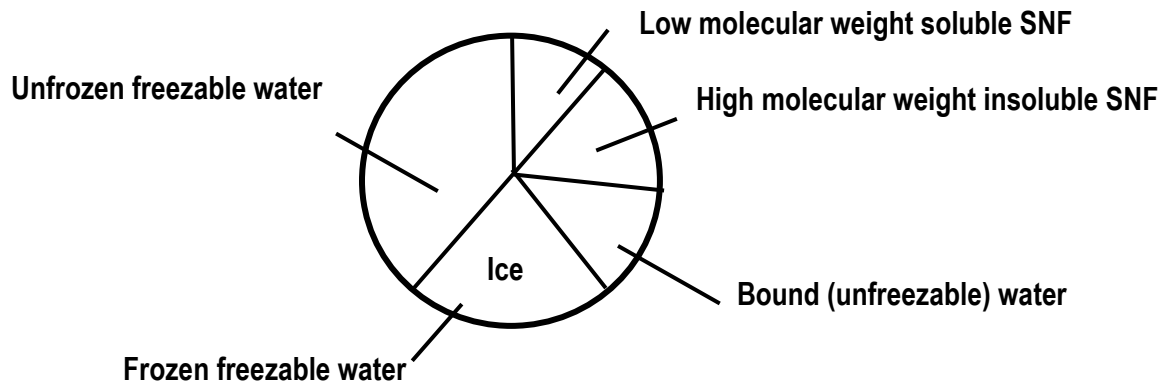


**Fig.1.** Representation of the mass composition of a non-fatty food above freezing.

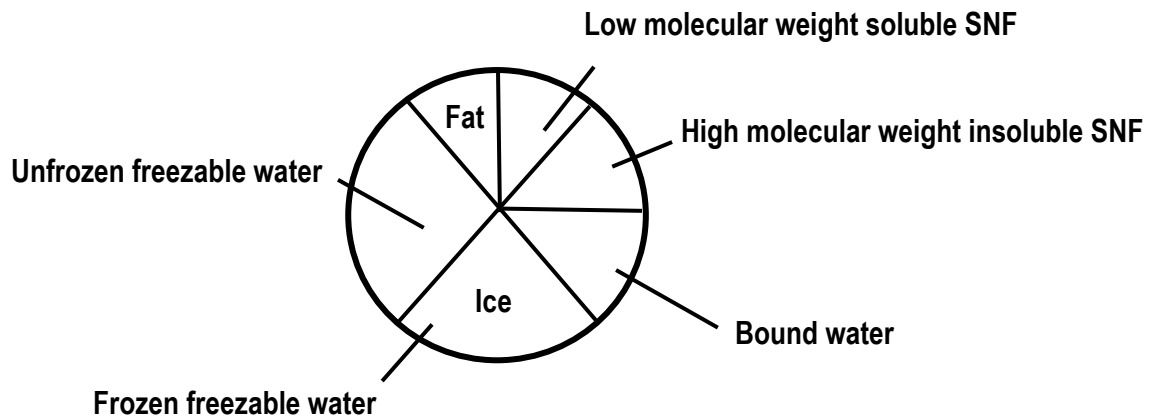


**Fig. 2.** Representation of the mass composition of a fatty food above freezing.

At temperatures below freezing, the compositions must be presented as shown in Figures 3 and 4.



**Fig 3. Representation of the mass composition of a non-fatty food below freezing.**



**Fig. 4. Representation of the mass composition of a fatty food below freezing.**

The only difference between Figs. 3 and 4, and between Figs. 1 and 2, is the fat content.

### ***Bound water and freezable water***

The total water content of a food comprises bound water and freezable (free, solvent) water. Bound water cannot be frozen (i.e. turned to ice) because it is attached (i.e. bound), usually by hydrogen bonds, to substances in the SNF. The freezable water, which can be turned to ice, is the total water minus the bound water. The concept of bound “immobilized” water has been challenged. There is experimental evidence that the mobility of water is reduced but cannot be immobilized.

### ***Soluble and insoluble SNF, and freezable water***

Soluble and insoluble SNF are differentiated in Figs. 3 and 4 merely to make the point that the soluble SNF is dissolved in the freezable (free) water. The initial freezing point of a food is the initial freezing point of this solution. As the temperature is lowered below the initial freezing point, freezable water becomes ice. If the temperature was dropped to a sufficiently low value, all the freezable water would be turned to ice and no liquid water (unfrozen freezable water) would remain. Frozen foods are not always cooled to a sufficiently low temperature for this to happen.

The point to note at this stage is that the phase change **water** ↔ **ice** occurs over a temperature **range** when a solution (and therefore when a food) is frozen, and **not** at a single constant freezing point, as in the case of pure water. This, and its significance, will be discussed in more detail later.

### ***Mass fractions***

In using food composition data in thermophysical property prediction, it is convenient to express a food's composition in terms of mass fractions.

$$\text{Mass fraction} = x = \frac{\text{percentage}}{100}$$

For example, the composition of avocado (Table 1) in terms of mass fractions is

$$\begin{array}{rcl} x_{PR} & = & 0.018 \\ x_{CA} & = & 0.007 \\ x_{FI} & = & 0.029 \\ x_{AS} & = & 0.039 \\ x_{fat} & = & 0.26 \\ x_w & = & \frac{0.647}{1.000} \end{array}$$

where PR = protein, CA = available carbohydrate, FI = fiber, AS = ash, fat = fat, and w = water.

Note that, because the figures are **fractions**, they must add up to 1.0.

Similarly, for foods above freezing:

- For non-fatty food  $x_{SNF} + x_w = 1$  (2)

- For a fatty food  $x_{SNF} + x_{fat} + x_w = 1$  (3)



For foods below freezing temperature:

- Non-fatty food  $x_{SNF} + x_{BW} + x_{ice} + (x'_w - x_{ice}) = 1$  (4)

- Fatty food  $x_{SNF} + x_{BW} + x_{fat} + x_{ice} + (x'_w - x_{ice}) = 1$  (5)

where

$BW$  means bound water

$x_{BW}$  = bound water fraction

$x'_w = (x_w - x_{BW})$  = mass fraction of freezable water

$x_{ice}$  = mass fraction of ice or  
= mass fraction of **frozen** freezable water

$(x'_w - x_{ice})$  = mass fraction of **unfrozen** freezable water

$x_w = x_{BW} + x'_w$  is the **total** water content of the food

**Table 1. Proximate compositions of the edible parts of a selection of foods.**

Food	Protein	Available Carbohydrate	Fiber	Ash	SNF	Fat	Water
<b>Dairy products</b>							
Pasteurized whole milk	3.3%	4.7%	0.0%	0.71%	<b>8.71%</b>	<b>4.0%</b>	<b>87.3%</b>
Skim milk	3.46	4.9	0.0	0.73	<b>9.09</b>	0.2	<b>90.9</b>
Trim milk	4.3	5.6	0.0	0.92	<b>10.8</b>	0.42	<b>89.2</b>
Cream	2.0	3.0	0.0	0.38	<b>5.4</b>	<b>40.0</b>	<b>54.6</b>
Natural unsweetened yogurt	4.8	4.6	0.0	0.95	<b>10.3</b>	0.8	88.8
Cheddar cheese	24.9	0.0	0.0	3.8	<b>28.7</b>	<b>35.2</b>	<b>36.1</b>
Processed cheese	21.3	0.0	0.0	5.3	<b>26.6</b>	<b>27.9</b>	<b>45.5</b>
Cream cheese	3.0	5.0	0.0	2.0	<b>10.0</b>	<b>37.0</b>	<b>53.0</b>
Cottage cheese	14.0	2.1	0.0	1.29	<b>17.4</b>	<b>3.5</b>	<b>79.1</b>
<b>Sugars, etc</b>							
Honey	1.4%	78.1%	0.0%	0.5%	<b>80.0%</b>	0.0%	<b>20.0%</b>
Chocolate (plain)	6.1	54.6	1.1	1.7	<b>63.5</b>	<b>35.0</b>	<b>1.5</b>
<b>Cereals</b>							
Wheat (whole grains)	11.8	66.2	12.0	1.6	<b>91.6</b>	1.8	<b>6.6</b>

Food	Protein	Available Carbohydrate	Fiber	Ash	SNF	Fat	Water
<b>Bakery products</b>							
Whole-meal flour	12.7	66.9	11.8	1.4	92.8	2.0	5.2
White flour (78% extraction)	11.5	72.1	3.1	0.6	87.3	1.3	11.4
Whole-meal bread	8.1	40.8	5.7	2.0	56.6	1.4	42.0
White bread	7.3	47.7	2.8	1.9	59.7	0.9	39.4
Biscuits	7.3	55.2	1.7	0.9	65.1	30.0	4.9
Banana cake	5.3	46.5	1.3	1.1	54.2	13.6	32.2
Chocolate cake	6.4	51.3	1.2	1.0	59.9	20.6	19.5
Short pastry	6.4	62.3	1.9	1.5	72.1	25.6	2.3
<b>Oils and fats</b>							
Pure edible oils and fats	0.0	0.0	0.0	0.0	0.0	100	0.0
Butter	.55	0.62	0.0	1.5	2.67	81.5	15.8
<b>Vegetables</b>							
Silver beet	2.6	0.4	2.9	1.3	9.3	0.3	90.4
Butternut squash	1.3	9.4	3.5	0.76	14.9	0.1	84.9
Potato	2.0	15.6	0.9	0.93	19.4	0.0	80.6
Onion	1.3	8.8	1.7	0.47	12.3	0.1	87.6
Asparagus	2.4	3.0	1.9	0.74	8.0	0.4	91.9
Tomato	0.74	2.2	1.1	0.49	4.5	0.2	95.3
Mushroom	2.4	2.2	1.4	0.80	6.8	0.2	93.0
<b>Fruits and nuts</b>							
Avocado	1.8	0.7	2.9	3.9	9.3	26.0	64.7
Kiwifruit	0.79	8.5	3.9	0.70	13.9	0.8	85.3
Apple (Granny Smith)	0.27	10.6	1.9	0.21	12.9	0.6	86.4
Nectarine	1.1	8.1	1.6	0.65	11.4	0.5	88.0
Strawberry	0.76	6.6	1.8	0.60	9.8	0.4	89.8
Cashew	16.9	26.0	4.7	2.5	50.1	45.9	4.0
Peanut	28.1	11.2	4.8	2.4	46.5	49.0	4.5
Peanut butter	29.0	13.4	5.2	2.5	50.1	48.0	1.9
<b>Meat</b>							
Raw whole chicken	17.5%	0.0%	0.0%	0.87%	18.4%	14.1%	67.5%
Chicken breast	22.3	0.0	0.0	1.09	23.4	2.1	74.5
Chicken thigh	17.0	0.0	0.0	0.9	17.9	13.8	68.3
Lean beef	22.2	0.0	0.0	1.0	23.2	0.0	76.8
Canned corned beef	22.3	0.0	0.0	3.5	25.8	15.7	58.5
Ham	15.5	0.0	0.0	2.9	18.4	49.5	32.1

<b>Food</b>	<b>Protein</b>	<b>Available Carbohydrate</b>	<b>Fiber</b>	<b>Ash</b>	<b>SNF</b>	<b>Fat</b>	<b>Water</b>
Pork sausage	10.7	10.6	0.0	0.8	<b>14.6</b>	<b>11.5</b>	<b>73.9</b>
<b>Whole egg</b>	131.5	0.32	0.0	0.8	<b>14.6</b>	<b>11.5</b>	<b>73.9</b>
<b><i>Fish</i></b>							
Cod	17.0	0.0	0.0	-	<b>17.0</b>	0.5	<b>82.5</b>
Salmon	20.0	0.0	0.0	-	<b>20.0</b>	<b>14.0</b>	<b>66.0</b>
Lobster	21.2	0.0	0.0	-	<b>21.2</b>	<b>3.4</b>	<b>75.4</b>
<b><i>Pickles and sauces</i></b>							
Mayonnaise	3.3	11.2	0.0	2.1	<b>16.6</b>	<b>36.0</b>	<b>47.4</b>

### Gas in foods

Foods often contain undissolved gas (e.g.  $CO_2$  in breadcrumbs, intracellular air in fruit and vegetable tissues). Gas is not counted as part of the mass composition of a food because the mass of gas will be very, very small compared with the masses of solid and liquid components (in a given quantity of the food). Thus the presence of gas can be ignored in predicting the specific heat, enthalpy change and latent heat of foods. However, gas does form a significant proportion of the volumetric composition of a food, because of its low density. Gas-filled spaces in the food represent porosity, which has to be taken into account in predicting density, thermal conductivity and thermal diffusivity.

### 3. THE THERMOPHYSICAL PROPERTIES OF FOOD COMPONENTS

Table 2 shows a set of empirical equations that may be used to predict the thermophysical properties specific heat, density, thermal conductivity and thermal diffusivity of the major food components (e.g. proteins, carbohydrate, etc). Each equation is valid for the temperature range  $-40$  to  $150^\circ C$ .

Values of these properties for the mid-point ( $-20^\circ C$ ) of the below freezing range ( $-40$  to  $0^\circ C$ ), the mid-point ( $75^\circ C$ ) of the above freezing range ( $0$  to  $150^\circ C$ ) and the mid-point ( $55^\circ C$ ) of the full range ( $-40$  to  $150^\circ C$ ) are given in Table 3. With the exception of the properties of water substance for temperatures  $\geq 0^\circ C$ , these values have been calculated using the equations in Table 2. The properties of water substance for temperatures  $\geq 0^\circ C$  are taken from Steam Tables.

All the equations and data in Table 2 and Table 3 respectively will be referred to and used in various ways in the remainder of this document.

All the equations in Table 2, except that for air, are taken from Choi & Okos (1986). The equation for the thermal conductivity of air is taken from Murikami & Okos (1988).

**Table 2. Temperature dependent equations for predicting the thermophysical properties of the major components of food. (From Choi & Okos, 1986), and Murakami and Okos, 1988).**

<u>Property</u>	<u>Food Component</u>	<u>Temperature Dependent Equation</u>	<u>Eq. No.</u>
<b>Specific heat</b> ( $kJ/(kg \cdot K)$ )	Protein	$c = 2.0082 + 1.2089 \times 10^{-3} \theta - 1.3129 \times 10^{-6} \theta^2$	(6)
	Carbohydrate	$c = 1.5488 + 1.9625 \times 10^{-3} \theta - 5.9399 \times 10^{-6} \theta^2$	(7)
	Fiber	$c = 1.8459 + 1.8306 \times 10^{-3} \theta - 4.6509 \times 10^{-6} \theta^2$	(8)
	Ash	$c = 1.0926 + 1.8896 \times 10^{-3} \theta - 3.6817 \times 10^{-6} \theta^2$	(9)
	Fat	$c = 1.9842 + 1.4733 \times 10^{-3} \theta - 4.8008 \times 10^{-6} \theta^2$	(10)
	Water ( $-40 - 0^\circ C$ )	$c = 4.0817 - 5.3062 \times 10^{-3} \theta + 9.9516 \times 10^{-4} \theta^2$	(11)
	Water ( $0 - 150^\circ C$ )	$c = 4.1762 - 9.0864 \times 10^{-5} \theta + 5.4731 \times 10^{-6} \theta^2$	(12)
	Ice	$c = 2.0623 + 6.0769 \times 10^{-3} \theta$	(13)
<b>Density</b> ( $kg/m^3$ )	Protein	$\rho = 1.3299 \times 10^3 - 5.1840 \times 10^{-1} \theta$	(14)
	Carbohydrate	$\rho = 1.5991 \times 10^3 - 3.1046 \times 10^{-1} \theta$	(15)
	Fiber	$\rho = 1.3115 \times 10^3 - 3.6589 \times 10^{-1} \theta$	(16)
	Ash	$\rho = 2.4238 \times 10^3 - 2.8063 \times 10^{-1} \theta$	(17)
	Fat	$\rho = 9.2559 \times 10^2 - 4.1757 \times 10^{-1} \theta$	(18)
	Water	$\rho = 9.9718 \times 10^2 + 3.1439 \times 10^{-3} \theta - 3.7574 \times 10^{-3} \theta^2$	(19)
	Ice	$\rho = 9.1689 \times 10^2 + 1.3071 \times 10^{-1} \theta$	(20)
<b>Thermal Conductivity</b> ( $W/(m \cdot K)$ )	Protein	$\lambda = 1.7881 \times 10^{-1} + 1.1958 \times 10^{-3} \theta - 2.7178 \times 10^{-6} \theta^2$	(21)
	Carbohydrate	$\lambda = 2.0141 \times 10^{-1} + 1.3874 \times 10^{-3} \theta - 4.3312 \times 10^{-6} \theta^2$	(22)
	Fiber	$\lambda = 1.8331 \times 10^{-1} + 1.2497 \times 10^{-3} \theta - 3.1683 \times 10^{-6} \theta^2$	(23)
	Ash	$\lambda = 3.2962 \times 10^{-1} + 1.4011 \times 10^{-3} \theta - 2.9069 \times 10^{-6} \theta^2$	(24)
	Fat	$\lambda = 18071 \times 10^{-1} - 2.267 \times 10^{-4} \theta - 1.7749 \times 10^{-7} \theta^2$	(25)
	Water	$\lambda = 5.7109 \times 10^{-1} + 1.7625 \times 10^{-3} \theta - 6.77036 \times 10^{-6} \theta^2$	(26)
	Ice	$\lambda = 2.2196 - 6.289 \times 10^{-3} \theta + 1.0154 \times 10^{-4} \theta^2$	(27)
	Air	$\lambda = 2.382 \times 10^{-2} + 6.75 \times 10^{-5} \theta$	(27a)
<b>Thermal Diffusivity</b> $\times 10^6$ ( $m^2/s$ )	Protein	$\alpha = 6.8714 \times 10^{-2} + 4.7578 \times 10^{-4} \theta - 1.4646 \times 10^{-6} \theta^2$	(28)
	Carbohydrate	$\alpha = 8.0842 \times 10^{-2} + 5.3052 \times 10^{-4} \theta - 2.3218 \times 10^{-6} \theta^2$	(29)

<u>Property</u>	<u>Food Component</u>	<u>Temperature Dependent Equation</u>	<u>Eq. No.</u>
<b>Thermal Diffusivity</b> $\alpha \times 10^6$ ( $m^2 / s$ )	Fiber	$\alpha = 7.3976 \times 10^{-2} + 5.1902 \times 10^{-4} \theta - 2.2202 \times 10^{-6} \theta^2$	(30)
	Ash	$\alpha = 1.2461 \times 10^{-1} + 3.7321 \times 10^{-4} \theta - 1.2244 \times 10^{-6} \theta^2$	(31)
	Fat	$\alpha = 9.8777 \times 10^{-2} - 1.2569 \times 10^{-4} \theta - 3.8286 \times 10^{-8} \theta^2$	(32)
	Water	$\alpha = 1.3168 \times 10^{-1} + 6.2477 \times 10^{-4} \theta - 2.4022 \times 10^{-6} \theta^2$	(33)
	Ice	$\alpha = 1.1756 - 6.0833 \times 10^{-3} \theta + 9.5037 \times 10^{-5} \theta^2$	(34)

**Table 3. Values of the thermophysical properties of the major food components at -20, 55 and 75°C, calculated (except for some water properties) using the equations in Table 2.**

<b>Property</b>	<b>Component</b>	<b>Temperature (°C)</b>		
		<b>-20</b>	<b>55</b>	<b>75</b>
<b>Specific heat</b> ( $kJ / (kg \cdot K)$ )	Protein	1.983	2.071	2.091
	Carbohydrate	1.507	1.639	1.662
	Fiber	1.807	1.932	1.957
	Ash	1.053	1.185	1.214
	Fat	1.953	2.051	2.068
	Water	4.586	4.182	4.194
	Ice	1.941	-	-
<b>Density</b> ( $kg / m^3$ )	Protein	1340	1301	1291
	Carbohydrate	1605	1582	1576
	Fiber	1319	1291	1284
	Ash	2429	2408	2403
	Fat	933.9	902.6	894.3
	Water	977.2	985.2	974.6
	Ice	919.5	-	-
<b>Thermal Conductivity</b> ( $W / (m \cdot K)$ )	Protein	0.154	0.236	0.253
	Carbohydrate	0.172	0.265	0.281
	Fiber	0.157	0.242	0.259
	Ash	0.300	0.398	0.418
	Fat	0.185	0.168	0.163
	Water	0.533	0.649	0.666
	Ice	2.385	-	-
<b>Thermal Diffusivity</b> $\alpha \times 10^6$ ( $m^2 / s$ )	Air	0.0225	0.0272	0.0289
	Protein	0.0586	0.0904	0.0961
	Carbohydrate	0.0693	0.103	0.107
	Fiber	0.0627	0.0958	0.100
	Ash	0.117	0.141	0.146
	Fat	0.101	0.0917	0.089

Property	Component	Temperature ( $^{\circ}\text{C}$ )		
		-20	55	75
Thermal	Water	0.118	0.158	0.163
Diffusivity	Ice	1.335	-	-
$\times 10^6$				
$(\text{m}^2 / \text{s})$				

## 4. TEMPERATURE AND HEAT: FUNDAMENTAL CONCEPTS

### 4.1 Temperature

The temperature of an object is a property that determines the direction of heat flow when the object is brought into thermal contact with other objects; heat flows from regions of higher to those of lower temperatures.

When two objects are in thermal equilibrium, no heat transfer takes place between them; they are at the same temperature.

Temperature is a measure of the kinetic energy of the molecules, atoms, or ions of which an object or material is composed.

Temperature is usually expressed in *degrees Celsius* ( $^{\circ}\text{C}$ ). The basic physical quantity, the thermodynamic temperature, is expressed in *Kelvins* ( $\text{K}$ ).

0 K (absolute zero) =  $-273.15^{\circ}\text{C}$ . Therefore a given temperature expressed in  $\text{K}$  is bigger by 273.15 than the same temperature expressed in  $^{\circ}\text{C}$ , e.g.  $293.15 \text{ K} = 20^{\circ}\text{C}$ . But note that a temperature **difference** expressed in  $\text{K}$  has exactly the same value as the same temperature difference expressed in  $^{\circ}\text{C}$ , e.g.  $(293.15 - 278.15) \text{ K} = (20 - 5)^{\circ}\text{C} = 15 \text{ K}$  or  $^{\circ}\text{C}$ .

### 4.2. Heat

When an energy transfer between two materials takes place by virtue of a temperature difference **exclusively**, this energy transfer is called a **heat flow**, i.e. heat is a form of energy. Strictly speaking, the word “heat” should be used only when referring to this method of energy transfer, and to refer to the energy so transferred. It is meaningless to say a material **contains** a certain amount of heat. However, one can say that a material possesses enthalpy. Enthalpy is defined in the next section.

## 5. SPECIFIC HEAT, ENTHALPY AND LATENT HEAT

### 5.1. Basic definitions and interrelationships

#### *Specific heat*

The specific heat capacity (commonly called specific heat) of a material is defined as the quantity of thermal or heat energy required to raise the temperature of unit mass of the material by  $1^{\circ}\text{C}$  or  $1 \text{ K}$ ; its units are  $\text{J}/(\text{kg} \cdot \text{K})$ .

Specific heat is generally temperature dependent to a greater or lesser extent, so the amount of heat energy to be added or removed to effect a given temperature change is given by the equation

$$q = \int_{\theta_1}^{\theta_2} c(\theta) d\theta \quad (J / kg) \quad (35)$$

where

- $q$  = quantity of heat energy ( $J / kg$ )
- $\theta$  = temperature ( $^{\circ}C$ )
- $\theta_2 - \theta_1$  = temperature change ( $\theta_1$  to  $\theta_2$  or  $\theta_2$  to  $\theta_1$ ) brought about by adding or removing  $q(^{\circ}C)$
- $c(\theta)$  = specific heat expressed as some function of temperature ( $J / (kg \cdot K)$ )

For solids and liquids (in general a food is either one or the other), in the absence of kinetic energy and potential energy effects, and significant chemical reaction, the heat added to or removed from the material is equal to the change in enthalpy of the material, so

$$\Delta h = \int_{\theta_1}^{\theta_2} c(\theta) d\theta \quad (J / kg) \quad (36)$$

where  $\Delta h$  is the enthalpy change per unit mass between temperatures  $\theta_1$  and  $\theta_2$ . Enthalpy is a thermodynamic property of a material. Kinetic and potential energies changes in food during heating and cooling operations are usually small enough, relative to the heat transferred, so they will be ignored.

Equation (36) is important to remember. It shows that if we have a temperature dependent expression for specific heat, we can integrate it to obtain an expression for enthalpy change.

As demonstrated the specific heat in equations (35) and (36) is the specific heat at either constant pressure or constant volume (in fact it was shown in ABE 202 that these are equals for liquids or solids, in fact for any incompressible material). Thus we will assume that the two can be taken as equal for solids and liquids, which for practical purposes may be considered incompressible.

### ***Temperature dependence of specific heat***

Specific heat is generally temperature dependent, as mentioned above. Often, however, if no phase change (**solid**  $\leftrightarrow$  **liquid**) occurs in the temperature range of interest, the temperature dependence may be ignored. Equation (36) can then be written

$$\Delta h = c \int_{\theta_1}^{\theta_2} d\theta = c(\theta_2 - \theta_1) = c\Delta\theta \quad (J / kg) \quad (37)$$

where  $c$  = temperature independent specific heat = constant ( $J / (kg \cdot K)$ ).

If  $c$  is only slightly temperature dependent, one can use an average value for the temperature range of interests. Then,

$$\Delta h = \bar{c} \Delta \theta \text{ (J/kg)} \quad (38)$$

where  $\bar{c}$  = average specific heat for the temperature range  $\theta_1$  to  $\theta_2$  (J/(kg · K)).

### **Enthalpy**

We cannot determine absolute values of enthalpy. However, equation (36) may be used to calculate enthalpy,  $h$ , at any temperature,  $\theta_2$ , relative to an arbitrarily assumed value of  $h = 0$  at temperature  $\theta_0$ .  $\theta_0$  is called the **datum temperature** in this case. Enthalpies expressed in this way are analogous to heights above mean sea level, mean sea level being specified as the datum at which height is arbitrarily made zero.

A mathematical expression,  $c(\theta)$ , relating  $c$  to temperature, is required to integrate equation (36). Such expressions have been developed for foods, as shown later in these notes

The datum temperature can be any convenient value, for example:

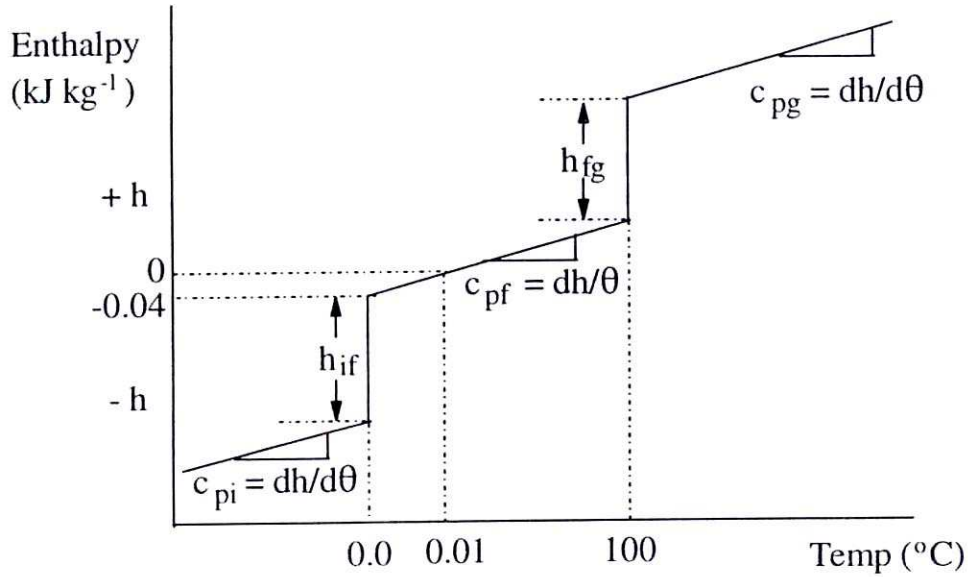
- 0.01°C     (the triple point of water) in steam tables;
- 0<sub>if</sub>°C     the initial freezing point of a food;
- 50°C     sometimes used when tabulating enthalpies of foods in the freezing region of temperature.

We will tend to use  $\theta_{if}$  or 0.01°C

Tabulations or plots of enthalpy versus temperature provide convenient ways of finding enthalpy values for the purpose of determining enthalpy changes, which are what we are always interested in practice; enthalpy changes represent energy demands for heating and cooling during processing. We can of course, as stated above, calculate enthalpy change,  $\Delta h$ , directly provided we are able to integrate the right-hand side of equation (36) to give an expression for doing so. We will see later how this can be done for foods.

A diagrammatic enthalpy-temperature plot for water substance at atmospheric pressure is shown in Fig. 5, as an example of such a plot. These data are tabulated in steam tables.





**Figure 5. Enthalpy against temperature plot for water substance at atmospheric pressure. Datum temperature = 0.01°C**

Note in Fig. 5 that:

$h = 0$  at the datum temperature of 0.01°C.

$h$  is positive at  $\theta > 0.01^\circ\text{C}$ .

$h$  is negative at  $\theta < 0.01^\circ\text{C}$ .

As temperature increases from some value below 0°C,  $h$  increases steadily except at the phase change temperatures 0°C and 100°C. At each of these, **latent** heat is supplied at constant temperature, and a large step increase in enthalpy results.

With the assumption of  $h = 0$  at  $\theta_1$ , equation (36) can be differentiated to give:

$$\frac{dh(\theta)}{d\theta} = c(\theta) \left( \frac{J}{kg K} \right) \quad (39)$$

where  $\frac{dh(\theta)}{d\theta}$  is the rate of change of enthalpy with temperature expressed as some function of temperature.

If  $c$  is independent of temperature, as in each of the sensible heat parts of the curve in Fig. 5, then equation (39) can be written

$$\frac{dh(\theta)}{d\theta} = c = \text{constant} \quad (J / (kg \cdot K)) \quad (40)$$

Equations (39) and (40) are important. They show that **the specific heat at a given temperature is equal to the rate of change of enthalpy with temperature at that temperature.**

They also show that the specific heat of a material (e.g. a food) can be determined by **differentiating** experimental enthalpy-temperature data. Using equation (39) to determine specific heat is the opposite of using equation (36) to determine enthalpy change.

### **Latent heat**

At each of the phase change temperatures  $0^\circ C$  and  $100^\circ C$ ,  $d\theta = 0$  and  $dh/d\theta = c = \infty$ , because there is no temperature change even though the enthalpy changes (Fig. 5). At these temperatures,

$$\Delta h = L \quad (J / kg) \quad (41)$$

where

$L =$  latent heat  $(J / kg)$ .

At  $0^\circ C$ ,  $L = h_{if}$  = latent heat of fusion

At  $100^\circ C$ ,  $L = h_{fg}$  = latent heat of evaporation.

## **5.2. Enthalpy changes and specific heats of foods**

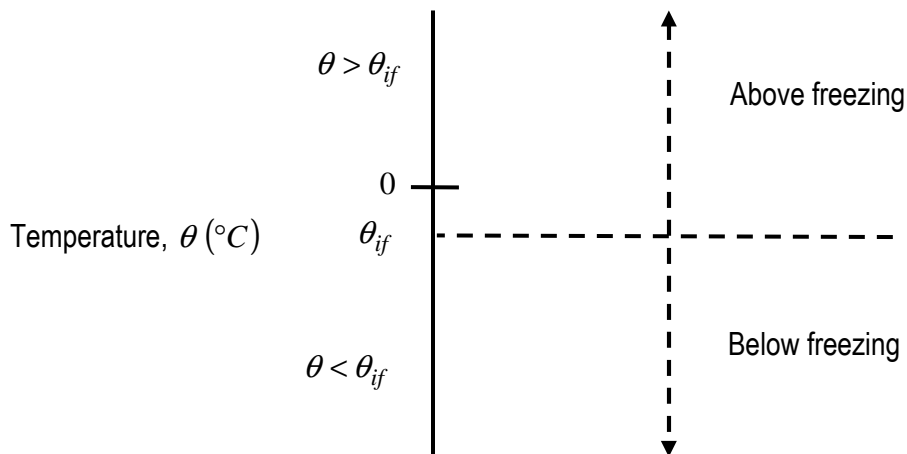
If tabulations or plots of enthalpy versus temperature are not available for a particular food of interest (they often are not!), we can still calculate enthalpy change  $\Delta h$  using equation (36) provided we have a valid temperature dependent expression for specific heat that we can integrate. The development of such expressions and their integration is covered in detail below.

Conversely, we can determine the specific heat of a food at a particular temperature by differentiating experimental enthalpy-temperature data, as shown by equation (39).

### **5.2.1. Enthalpy and specific heat of foods: general points**

The objective of all that follows in the remainder of Section 5 is the derivation of relationships that allow the calculation (prediction) of the enthalpy change in a food between any two given temperatures. Such relationships allow the technologist to calculate **HOW MUCH?** heat must be added or removed to heat or to cool the material by the required amount.

The overall temperature range to be considered can be represented as in Fig. 6.



**Fig 6. Temperature range considered in developing expressions for specific heat and enthalpy.  $\theta_{if}$  = initial freezing point.**

We will develop equations for calculating the enthalpy change between:

- any two temperatures above freezing,
- any two temperatures below freezing, and
- any two temperatures one of which is above freezing and one below.

We will do this for:

- non-fatty foods first, and then
- fatty foods

The establishment of an equation for enthalpy change involves first developing a temperature dependent expression for specific heat, then inserting it into equation (36) and then integrating with respect to temperature between the limits  $\theta_1$  and  $\theta_2$ .

The specific heats, and thus the enthalpies of foods, depend on **composition** and **temperature**. (For a pure material like water substance, the composition is constant, and specific heat and enthalpy depend only on temperature (Fig. 5)).

We will consider non-fatty foods initially (both above and below freezing) because enthalpy changes in fats complicate the picture. We will then look at how to deal with foods that do have appreciable fat contents (i.e.  $\geq 2.0\%$  fat).

### **5.2.2. Enthalpy: general remarks**

For a given food, i.e. a given chemical composition, enthalpy depends on temperature only. A typical enthalpy – temperature plot is shown in Fig. 7. The datum temperature

(the temperature at which enthalpy is arbitrarily assumed to be zero) is, in this case,  $-40^{\circ}\text{C}$ .

Looking at Fig. 7, note the following:

- $\theta_{if} < 0^{\circ}\text{C}$  : there is depression of freezing point owing to the solutes in the water in the food.
- At temperatures above  $\theta_{if}$ , enthalpy  $h$  is more or less linearly related to temperature (i.e.  $dh/d\theta \approx \text{constant}$ ), as for water substance.
- At temperatures between  $\theta_{if}$  and about  $-30^{\circ}\text{C}$ , enthalpy  $h$  is related to temperature in a highly non-linear way. The reason is that the phase change **water**  $\leftrightarrow$  **ice** does not occur at  $\theta_{if}$  but over a freezing range between  $\theta_{if}$  and about  $-30^{\circ}\text{C}$ . Latent heat of fusion of water substance is absorbed or released over this temperature **range**, and not at a single constant temperature ( $0^{\circ}\text{C}$ ) as in the case of pure water substance.
- At temperatures lower than about  $-30^{\circ}\text{C}$  all the freezable water is frozen, and enthalpy again becomes linearly related to temperature (as in the case of pure ice).

We will consider all this in more detail later.

### 5.2.3. *Specific heat: general remarks*

Remembering that

$$\frac{dh}{d\theta}(\theta) = c(\theta) \quad \left(\frac{\text{J}}{\text{kg K}}\right) \quad (39)$$

it is realized that the slope of the enthalpy – temperature plot in Fig. 7 at a particular temperature is equal to the specific heat at that temperature.

If slopes (i.e. specific heats) are plotted against temperature, we get a plot like that shown in Fig. 8. Looking at this plot, note the following points:

- For  $\theta > \theta_{if}$ , specific heat is more or less constant, i.e. independent of temperature. This is because the slope of the curve in Fig. 7 ( $= dh/d\theta$ ) is constant for temperatures above  $\theta_{if}$ .

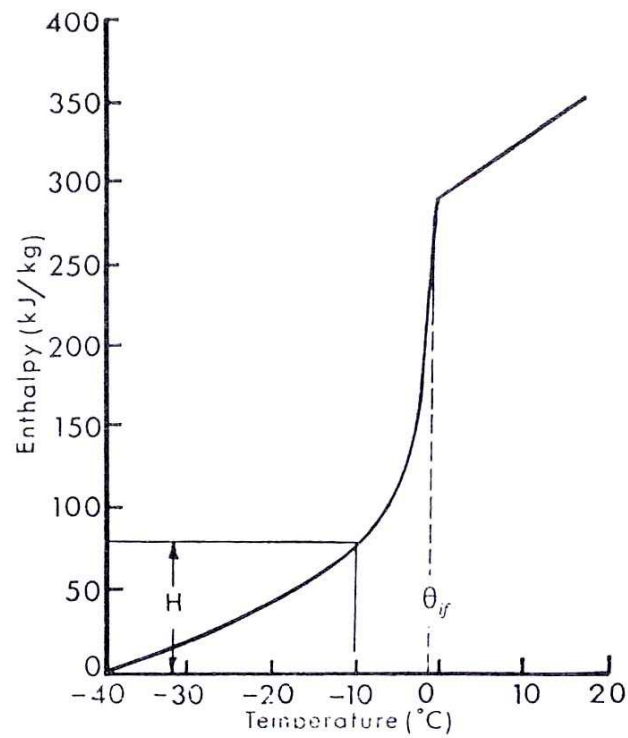


Fig. 7. Curve showing typical variation of enthalpy with temperature for a non-fatty food.  
 $h = 0$  at  $40^\circ\text{C}$ . (From Mellor, 1978).

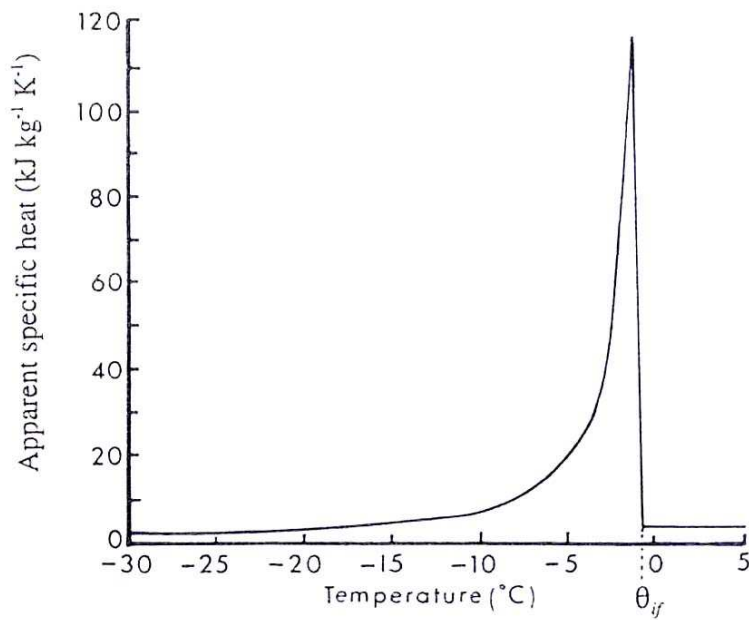


Fig. 8. Curve showing typical variation of apparent specific heat with temperature for a non-fatty food. (From Mellor, 1978).

- There is a marked peak in the plot just below  $\theta_{if}$  corresponding to the very large slope of the plot in Fig. 7 at the same position.
- As temperature decreases, specific heat decreases again. This corresponds to the decrease in the slope of the plot in Figure 7 as temperature decreases through the freezing point range.

Over this range, both sensible heat and latent heat changes are occurring simultaneously. These two changes cannot be separated and thus the specific heat is actually an **apparent** specific heat: it lumps together both the sensible and latent heat effects.

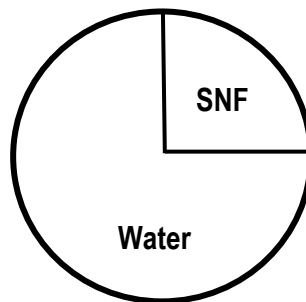
- At temperatures lower than the lower end of the freezing point range (about  $-30^{\circ}\text{C}$ ) specific heat again becomes constant. This corresponds to the constant slope below  $-30^{\circ}\text{C}$  in Figure 7.

We will now look in detail at how the specific heat of, and enthalpy change in, non-fatty foods are related to temperature and composition above and below freezing.

### 5.3. Specific heat of, and enthalpy change in, non-fatty foods above freezing: relationships with temperature and composition.

#### 5.3.1. Specific heat

Non-fatty foods at temperatures above  $\theta_{if}$  can be considered to consist of two components: SNF and water. This is shown in Fig. 1, which is given again here:



**Fig. 1 Representation of the composition of a non-fatty food above freezing**

In the temperature range above  $\theta_{if}$  only sensible heat has to be added or removed to heat or cool a non-fatty food.

Therefore, at a given temperature, the food's specific heat,  $c$ , can be expressed as the sum of the specific heats of the individual components weighted according to their mass fractions:

$$c = c_{SNF} x_{SNF} + c_w x_w \quad (42)$$

where

$$\begin{aligned} c &= \text{specific heat of non-fatty food } (J \text{ kg}^{-1} K^{-1}) \\ c_{SNF} &= \text{specific heat of SNF } (J \text{ kg}^{-1} K^{-1}) \\ c_w &= \text{specific heat of liquid water } J \text{ kg}^{-1} K^{-1} \\ x_{SNF} &= \text{mass fraction of SNF} \\ x_w &= \text{mass fraction of water substance} \end{aligned}$$

Because  $x_{SNF}$  and  $x_w$  are fractions,

$$x_{SNF} + x_w = 1 \quad (2)$$

As the SNF comprises protein (PR), available carbohydrate (CA), fiber (FI) and ash (AS), we could expand equation (42) to give

$$c = c_{PR} x_{PR} + c_{CA} x_{CA} + c_{FI} x_{FI} + c_{AS} x_{AS} + c_w x_w \quad \left( \frac{J}{\text{kgK}} \right) \quad (43)$$

where

$$x_{PR} + x_{CA} + x_{FI} + x_{AS} + x_w = 1 \quad (44)$$

For many foods,  $x_{AS}$  is very small, and the term  $c_{AS} x_{AS}$  in equation (43) is small enough to be neglected. Similarly,  $x_{FI}$  is very small or zero for many foods, and the term  $c_{FI} x_{FI}$  in equation (43) may be neglected. Equation (43) can then be written

$$c = c_{PR} x_{PR} + c_{CA} + c_w x_w \quad \left( \frac{J}{\text{kg K}} \right) \quad (45)$$

Shorthand ways of writing equations (42), (43) and (45), and equations (2) and (44), are:

$$c = \Sigma (c_i x_i) \quad \left( \frac{J}{\text{kgK}} \right) \quad (46)$$

and

$$\Sigma x_i = 1 \quad (47)$$

where  $i$  means the  $i$ th component.

To be able to calculate specific heat using equation (42), (43), (45) or (46) we need

- Numerical values of  $x_i$
- Numerical values of  $c_i$

Values of  $x_i$  must be found by measuring the food's composition using the standard methods of gravimetric food analysis, or by taking representative values from published

composition data like those shown in Table 1. **It is always more accurate to analyze a sample of the actual food whose specific heat you wish to predict.**

Values of  $c_i$  may be calculated using equations (6), (7), (8), (9) and (11) (Table 2, Section 3), inserting the desired value for the temperature,  $\theta$ , in each equation.

Equation (43) and (45) can be made fully temperature dependent by inserting the appropriate equations for  $c_i$  in place of  $c_{PR}$ ,  $c_{CA}$ , etc. Equation (45), for example, would then become:

$$\begin{aligned}
 c = & \left( 2.0082 + 1.2089 \times 10^{-3} \theta - 1.3129 \times 10^{-6} \theta^2 \right) x_{PR} \\
 & + \left( 1.5488 + 1.9625 \times 10^{-3} \theta - 5.9399 \times 10^{-6} \theta^2 \right) x_{CA} \\
 & + \left( 4.1762 - 9.0864 \times 10^{-5} \theta + 5.4731 \times 10^{-6} \theta^2 \right) x_w \quad \left( \frac{kJ}{kgK} \right)
 \end{aligned} \tag{48}$$

As the specific heats of food components are not particularly temperature sensitive, it is probably adequate for engineering purposes to use the values of  $c_i$  evaluated at  $75^\circ C$  (Table 3) for any temperature in the range  $0-150^\circ C$ . These values are repeated here for convenience:

$$c_{PR} = 2.09 \quad \frac{kJ}{kgK} \quad \text{at } 75^\circ C$$

And for the same temperature

$$c_{CA} = 1.66 \quad \frac{kJ}{kgK}$$

$$c_{FI} = 1.96 \quad \frac{kJ}{kgK}$$

$$c_{AS} = 1.21 \quad \frac{kJ}{kgK}$$

$$c_w = 4.19 \quad \frac{kJ}{kgK}$$

For any temperature in this range, equation (48), for example, could be written

$$c = 2.09 x_{PR} + 1.66 x_{CA} + 4.19 x_w \quad \left( kJ \, kg^{-1} K^{-1} \right) \tag{49}$$

It should be noted that all equations of the form of equations of the form of equation (46) ( $c = \sum(c_i x_i)$ ) are thermodynamically valid only if there are no chemical or physio-chemical interactions of any kind between the components that would change their specific heats from what they would be if each component was in the pure state. For engineering purposes, it is assumed that no interactions take place.



### Example 1

Calculate the specific heat of a pork sausage mix containing 10.7% protein, 10.6% available carbohydrate and 78.7% water.

Answer:

$$c = (2.09 \times 0.107) + (1.66 \times 0.106) + (4.19 \times 0.787) = 3.69 \frac{\text{kJ}}{\text{kgK}}$$

Comment: Be consistent with units. Do not have  $\frac{\text{kJ}}{\text{kgK}}$  and  $\frac{\text{J}}{\text{kgK}}$  in the same equation.

### Relationships between specific heat and water content, $x_w$

Because of the effort required to measure necessary values of  $x_i$ , it is much more convenient if we can relate  $c$  to just  $x_w$ , which is relatively easy to measure. Furthermore, for many foods the water they contain, with its relatively high specific heat, is the major determinant of the specific heat of the food. A number of food researchers have developed empirical relationships between  $c$  and  $x_w$  of the following form:

$$c = a + bx_w \quad \left( \frac{\text{kJ}}{\text{kgK}} \right) \quad (50)$$

where  $a$  and  $b$  are empirical constants. Typical pairs of values of  $a$  and  $b$  (the units of each are  $\frac{\text{kJ}}{\text{kgK}}$ ) are given in Table 4.

$a$ $\left( \frac{\text{kJ}}{\text{kgK}} \right)$	$b$ $\frac{\text{kJ}}{\text{kgK}}$
1.2	2.99
1.67	2.51
1.39	2.81
1.26	2.93
1.38	2.93
0.84	3.35
1.47	2.72
1.40	3.22

Table 4. Typical pairs of values of the constants  $a$  and  $b$  in equation (50)

The eight pairs of  $a$  and  $b$  values shown in Table 4, when inserted in turn into equation (50), give values of the specific heat of the pork sausage in Example 1 ( $x_w = 0.787$ ) ranging from 3.48 to 3.93  $\frac{kJ}{kg K}$ .

The eight versions of equation (50) are plotted in Fig. 9. The curves are linear because equation (47) is, of course, the equation of a straight line. Slopes and intercepts differ but most of the curves converge on the value of the specific heat of water ( $c_w = 4.18 \frac{kJ}{kg K}$ ) at  $x_w = 1$  as would be expected.

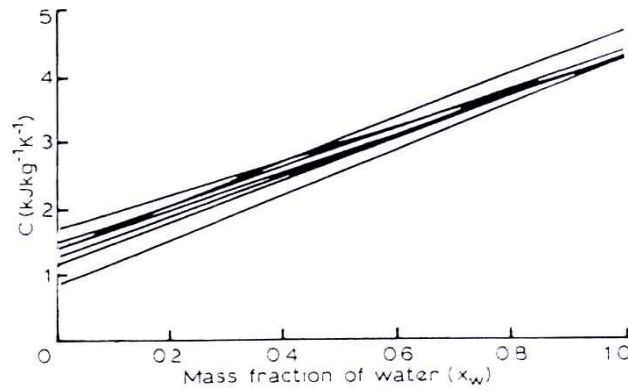


Fig. 9. Plots of  $c = a + bx_w$  (equation (50)) using the eight pairs of  $a$  and  $b$  values from Table 4. (From Miles et al, 1983).

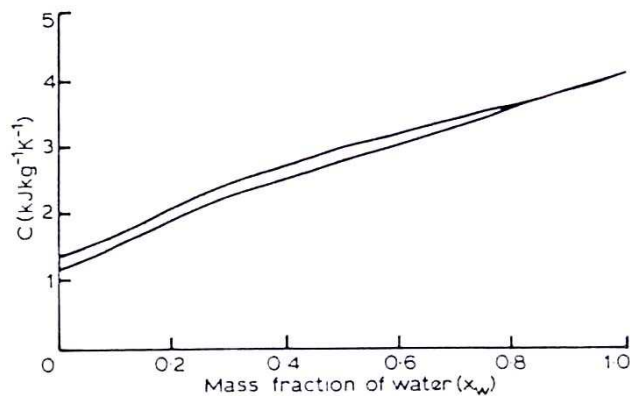


Fig. 10 Plots of equation (54) using the eight pairs of  $\delta$  and  $\beta$  values given in Table 5 lie in the narrow band shown on this graph. (From Miles et al, 1983).

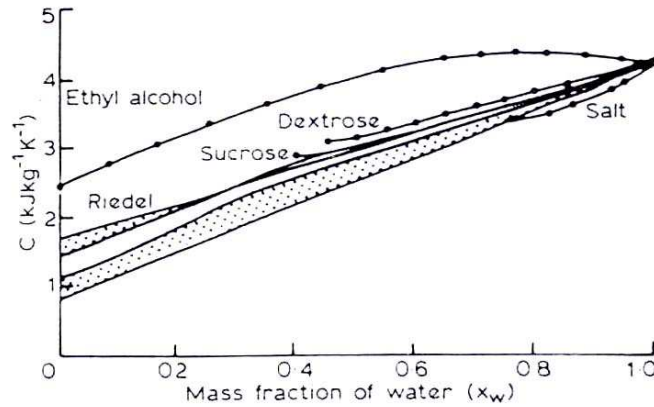


Fig. 11 Comparison of the equation (50) plots from Fig. 9 (shaded area) with the narrow band from Fig. 10 (equation (54)). Data for aqueous solutions are superimposed. (From Miles et al, 1983).

Disagreement among the eight equations is greatest at low moisture content (low  $x_w$ ), as is evident from the marked differences between the intercepts (Fig. 9). This is a reflection of the fact that the composition of the SNF is different for different foods. (When  $x_w = 0$ , the intercept on the  $c$  axis is equal to  $c_{SNF}$ ).

This problem has been overcome, and an equation more sophisticated than equation (50) developed, as follows. Equation (42) can be written as:

$$c = c_{SNF}(1 - x_w) + c_w x_w \quad (51)$$

where  $(1 - x_w) = x_s$  (equation (2)). Riedel, a German food engineer who, in the 1950s, made many precise measurements of the enthalpies and specific heats of foods, found empirically that, if  $x_w > 0.4$  (i.e. moisture content >40%), equation (51) predicts  $c$  well for a number of non-fatty food materials provided  $c_{SNF}$  is calculated from:

$$c_{SNF} = (\delta + 0.001\theta) \times 4.18 \quad \left( \frac{kJ}{kgK} \right) \quad (52)$$

where

$\theta$  = temperature in  $^{\circ}C$

$\delta$  = a food-specific constant  $\left( \frac{cal}{gK} \right)$

Typical values of  $\delta$  are given in Table 5.

The multiplier 0.001 in equation (52) has the units  $\frac{\text{cal}}{\text{g K}^2}$ . The multiplier 4.18 converts  $\text{cal} \frac{\text{cal}}{\text{g K}}$  to  $\frac{\text{kJ}}{\text{kgK}}$ .

Substituting equation (52) for  $c_{SNF}$  in equation (51) gives:

$$c(\theta) = [(\delta + 0.0010) \times 4.18](1 - x_w) + c_w x_w \left( \frac{\text{kJ}}{\text{kgK}} \right) \quad (53)$$

where  $c(\theta)$  is the specific heat of the food at temperature  $\theta$ . Equation (53) thus allows for some temperature dependence of specific heat.

**You must use  $c_w = 4.194 \frac{\text{kJ}}{\text{kg K}}$  (Table 3) (and not  $c_w = 4194 \frac{\text{J}}{\text{kg K}}$ ) when using equation (53).**

**Table 5. Numerical values of the coefficients  $\delta$  and  $\beta$  (See equations (52), (53) and (54))**

	$\delta$ $\left( \frac{\text{cal}}{\text{g K}} \right)$	$\beta$ $\left( \frac{\text{cal}}{\text{g K}} \right)$
Beef	0.385	0.08
Saltwater fish	0.410	0.12
Egg white	0.330	0.06
Low-fat cheese	0.390	0.10
Baker's yeast	0.395	0.10
White bread	0.350	0.09
Potato starch	0.340	0.06
Coffee extract	0.390	0.13

Equation (53), while an improvement over equations of the form  $c = a + b x_w$  (equation (50)), is valid only for relatively high  $x_w$  ( $x_w > 0.4$ ). For low  $x_w$ , the true specific heat is less than that predicted by equation (53). Riedel developed the following empirical equation valid for both low and high  $x_w$ :

$$c(\theta) = [(\delta + 0.0010) \times 4.18] (1 - x_w) + c_w x_w - 4.18 \beta \cdot \exp(-42 x_w^{2.3}) \left( \frac{kJ}{kgK} \right) \quad (54)$$

where  $\beta$  = another food-specific constant  $\left( \frac{cal}{gK} \right)$ .

Typical values of  $\beta$  are given in Table 5.

Equation (54) is equation (53) plus an extra term on the right-hand side. This extra term becomes of significant size only when  $x_w$  is, in fact, quite small. For  $x_w > 0.2$ , the error incurred by **ignoring** the term is <6%. But at  $x_w = 0.1$ , for example, the error is >13%, which is unacceptably high. It is always wise to include the term in the equation and calculate its value.

If equation (54) is plotted eight times, using the eight pairs of  $\delta$  and  $\beta$  values shown in Table 5 (and a constant value of temperature  $\theta$ ) all the curves lie in a narrow band Fig. 10); the discrepancies among the intercepts in Fig. 9 have largely disappeared.

If **mean** values of  $\delta$  ( $\delta = 0.37$ ) and  $\beta$  ( $\beta = 0.09$ ) are used in equation (54), we have:

$$c(\theta) = [(0.37 + 0.0010) \times 4.18] (1 - x_w) + c_w x_w - 0.376 \exp(-43 x_w^{2.3}) \left( kJ kg^{-1} K^{-1} \right) \quad (55)$$

Equation (55) is accurate even at low  $x_w$ .

Although based on data for just eight non-fatty foods (table 5), equation (55) can be extended to all non-fatty foods. It will predict specific heat at any moisture content with accuracy sufficient for most engineering purposes.

Equation (55) will work quite well for aqueous solutions of substances such as salt ( $NaCl$ ), sucrose and dextrose (glucose), but not for ethyl alcohol solutions. This is shown in Fig. 11 where the eight versions of equation (50) from Fig. 9, represented by the shaded area, and the eight versions of equation (54), represented by the clear area (as in Fig. 10), are plotted together with experimental specific heat data for aqueous solutions. The measured (true) specific heats of alcohol solutions are much higher than would be predicted by equation (55). You must be aware of this if you are dealing with fermentation liquors or alcoholic beverages; for these you would have to use experimental specific heat data.

### 5.3.2. Enthalpy change

An equation for calculating the enthalpy change in a food that occurs if the food is heated from  $\theta_1$  to  $\theta_2$ , or cooled from  $\theta_2$  to  $\theta_1$ , may be obtained by integrating the right-hand side of equation (36), with  $\theta_1$  and  $\theta_2$  as the limits:

$$\Delta h_{(\theta_1 \leftrightarrow \theta_2)} = \int_{\theta_1}^{\theta_2} c(\theta) d\theta \left( \frac{J}{kg} \right) \quad (36)$$

$c(\theta)$  represents a temperature dependent expression for specific heat. We could use for  $c(\theta)$  an expression of the form of equation (48), which includes temperature dependent expressions (from Table 2) for the specific heats of the food's individual components. This would be perfectly valid, but the resulting equation for calculating  $\Delta h$  would be rather cumbersome. Moreover, its use would require the prior determination of all necessary  $x_i$  values.

A neater and easier approach, which requires the prior determination of  $x_w$  only, is to use equation (55) for  $c(\theta)$ . Substitution of the right-hand side of equation (55) into equation (36) gives:

$$\Delta h_{(\theta_1 \leftrightarrow \theta_2)} = \int_{\theta_1}^{\theta_2} \left[ ((0.37 + 0.001\theta) \times 4.18)(1 - x_w) + c_w x_w - 0.376 \exp(-43x_w^{2.3}) \right] d\theta \quad (56)$$

Expansion of the brackets inside the integral, followed by simple integration of each of the resulting terms, insertion of the limits and rationalizing, gives the final equation for  $\Delta h_{(\theta_1 \leftrightarrow \theta_2)}$ :

$$\begin{aligned} \Delta h_{(\theta_1 \leftrightarrow \theta_2)} = & 1.55(1 - x_w)(\theta_2 - \theta_1) \\ & + 2.09 \times 10(1 - x_w)(\theta_2^2 - \theta_1^2) \\ & + c_w x_w(\theta_2 - \theta_1) \\ & - 0.376 \exp(-43x_w^{2.3})(\theta_2 - \theta_1) \left( \frac{kJ}{kg} \right) \end{aligned} \quad (57)$$

When using equation (57), you must use  $c_w = 4.19 \frac{kJ}{kgK}$ . Also, always substitute the higher temperature for  $\theta_2$  and the lower temperature for  $\theta_1$ . The equation will then always give a positive numerical value for  $\Delta h_{(\theta_1 - \theta_2)}$ . This amount of thermal energy **must be added** to the food to heat it from  $\Delta h_{(\theta_1 - \theta_2)}$ , **or removed** from the food to cool it from  $\Delta h_{(\theta_2 - \theta_1)}$ .

If  $\theta_1$  is a preselected datum temperature, equation (57) will give the enthalpy of the material at  $\theta_2$  relative to an assumed zero enthalpy at the datum temperature  $\theta_1$ .

### Example 2

How much thermal energy is required to heat 4 tons of lean beef (moisture content = 74%) from  $10^\circ\text{C}$  to  $35^\circ\text{C}$ ?

Answer:

$$\begin{aligned}x_w &= 0.74 \\ \theta_1 &= 10^\circ\text{C} \\ \theta_2 &= 35^\circ\text{C} \\ c_w &= 4.194 \frac{\text{kJ}}{\text{kg K}} \text{ Table 3)}\end{aligned}$$

Using equation (57):

$$\begin{aligned}\Delta h_{(10 \leftrightarrow 35)} &= 1.55(1-0.74)(35-10) \\ &\quad + 2.09 \times 10^{-3}(1-0.74)(35^2-10^2) \\ &\quad + 4.18 \times 0.74(35-10) \\ &= 10.07 \\ &\quad + 0.61 \\ &\quad + 77.33 \\ &\quad - 4.26 \times 10^{-9} \\ &= 88.0 \frac{\text{kJ}}{\text{kg}}\end{aligned}$$

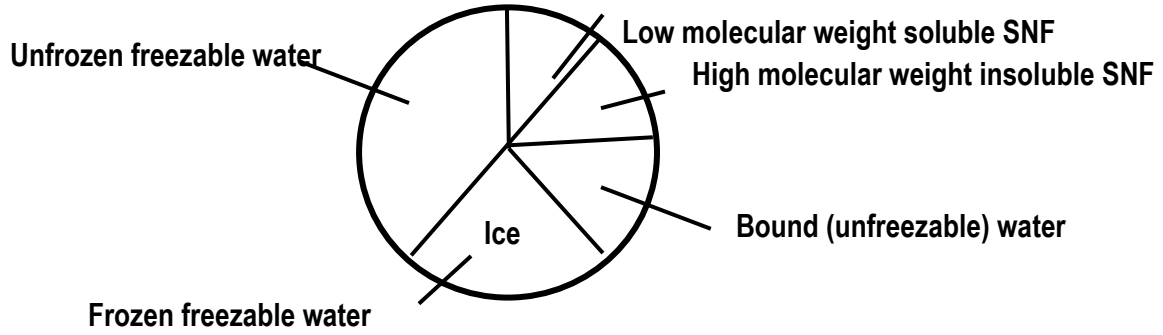
The last term  $(-4.26 \times 10^{-9})$  is clearly negligibly small at the high  $x_w$  of 0.74.

$$\begin{aligned}\text{Total thermal energy required} &= 88.0 \left( \frac{\text{kJ}}{\text{kg}} \right) \times 4000 \text{ kg} \\ &= 3.52 \times 10^5 \text{ kJ}\end{aligned}$$

Comment: This amount of thermal energy would have to be removed from the four tons of beef if the beef had to be cooled from  $35^\circ\text{C}$  to  $10^\circ\text{C}$ .

### 5.4. Specific heat of, and enthalpy change in, no-fatty food below freezing

The composition of a non-fatty food below freezing is shown in Fig. 3, which is given again here:



**Fig. 3. Representation of the mass composition of a fatty food below freezing**

As explained in Section 2, the fractional composition of the food in Fig. 3 is

$$x_{SNF} + x_{BW} + x_{ice} + (x'_w - x_{ice}) = 1 \quad (4)$$

where

$$\begin{aligned} x_{SNF} &= \text{mass fraction of SNF (soluble + insoluble)} \\ x_{BW} &= \text{mass fraction of bound water} \\ x_{ice} &= \text{mass fraction of ice} \\ &= \text{mass fraction of **frozen** freezable water} \\ (x'_w - x_{ice}) &= \text{mass fraction of **unfrozen** freezable water} \end{aligned}$$

and

$$x'_w = (x_w - x_{BW}) \quad (58)$$

where

$$x_w = \text{total water content}$$

The fact that some of the water substance in the food is in the form of ice is highly **significant** with respect to the properties specific heat and enthalpy because, below freezing (as shown in Table 3),

$$c_w = 4.586 \frac{kJ}{kg \ K}, \text{ whereas}$$

$$c_{ice} = 1.941 \frac{kJ}{kg \ K}$$

$c_{ice}$  is less than half the value of  $c_w$ ; clearly the value of  $x_{ice}$  at any temperature  $< \theta_{if}$  will have a profound effect on the specific heat and thus the enthalpy of the food at that temperature.

How can we predict specific heat (a necessary prerequisite for being able to predict enthalpy change)?



We could write:

$$c = \sum (c_i x_i) \quad (46)$$

which, on expanding, could be written (see equation (4)) as:

$$c = c_{SNF} x_{SNF} + c_{BW} x_{BW} + c_{ice} x_{ice} + c_w (x'_w - x_{ice}) \quad (59)$$

Could we calculate  $c$  from equation (59) if we knew  $x_{ice}$ ?

Not quite!

Remember that as temperature changes in the “below freezing” region there is a latent heat of fusion effect due to the phase change **water**  $\leftrightarrow$  **ice** and that this effect is confounded with the sensible heat effect. We thus define an **apparent** specific heat  $c_{app}$ , which lumps the two effects together. An equation of the form of equation (59) must therefore have in it an **extra term** that accounts for the latent heat effect if it is to accurately predict  $c_{app}$ .

In developing a more valid equation that does contain such a term the following facts must be considered:

- The water  $\leftrightarrow$  ice phase change occurs over a temperature range (the upper limit of which is  $\theta_{if}$ ). Therefore  $x_{ice}$  **depends on temperature**.
- The **rate of change of  $x_{ice}$  with temperature** also depends on temperature. Therefore the latent heat effect depends on temperature.

We therefore need to have a way of predicting  $x_{ice}$ , and its rate of change with temperature, at any temperature lower than  $\theta_{if}$ . To understand how to handle this apparently complex situation we need to consider:

- How pure water freezes,
- How a simple solution freezes, and then
- How a food freezes.

#### **5.4.1. How pure water freezes**

This is fully described in the caption to Figure 12. The main thing to note is that, as mentioned previously, the water  $\leftrightarrow$  ice phase change occurs at a constant temperature ( $= 0^\circ\text{C}$  at atmospheric pressure).

### 5.4.2. How a simple solution freezes

This also is explained in the caption to Figure 12. The first thing to note is that the freezing of a solution occurs over a temperature **range** between F and G. The composition of the partly frozen mixture therefore changes over this range because of the phase change  $\text{water} \leftrightarrow \text{ice}$ . Note that until the eutectic mixture begins to solidify, only water changes phase (to ice) as the temperature drops; the unfrozen water and the solute merely get colder.

The way in which composition changes in the case of a NaCl solution is shown by the freezing point depression curve in Figure 13. This figure – which also includes the solubility curve – is called a **phase diagram**.

The second thing to note, from Figure 13, is that a solution of composition B, the eutectic mixture, behaves as if it was pure compound: it freezes/solidifies (or melts) at a distinct constant temperature.

The third thing to note (again from Figure 13) is that the freezing point depression curve, since it is a plot of temperature versus composition, allows the prediction of  $x_{ice}$  at any temperature below the initial freezing point for a solution of known unfrozen composition (e.g. the solution of composition X identified in Figure 13). This is explained more fully below.

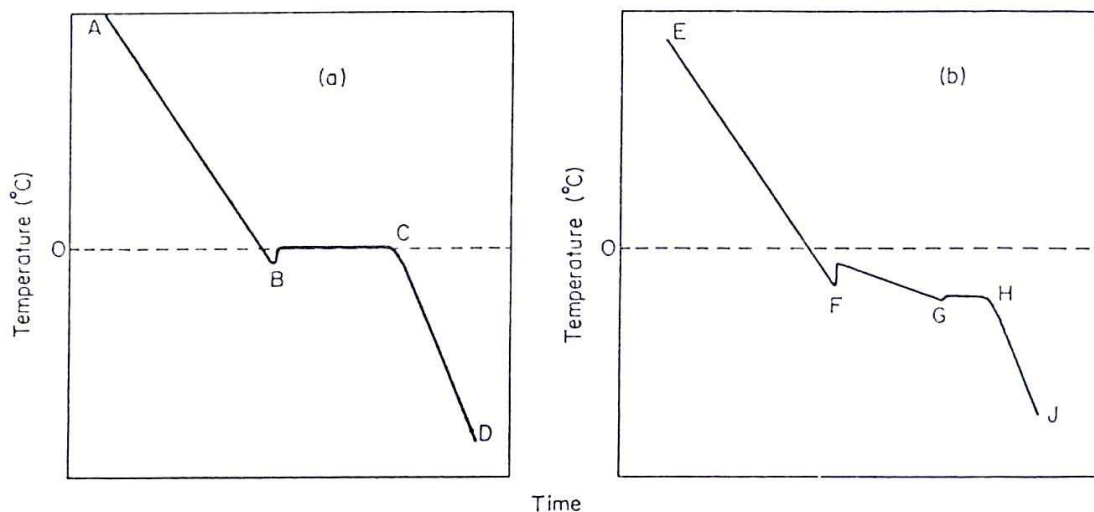


Fig. 12. Cooling curves observed with stirred liquids.

(a) Removal of heat from pure water.

AB represents the cooling and slight super-cooling of pure liquid water. With the onset of freezing the temperature rises abruptly to the freezing point and the system remains at this temperature (the so-called thermal arrest) until all the water becomes ice.

CD represents the cooling of ice by the continued abstraction of heat. CD is almost twice as steep as AB because the specific heat of ice is smaller (in fact 0.423 times) than that of liquid water. The evolution of latent heat of fusion gives rise to the thermal arrest.

- (b) Removal of heat from a dilute aqueous solution containing one solute.

EF represents the cooling and slight super-cooling of the solution. When freezing is initiated the temperature rises abruptly to the freezing point of the solution. Further cooling gives rise to a gradual fall in temperature to G, during which period in time water gradually is converted into ice and the remaining solution becomes progressively more concentrated until the eutectic composition is reached (in the case of NaCl solution the temperature and composition would follow curve AB of Fig. 14). At G the system is slightly super-cooled and the temperature rises sharply to the freezing point the eutectic point as the latter begins to crystallize. Further removal of heat results only in a change in state with no fall in temperature while the eutectic crystallizes into a solid of identical composition. At point H crystallization is complete, and continued removal of heat merely reduces the temperature. (From Rolfe, 1968).

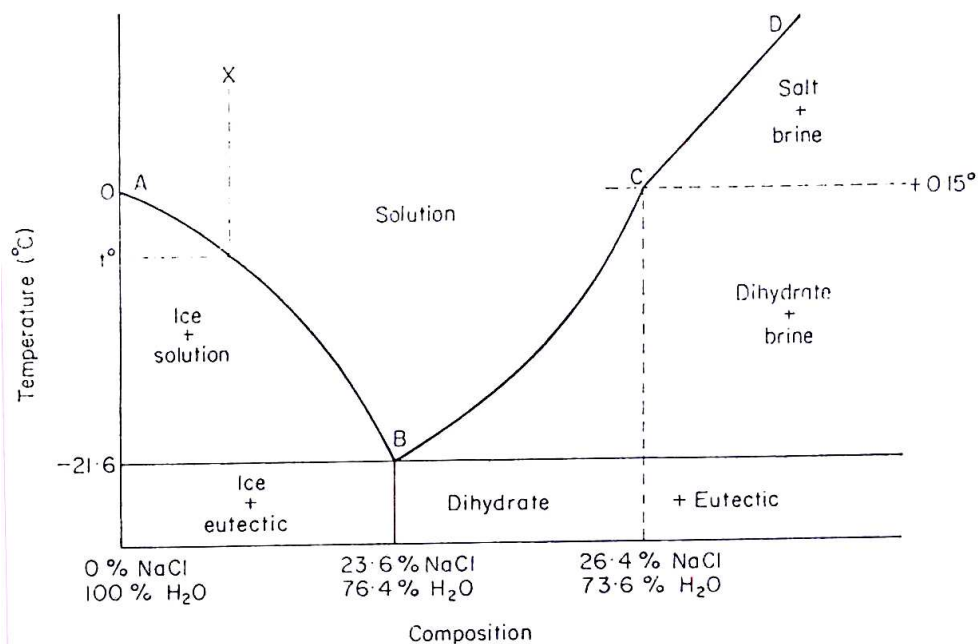


Fig. 13. Phase diagram for aqueous solutions of common salt. Composition axis is not drawn to scale.

AB represents the temperatures at which solutions of given composition are in equilibrium with ice, i.e. is the freezing point depression curve.

BCD represents the temperatures at which solutions of given composition are in equilibrium with salt, i.e., the solubility curve.

Point A represents the melting point of pure water at  $0^{\circ}\text{C}$ , and B represents the melting point and composition of the eutectic mixture. A solution of composition B will remain liquid when cooled until the temperature falls to  $-21.6^{\circ}\text{C}$  when the solution will freeze at a constant temperature into a solid of the same composition as though it were a pure compound.

C represents the transition temperature between crystals of NaCl and  $\text{NaCl}\cdot 2\text{H}_2\text{O}$ .

#### **5.4.3. How a food freezes**

As explained previously (Section 1), the aqueous part of a food comprises the soluble SNF dissolved in the freezable water. In high moisture foods (e.g. vegetables, meats, fish), this aqueous part is essentially a dilute solution, though with a mixture of solutes. It therefore freezes in much the same way as a dilute binary solution such as NaCl in water. This is illustrated in Figs. 14 and 15.

In Fig. 14, which is analogous to Figs. 12(a) and 12(b), the curve after the initial freezing point (point F) has been passed, appears to be one continuous line. In fact, the curve is the net result of the behavior of all the solutes making up the soluble SNF, each solute would exhibit a curve like FGHJ in Fig. 12(b) if it was in pure solution by itself.

Fig. 15 shows an experimental freezing point depression curve (of temperature against % total soluble solids) for fruit juices. The curve, analogous to the curve AB for NaCl solutions shown in Fig. 13, was obtained by the German researcher Riedel. Also shown on the plot in Fig. 15 are the phase diagram curves for the sugars glucose (G) and sucrose (S). These curves are shown separately in Fig. 16 for clarity. Compare them with the freezing point depression and solubility curves for NaCl shown in Fig. 13.

Fig. 15 shows that the freezing point depression curve for fruit juices lies close to those for glucose and sucrose. This is hardly surprising, as these sugars are the principal solutes in fruit juices.

Another example: it has been found experimentally that the juice from beef muscle, and therefore beef muscle itself, has the same freezing point depression curve as a 0.28 M KCl solution.

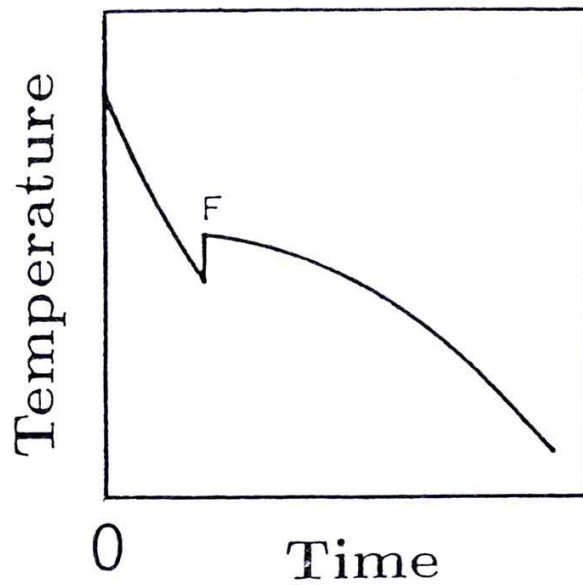


Fig. 14. Typical cooling curve for a food. Point F is the initial freezing point. (From Rahman, 1995).

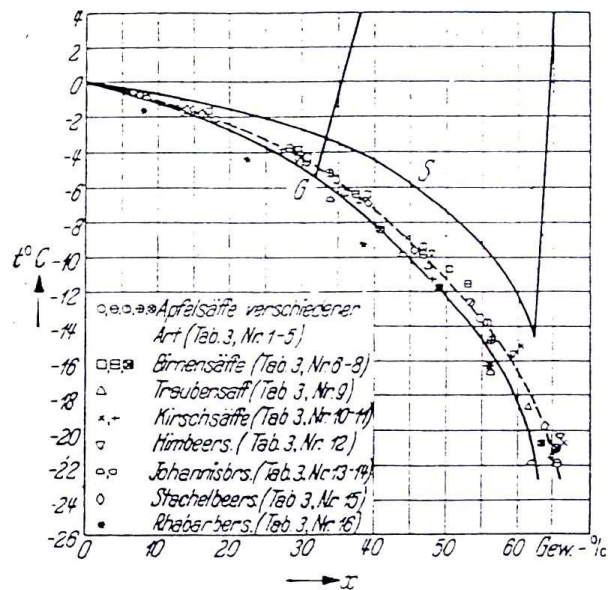


Figure 15. Plot of initial freezing point ( $t^{\circ}\text{C}$  in this figure) against % total solids for fruit juices. The phase diagram curves for glucose in water (G) and sucrose in water (S) are superimposed. (From Riedel, 1949).

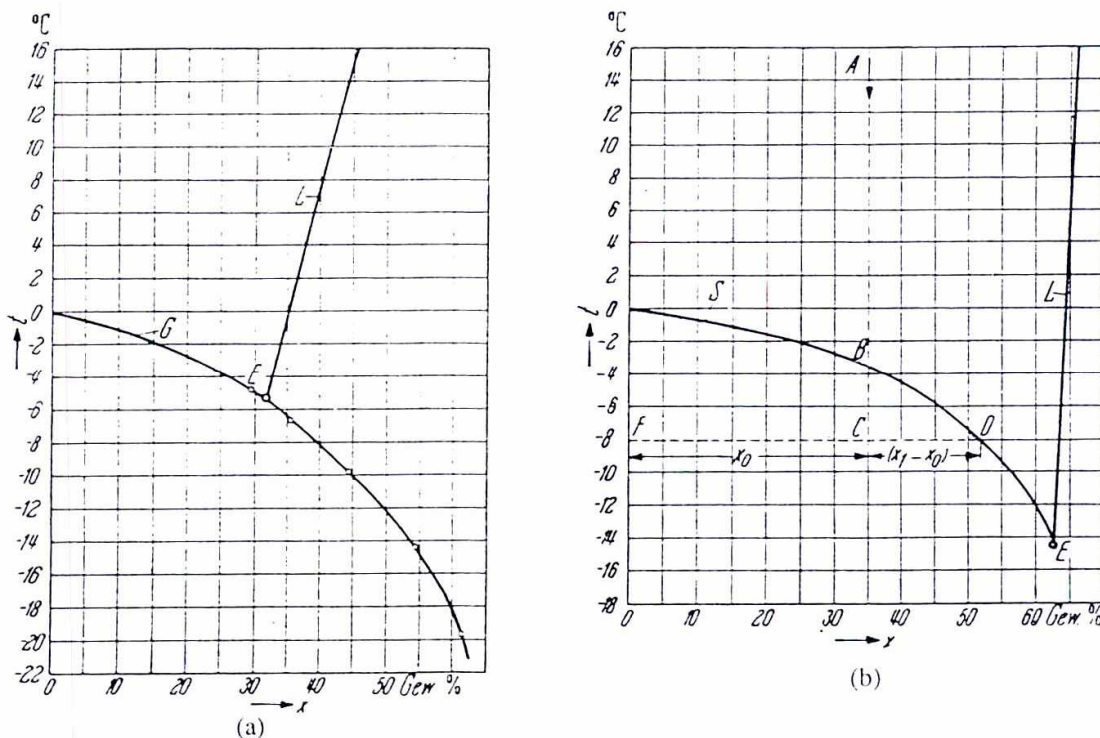


Fig. 16. Phase diagrams for (a) glucose in water and (b) sucrose in water. (From Riedel, 1949).

It is perhaps interesting to note here, as an aside, the so-called state diagram of an aqueous binary system (solute plus water) (Fig. 17). Just as the phase diagram of a food (e.g. fruit juice) is similar to that of a binary system containing a simple solute (e.g. sucrose) (Fig. 15), a state diagram of a food is similar to the state diagram of a binary system.

The state diagram (Fig. 17) is essentially an extension of the phase diagram (Fig. 13). Under certain conditions and for certain solutes (e.g. glucose, Fig. 16(a)), the mixture at the eutectic point does not crystallize (solidify) on further cooling, but merely gets colder. The mixture then consists of ice and a supersaturated (SS) solution. If this mixture is cooled still further, eventually the so-called glass transition temperature ( $T_g'$ ) is reached. At this point, the supersaturated solution becomes an amorphous (non-crystalline) "glass". The glass can be thought of as a liquid with an extremely high viscosity ( $10^{10}$  to  $10^{14}$  Pa s).

The significance of this is that if the temperature of the system (binary system or food) is maintained at a value at or below the glass transition curve, the extremely high glass viscosity means that deteriorative chemical reactions (which occur in aqueous solution) can proceed only very, very slowly indeed. Thus if a food is stored below its glass transition temperature, it will remain stable for very long periods of time (i.e. many years).

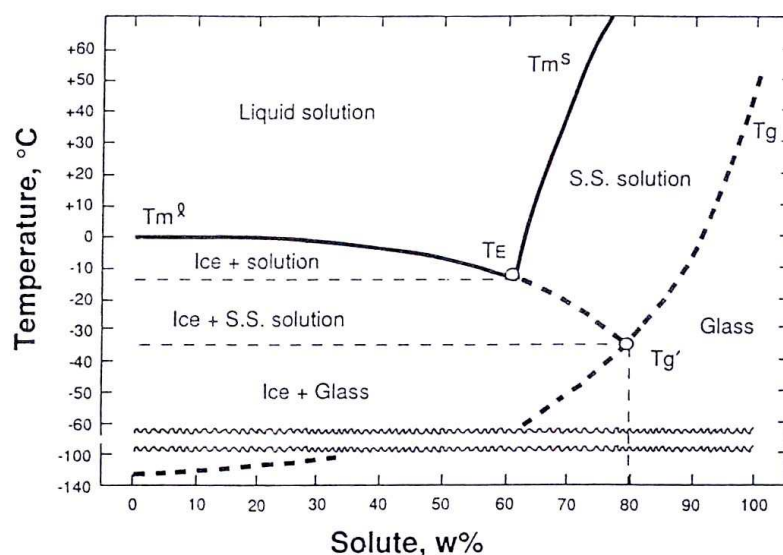


Fig. 17. State diagram of a binary system. Assumptions: maximal freeze concentration, no solute crystallization, constant pressure, no time dependence.  $T_m^l$  is the melting point curve.  $T_E$  is the eutectic point,  $T_m^s$  is the solubility curve,  $T_g$  is the glass transition curve, and  $T_g'$  is the solute-specific glass transition temperature of a maximally freeze-concentrated solution. Heavy dashed lines represent conditions of metastable equilibrium. All other lines represent conditions of equilibrium. (From Fennema, 1996).

#### 5.4.4. Variation of $x_{ice}$ with temperature

As mentioned above, a phase diagram allows the determination of  $x_{ice}$  at any temperature below the initial freezing point for a solution of known unfrozen composition.

To understand how, look at Figure 13. If a solution of composition X is cooled to a given temperature lower than its initial freezing point  $\theta_{if}$ , some of the water will crystallize out as ice. The remaining solution will now be more concentrated and its freezing point will be that lower temperature. In other words, we will now be at some point further to the right on the curve AB in Fig. 13.

The freezing point depression curve tells you the composition of the more concentrated solution (i.e., the unfrozen part) at the new lower freezing point. Since now both this composition and the original composition are known it is a simple matter to calculate the mass fraction of ice present at the lower temperature.

For instance, let composition X be 10% NaCl and 90% water. Let this mixture be cooled to some temperature lower than  $\theta_{if}$ . At this lower temperature the mixture will consist

of ice and a more concentrated salt solution. Suppose this more concentrated solution has the composition 19% NaCl and 81% water. What is  $x_{ice}$ ?

1 kg of the unfrozen mixture contains

0.1 kg NaCl, and  
0.9 kg liquid water

1 kg of the partly frozen mixture will contain

$$\frac{0.1 \times 100}{19} = 0.53 \text{ kg}$$

of more concentrated but unfrozen solution. Since the total weight is still 1 kg, the amount of ice present is

$$1 - 0.53 = 0.47 \text{ kg}$$

and therefore  $x_{ice} = 0.47$

The ice content expressed as a fraction of the water substance (rather than of the total material) is

$$\frac{x_{ice}}{x_w} = \frac{0.47}{0.9} = 0.52$$

Note therefore that  $x_{ice}$  may be expressed as

$$\begin{aligned} x_{ice} &= \frac{x_{ice}}{x_w} \times x_w \\ &= 0.52 \times 0.9 \\ &= 0.47 \end{aligned} \tag{60}$$

(Note that for a solution containing a simple low molecular weight solute such as NaCl, **all** the water is freezable and none of it is bound, i.e.,  $x_w' = x_w$ ).

Unfortunately, very few phase diagrams, which have to be determined experimentally, exist for foods. Two examples of the few that have been developed, and which are plotted in a way that allows easy determination of  $(x_{ice}/x_w)$  and thus of  $x_{ice}$  (see equation (60)), are shown in Figs. 20 and 21.

A more general way of finding  $x_{ice}$ , that is applicable to **any** food, is needed. The simplest approach is to assume that the **depression** in freezing point of an aqueous



solution, which is **numerically** equal to  $\theta_{if}$ , is proportional to the mass fraction of solute in the solution. (The mass fraction of solute in a 10% NaCl solution, for example, is 0.1).

On the basis of this assumption, the following quite simple equation for the fraction of water substance frozen can be derived:

$$\frac{x_{ice}}{x_w} = \left(1 - \frac{\theta_{if}}{\theta}\right) \quad (61)$$

Therefore,

$$x_{ice} = x_w \left(1 - \frac{\theta_{if}}{\theta}\right) \quad (62)$$

In the case of a food, the solution that freezes consists of the soluble SNF and the **freezable** water, and equation (61) must be written as:

$$\begin{aligned} x_{ice} &= x'_x \left(1 - \frac{\theta_{if}}{\theta}\right) \\ &= (x_w - x_{BW}) \left(1 - \frac{\theta_{if}}{\theta}\right) \end{aligned} \quad (63)$$

Note that in equations (61), (62) and (63),  $\theta_{if}$ , which itself is lower than  $0^\circ\text{C}$ . Therefore, both  $\theta_{if}$  and  $\theta$  are **negative** temperatures.

If  $x_{ice} / x'_w$  is plotted against temperature according to equation (63), the result is the curve shown in Fig. 18. Note the following points.

- Ice begins to form at  $\theta_{if}$  (which is  $< 0^\circ\text{C}$ ) when the food is cooled.
- The rate of increase of  $x_{ice} / x'_w$  with decreasing temperature is initially very rapid; the plot has a very steep slope.
- The rate of increase levels off as temperature decreases further and as  $x_{ice} / x'_w$  approaches the value of 1.0, the maximum value it can have.

The plot in Figure 18, together with the knowledge that the thermophysical properties of water and of ice are very different, is the key to understanding how the thermophysical properties of biological materials vary with temperature over the freezing region. **Note it well.**

For example, compare Figure 18 with Figures 7 and 8. In Figure 7 the high rate of change of enthalpy with temperature just below  $\theta_{if}$  corresponds to the high rate of change of  $x_{ice}$  with temperature in the same region. In this region a large latent heat effect must be satisfied to achieve a small change in temperature.

This large latent heat effect is again reflected by the peak in the plot of  $c_{app}$  (which lumps together latent and sensible heat effects) against temperature in Figure 8.

Equation (63), though based on a simple assumption, works very well for high moisture foods, as will be demonstrated in Section 5.4.6.

Now that we have a means of calculating  $x_{ice}$  at any temperature lower than  $\theta_{if}$ , we can proceed to develop a full expression for enthalpy change in the *below freezing* region, for non-fatty foods.

First, we must develop a temperature dependent expression for specific heat.

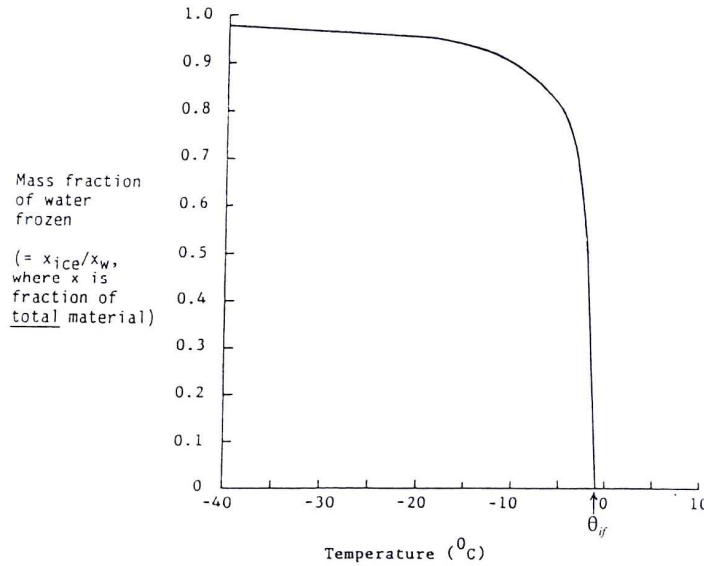


Fig. 18. Typical plot, for a non-fatty food, of mass fraction of water substance frozen (i.e. water substance in the form of ice) against temperature. This is a plot of equation (63).

#### 5.4.5. Prediction of the specific heat of non-fatty foods below freezing

As stated earlier, we can predict  $c$  using equation of the form

$$c = \sum (c_i x_i) \quad (46)$$

**provided** we put an extra term on the right-hand side that will account for the latent heat of fusion of water substance effect.  $c$  is in fact  $c_{app}$  because of this effect. We can predict  $c_{app}(\theta)$  at a given temperature below freezing if we know

- The food's composition (including  $x_{ice}$ ) at that temperature, and
- The rate of change of  $x_{ice}$  with temperature at that temperature; the latent heat effect depends on this.

We develop an equation for apparent specific heat below freezing ( $c_{app}(\theta)$ ) as follows. We start by remembering that specific heat is defined as the rate of change of enthalpy with temperature (equation (39)).

$$c_{app}(\theta) = c_{app,\theta} = \frac{dh(\theta)}{d\theta} = \left( \frac{dh}{d\theta} \right)_{sensible,\theta} + \left( \frac{dh}{d\theta} \right)_{latent,\theta} \quad (64)$$

where  $(\theta)$  and the subscript  $\theta$ , both mean *at temperature  $\theta$* .

Putting  $x_{ice}$ , and two minus signs, into the top and bottom of the last term of the right-hand side of equation (64) allows us to write:

$$c_{app,\theta} = \left( \frac{dh}{d\theta} \right)_{sensible,\theta} + \left( \frac{-dh}{dx_{ice}} \right)_{\theta} \left( \frac{-dx_{ice}}{d\theta} \right)_{\theta} \quad (65)$$

$$= c_{sensible,\theta} + \left( \frac{-dh}{dx_{ice}} \right)_{\theta} \left( \frac{-dx_{ice}}{d\theta} \right)_{\theta} \quad (66)$$

$(-dx_{ice}/d\theta)$  is the rate of change of ice mass fraction with temperature. It is **negative** because the ice mass fraction increases as temperature decreases.

$(-dh/dx_{ice})$  is the rate of change of enthalpy with ice mass fraction that is due **solely** to the **phase change water  $\leftrightarrow$  ice**. It is negative because an increase in ice fraction is brought about by a reduction in enthalpy (i.e., a removal of thermal energy).

Therefore,

$$\left( \frac{-dh}{dx_{ice}} \right) = L \left( \frac{J}{kg} \right) \quad (67)$$

where  $L$  = latent heat of fusion of pure water substance.

Strictly, allowance should be made for the fact that  $L$  is somewhat temperature dependent. However, for engineering prediction purposes  $L$  may be assumed constant at  $L = 334 \text{ kJ kg}^{-1}$ . The subscript  $\theta$  on the term on the left-hand side of equation (67) is therefore left out.

Substitution of equation (67) into equation (66) gives:

$$c_{app,\theta} = c_{sensible,\theta} + L \left( \frac{-dx_{ice}}{d\theta} \right) = c_{sensible,\theta} - L \left( \frac{dx_{ice}}{d\theta} \right) \quad (68)$$

The term  $-L(dx_{ice}/d\theta)$  does in fact turn out to be positive when the appropriate form of  $(-dx_{ice}/d\theta)$  is used (see below) and when numbers are put in;  $c_{app,\theta}$  is larger than  $c_{sensible,\theta}$  because of the latent heat effect (see Figure 8).

We will now develop, in turn, expressions for the two terms on the right-hand side of equation (68). We will then substitute this expression into equation (68) to give the final equation for  $c_{app,\theta}$ .

The first term,  $c_{sensible,\theta}$ , can be calculated using equation (46):

$$c = \sum (c_i x_i) \quad (46)$$

Therefore,

$$c_{sensible,\theta} = c_{SNF} x_{SNF} + c_{BW} x_{BW} + c_{ice} x_{ice} + c_x (x'_w - x_{ice}) \quad (69)$$

But

$$\begin{aligned} \blacksquare \quad x_{SNF} &= (1 - x_w) \end{aligned} \quad (2)$$

$$\blacksquare \quad c_{BW} \approx c_{ice} \text{ (found experimentally)}$$

$$\blacksquare \quad x_{ice} = x'_w \left( 1 - \frac{\theta_{if}}{\theta} \right) = \left( x'_w - x'_w \frac{\theta_{if}}{\theta} \right) \quad (63)$$

Thus equation (69) becomes:

$$\begin{aligned} c_{sensible,\theta} &= c_{SNF} (1 - x_w) + c_{ice} x_{BW} \\ &+ c_{ice} x'_w \left( 1 - \frac{\theta_{if}}{\theta} \right) \\ &+ c_w \left( x'_w - \left( x'_w - x'_w \frac{\theta_{if}}{\theta} \right) \right) \end{aligned} \quad (70)$$

Rearranging equation (70) gives:

$$\begin{aligned} c_{sensible,\theta} &= c_{SNF} (1 - x_w) + c_{ice} x_{BW} \\ &+ c_{ice} x'_w \left( 1 - \frac{\theta_{if}}{\theta} \right) + c_w x'_w \frac{\theta_{if}}{\theta} \end{aligned} \quad (71)$$

We will now consider the second term on the right hand side of equation (68):

$$\begin{aligned}
\text{Latent heat contribution to } c_{app,\theta} &= -L \left( \frac{dx_{ice}}{d\theta} \right) \\
&= -L \frac{d(x'_w - x'_w \frac{\theta_{if}}{\theta})}{d\theta} \\
&= -L \frac{d(x'_w - x'_w \theta_{if} \theta^{-1})}{d\theta} \\
&= -L (0 - x'_w \theta_{if} (-\theta^{-2})) \\
&= -L x'_w \left( \frac{\theta_{if}}{\theta^2} \right)
\end{aligned} \tag{72}$$

Because both  $\theta_{if}$  and  $\theta$  are **negative** temperatures, the value of this term is positive when numbers are put in.

Substitution of equations (71) and (72) into equation (68) now gives the final equation for  $c_{app,\theta}$ , the apparent specific heat of a non-fatty food at a given temperature  $\theta$  below freezing:

$$\begin{aligned}
c_{app,\theta} &= c_{SNF} (1 - x_w) + c_{ice} x_{BW} + c_{ice} x'_w \left( 1 - \frac{\theta_{if}}{\theta} \right) \\
&\quad + c_w x'_w \left( \frac{\theta_{if}}{\theta} \right) - L x'_w \left( \frac{\theta_{if}}{\theta^2} \right)
\end{aligned} \tag{73}$$

If  $c$  and  $L$  are in  $\frac{kJ}{kgK}$  and  $\frac{kJ}{kg}$  respectively, this equation will give a result in  $\frac{kJ}{kgK}$ , if in  $\frac{J}{kg K}$  and  $\frac{J}{kg}$ , the result will be in  $\frac{J}{kg K}$ . **PLEASE DO NOT MIX UNITS!**

#### 5.4.6. Prediction of enthalpy change in non-fatty foods below freezing

The enthalpy change between the initial freezing point  $\theta_{if}$  and some **lower** temperature  $\theta$  can be predicted using the following form of equation (36):

$$\Delta h(\theta \leftrightarrow \theta_{if}) = \int_{\theta}^{\theta_{if}} c(\theta) d\theta \tag{74}$$

where  $c(\theta)$  is an appropriate temperature dependent expression for specific heat. Equation (73) is just such an expression. Therefore, we can obtain an equation for enthalpy change simply by integrating equation (73) between the limits  $\theta$  and  $\theta_{if}$ .

Substitution of equation (73) into equation (74) gives:

$$\begin{aligned}\Delta h(\theta \leftrightarrow \theta_{if}) = & \int_{\theta}^{\theta_{if}} (c_{SNF}(1 - x_w) + c_{ice} x_{BW}) \\ & + c_{ice} x_w' \left(1 - \frac{\theta_{if}}{\theta}\right) + c_w x_w' \left(\frac{\theta_{if}}{\theta}\right) \\ & - L x_w' \left(\frac{\theta_{if}}{\theta^2}\right) d\theta\end{aligned}\quad (75)$$

Expansion of the brackets inside the integral, followed by simple integration of each of the resulting terms, insertion of the limits and rationalizing, gives the final equation for  $\Delta h(\theta \leftrightarrow \theta_{if})$ :

$$\begin{aligned}\Delta h(\theta \leftrightarrow \theta_{if}) = & c_{SNF}(1 - x_w)(\theta_{if} - \theta) \\ & + c_{ice} x_{BW}(\theta_{if} - \theta) \\ & + c_w x_w' \theta_{if} \ln\left(\frac{\theta_{if}}{\theta}\right) \\ & + c_{ice} x_w'(\theta_{if} - \theta) \\ & - c_{ice} x_w' \theta_{if} \ln\left(\frac{\theta_{if}}{\theta}\right) \\ & - L x_w' \left(\frac{\theta_{if}}{\theta} - 1\right)\end{aligned}\quad (76)$$

Remember that  $\theta < \theta_{if}$ .

If  $c$  and  $L$  are in  $\frac{J}{kg K}$  and  $\frac{J}{kg}$  respectively, this equation will give a result in  $\frac{J}{kg}$ , if in  $\frac{kJ}{kg K}$  and  $\frac{kJ}{kg}$ , the result will be in  $\frac{kJ}{kg}$ . Again, **DO NOT MIX UNITS!**

Equation (76) will always give a positive value  $\Delta h(\theta \leftrightarrow \theta_{if})$ . But note that this amount of thermal energy must be **removed** from the food to **cool** it from  $\theta_{if}$  to  $\theta$ , or **added** to the food to **heat** it from  $\theta$  to  $\theta_{if}$ .

**Notes on  $x_{ice}, x_{BW}$  and  $\theta_{if}$  and  $x_{ice}$ , the ice mass fraction**

More complex expressions than equation (63),

$$x_{ice} = x_w' \left( 1 - \frac{\theta_{if}}{\theta} \right) = (x_w - x_{BW}) \left( 1 - \frac{\theta_{if}}{\theta} \right) \quad (63)$$

have been developed for calculating  $x_{ice}$ . Some of them are very complex and the expressions for specific heat and enthalpy change derived on the basis of them are correspondingly very complex.

Fortunately, equation (63), although strictly valid only for dilute solutions, does work well for high moisture foods. It is simple in terms of the data required and in terms of the consequential expressions for specific heat and enthalpy change.

The data required are  $x_w$  (which is quite easy to measure),  $x_{BW}$  and  $\theta_{if}$ .

#### $x_{BW}$ , the bound water fraction

This has to be determined experimentally using accurate calorimetry, nuclear magnetic resonance (NMR) or other methods. The most reliable values are probably those measured by calorimetry.

Bound water is usually measured and expressed in terms of

*BW kg of bound water per kg of SNF*

Therefore,

$$x_{BW} = BW \cdot X_{SNF} \quad (77)$$

$BW$  can be surprisingly high, e.g. 0.34 kg bound water per kg SNF for meat (see Figures 19 and 20). For lean meat containing 74% moisture, for example,

$$\begin{aligned} x_{BW} &= 0.34 (1 - 0.74) \\ &= 0.088 \end{aligned}$$

Other typical data for  $BW$  are as follows:

Egg white	0.109 kg per kg SNF
Egg yolk	0.104
White bread	0.143
Whole-meal bread	0.111
Sucrose solution	0.30

#### $\theta_{if}$ , the initial freezing point

Values of  $\theta_{if}$  for some foods can be found in the literature (see, for example, Fig. 20). If a value cannot be found,  $\theta_{if}$  must be determined experimentally. One way of doing this is to obtain experimentally a curve like that in Fig. 14 by **thawing** the **frozen** food

with a steady rate of heat input and recording the change of temperature with time.  $\theta_{if}$  is obtained as the temperature at the upper end (point F) of the below freezing part of the curve. Obtaining the curve while thawing upper end (point F) of the below freezing part of the curve. Obtaining the curve while thawing rather than while freezing avoids the super cooling kink in the curve at point F; this would make the precise identification of  $\theta_{if}$  difficult.

The following are typical ranges of  $\theta_{if}$  for foods:

Fresh vegetables	$-0.8$ to $-2.8^{\circ}\text{C}$
Fresh fruits	$-0.9$ to $-2.7$
Fresh meat and fish	$-0.8$ to $2.9$
Skim milk	$-0.6(x_{SNF} = 0.10)$ to $-4.1(x_{SNF} = 0.40)$
Coffee	$-0.3(x_{SNF} = 0.05)$ to $-3.7(x_{SNF} = 0.40)$
Grape juice	$-1.2(x_{SNF} = 0.10)$ to $-4.4(x_{SNF} = 0.30)$
Sucrose solution	$-0.3(x_{SNF} = 0.05)$ to $-4.7(x_{SNF} = 0.40)$

Note that when a food is concentrated,  $x_{SNF}$  increases and  $x_w$  decreases. Therefore the concentration of soluble SNF increases, increasing the freezing point depression and lowering  $\theta_{if}$ .

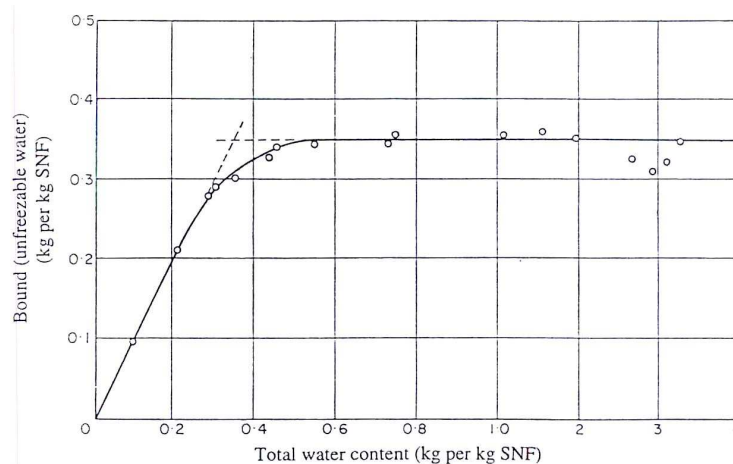


Fig. 19 Plot of bound (unfreezable) water against total water content for lean meat. (From Rolfe, 1968).

***A comparison between predicted and measured enthalpy change below freezing: a test of equation (76).***

We will compare an enthalpy change for lean beef (a non-fatty food) predicted using equation (76) with a value obtained from the empirical data plotted in Fig. 20. Fig. 20 itself will be discussed first.



Fig. 20 is a plot of enthalpy (relative to zero enthalpy at a datum temperature of  $-40^{\circ}\text{C}$ ) against water content (% water by weight). The units of enthalpy are  $\frac{\text{kcal}}{\text{g}}$ ; enthalpy values from the figure must therefore be multiplied by 4.18 to convert them to  $\frac{\text{kJ}}{\text{kg}}$ .

The parameters on the plot are temperature ( $^{\circ}\text{C}$ ) and % of total water substance frozen (i.e., in the form of ice),  $\Psi$ . Therefore,

$$\Psi = \frac{x_{ice}}{x_w} \times 100\%$$

and

$$x_{ice} = x_w \frac{\Psi}{100}$$

To see how the plot works, consider lean beef with 74% water:

$$\begin{aligned} x_w &= 0.74 \\ x_{SNF} &= (1 - x_w) = (1 - 0.74) = 0.26 \end{aligned}$$

There is a vertical dashed line on the plot in Fig. 20 at a water content of 74%. The point where this line intercepts the dashed line representing  $\Psi$  is, of course,  $> 0\%$ . At  $-14^{\circ}\text{C}$ , for example,  $\Psi = 85\%$ , and therefore

$$\begin{aligned} x_{ice} &= 0.74 \times \frac{85}{100} \\ &= 0.629 \end{aligned}$$

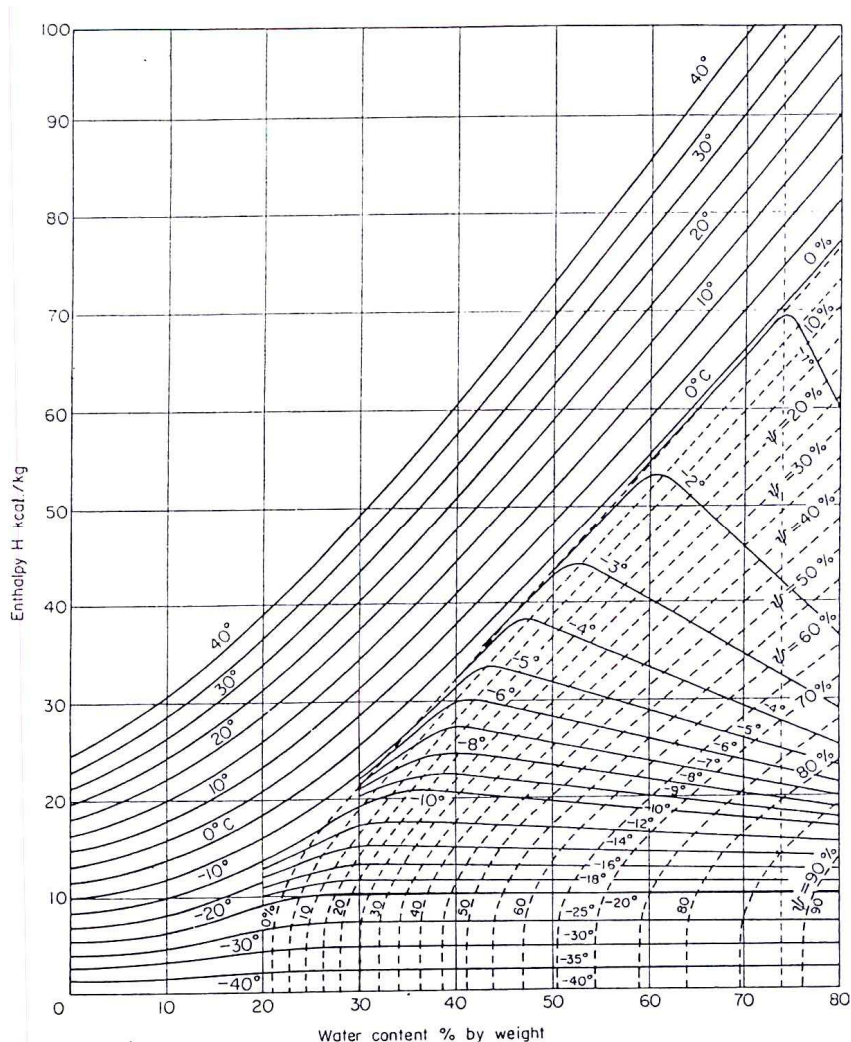


Fig. 20. Enthalpy – Composition diagram for lean beef. The enthalpy isotherms are drawn assuming a value of 0 at  $-40^{\circ}\text{C}$ , and are related to the water content (g water/100 g meat) of the lean beef. The curves were obtained by direct measurement on meats dried to appropriate moisture contents in a stream of air. The dotted lines show the percentage of total water frozen out as ice ( $\phi$ ) related to both temperature and water content of the meat. The curve  $\phi = 0$  gives the temperatures at which the freezing of lean beef begins. Assume fresh lean beef contains 74% water. The ice content at  $-14^{\circ}\text{C}$  is 85% of total water content, i.e., the quantity of ice formed is  $0.85 \times 0.74 = 0.629$  kg ice/kg/meat. With further cooling to  $-30^{\circ}\text{C}$ , the ice fraction  $\phi$  becomes constant at about 88%. The remaining 12% water is bound water and remains unfrozen. This bound water is  $0.12 \times 0.74 = 0.0888$  kg/kg meat, i.e.,  $0.0888 \text{ kg}/0.26 \text{ kg dry substance} = 0.34 \text{ kg bound water/kg dry substance}$ . Curve  $\phi = 0\%$  defines the temperature at which freezing begins, e.g. partially dried meat containing 30% water will commence to freeze at  $-7^{\circ}\text{C}$ . Riedel, L. (1957). *Kalketechnik* 9,38. Reproduced by kind permission of the author and publisher. (From Rolfe, 1968).

Below about  $-30^{\circ}\text{C}$ ,  $\Psi$  becomes constant at 88%, instead of increasing, with decreasing temperature. In other words, once the temperature is down to  $-30^{\circ}\text{C}$ , all the freezable water has been frozen (i.e., converted to ice). At this point,

$$\frac{x_{ice}}{x_w} = \frac{\Psi}{100} = \frac{88}{100} = 0.88$$

The fraction **of the water substance** remaining unfrozen therefore  $= 1 - 0.88$   
 $= 0.12$

This fraction is **bound** water.

Therefore,

$$\begin{aligned} x_{BW} &= 0.12 \times x_w \\ &= 0.12 \times 0.74 \\ &= 0.089 \end{aligned}$$

Therefore,

$$\begin{aligned} BW &= \frac{x_{BW}}{x_{SNF}} \\ &= \frac{0.089}{0.26} \\ &= 0.34 \text{ kg BW per kg SNF.} \end{aligned} \tag{77}$$

This figure agrees with the data in Fig. 19.

We can now compare a prediction made using equation (76) with the enthalpy data in Fig. 20.

Consider the enthalpy change,  $\Delta h_{(-10 \leftrightarrow \theta_{if})}$ , in lean beef between  $\theta = -10^{\circ}\text{C}$  and  $\theta_{if} = -0.5^{\circ}\text{C}$ . The following are the other data needed for equation (76):

$$\begin{aligned} x_{BW} &= 0.089 \\ x_w &= 0.74 \\ x'_w &= (x_w - x_{BW}) = 0.74 - 0.089 = 0.651 \\ C_{SNF} &= C_{PR} = 1.98 \frac{\text{kJ}}{\text{kg K}} \quad (\text{Table 3}) \\ c_w &= 4.59 \frac{\text{kJ}}{\text{kg K}} \quad (\text{Table 3}) \\ c_{ice} &= 1.94 \frac{\text{kJ}}{\text{kg K}} \quad (\text{Table 3}) \\ L &= 334 \text{ kJ / kg} \end{aligned}$$

Substituting all these data into equation (76) gives:

$$\begin{aligned}
\Delta h_{(-10 \leftrightarrow -0.5)} &= 1.98 (1 - 0.74) (-0.5 - (-10)) \\
&+ 1.94 (0.089) (-0.5 - (-10)) \\
&+ 4.59 (0.651) (-0.5) \ln \left( \frac{-0.5}{-10} \right) \\
&+ 1.94 (0.651) (-0.5 - (-10)) \\
&- 1.94 (0.651) (-0.5) \ln \left( \frac{-0.5}{-10} \right) \\
&- 334 (0.651) \left( \left( \frac{-0.5}{-10} \right) - 1 \right) \\
&= 4.89 \\
&+ 1.64 \\
&+ 4.47 \\
&+ 11.99 \\
&- 1.89 \\
&- (-206.6) \\
&= 227.7 \text{ kJ / kg}
\end{aligned}$$

What enthalpy change does the plot in Fig. 20 give for the same temperature change?

From the plot:

$$\begin{aligned}
\text{Enthalpy at } -0.5^\circ\text{C (relative to } h = 0 \text{ at } -40^\circ\text{C)} \\
&= 69.5 \text{ kcal / kg} \\
&= 69.5 \times 4.18 \text{ kJ / kg} \\
&= 290.5 \text{ kJ / kg}
\end{aligned}$$

$$\begin{aligned}
\text{Enthalpy at } -10^\circ\text{C} &= 17.5 \text{ kcal / kg} \\
&= 17.5 \times 4.18 \text{ kJ / kg} \\
&= 73.1 \text{ kJ / kg}
\end{aligned}$$

Therefore,

$$\begin{aligned}
\Delta h_{(-10 \leftrightarrow -0.5)} &= 290.5 - 73.1 \\
&= 217.4 \frac{\text{kJ}}{\text{kg}}
\end{aligned}$$

The result given by equation (76) (227.7 kJ / kg) is within 5% of this very accurate piece of empirical data, demonstrating that equation (76) works well for high moisture foods. Equation (76) is not so accurate for low moisture (high SNF) non-fatty food because, then, the solution of soluble SNF in freezable water is more concentrated, and as a result, equation (63) for  $x_{ice}$  is less valid.

This is not however, a serious drawback because foods that are frozen, and for which one might need to calculate enthalpy changes below freezing, are nearly all high moisture foods anyway. This is why freezing is a good way of preserving them;

intermediate and low moisture foods are preserved mainly by their low water activities and do not need to be frozen. Fig. 20 is a good example of high-quality published empirical enthalpy data. Another example is the phase diagram for fruit and vegetable juices, also developed by Riedel, shown in Fig. 21. This also is essentially a plot of enthalpy (in the English engineering units  $\frac{Btu}{lb}$ ) against both % SNF (called  $x_o$ ) and refractive index ( $n$ ) (which are directly related to each other). The parameters on the plot are temperature (in  $^{\circ}F$ ) and  $\Psi (= (x_{ice} / x_w) \times 100\%)$ .

At this point, before going on to deal with the specific heat of, and enthalpy change in, fatty foods, it is helpful to summarize the equations developed above for non-fatty foods. This is done in the next section.

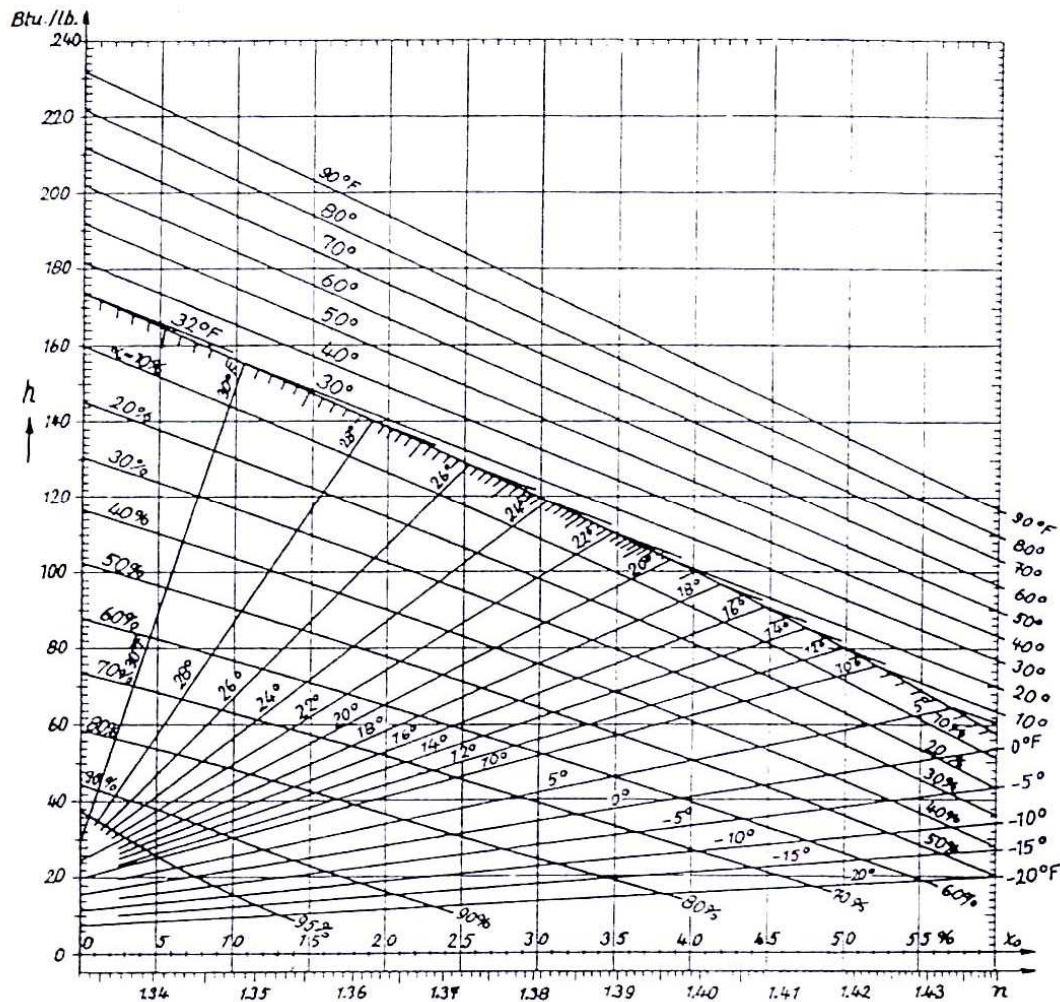
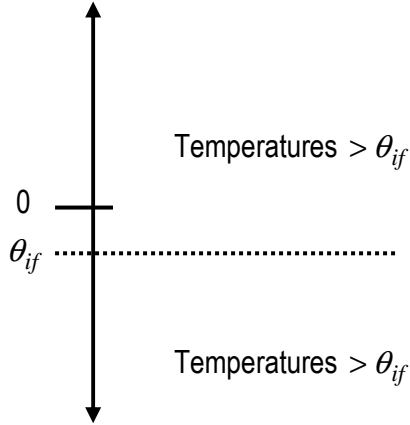


Fig. 21 Plot of enthalpy  $\left(\frac{Btu}{lb}\right)$  against both %SNF ( $= X_o$ ) and refractive index ( $= n$ ). The parameters on the plot are temperature ( $^{\circ}F$ ) and  $((x_{ice} / x_w) \times 100)(= \alpha)$ .  $h = 0$  at  $-40^{\circ}F$ . (From Riedel, 1951).

## 5.5. Summary of equations for calculating the specific heat of and enthalpy change in non-fatty foods above and below freezing

### 5.5.1. Specific heat

The overall temperature range of interest is:



**To calculate specific heat at  $\theta$  when  $\theta > \theta_{if}$**

Use equation (55):

$$c(\theta) = [(0.37 + 0.001 \theta) \times 4.18] (1 - x_w) + c_w x_w - 0.376 \exp(-43 x_w^{2.3}) \left( \frac{kJ}{kg K} \right) \quad (55)$$

where  $c_w = 4.19 \frac{kJ}{kgK}$

$\theta$  = temperature in  $^{\circ}C$ .

**To calculate specific heat at  $\theta$  when  $\theta < \theta_{if}$**

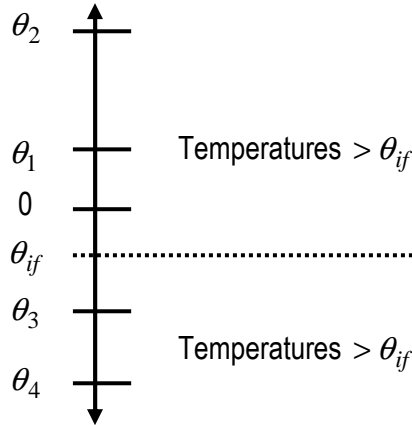
Use equation (73):

$$c_{app, \theta} = c_{SNF} (1 - x_w) + c_{ice} x_{BW} + c_{ice} x_w' \left( 1 - \frac{\theta_{if}}{\theta} \right) + c_w x_w' \left( \frac{\theta_{if}}{\theta} \right) - L x_w' \left( \frac{\theta_{if}}{\theta} \right) \quad (73)$$

The units of  $c_{app, \theta} \left( \frac{J}{kg} \text{ or } \frac{kJ}{kgK} \right)$  depend upon whether the units of  $c$  and  $L$  are based on  $J$  or  $kJ$ . **DO NOT MIX THESE!**

## Enthalpy

The overall temperature range of interest is:



**To calculate enthalpy change above freezing (e.g. between  $\theta_1$  and  $\theta_2$ )**

Use equation (57):

$$\begin{aligned} \Delta h_{(\theta_1 \leftrightarrow \theta_2)} = & 1.55(1-x_w)(\theta_2 - \theta_1) \\ & + 2.09 \times 10^{-3}(1-x_w)(\theta_2^2 - \theta_1^2) \\ & + c_w x_w (\theta_2 - \theta_1) \\ & - 0.376 \exp(-43 x_w^{2.3})(\theta_2 - \theta_1) \quad \left( \frac{kJ}{kg} \right) \end{aligned} \quad (57)$$

where  $c_w = 4.19 \frac{kJ}{kgK}$ . **DO NOT** use  $c_w$  expressed in  $\frac{J}{kg K}$ .

**To calculate enthalpy change between some temperature  $\theta$  below freezing and the initial freezing point (e.g., between  $\theta_3$  and  $\theta_{if}$ ).**

Use equation (76):

$$\begin{aligned} \Delta h(\theta \leftrightarrow \theta_{if}) = & c_{SNF}(1-x_w)(\theta_{if} - \theta) \\ & + c_{ice} x_{BW}(\theta_{if} - \theta) \\ & + c_w x_w' \theta_{if} \ln\left(\frac{\theta_{if}}{\theta}\right) \\ & + c_{ice} x_w'(\theta_{if} - \theta) \\ & - c_{ice} x_w' \theta_{if} \ln\left(\frac{\theta_{if}}{\theta}\right) \\ & - L x_w' \left( \frac{\theta_{if}}{\theta} - 1 \right) \end{aligned} \quad (76)$$

The units of  $\Delta h \left( \frac{J}{kg} \text{ or } \frac{kJ}{kg} \right)$  depend upon whether the units of  $c$  and  $L$  are based on  $J$  or  $kJ$ . **DO NOT MIX THESE!**

**To calculate enthalpy change between two temperature both of which are below freezing (e.g.  $\theta_3$  and  $\theta_4$ ).**

To do this, equation (76) must be applied **twice**, because it must always include  $\theta_{if}$  as the higher temperature:

$$\Delta h(\theta_4 \leftrightarrow \theta_3) = \Delta h(\theta_4 \leftrightarrow \theta_{if}) - \Delta h(\theta_3 \leftrightarrow \theta_{if}) \quad (78)$$

Each of the terms on the right-hand side is calculated using equation (76). **It is meaningless to insert  $\theta_4$  and  $\theta_3$  directly into equation (76) in place of  $\theta$  and  $\theta_{if}$  respectively.**

**To calculate enthalpy change between some temperatures below freezing (e.g.  $\theta_4$ ) and some temperature above freezing (e.g.  $\theta_1$ ).**

Equation (76) must be applied for the *below freezing* part of the overall temperature change, and equation (57) for the *above freezing* part:

$$\Delta h(\theta_4 \leftrightarrow \theta_1) = \Delta h(\theta_4 \leftrightarrow \theta_{if}) + \Delta h(\theta_{if} \leftrightarrow \theta_1)$$

$\uparrow$   
 Calculate  
using equation  
(76)

$\uparrow$   
 Calculate  
using equation  
(57)

Note that  $\theta_{if}$  represents both the upper limit of the *below freezing* region and the lower limit of the *above freezing* region.

### **Example 3: using equation (79)**

A fish processing company wishes to thaw 2.5 tons per day of frozen blue cod (a non-fatty fish) and partly cook it by heating it to  $70^\circ\text{C}$ .

If the frozen fish is taken from the cold store at  $-30^\circ\text{C}$ , how much heat energy, expressed in  $kJ/day$ , must the company expend to do the job?

Data available:

Water content of blue cod	=	78% by weight
Bound water content of blue cod	=	0.34 kg per kg SNF



Initial freezing point of blue cod	=	$-1.0^{\circ}\text{C}$
Specific heat of blue cod SNF	=	$2.07 \frac{\text{kJ}}{\text{kg K}}$
Specific heat of water	=	$4.18 \frac{\text{kJ}}{\text{kg K}}$
Specific heat of ice	=	$1.94 \frac{\text{kJ}}{\text{kg K}}$
Latent heat of fusion of water substance=		$334 \frac{\text{kJ}}{\text{kg}}$

(The specific heats of blue cod SNF (which is protein) and water given above are average values for the whole temperature range *below freezing* plus *above freezing*. (See Table 3).

## 5.6. Specific heat of, and enthalpy change in, fatty foods

Fatty foods have been defined here as those containing  $\geq 2.0\%$  fat. Examples are fatty cuts of meat, peanuts, whole milk and avocados.

The fat in a food is not a single pure substance; it is a mixture of triglycerides, each with its own characteristic melting/solidifying point. When an edible fat is heated or cooled, phase changes (***solid triglyceride***  $\leftrightarrow$  ***liquid triglyceride***), and therefore latent heat of fusion effects, occur at several temperatures.

When a food contains fat as a significant component, the enthalpy changes in the fat are superimposed upon the enthalpy change in the non-fatty part of the material. The latter enthalpy change we have a course already dealt with.

The picture for fatty foods is therefore somewhat more complex than for non-fatty foods. Nevertheless, we can predict enthalpy change and specific heat for a fatty food quite easily by considering the food as made up of

- a fatty fraction containing just the fat, and
- a non –fatty fraction consisting of
  - ▶ SNF and water above freezing, or
  - ▶ SNF, bound water, ice and unfrozen freezable water below freezing

With this in mind, we look first at how to predict enthalpy for fatty materials and then at how to predict specific heat.

### 5.6.1. Prediction of enthalpy change in a fatty food

The enthalpy change in a fatty food between any two given temperatures (in the overall *below freezing* plus *above freezing* range) can be expressed as:

$$\Delta h_{fatty\ food} = x_{fat} \Delta h_{fat} + x_{non-fat} \Delta h_{non-fat} \quad (80)$$

where subscript *fat* means the fatty fraction, and subscript *non-fat* means the non-fatty fraction. Of course,

$$x_{fat} + x_{non-fat} = 1 \quad (81)$$

$\Delta h_{non-fat}$  is calculated using the appropriate equation from among those already developed for non-fatty foods and summarized in Section 5.5. In other words, the non-fatty fraction of the fatty food is treated as if it was a non-fatty food in its own right.

$\Delta h_{fat}$  is found by treating the fatty fraction as an edible fat in its own right. Enthalpy changes in edible fats have to be determined from published tables and graphs of empirical data (e.g. Table 6); they cannot usually be calculated.

**Example 4: the use of equation (80)**

How much thermal energy in  $kJ / kg$  is required to heat fatty beef (40% fat, 42% water) from 10 to 40°C?

Answer:

The fractional composition of the beef is:

$$\begin{aligned} x_w &= 0.42 \\ x_{fat} &= 0.40 \\ x_{SNF} &= \frac{0.18}{1.00} (= 1 - (0.42 + 0.40)) \end{aligned}$$

or

$$\begin{aligned} x_{fat} &= 0.40 \\ x_{non-fat} &= \frac{0.60}{1.00} \end{aligned}$$

Using equation (80),

$$\Delta h_{fatty\ beef, (10 \leftrightarrow 40)} = x_{fat} \Delta h_{fat, (10 \leftrightarrow 40)} + x_{non-fat} \Delta h_{non-fat, (10 \leftrightarrow 40)}$$

**Calculation of  $\Delta h_{fat, (10 \leftrightarrow 40)}$ :**

From empirical data obtained by Riedel (Table 6) the enthalpies of beef fat (rinderfett in German) relative to  $h = 0$  at a datum temperature of  $-50^\circ C$  are:

$$\begin{aligned}
h_{10} &= 26.97 \frac{\text{cal}}{\text{g}} \\
&= 26.97 \times 4.18 \frac{\text{kJ}}{\text{kg}} \\
&= 112.7 \frac{\text{kJ}}{\text{kg}} \\
h_{40} &= 53.27 \frac{\text{cal}}{\text{g}} \\
&= 222.7 \frac{\text{kJ}}{\text{kg}}
\end{aligned}$$

Therefore,

$$\begin{aligned}
\Delta h_{fat, (10 \leftrightarrow 40)} &= h_{40} - h_{10} \\
&= 222.7 - 112.7 \\
&= 110 \frac{\text{kJ}}{\text{kg}}
\end{aligned}$$

**calculation of  $\Delta h_{non-fat, (10 \leftrightarrow 40)}$ :**

**This is calculated using equation (57), the equation for calculating enthalpy change in non-fatty foods above freezing.**

But what figure should be used for  $x_w$  in this equation? We are considering the **non-fatty fraction as a non-fatty material in its own right**. It would therefore be **incorrect** to use  $x_w = 0.42$  because this is the fractional water content of the **whole fatty** beef.

The water content of the non-fatty fraction of the beef must be expressed as a fraction of this non-fatty fraction, that is

$$\begin{aligned}
x_{w, non-fat} &= \frac{x_{w, whole fatty food}}{x_{non-fat}} \\
&= \frac{0.42}{0.6} \text{ in this example} \\
&= 0.7
\end{aligned} \tag{82}$$

Also, similarly,

$$x_{BW, non-fat} = \frac{x_{BW, whole fatty food}}{x_{non-fat}} \tag{82a}$$

and

$$\begin{aligned}x'_{w, non-fat} &= \frac{x'_{w, whole\ fatty\ food}}{x_{non-fat}} \\&= \frac{(x_w - x_{BW})_{whole\ fatty\ food}}{x_{non-fat}}\end{aligned}\tag{82b}$$

**Equations (82), (82a), and (82b) are important ones to remember** when calculating enthalpy changes in (and specific heats of) fatty foods.

Table 6. Empirical enthalpy against temperature data for some edible oils and fats. Units: cal/g

Temperatur °C	Palmkernöl	Kokosöl	Butterfett (Sommer)	Butterfett (Winter)	Schweinefett (deutsch)	Schweinefett (amerik.)	Rinderfett	Rinder- klauenöl	Walöl (roh)	Walöl (gehärtet)	Heringöl	Tafel- margarine	Margarine (Markenware)
0	22.30	20.72	24.29	23.25	23.00	27.21	20.58	29.65	30.65	21.17	28.41	24.00	25.02
1	23.06	21.49	25.07	24.06	24.19	28.70	21.05	30.75	31.24	21.77	29.16	24.82	25.90
2	23.84	22.29	25.88	24.87	25.47	30.26	21.55	31.92	31.83	22.39	29.92	25.66	26.80
3	24.63	23.11	26.72	25.69	26.77	31.74	22.09	33.17	32.44	23.03	30.68	26.52	27.72
4	25.45	23.97	27.60	26.53	27.99	33.03	22.67	34.51	33.06	23.67	31.44	27.39	28.66
5	26.29	24.88	28.51	27.40	29.06	34.12	23.29	35.93	33.69	24.31	32.20	28.28	29.61
6	27.15	25.84	29.46	28.31	30.00	35.08	23.95	37.44	34.33	24.95	32.93	29.18	30.58
7	28.04	26.83	30.45	29.26	30.86	35.96	24.64	39.00	35.00	25.58	33.64	30.10	31.56
8	28.94	27.87	31.49	30.24	31.68	36.80	25.37	40.57	35.70	26.20	34.32	31.03	32.57
9	29.85	28.97	32.60	31.25	32.46	37.61	26.15	41.94	36.41	26.81	34.98	31.96	33.60
10	30.76	30.11	33.77	32.26	33.21	38.37	26.97	42.89	37.11	27.43	35.63	32.91	34.65
11	31.66	31.30	35.02	33.27	33.92	39.11	27.85	43.55	37.82	28.05	36.26	33.87	35.72
12	32.56	32.54	36.32	34.28	34.60	39.81	28.79	44.11	38.50	28.67	36.88	34.83	36.83
13	33.44	33.86	37.66	35.29	35.26	40.49	29.80	44.61	39.17	29.29	37.50	35.80	37.96
14	34.31	35.24	39.00	36.30	35.90	41.14	30.87	45.09	39.83	29.89	38.11	36.77	39.13
15	35.17	36.73	40.32	37.32	36.52	41.79	31.99	45.56	40.49	30.48	38.72	37.75	40.31
16	36.08	38.31	41.58	38.40	37.14	42.42	33.14	46.04	41.15	31.06	39.32	38.73	41.51
17	37.11	40.00	42.82	39.56	37.75	43.04	34.27	46.52	41.80	31.62	39.91	39.67	42.70
18	38.29	41.76	44.04	40.80	38.37	43.66	35.32	46.99	42.46	32.23	40.50	40.62	43.84
19	39.63	43.59	45.22	42.15	38.99	44.30	36.27	47.47	43.11	32.94	41.08	41.55	44.98
20	41.18	45.58	46.25	43.56	39.61	44.95	37.10	47.94	43.76	33.80	41.65	42.47	46.09
21	42.97	47.80	47.07	45.09	40.26	45.66	37.82	48.42	44.41	34.78	42.22	43.36	47.09
22	45.01	50.27	47.78	46.63	40.95	46.43	38.48	48.90	45.05	35.88	42.79	44.24	48.01
23	47.28	53.04	48.47	47.96	41.70	47.26	39.12	49.37	45.68	37.05	43.34	45.08	48.85
24	49.75	55.91	49.14	48.94	42.51	48.17	39.76	49.85	46.30	38.26	43.86	45.87	49.70
25	52.30	57.56	49.79	49.72	43.40	49.19	40.40	50.32	46.93	39.52	44.34	46.64	50.60
26	54.83	58.13	50.44	50.48	44.39	50.31	41.05	50.80	47.54	40.85	44.81	47.44	51.48
27	57.21	58.60	51.12	51.26	45.52	51.58	41.71	51.28	48.09	42.31	45.27	48.25	52.36
28	58.66	59.07	51.87	52.08	46.81	53.00	42.36	51.75	48.60	43.88	45.74	49.09	53.26
29	59.22	59.54	52.67	52.95	48.29	54.39	42.99	52.23	49.08	45.52	46.21	50.00	54.15
30	59.71	60.01	53.51	53.87	49.99	55.23	43.63	52.70	49.55	47.22	46.67	50.97	55.05
31	60.19	60.48	54.39	54.83	51.98	55.87	44.30	53.18	50.02	48.96	47.14	52.00	55.97
32	60.67	60.95	55.27	55.82	54.02	56.51	45.05	53.66	50.49	50.75	47.61	53.01	56.91
33	61.16	61.42	56.12	56.84	55.13	57.15	45.90	54.13	50.95	52.53	48.08	54.02	57.84
34	61.64	61.89	56.93	57.84	55.90	57.75	46.84	54.61	51.42	54.26	48.55	55.02	58.73
35	62.13	62.36	57.70	58.83	56.66	58.34	47.84	55.09	51.89	55.91	49.02	56.01	59.56
36	62.61	62.83	58.38	59.69	57.40	58.93	48.87	55.57	52.36	57.40	49.49	57.02	60.33
37	63.10	63.30	58.99	60.35	58.12	59.52	49.92	56.05	52.83	58.63	49.97	58.10	61.00
38	63.58	63.77	59.54	60.87	58.85	60.12	51.00	56.52	53.29	59.42	50.44	59.20	61.55
39	64.07	64.24	60.06	61.35	59.58	60.73	52.11	57.00	53.76	59.92	50.91	60.24	62.05
40	64.55	64.71	60.57	61.83	60.30	61.35	53.27	57.49	54.23	60.40	51.38	61.07	62.54
41	65.04	65.18	61.07	62.31	61.04	61.97	54.50	57.97	54.70	60.83	51.85	61.69	63.03
42	65.53	65.65	61.55	62.79	61.78	62.60	55.79	58.45	55.17	61.37	52.33	62.22	63.52
43	66.01	66.12	62.04	63.27	62.53	63.23	57.15	58.93	55.64	61.85	52.80	62.71	64.01
44	66.50	66.59	62.52	63.75	63.30	63.85	58.56	59.41	56.11	62.34	53.27	63.20	64.51
45	66.99	67.06	63.01	64.23	64.07	64.42	60.03	59.90	56.58	62.82	53.74	63.69	65.00
46	67.48	67.54	63.49	64.71	64.87	64.91	61.55	60.38	57.05	63.30	54.21	64.18	65.49
47	67.97	68.01	63.98	65.19	65.69	65.40	63.09	60.86	57.52	63.79	54.69	64.67	65.98
48	68.45	68.48	64.46	65.67	66.56	65.88	64.67	61.35	58.00	64.27	55.16	65.16	66.47
49	68.94	68.96	64.95	66.15	67.45	66.37	66.16	61.84	58.47	64.76	55.63	65.65	66.96
50	69.43	69.43	65.44	66.63	68.28	66.85	67.12	62.32	58.94	65.24	56.10	66.14	67.46
51	69.92	69.90	65.93	67.11	68.90	67.33	67.62	62.81	59.41	65.72	56.57	66.63	67.95
52	70.41	70.37	66.41	67.59	69.39	67.82	68.10	63.29	59.88	66.21	57.05	67.12	68.44
53	70.90	70.86	66.90	68.06	69.87	68.31	68.58	63.78	60.35	66.69	57.52	67.61	68.94
54	71.39	71.32	67.38	68.54	70.36	68.79	69.06	64.27	60.82	67.18	58.00	68.10	69.43
55	71.88	71.79	67.87	69.02	70.84	69.28	69.53	64.76	61.29	67.66	58.47	68.59	69.92

Using  $x_w = x_{w, non-fat} = 0.7$  in equation (57), we have:

$$\begin{aligned}
 \Delta h_{non-fat, (10 \leftrightarrow 40)} &= 1.55 (1 - 0.7) (40 - 10) \\
 &\quad + 2.09 \times 10^{-3} (1 - 0.7) (40^2 - 10^2) \\
 &\quad + 0.7 \times 4.18 (40 - 10) \\
 &\quad - 0.376 \exp(-43 (0.7)^{2.3}) (40 - 10) \\
 &= 13.95 \\
 &\quad + 0.94 \\
 &\quad + 87.78 \\
 &\quad - 6.76 \times 10^{-8} \\
 &= 102.7 \frac{kJ}{kg}
 \end{aligned}$$

Using equation (80), the final answer is:

$$\begin{aligned}
 \Delta h_{fatty, beef, (10 \leftrightarrow 40)} &= x_{fat} \Delta h_{fat, (10 \leftrightarrow 40)} + x_{non-fat, (10 \leftrightarrow 40)} \\
 &= (0.4 \times 110) + (0.6 \times 102.7) \\
 &= 105.6 \frac{kJ}{kg}
 \end{aligned}$$

Remember that in calculating enthalpy change in a fatty material,  $\Delta h_{non-fat}$  is calculated using an appropriate equation from among those summarized in Section 5.5, while  $\Delta h_{fat}$  must be determined from published empirical data.

### 5.6.2. Prediction of the apparent specific heat of a fatty food

For a fatty material, the specific heat is always an **apparent** specific heat because of phase changes (**solid triglycerides**  $\leftrightarrow$  **Liquid triglycerides**) in the fat. In the *below freezing* region, of course, the **water**  $\leftrightarrow$  **ice** phase change occurs as well.

To predict specific heat, we again consider the fatty food to consist of a fatty fraction and a non-fatty fraction. Therefore,

$$c_{app, \theta, fatty\ food} = x_{fat} c_{app, \theta, fat} + x_{non-fat} c_{app, \theta, non-fat} \quad (83)$$

$c_{app, \theta, non-fat}$  is calculated using equation (55) for  $\theta > \theta_{if}$  or equation (73) for  $\theta < \theta_{if}$ .

$c_{app, \theta, fat}$  can vary quite markedly with temperature because of phase change (see Fig. 22). For approximate calculations, it can be calculated at the desired temperature using equation (10) (Table 2), or the value of  $55^\circ C$  calculated using equation (10) could be used at any temperature with only small errors. This value is:

$$c_{fat, 55^{\circ}C} = 2.05 \frac{kJ}{kg K} \quad \text{from Table 3}$$

For accurate calculations, a value of  $c_{app, \theta, fat}$  should be read from a plot like that shown in Fig. 22 (if such data exists for the fat in question). Alternatively, a value could be calculated as:

$$c_{app, \theta, fat} = \frac{dh_{fat}(\theta)}{d\theta} \quad (39)$$

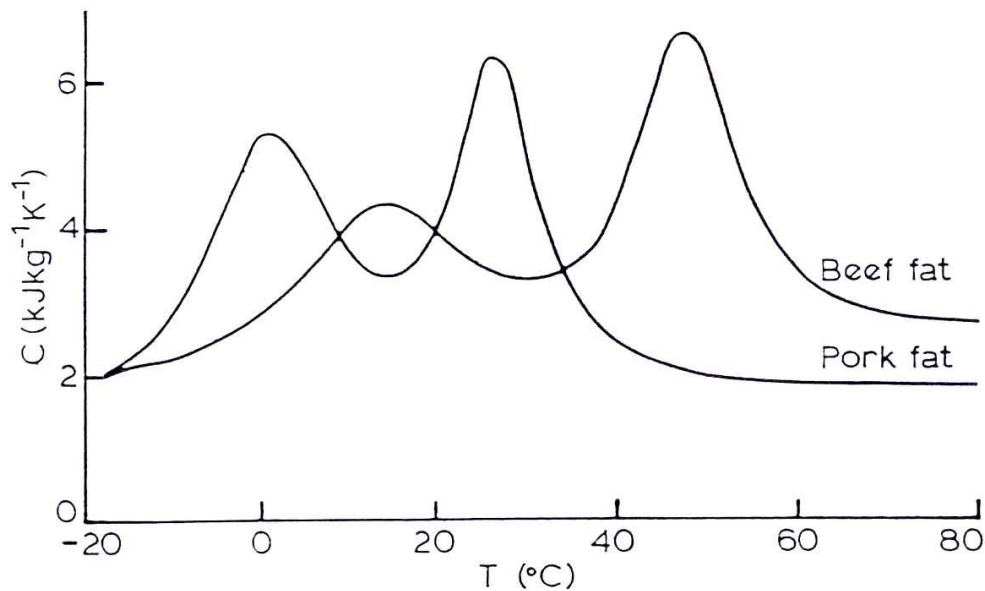


Fig. 22. Plot of specific heat against temperature for beef fat and pork fat. (From Miles *et al*, 1983).

where  $\frac{dh_{fat}(\theta)}{d\theta}$  is the **slope** of a plot of available empirical enthalpy data (e.g. from Table 6) against temperature for the fat in question.

**Example 5: using equation (83)**

Calculate the specific heat at 50°C of the fatty beef considered in the last example.

Answer:

$$\begin{aligned}
c_{app,50, fatty beef} &= x_{fat} c_{app,50, fat} + x_{non-fat} c_{app,50, non-fat} \\
x_{fat} &= 0.4 \\
x_{non-fat} &= 0.6 \\
c_{app,50, fat} &= 6.5 \frac{kJ}{kg K} \quad (\text{From the plot in Fig.22})
\end{aligned}$$

The water content of the fatty beef expressed as **a fraction of the non-fatty fraction** is 0.7. This value must be used for  $x_w$  in equation (55) to calculate  $c_{app,50, non-fat}$ :

$$\begin{aligned}
c_{app,50, non-fat} &= \left[ (0.37 + (0.001)(50)(4.18)) \right] \\
&\quad + (4.19)(0.7) \\
&\quad - 0.376 \exp \left( -43(0.7)^{2.3} \right) \\
&= 0.174 \\
&\quad + 2.93 \\
&\quad - 2.25 \times 10^{-9} \\
&= 3.10 \frac{kJ}{kg K}
\end{aligned}$$

Using equation (83), the final answer is:

$$\begin{aligned}
c_{app,50, fatty beef} &= (0.4 \times 6.5) + (0.6 \times 3.10) \\
&= 4.46 \frac{kJ}{kg K}
\end{aligned}$$

## 5.7. Latent heat evaporation of foods

We have already covered the effects of latent heat of fusion of water substance and of triglycerides in foods. We now look at latent heat effects when solvents are evaporated (boiled off) from food, e.g. water in the evaporation of milk, water plus ethanol in distilling.

### ***Foods with only one major volatile component***

These are foods in which the vapor produced by boiling has only one major component, e.g. water substance in the case of milk (and, indeed, most foods). The latent heat of evaporation of the food is in fact expressed as the latent heat of evaporation  $\frac{kJ}{kg}$  **of the substance evaporated**. The value of this is found from tables at the **pressure** at which



evaporation (boiling) occurs or at the **temperature** at which the vapor would condense at the prevailing pressure. It is **not** found at the temperature at which the food boils. The reason for this is the boiling point elevation caused by the solutes (soluble SNF) in the food.

### Example 6

How much thermal energy (in *kJ per kg of original milk*) is required to concentrate 1500 kg of whole milk from 88% water to 60% water by evaporation at a pressure of 12.34 *kPa* absolute (-88.96 *kPa gauge*)? (Milk and other heat sensitive foods are commonly evaporated at reduced pressure to lower their boiling points and thus minimize heat damage).

Answer:

From Steam Tables

$$h_{fg} \text{ at } 12.34 \text{ kPa absolute} = 2383 \frac{\text{kJ}}{\text{kg}}$$

1500 *kg* of the original milk contained

$$\begin{aligned} 0.88 \times 1500 &= 1320 \text{ kg water} \\ (1500 - 1320) &= 180 \text{ kg total solids (fat plus SNF)}. \end{aligned}$$

The total weight of concentrated milk (which contains all of the total solids)

$$= \frac{180 \times 100}{(100 - 60)} = 450 \text{ kg}$$

Therefore,

$$\begin{aligned} \text{Mass of water evaporated} &= 1500 - 450 \\ &= 1050 \text{ kg} \end{aligned}$$

Therefore,

$$\begin{aligned} &= 1050 \times h_{fg} \text{ kJ} \\ \text{Thermal energy requirement} &= 1050 \times 2383 \text{ kJ} \\ &= 2.5 \times 10^6 \text{ kJ} \end{aligned}$$

Therefore, the thermal energy requirement per *kg* of original milk

$$\begin{aligned} &= \frac{2.5 \times 10^6}{1500} \\ &= 1.7 \times 10^3 \frac{\text{kJ}}{\text{kg}} \end{aligned}$$

### ***Systems with more than one volatile component***

Distillation commonly involves such a system. For example, if ethanol is to be recovered from fermented fodder beet a separation process is required in which the ethanol is removed from the mixed fermented liquor by evaporation (i.e. distillation). In this process mixtures of water vapor and are produced. The latent heat of evaporation of the system is calculated as the average of the latent heats of the pure components evaporated weighted according to their mass fractions in the **vapor**.

If the components are *a*, *b*, *c*, etc, then

$$x_a + x_b + x_c + \dots = 1 \quad (84)$$

where *x* = mass fraction of component in vapor.

The latent heat of evaporation of the liquor being evaporated is expressed as the latent heat of evaporation needed to produce the mixed vapor. This is calculated as:

$$h_{fg} = h_{fg,a} x_a + h_{fg,b} x_b + h_{fg,c} x_c + \dots \left( \frac{kJ}{kg} \right) \quad (85)$$

where  $h_{fg,a}$  = latent heat of evaporation  $\left( \frac{kJ}{kg} \right)$  of a pure component “*a*” determined at the pressure at which evaporation occurs or at the temperature (at the prevailing pressure) at which the mixed vapor would condense.  $h_{fg,b}$ ,  $h_{fg,c}$  .....are the latent heat of evaporation of the other components in the mixture.