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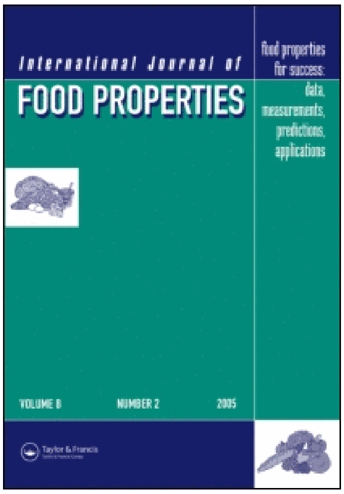

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Apparent Specific Heat Capacity of Chilled and Frozen Meat Products

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APPARENT SPECIFIC HEAT CAPACITY OF CHILLED AND FROZEN MEAT PRODUCTS

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In this article, apparent specific heat capacities of meat and meat products, minced beef, hamburger patties, soudjouk, minced turkey meat, turkey sausage, and turkey soudjouk, were measured at temperatures ranging from –60°C to +40°C, using a differential scanning calorimeter. Experimental data were compared with values calculated from different predictive models given in the literature. Measured apparent specific heat capacities were also mathematically interpreted as a function of temperature, moisture and fat content by application of nonlinear regression analysis for frozen and unfrozen samples. The developed models were found to be in good agreement with the experimental data.

Keywords: ***Specific heat, Foods, Mathematical model, Meats, Meat products, Turkey meat, Soudjouk.***

INTRODUCTION

Knowledge of physical and thermal properties of foods is essential in food freezing equipment design and processes. The computation of refrigeration requirements and freezing times can be done only when quantitative information on food properties is available. Considerable research has been done to measure and model properties of foods undergoing various processing treatments. The key properties of interest in food freezing include density, thermal conductivity and specific heat capacity.[1]

There are several methods for the determination of specific heat capacity of foods as a function of temperature. Most widely used methods are adiabatic calorimetry, differential scanning calorimetry (DSC), the method of mixtures and microcalorimetry.[2,3] The advantages of DSC are that it works rapidly and simply; much valuable information can be obtained by a single thermogram and a very small amount of sample can yield accurate results. This technique has been used to analyze thermal properties of frozen foods in different studies.[4–11] In DSC, the sample material is subjected to a linear temperature

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program, and the heat flow rate into the sample is continuously measured; the flow rate is proportional to the instantaneous specific heat capacity of the sample.[12]

Thermal properties depend strongly on temperature and composition of the product.[13,14] Specific heat capacity data of meat and meat products are available in the literature especially for beef muscle.[15,16] In general, specific heat capacity of foods can also be calculated using either semi-theoretical equations that are based on the thermodynamic principles of freezing point depression or on reliable empirical equations that are derived from regression analysis of experimental data. However, they may not be applicable to a wide range of different foods and conditions. Schwartzberg[17] applied the theory of freezing point depression to derive a predictive equation that can be used to correlate enthalpies and heat capacities as functions of temperature and moisture content during freezing and thawing of food materials. Chen[18] also derived equations of enthalpies and heat capacities as functions of temperature and moisture content using the principles of freezing point depression. Chen’s equation requires moisture content and effective molecular weight of solute. Tocci, Flores, and Mascheroni[10] measured specific heat capacity and the enthalpy of boneless mutton using a differential scanning calorimeter (DSC) in the temperature range of −40°C to 40°C. They presented empirical equations obtained by fitting their experimental data as functions of temperature and moisture content.

During the freezing process, water changes gradually from the liquid phase to solid ice. Since the properties of ice are different from those of liquid water, the properties of food determined at temperatures above freezing are often not valid for subfreezing conditions. The most dramatic change in these properties is observed at temperatures close to the freezing point.[1] In the literature, there are many reports on the measured values of thermal properties, as well as on mathematical models for their calculation. However, because of the great variation in origin, composition and processing of foods it is often necessary to make measurements for each special case, or at least to check the literature values or the calculation models.[8] In this study, specific heat capacities of meat and meat products in the frozen and unfrozen state are determined, and the data obtained is used to develop a mathematical model for predicting specific heat capacity of meat products as a function of temperature, water, and fat contents.

MATERIAL AND METHODS

Material

The meat samples used in experiments were beef and turkey meat samples such as minced beef, hamburger patties, soudjouk, minced turkey meat, turkey sausage, and turkey soudjouk. Turkish fermented sausage (soudjouk) is similar to semi-dried fermented meat products in Europe and the USA. The soudjouk is produced mainly from beef meat and/or turkey meat and tail fat from sheep.[19]

All samples used for the experiments were obtained from a meat processing plant in Izmir, Turkey. Beef and turkey meat samples were ground and pressed to pass through 5 mm sieve. Other meat products were obtained from the processing plant just before the filling process, in the form of meat dough. Compositions of the material were determined according to AOAC[20] methods and given in Table 1.

Table 1 Compositions of the material used in the study (% wet basis).

Material	Water	Protein	Fat	Ash	Carbohydrate[a]
Minced beef	65.39	17.78	16.18	0.65	–
Hamburger patties	59.45	14.73	18.36	2.48	4.98
Beef soudjouk	52.99	19.75	22.96	2.83	1.47
Minced turkey meat	69.64	20.97	7.93	1.46	–
Turkey sausage	67.38	14.62	12.20	2.78	3.02
Turkey soudjouk	54.40	19.57	22.67	3.37	–

[a] Carbohydrate contents were calculated from the difference.

Methods

Apparent specific heat capacity measurements. Specific heat capacities were measured using a TA 2920 Modulated DSC (TA Instruments Inc., New Castle, DE, USA). The DSC was fully computer controlled with rapid energy compensation and equipped with automatic data analysis software. A mass of homogenized meat sample between 18–20 mg was sealed hermetically in an aluminum DSC pan (Diameter of 4 mm) and very precisely weighed. The samples were frozen in situ in the calorimeter with liquid nitrogen cooling stabilized at –60 °C and then heated from –60°C to 40°C, at a scan rate of 2 °C/min. This low heating rate is also used by Wang and Kolbe,[5] Tocci, Flores and Mascheroni,[10] Tocci and Mascheroni,[11] as it minimizes the temperature lags likely to occur in the event of a poor thermal contact of the sample-capsule-base system and this heating rate. Prior to measurements, the DSC was calibrated for temperature and energy sensitivities using indium and sapphire. Baseline was optimized using two empty pans (one placed in the reference oven compartment and the other in the sample oven compartment). TA heat analysis software was used to calculate apparent specific heat capacity from the heat flow data.

Regression model application. Specific heat represents the rate of enthalpy change with the temperature. Since latent heat removal occurs over the freezing temperature domain, it is usual to include the latent heat contribution in the specific heat, which is then called the apparent specific heat.[6,7,21] In food materials, latent heat is not released at one single temperature as in pure substances, but over a very wide range of temperatures. For this reason, it is incorporated the latent heat into the apparent specific heat also for the food materials. Both experimental and mathematical modeling approaches have been used to determine enthalpy and apparent specific heat of frozen foods.

In this article, it is considered that the food materials were composed of liquid unfrozen water, frozen water, fat, and non-fat solid materials at any time during thawing and freezing processes. Enthalpy per unit mass of food, H, is:

$$H = [H_{wl}(1-p) + H_{ws}p].W + SH_o + FH_F \tag{1}$$

Apparent specific heat of food is obtained by differentiating Eq. (1) with respect to temperature, T.

$$C_p = \frac{dH}{dT} = W\left\{\frac{d[H_{wl}(1-p)]}{dT} + \frac{d(H_{ws}p)}{dT}\right\} + S\frac{dH_o}{dT} + F\frac{dH_F}{dT} \tag{2}$$

$$C_P = W\left[C_{Pw} + p(C_{Pi} - C_{Pw}) + (H_{ws} - H_{wl})\frac{dp}{dT}\right] + SC_{Ps} + FC_{PF} \tag{3}$$

The fraction of solidified water in food is approximated by Heiss' empirical equation;[22,23]

$$P \cong 1 - \frac{T_{cr}}{T} \tag{4}$$

where p is the fraction of solidified water in food: T_{cr} and T are temperatures in °C. The difference of enthalpies of solidified and liquid water at the same temperature, H_{ws}–H_{wl}, is the negative latent heat of freezing: -ΔH_w. Latent heat of freezing can be obtained using an empirical regression equation as a function of temperature according to Lacey and Payne[24] as given below:

$$-\Delta H_w = a + bT + cT^2 \tag{5}$$

Combining Eqs. (2), (3), (4), and (5):

$$C_P = W(C_{pi} + cT_{cr}) + SC_{ps} + FC_{pF} + W(b + C_{pw} - C_{pi})\frac{T_{cr}}{T} + Wa\frac{T_{cr}}{T^2} \tag{6}$$

The terms C_{pw}, C_{pi}, C_{pF} and C_{ps} are typically linear function of temperature.[3,22,25] Therefore, variation of apparent specific heat with respect to temperature is given in a general form of equation:

$$C_P = A + \frac{B}{T} + \frac{C}{T^2} \tag{7}$$

where T is temperature in °C and A, B, C are regression parameters that are dependent on moisture and fat contents.[22]

In order to account for the linear relationship of apparent specific heat capacity with respect to moisture and fat contents,[13,22,25] the form of Eq. (7) can be modified as follows:

$$C_P = AW + A'F + \frac{(B + B'W)}{T} + \frac{C}{T^2} \tag{8}$$

where A, B, C, A′ and B′ are parameters; and, W and F are moisture and fat contents of product (kg/kg), respectively. Eq. (8) provides an overall semi-empirical description of the apparent specific heat capacity of the product at freezing temperatures.

At temperatures above the initial freezing point the variation of specific heat capacity of food products is also described in the literature as a linear function of temperature and the composition of the material:[16,17,22,26]

$$C_P = aT + bW + cF + d \tag{9}$$

where a, b, c, and d are regression parameters. For the samples used in this study coefficients of Eq. (8) and Eq. (9) were determined by using SPSS 11.5 (Statistical Package for Social Sciences, Chicago, IL) software package.

RESULTS AND DISCUSSION

The data obtained from apparent specific heat capacity measurements are shown in Fig. 1 for beef and Fig. 2 for turkey meat samples. Each value of apparent specific heat capacity given is the average of six replicates. In all cases, the mean value of specific heat

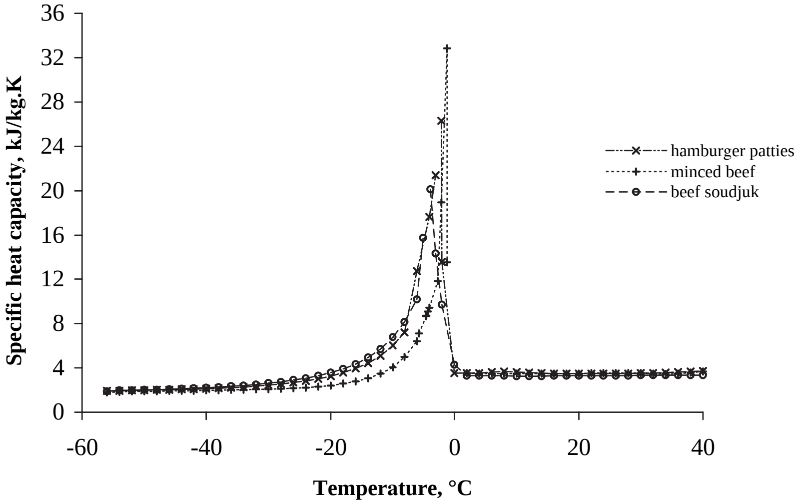

Figure 1 Experimental data of apparent specific heat capacity versus temperature for beef samples.

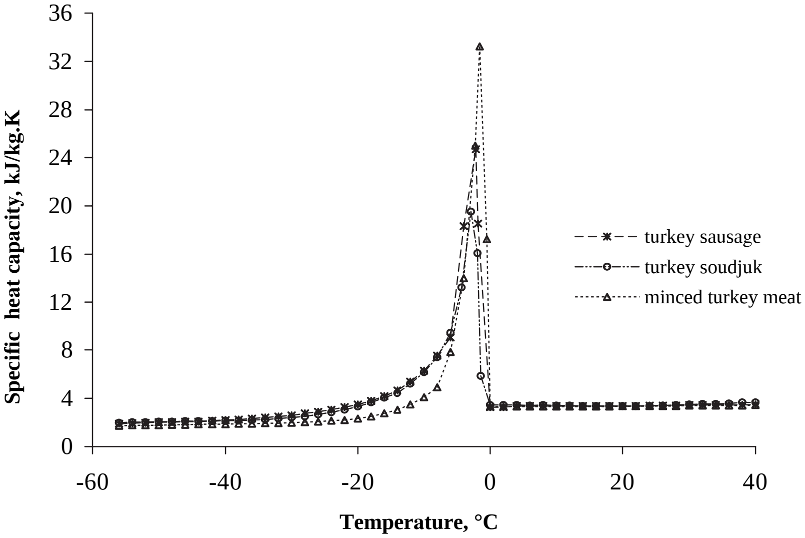

Figure 2 Experimental data of apparent specific heat capacity versus temperature for turkey meat samples.

and the standard deviation gave a coefficient of variation lower then 10%, indicating that the variability in the measurements was not excessive.

The apparent specific heat capacity values of meat samples increased from about 2 kJ/kg.K at –40°C to peak values at the initial freezing point (Fig. 1 and Fig. 2). The apparent specific heat capacity peak values and initial freezing points for the samples are given in Table 2. For the samples with the higher moisture contents, the rates of change of apparent specific heat capacity remained low with increasing temperature until close to the critical temperature when abrupt increases were observed because samples with higher moisture contents behaved more similar to pure ice with sharper phase changes and peaks. This can be seen clearly for minced beef and minced turkey meat samples from Fig. 1 and 2. The results show more gradual phase change in the samples with lower moisture such as beef soudjouk, hamburger patties and turkey soudjouk.

Measured specific heat capacities of the samples increased with increasing temperature close to about –2 °C due to phase change and dropped significantly from the peak values to about 3.4 kJ/kg.K and subsequently increased slightly with increasing temperature in the unfrozen state. The specific heat capacity values of 3.42, 3.18, 3.01, 3.45, 3.36, 3.06 kJ/kg.K were obtained at 30°C for minced beef meat, hamburger patties, soudjouk, minced turkey meat, turkey sausage, and turkey soudjouk samples, respectively.

The patterns of variations of apparent specific heat capacity obtained in this study for beef and turkey samples are typical and similar to the results reported in the literature for boneless mutton,[10] for minced beef,[8] and for beef and pork.[11] Literature on the calculation of thermal properties of meats presents several expressions of similar accuracy for the prediction of apparent specific heat capacity. Eqs (10–19) are given in Table 3, are semi-theoretical as they are based on the theory of freezing point lowering of solutions but also need some empirical parameters. The equations were used to be tested with the experimental data of apparent specific heat capacity determined in this work. The corresponding equations for the calculation of apparent specific heat capacity, as well as the values of different parameters and properties needed for the calculation, are given in Table 3.

Coefficients of regression models given in Eq.(8) and Eq. (9) are determined for calculation of apparent specific heat capacity of meat samples used in this study as a function of moisture and fat contents and temperature, in the frozen and unfrozen state, by application of nonlinear regression analysis to the measured values using the SPSS 11.5 software package. Regression coefficient was found at 95% confidence interval as $R^2 = 0.9501$ with standard error of estimate $(E_s) = 2.7257$ for Eq. (20) for frozen state. In the unfrozen state $R^2 = 0.913$ with standard error of estimate $(E_s) = 0.23916$ was calculated for Eq. (21).

$$C_P = -1.4842W - 0.0191F + \frac{(-94.8594 + 87.8803W)}{T} + \frac{2.3441}{T^2} \tag{20}$$

Table 2 Initial freezing points and the apparent specific heat capacity peak values for the samples.

Material	T_{cr} (°C)	C_p (kJ/kg.K)
Minced beef	–2.37 ± 0.06	32.86 ± 3.19
Hamburger patties	–2.69 ± 0.10	26.32 ± 2.26
Beef soudjouk	–4.05 ± 0.11	20.13 ± 1.88
Minced turkey meat	–2.35 ± 0.08	33.25 ± 3.26
Turkey sausage	–2.62 ± 0.13	24.68 ± 1.97
Turkey soudjouk	–3.24 ± 0.26	19.55 ± 1.86

Table 3 Predictive equations for specific heat capacity of meat products for comparison with experimental data.

Predictive equations for meats		Author
T < T$_{cr}$; $C_p = C_{ps}(1-W) + 2.10W - \frac{335WT_{cr}}{T^2} + \frac{2.09WT_{cr}}{T}$	(10)	Mellor[27,28]
T ≥ T$_{cr}$; $C_P = C_{Ps}(1-W) + 4.19W$	(11)	
T < T$_{cr}$; $C_P = 3.874 - 2.534W + \frac{902.893\,(1-W)}{T^2}$	(12)	Mascheroni[27]
T ≥ T$_{cr}$; $C_P = 1.448(1-W) + 4.187W$	(13)	
T < T$_{cr}$; $C_P = C_{P0} + [W - b(1-W)]\left[C_{Pi} - C_{PW} - \frac{\Delta H_w T_{cr}}{T^2}\right]$	(14)	Schwartzberg[17]
T ≥ T$_{cr}$; $C_P = C_{Po}$	(15)	
T < T$_{cr}$; $C_p = (-0.055 + 0.662W) - \frac{(233.883 - 2115.116W)}{(T-1)^2} - \frac{(72.500 - 4230.208W)}{(T-1)^3}$	(16)	Tocci[10]
T ≥ T$_{cr}$; $C_P = 1.920 + 1.433W$	(17)	
T < T$_{cr}$; $C_p = 0.51W - 3.37F + \frac{(-60.18 + 42.53W)}{T} + \frac{133.85}{T^2}$	(18)	Ngadi[22]
T ≥ T$_{cr}$; $C_P = -0.88 + 0.007T + 5.20W + 15.32F$	(19)	

C_{ps} = 1.31 (kJ/kg.°C) in Eq. (10) and Eq. (11); T_{cr} = –1°C in Eq. (10) and Eq. (14).

C_{po} = 3.48 kJ/kg.K in Eq. (14) and Eq. (15); b = 0.255 (for meats) in Eq. (14).

Eqs. from (10) to (15) are for lean beef; Eqs. (16) and (17) are for boneless mutton; and, Eqs. (18) and (19) are for fried shrimps.

$$C_P = 0.00281T + 5.171132W + 2.87307F - 0.4615 \tag{21}$$

For purpose of clarity, Fig. 3 compares experimental data of apparent specific heat capacity for minced beef with predictions of some theoretical models given in Table 3, as an example.

In Table 4, comparison of the experimental values obtained in this study and the values predicted by using Mellor, Mascheroni, Schwartzberg and Tocci equations, given in Table 3, is given for all samples. The results of calculations using Eq. (20) and Eq. (21) are also given in Table 4 and Fig. 3.

It can be seen from the Fig. 3 and Table 4 that Schwartzberg, Mellor, and Mascheroni equations give good agreement with the experiments for the meat and meat products except at temperatures close to the initial freezing point. Specific heat capacity values calculated from Eq. (20) and Eq. (21) were in closer agreement with those obtained experimentally.

CONCLUSIONS

The specific heat capacities of different meat samples were determined in the temperature range from –60 to +40°C using the differential scanning calorimeter. The samples used in the experiments were of different compositions. Due to phase change the apparent specific heat capacity of all samples increased with increasing temperature to a

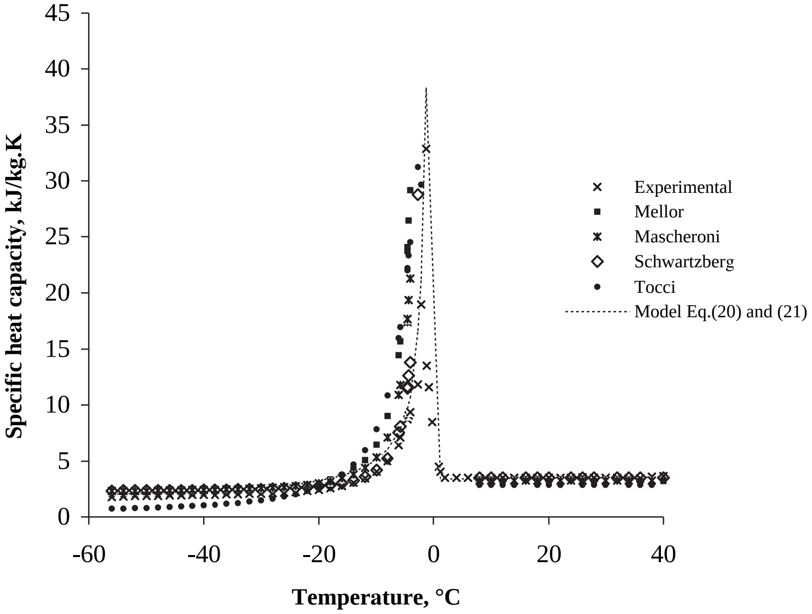

Figure 3 Experimental data of apparent specific heat capacity versus temperature for minced beef samples including calculated values of some theoretical models given in Table 3.

Table 4 Experimental and calculated values of specific heat capacity for meat samples at different temperatures.

Material	T(°C)	Experimental	Mellor	Mascheroni	Schwartzberg	Tocci	Eqs. (20) and (21)
Minced beef	–40	2.199 ± 0.036	2.169	2.412	2.399	1.022	2.305
	–20	2.953 ± 0.019	3.058	2.998	2.754	2.693	3.240
	–10	4.946 ± 0.037	6.481	5.342	4.175	7.852	5.109
	+20	3.483 ± 0.075	3.193	3.239	3.480	2.857	3.435
Hamburger patties	–40	2.228 ± 0.055	2.090	2.596	2.541	0.912	2.523
	–20	3.261 ± 0.054	2.899	3.283	2.850	2.396	3.588
	–10	6.001 ± 0.024	6.011	6.028	4.084	6.963	5.719
	+20	3.175 ± 0.032	3.022	3.076	3.480	2.771	3.196
Beef soudjouk	–40	2.296 ± 0.060	2.050	2.350	2.697	0.791	2.760
	–20	3.557 ± 0.125	2.727	2.903	2.954	2.071	3.968
	–10	6.177 ± 0.376	5.501	5.112	3.984	5.996	6.382
	+20	3.011 ± 0.022	2.836	2.899	3.480	2.679	2.995
Minced turkey meat	–40	1.984 ± 0.084	2.225	2.281	2.297	1.101	2.150
	–20	2.404 ± 0.084	3.172	2.794	2.686	2.905	2.991
	–10	4.384 ± 0.238	6.817	4.850	4.241	8.487	4.675
	+20	3.447 ± 0.032	2.939	3.355	3.480	2.919	3.423
Turkey sausage	–40	2.194 ± 0.032	2.195	2.351	2.352	1.059	2.233
	–20	3.299 ± 0.040	3.111	2.903	2.722	2.792	3.123
	–10	6.315 ± 0.186	6.638	5.112	4.206	8.149	4.906
	+20	3.357 ± 0.036	3.251	3.294	3.480	2.886	3.429
Turkey soudjouk	–40	2.245 ± 0.081	2.024	2.753	2.663	0.818	2.708
	–20	3.331 ± 0.179	2.765	3.525	2.931	2.143	3.885
	–10	6.174 ± 0.661	6.174	5.612	6.613	6.207	6.237
	+20	3.048 ± 0.023	2.877	2.938	3.480	2.700	3.059

peak value at the initial freezing point close to −2°C. Above the initial freezing point, the specific heat capacity increased linearly with temperature for each sample. It was possible to predict the apparent specific heats for the meat products in the frozen and unfrozen states.

NOMENCLATURE

b	Amount of bound water
T	Temperature (°C)
W	Mass fraction of water (kg/kg)
F	Mass fraction of fat (kg/kg)
C_p	Apparent specific heat capacity (kJ/kg.K)
C_{pF}	Specific heat capacity of fat (kJ/kg.K)
C_{pi}	Specific heat capacity of ice (kJ/kg.K)
C_{po}	Specific heat capacity of unfrozen meat (kJ/kg.K)
C_{ps}	Specific heat capacity of dry matter (kJ/kg.K)
C_{pw}	Specific heat capacity of water (kJ/kg.K)
H_{wl}	Enthalphy of liquid water (kJ/kg)
H_{ws}	Enthalphy of frozen water (kJ/kg)
ΔH_w	Latent heat of fusion (kJ/kg)
S	Mass fraction of solid (kg/kg)
T_{cr}	Initial freezing point (°C)

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