Lebensm.-Wiss. u.-Technol., 29, 659–663 (1996)

An Empirical Equation for Estimating Food Enthalpy in a Freezing Temperature Range

Hidemasa Miki and Kan-ichi Hayakawa*

H. Miki: Faculty of Fisheries, Kagoshima University, 4-50-20, Shimoarata, Kagoshima 890 (Japan)
K. Hayakawa: Food Science Department, New Jersey Agricultural Experiment Station, Cook College, Rutgers University, P.O. Box 231, New Brunswick, NJ 08903 (U.S.A.)

(Received June 23, 1995; accepted January 3, 1996)

Food enthalpies (Hs) need to be estimated accurately, as a function of temperature, in order to analyse heat transfer in food undergoing freezing or thawing. Therefore, several predictive equations have been published in the literature. Since there was a need for simple-to-use equations, a semitheorical equation containing three coefficients was derived using a published empirical equation for estimating frozen fraction of water in food. The three coefficients were functions of initial freezing point, moisture content, and effective specific heat of solid components. However, these coefficients were treated as empirical parameters that were estimated from Hs by an optimization method. The reliability of the equation was examined using 74% lean beef meat enthalpies. The maximum error of the estimated enthalpies was 1.10 kJ/kg which was about half of the most reliable, theoretical equation among those available in the literature. Because of the reliability of the developed formula, the values of the coefficients were determined for 21 different foods using published H values. The maximum absolute errors of Hs estimated using these coefficients were less than 3 kJ/kg for most foods.

Introduction

Food enthalpies must be estimated accurately in order to analyse heat transfer in food undergoing freezing or thawing. This can be accomplished using reliable theoretical equations based on the thermodynamic principles of phase change, or using reliable empirical equations based on the regression analysis of enthalpy data. Schwartzberg (1) obtained his predictive equation using a freezing point depression equation. His equation contains five parameters (nonfreezable water fraction, moisture mole fraction, solute mole fraction, effective molecular weight of solute, and specific heat of food above freezing point) that were estimated by analysing published enthalpy data. Succar and Hayakawa (2) obtained an empirical equation that retained the mathematical structure of Schwartzberg's. Their equation contains four empirical parameters that were estimated directly from enthalpy data by an optimization method. Chen (3) obtained a thermodynamic equation for estimating a temperature dependent rate of ice formation. He then derived an enthalpy equation using his frozen water fraction equation together with an empirical specific heat equation of frozen food. His enthalpy equation includes two parameters, moisture content and effective molecular weight of solute. Lacey and Payne (4) refined Schwartzberg's equation by introducing one additional parameter (ratio of soluble solid fraction and total solid fraction) and incorporating temperature dependent latent fusion heat of pure water. According to their analysis, this refined equation estimated food enthalpy most accurately compared to other published equations.

Empirical equations are easy-to-use since they are mathematically simple although they are not applicable to different foods without estimating equation parameters for each food. The aim of the present work was to develop a reliable empirical enthalpy equation.

Materials and Methods

A semitheoretical equation used for the present work was obtained assuming that food consists of water and other materials that go through no phase changes during freezing.

An enthalpy per unit mass of food, H, is:

$$\mathrm{H} = \{H_{w\ell}\,(1-p) + H_{ws}p\}W + (1-W)H_{\mathrm{o}} \qquad \text{Eqn [1]}$$

An effective specific heat of food, c_e, is obtained by differentiating Eqn [1] with respect to temperature, T.

$$\begin{aligned} C_e &= \mathrm{d}H/\mathrm{d}T = W\{\mathrm{d}[H_{w\ell}\,(1-p)]/\mathrm{d}T + \mathrm{d}(H_{ws}p)/\mathrm{d}T\} \\ &\quad + (1-W)\ \mathrm{d}H_{\mathrm{o}}/\mathrm{d}T \\ &= w\{C_{w\ell} + \mathrm{p}(C_{ws}-C_{w\ell}) + (H_{ws}-H_{w\ell})\ \mathrm{d}p/\mathrm{d}T\} \\ &\quad + (1-W)C_{\mathrm{o}} \qquad \text{Eqn [2]} \end{aligned}$$

The fraction of solidified water in food, p, is approximated by Heiss' empirical equation (cited by Watanabe (5)):

$$p \simeq 1-T_{sh}/T \qquad \text{Eqn [3]}$$

where T_{sh} and T are expressed in °C.

---

*To whom correspondence should be addressed.

0023-6438/96/070659 + 05$25.00/0 ©1996 Academic Press Limited

The difference of enthalpies of solidified and liquid water at the same temperature, H_{ws}–$H_{w\ell}$, is the negative latent heat of freezing, $-L_w$. According to Lacey and Payne (4), $-L_w$ may be estimated by:

$$\begin{aligned} -L_w &= 493.9 - 3.973\ (T + 273.15) + 0.00345\ (T + 273.15)^2 \\ &= -333.92\ -2.088\ T + 0.00345T^2 \\ &= a + bT + dT^2 \qquad \text{Eqn [4]} \end{aligned}$$

From Eqns [2], [3] and [4] one can obtain:

$$\begin{aligned} C_e &= W(C_{ws} + dT_{sh}) + (1-W)C_o \\ &\quad + W(b + C_{w\ell} - C_{ws})T_{sh}/T + WaT_{sh}/T^2 \\ &= C + B/T + A/T^2 \qquad \text{Eqn [5]} \end{aligned}$$

where

$$A = aWT_{Sh} \qquad \text{Eqn [6.1]}$$

$$B = (b + C_{w\ell} - C_{ws})\ WT_{sw} \qquad \text{Eqn [6.2]}$$

$$C = (C_{ws} + dT_{sh})\ W + C_o\ (1-W) \qquad \text{Eqn [6.3]}$$

Since water in food is solidified as ice crystalls during freezing, C_{ws} is specific heat of solidified water. According to a handbook (6), C_{ws} changed less than 10% within temperatures ranging from 0 to –20 °C (a food temperature range in many freezing processes). Therefore, temperature independent C_{ws} was assumed. The same was assumed for $C_{w\ell}$, specific heat of water in a food solution, as justified by Lacey and Payne (4). Based on these assumptions, coefficients A, B and C became temperature independent.

Food enthalpy was obtained integrating C_e with respective temperature.

$$\begin{aligned} H &= \int_{T_r}^{T} C_e dT \\ &= A\ (1/T_r - 1/T) + B\ell n(T/T_r) + C(T - T_r) \qquad \text{Eqn [7]} \end{aligned}$$

Equation [7] was used for the present work to estimate food enthalpy.

To validate Eqn [7], coefficients A, B, and C were determined using Riedel's enthalpy data that have been used widely by many researchers to validate enthalpy equations (cited in (7)). Since the equation should be applied to enthalpies below the initial freezing point, T_{sh}, of food, enthalpy data for the validation were selected out of published data using T_{sh} values estimated by Lacey and Payne (4). The coefficients A, B, and C were estimated from the selected data applying Levenberg–Marquardt optimization routine (a gradient method) available in a software package (8).

Results and Discussion

Equation [6] was fitted to Riedel's 74% moisture lean beef meat data, T_r = –40 °C, (cited in (2)) to examine the reliability. The optimized values of coefficients A, B, and C were 157.001 kJC/kg, –14.078 kJ/kg and 1.375 kJ/(kgC), respectively. **Table 1** compares enthalpies estimated by the proposed equation and Lacey and Payne's equation (LP) (4) since the LP equation was the most accurate among five published equations (4). The maximum absolute error of those estimated by the proposed and by LP equations were 1.10 and 2.13 KJ/kg, respectively. It is also of interest to note that LP equation underestimated at 11 successive data points, whereas the proposed underestimated at five successive data points and overestimated at five successive points.

Table 1 Estimated enthalpy values of lean beef meat (74% moisture)

Temperature (°C)	Published data (kJ/kg)	Lacey and Payne (kJ/kg) H	Lacey and Payne (kJ/kg) Error[a]	Proposed Eqn (kJ/kg) H	Proposed Eqn (kJ/kg) Error[a]
–40	0.00	0.00	0	0.00	0
–30	18.83	18.77	–0.05	19.11	+0.28
–20	40.60	40.40	–0.20	41.18	+0.58
–18	45.60	45.40	–0.20	46.29	+0.69
–16	51.90	50.80	–1.10	51.78	–0.12
–14	58.16	56.74	–1.42	57.81	–0.35
–12	64.85	63.48	–1.37	64.60	–0.25
–10	73.20	71.44	–1.76	72.54	–0.66
–9	78.24	76.11	–2.13[b]	77.14	–1.10[b]
–8	82.01	81.45	–0.56	82.35	+0.34
–7	88.28	87.70	–0.58	88.41	+0.13
–6	95.40	95.29	–0.11	95.69	+0.29
–5	104.60	104.88	+0.28	104.87	+0.27
–4	116.32	117.75	+1.43	117.24	+0.92
–3	136.40	136.51	+0.11	135.74	–0.66

[a] Estimated value less published data.
[b] Maximum absolute error.

The number of underestimated data points should be approximately equal to those of overestimated data points and there should not be over- or underestimation at several, successive data points when a regressed equation truly represents data points. In this aspect, further refinement is required for both the LP and proposed equation, especially the former.

According to published results (4), the maximum errors of formulas obtained by Schwartzberg (1), Succar and Hayakawa (2), and by Chen (3) were 8.45, 3.72, and 2.45 kJ/kg, respectively. Therefore, the proposed formula estimated the enthalpies with the least error compared to these and LP equations.

It should be noted that Lacey and Payne (4) used the standard deviation of errors as an indicator for goodness of equation fitting to data. However, the maximum absolute error was used for the present work as a reliability measure. This error is related more closely to the maximum absolute error of a freezing heat transfer analysis, a frequently used analytical error measure.

Table 2 shows the values of coefficients A, B, and C for 21 different foods estimated using Riedel's enthalpy data (7). Since Eqn [7] is applicable in a temperature range below the initial freezing point (T_{sh}) of food, the same table also shows published T_{sh} values (4).

The tabulated A values of all foods are positive. This is consistent with Eqn [6.1] (i.e. $A > 0$ since a = –333.92 and T_{sh} < 0). The same equation indicates that A is proportional to $|WT_{sh}|$. This proportionality held well for foods of a vegetable group, including tomato pulp (the first seven foods), when cucumber *A* was used as a reference value (about 10% errors in *A* values estimated applying the proportionality relationships). However, *A*s for a fruit group (the next eight foods) did not satisfy the proportionality when strawberry *A* was used as a reference value. For example, there were about 150% errors in *A* values of sweet cherry and plum estimated using the proportionality relationship. Similar large deviations were observed with the remaining foods when egg white *A* was used as a reference value.

Table 2 Values of coefficients in Eqn [6] estimated using published data

Food	*W* (kg/kg)	T_{sh}[a] (°C)	*A* (kJ·C/kg)	*B* (kJ/kg)	*C* (kJ/(kg·C))
Asparagus (peeled)	0.926	–0.75	145.789	–9.551	1.487
Carrot	0.875	–1.39	271.981	–8.768	1.632
Cucumber	0.954	–0.49	100.123	–5.481	1.602
Onion	0.855	–1.82	366.699	–6.781	1.792
Tall peas	0.758	–2.41	410.875	–9.735	1.681
Spinach	0.902	–0.68	138.056	–6.579	1.570
Tomato pulp	0.929	–0.83	174.821	–7.143	1.612
Apple sauce	0.824	–2.13	410.100	–7.618	1.783
Blueberry	0.851	–1.46	265.652	–10.924	1.548
Sweet cherry[b]	0.770	–3.33	200.521	–81.601	–0.373
Peach[b]	0.851	–1.95	382.079	–8.321	1.758
Pear	0.838	–2.05	396.669	–8.883	1.738
Plum[b]	0.803	–2.97	340.466	–47.861	0.666
Raspberry	0.827	–1.60	293.686	–9.705	1.627
Strawberry	0.893	–1.12	208.691	–11.954	1.476
Egg white	0.865	–0.59	130.615	2.255	1.709
Egg yolk	0.500	–3.75	36.556	–13.804	1.421
Cod	0.803	–1.11	203.459	–4.755	1.715
Haddock	0.836	–1.01	221.883	–0.049	1.858
Perch	0.791	–1.03	228.485	9.818	2.223
Beef	0.740	–0.99	157.001	–14.078	1.375

[a] Values estimaged by Lacey and Payne, 1991 (4).
[b] Without stones.

As for the *B* values, all tabulated values, except the value of perch, are negative and the absolute values of most *B*s are much smaller than the respective *A* values. The negative and small absolute *B* values are consistent with values expected from Eqn [6.2]. Since $b = -2.088$ [kJ/(kgC)], $C_{w\ell} = 4.180$, and $C_{ws} \simeq 2.2$, $b + C_{w\ell} - C_{ws} = 0.148 > 0$, and since $T_{sh} < 0$ and $W > 0$, *B* should be negative and the absolute value of |B| should be small. The same equation indicated that *B* should be proportional to WT_{sh}. This proportionality did not hold with the tabulated *B* values.

All but one *C* value was positive and small. This is consistent with Eqn [6.3]. The value of *d* in the equation is very small, 0.00345. Therefore, *C* is approximately equal to $C_{ws}\ W + C_o$ (1-*W*), the specific heat of completely frozen food. This value should be between 1.94 kJ/(kgC), ice, and 1.26, an approximate specific heat of solids in food (9). All except those of sweet cherry, plum, and perch are within this range.

Table 3 shows the errors, εs, of enthalpies estimated using Eqn [6] together with coefficients given in **Table 2** (ε = estimated – published data). The maximum absolute errors among them is also given for each food. There is excellent agreement between the estimated and published enthalpies for most foods. For example, the maximum absolute errors for 14 foods are less than 2 kJ/kg and those for five foods less than 3 kJ/kg. The maximum errors of sweet cherry, plum and perch were

Table 3 Errors (ε) of enthalpies estimates using Eqn [6] and coefficients given in **Table 2**

	ε (kJ/kg) at the following temperatures (°C)[a]														Maximum[b]
Food	–30	–20	–18	–16	–14	–12	–10	–9	–8	–7	–6	–5	–4	–3	|ε| (kJ/kg)
Asparagus (peeled)	0.17	0.01	–0.20	–0.09	0.46	0.64	–0.21	–0.10	0.54	–0.10	0.67	–1.58	0.33	1.71	1.71
Carrot	0.11	–0.48	0.22	0.40	0.26	0.12	0.51	0.09	–0.47	–0.81	–0.35	–1.05	1.14	0.96	1.14
Cucumber	0.43	–0.65	–0.31	0.23	1.06	0.30	–0.82	–0.53	0.11	0.23	0.06	0.00	–0.17	0.35	1.06
Onion	–0.07	–0.29	1.05	0.98	–0.26	–1.26	–0.33	0.25	–0.06	–0.82	0.75	0.00	–0.36	0.95	1.26
Tall pea	0.04	–0.35	1.32	0.68	0.01	–1.23	–0.25	0.03	–0.44	–0.12	0.84	–1.01	–0.61	2.11	2.11
Spinach	–0.26	–0.59	0.01	–0.12	0.13	–0.07	0.57	0.36	0.63	–0.54	–0.59	–1.22	–0.28	0.69	1.22
Tomato pulp	–0.36	–0.42	–0.48	–0.19	0.55	0.95	0.40	0.70	–0.42	–0.73	0.15	–1.11	–0.16	1.08	1.11
Apple sauce	0.44	0.19	–0.16	0.15	0.40	–0.98	–0.19	–0.05	0.33	0.45	1.17	–1.98	–1.00	2.15	2.15
Blueberry	–0.16	0.17	0.90	0.12	0.05	–1.01	–0.49	0.16	–0.32	0.43	0.99	–1.62	0.65	0.48	1.62
Sweet cherry	–4.59	–3.89	–2.92	–2.66	–1.72	–0.50	2.97	4.42	6.45	4.55	4.53	1.72	–5.42	[c]	6.45
Peach	0.16	0.49	0.01	0.16	0.20	–0.46	–0.06	–0.17	–0.13	–0.44	0.70	–0.29	–1.57	2.43	2.43
Pear	0.24	–0.16	0.46	0.73	–0.06	–0.49	–0.79	0.30	0.59	–0.40	0.15	–1.27	–0.72	2.63	2.63
Plum	–1.73	–1.99	–1.73	–1.40	–0.63	–0.87	0.86	2.36	3.39	3.52	2.67	0.41	–3.22	–8.41	8.41
Raspberry	1.50	–0.40	–0.49	–0.06	1.11	–0.64	–0.73	0.19	0.04	0.20	0.32	–0.50	–1.02	1.87	1.87
Strawberry	–0.06	–0.97	–0.60	0.21	0.62	0.90	0.51	0.57	–0.65	–0.85	0.44	–0.95	0.63	–0.07	0.97
Egg white	0.83	0.01	0.39	–0.02	–0.14	0.19	–0.81	–0.41	–0.62	0.72	–0.11	0.36	0.10	0.35	0.83
Egg yolk	0.48	–0.11	0.39	0.12	0.13	–0.47	–0.50	–0.22	0.33	–0.25	–0.33	–0.18	0.15	[c]	0.59
Cod	1.22	0.69	0.75	0.15	0.04	–0.38	–0.69	–1.21	–1.11	–0.13	0.16	0.53	0.48	1.52	1.52
Haddock	1.45	0.75	0.70	–0.04	–0.33	–0.97	–0.55	–0.22	–0.27	–0.44	–0.29	–0.03	0.93	1.30	1.45
Perch	2.31	2.37	2.05	0.93	0.11	–1.24	–1.78	–2.05	–2.81	–2.82	–3.67	4.38	7.84	1.72	7.84
Beef	0.28	0.58	0.69	–0.12	–0.35	–0.25	–0.66	–1.10	0.34	0.13	0.29	0.27	0.92	0.34	1.10

[a] ε=estimated H–published H.
[b] Maximum absolute value of ε.
[c] Data were not used for estimating the coefficients since the temperature is above T_{sh}.

between 5 and 10 kJ/kg. It is of interest to note that the values of the coefficients of these three foods deviated greatly from values expected by Eqns [6.1], [6.2] and [6.3]. This implies that Eqn [3] is not applicable to these foods.

Due to the empirical nature of Eqn [7], its parametric values should be estimated for each set of food enthalpy data. However, Eqns [6.1], [6.2] and [6.3] could provide a means for converting the coefficient values for food at one moisture level to those for the same food at different moisture levels. This was tested using 63% moisture lean beef enthalpies obtained from Riedel's Mollier chart (10) and the coefficient values for 74% moisture lean beef (**Table 1**). To convert C using Eqn [6.3], the value of C_o is required since all others are known. This was estimated substituting the C value of 74% moisture meat, 1.375, into the equation. The value obtained was –0.2347. Although this was an unrealistic value since C_o should be positive, this effective C_o was used together with the T_{sh} of 63% moisture beef, –1.76 °C, estimated by Succar and Hayakawa (2) for the C conversion. The calculated values of coefficient for 63% moisture beef were: A = 237.623, B = –21.307 and C = 1.138. Enthalpies estimated using these coefficient values deviated as much as 10 kJ/kg from the published data. Therefore, one needs to refine Eqns [6.1], [6.2] and [6.3] if one needs to use them for the coefficient conversion to different moisture levels of the same food.

The present study clearly shows the reliability of Eqn [7] for fitting enthalpy data of most foods in freezing temperature ranges. This equation may be used for accurate interpolation of tabulated enthalpy values whose errors are negligible. For this, three data points are required to estimate empirical constants A, B, and C (the estimation by a standard method for solving three simultaneous, linear algebraic equations). As an example, enthalpy values were interpolated using 74% moisture lean beef data at –3, –6, and –12 °C (**Table 1**) and using Eqn [7]. The maximum absolute error of the interpolated values was 0.68 kJ/kg at –9 °C. The maximum errors in the temperature range between –3 and –6 °C were below 0.2 kJ/kg. These errors were much less than those obtained through linear interpolation of 2 °C interval data (4.19 kJ/kg error for the linear interpolation of –3 and –5 °C data).

Conclusions

A semitheoretical equation was obtained for estimating food enthalpy using a published equation for estimating fraction of food moisture solidified as a function of temperature. The values of three empirical coefficients in the equation were determined through an optimization analysis of published enthalpy data of 21 different foods. The equation estimated enthalpies of 14 foods with the maximum errors less than 2 kJ/kg and those for four foods with the errors between 2 and 3 kJ/kg. The estimated enthalpies of the remaining three foods had maximum errors between 5 and 10 kJ/kg. The coefficient values of these three foods with the large errors deviated greatly from those estimated using the semitheoretical equations. The present formula did not convert coefficient values of one moisture level to those for different moisture levels of the same food. Future refinement is necessary for this coefficient conversion.

Acknowledgements

Mainframe computer time for the present work supported by Rutgers University Computer Services Center. The work was supported in part by U.S. Hatch Act Fund, NJ state funds, and Japanese Ministry of Education Overseas Visiting Scholarship. New Jersey Agricultural Experiment Station publication No. D-10103-1-95.

Nomenclature

A, B, C	Empirical coefficients in Eqn [7]. A (kJ·K/kg), B(kJ/kg), C(kJ/(kg·K))
a, b, d	Empirical coefficients in Eqn [4]. a = –333.92 kJ/kg, b = –2.088 kJ/(kg·C) and d = 0.00345 kJ/ (kg·C^2)
C_e	Effective heat capacity of food undergoing freezing and thawing (kJ/kg·C)
C_o, $C_{w\ell}$, C_{ws}	Specific heat of solid food components, liquid and solid water in a food solute system, respectively (kJ/(kg·C)
H	Enthalpy of food undergoing freezing and thawing (kJ/kg)
H_o	Enthalpy of solid components in food (kJ/kg)
L_w	Latent heat of water freezing (kJ/kg)
p	Mass ratio of solidified water and total water in food (kg/kg)
T	Food temperature (°C)
T_{sh}	Initial freezing point of food (°C)
T_r	Reference temperature (°C)
W	Mass fraction of moisture in food (kg/kg)
ε	Error of estimated enthalpy (kJ/kg)

References

1 Schwartzberg, H. G. Effective heat capacities for the freezing and thawing of food. *Journal of Food Science*, **41**, 152–156 (1976)

2 Succar, J. and Hayakawa, K. Empirical formulae for predicting thermal physical properties of food at freezing or defrosting temperatures. *Lebensmittel-Wissenschaft und-Technologie*, **16**, 326–331 (1983)

3 Chen, C. S. Thermodynamic analysis of the freezing and thawing of foods: Enthalpy and apparent specific heat. *Journal of Food Science*, **51**, 1158–1162 (1985)

4 Lacey, R. E. and Payne, F. A. A model to estimate thermodynamic properties of biological materials during freezing. *Transactions of the ASAE*, **34**, 1836–1841 (1991)

5 Watanabe, H. Freezing and refrigeration. In: Yano, T. and Toei, R. (Eds), *Heating and Cooling*. Tokyo: Korin Co., pp. 111–118 (1991)

6 Anonymous. *Psychrometrics, ASHRAE Handbook Fundamentals*. Atlanta, GA: The American Society of Heating, Refrigeration, and Air Conditioning Engineers, pp. 6.4–6.6 (1993)

7 Anonymous. *Thermal properties of foods, ASHRAE Handbook Fundamentals*. Atlanta, GA: The American Society of Heating, Refrigeration, and Air Conditioning Engineers, pp. 30.9–30.10 (1993)

8 Anonymous. *Fortran Subroutines for Mathematical Applications*. Houston, TX: IMSL, pp. 1017–1022 (1991)

9 Yano, T. Thermal properties of food. *New Food Industry*, **20**, 55–73 (1979)

10 Riedel, L. Kalorimetrische Untersuchengen über das Gefrieren von Fleish. *Kältetechnik*, **9**(2), 38–40 (1957)