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Thermal Properties of Model Foods in the Frozen State

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ABSTRACT

Thermal diffusivities and thermal conductivities of model food systems were measured by two transient methods: the flash method and the hot wire probe method.

Experimental runs were carried out between +20°C and −40°C with binary food gels: water+gelatin; water+ovalbumin; water+starch; water+sucrose. These results were compared with the main thermal conductivity models (series, parallel, Maxwell, series-parallel). The conductivity data which are very sensitive to the ice fraction are best fitted by the Maxwell's model.

NOMENCLATURE

$A=\frac{Q}{4\pi}$	Probe constant for eqn (1) (W/m)
B	Constant defined by eqn (1) (K)
ΔH_f	Enthalpy of fusion of ice (J/kmol)
m	Mass of component i (kg)
M_w, M_s	Molar mass of water and dry matter (kmol/kg)
N	Fraction of parallel part (eqn (4))
R	Gas constant (J/kmol K)
t	Time (s)
T	System temperature (K)

T_f	Gel initial freezing temperature (K)
$T_{f,0}$	Freezing temperature of pure water (K)
$y_i = \frac{m_i}{m_i + m_w}$	Mass fraction of component *i*
ε	Volume fraction of continuous dispersed phase
λ	Thermal conductivity of continuous dispersed phase

Subscripts

c	Continuous phase
d	Dispersed phase
f	Freezing
ice	Ice phase
0	Pure component
par	Parallel part
s	Dry matter
ser	Series part
unf	Unfrozen
w	Total water

1 INTRODUCTION

The thermophysical properties of foods, required in the simulation of freezing and thawing processes include density, conductivity and diffusivity. Unfortunately these data are only available for a small number of foods in the frozen state. Indeed the estimation of freezing times are necessary for designing freezing equipment.

When experimental data are lacking, theoretical models based on the properties of major food components are often used.

Between 0°C and -40°C the thermophysical properties of foods show important variations due to the continuous variation of ice content with temperature in this range and to the fact that the thermal conductivity of ice is about four times the value of unfrozen water. Moreover, unfreezable water which can be estimated from enthalpy data (Heldman, 1974, 1982; Miles *et al.*, 1983; Mannapperuma & Singh, 1988) is also an important parameter which must be taken into account. Most of the conductivity or diffusivity data for model foods (gels) were measured in the unfrozen state; so, the purpose of this work was to extend these measurements to the frozen state down to -40°C.

Experimental data were obtained with four types of gels: water + sucrose; water + gelatin; water + ovalbumin; water + starch. Furthermore, these data were interpreted by four heat transfer models: series, parallel, Maxwell and series–parallel. Two experimental transient methods, namely the pulse method (diffusivity) and the hot wire probe (conductivity) were used.

2 EXPERIMENTAL METHODS

2.1 Sample preparation

Different gel types were prepared with well defined protocols by controlling precisely the preparation conditions in order to obtain gels of reproducible texture for a given composition. In the case of sucrose and starch gels the addition of 4% agar–agar (mass ratio agar–agar/water) gives homogeneous structures (Renaud, 1990). Furthermore, hot solutions of gels were poured into measuring cells in order to achieve a good thermal contact with the temperature detector. The different gel compositions (by mass) are shown in Table 1.

2.2 Experimental set-up

The two transient methods selected have the main advantage of short experimental times and low thermal perturbations (Mohsenin, 1980; Renaud, 1990).

Hot wire probe method
This well-known method has been used with numerous materials, especially foodstuffs (Lentz, 1961; Sweat *et al.*, 1973).

The probe is made with a hypodermic needle (overall external diameter 0·6 mm and total length equal to 10 cm) inside which is placed a chromel–alumel heating wire and a very small thermocouple (diameter = 0·08 mm), all these components being carefully insulated

TABLE 1
Gel Composition. Mass Fraction of Dry Matter, y_i

Sucrose	10	20	30	40	50	—
Gelatin	5	10	15	20	30	40
Starch	5	10	20	30	—	—
Ovalbumin	5	10	14	24	—	—

with an epoxy resin. The linear heating power was about 10 W/m for a sample diameter of 10 cm. For these conditions the maximum temperature variation recorded was $\Delta T = 5$°C and $\Delta T = 1{\cdot}5$°C respectively for unfrozen and frozen materials; each experimental run lasted approximately 40 s.

Assuming a probe of low thermal capacity and a purely radial heat flow, a theoretical analysis shows that the temperature variation at the probe surface is given by:

$$T = \frac{A}{\lambda} \ln t + B \tag{1}$$

where $A = Q/4\pi$ is the probe constant, Q represents the heat flux by probe unit length and B is an experimental constant. The probe was first calibrated with very viscous liquids (glycerol, ethylene glycol) or gelatinized water with 4% agar–agar in order to obtain the actual value of A. Then, the thermal conductivity λ was calculated from the linear part of the curve $T = f(\ln t)$ in the time domain ranging from 6 to 40 s; the conductivity values reproducibility was around 5%.

Pulse method

This method, well known for inorganic materials was described in previous communications (Gonnet, 1987; Andrieu *et al.*, 1987). The front face of the sample, shaped as a disk of uniform thickness, is submitted to an uniform pulse of radiant energy. The temperature variation at the rear face of the specimen is recorded (maximum temperature change 0·5°C) and the thermograms analysis $T = f(t)$ gives the thermal diffusivity.

The thermal diffusivity identification can be carried out by the partial moments' method as described previously (Gonnet, 1987). Reproducibility values for diffusivity were around 5%.

These two sets of apparatus are entirely controlled by a microcomputer (Renaud, 1990). For simulating the freezing processes, experimental runs were carried out with temperature decreasing at a constant cooling rate of 3°C/h. This a low cooling rate was chosen in order to minimize the internal thermal gradients and the supercooling effects.

3· RESULTS

The whole set of experimental data for the four types of gels are presented in Figs 1–8. These figures show an important variation in

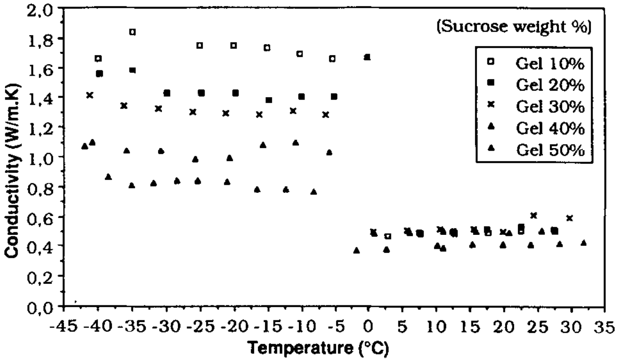

Fig. 1. Thermal conductivity of sucrose gels.

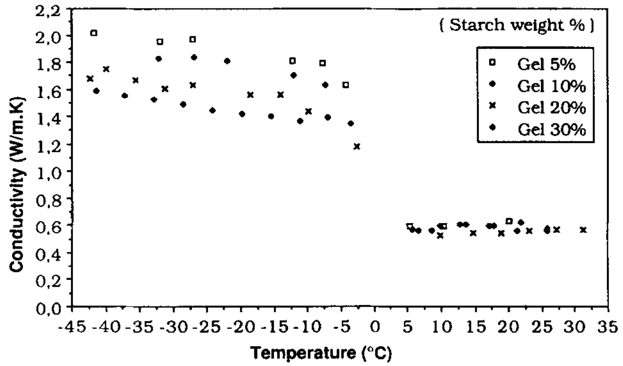

Fig. 2. Thermal conductivity of starch gels.

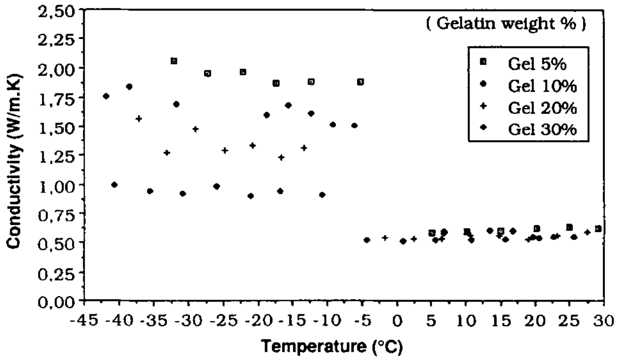

Fig. 3. Thermal conductivity of gelatin gels.

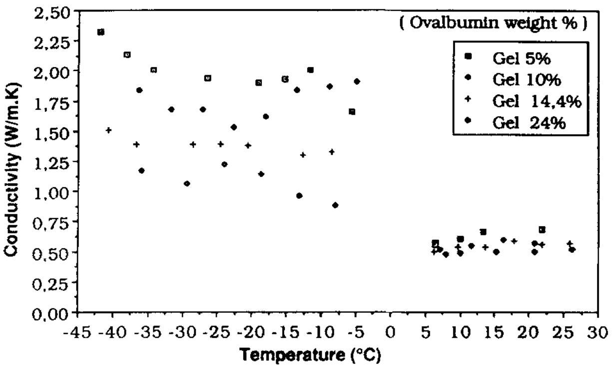

Fig. 4. Thermal conductivity of ovalbumin gels.

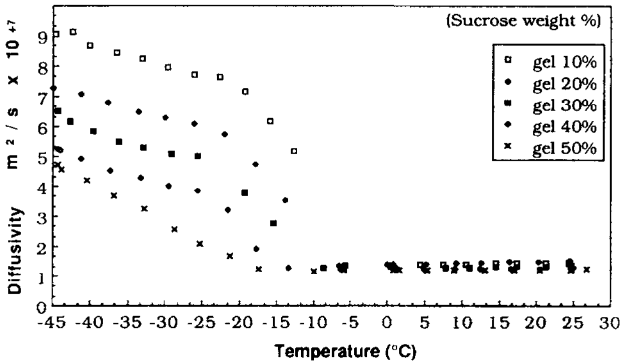

Fig. 5. Thermal diffusivity of sucrose gels.

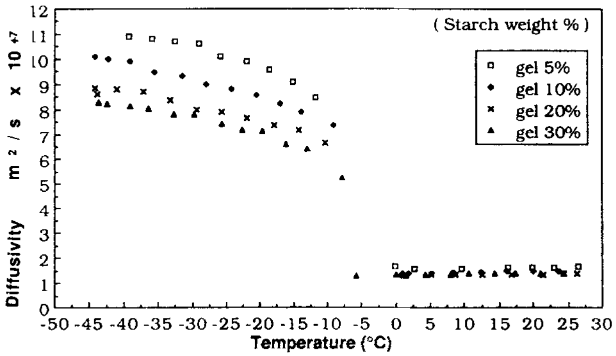

Fig. 6. Thermal diffusivity of starch gels.

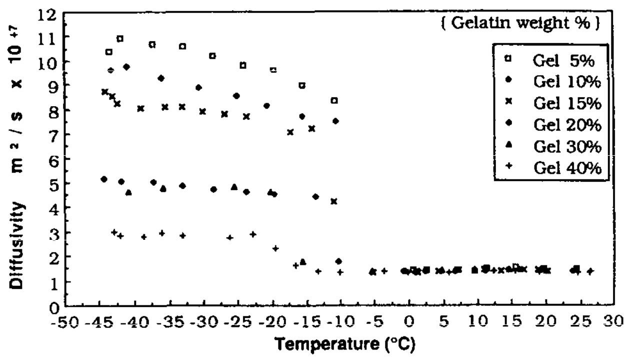

Fig. 7. Thermal diffusivity of gelatin gels.

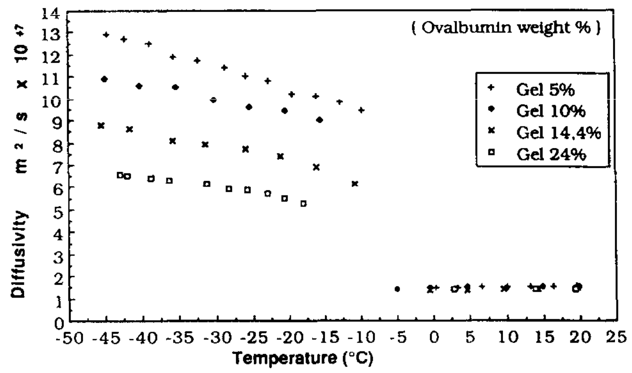

Fig. 8. Thermal diffusivity of ovalbumin gels.

thermal properties between 0°C and − 10°C as in the case of commercial products (Lentz, 1961; Sweat *et al.*, 1973; Heldman, 1982; Pham & Willix, 1989; Pham, 1990) due to a high variation of the ice fraction in this range. In the range − 10°C to − 40°C the dry matter concentration has the most important influence on the amount of ice frozen at a given temperature. This amount decreases with increase in dry matter concentration, all other things being equal.

The conductivity data for gelatin and ovalbumin gels, even repeated many times, are more scattered than the other ones probably because of the reproducibility of the ice crystallization; these gels were prepared without agar–agar addition.

4 INTERPRETATION

4.1 Ice fraction estimation

The estimation of the ice mass fraction y_{ice} of the food at $T < T_f$, where T_f represents the initial freezing point in K, was based on the following formula derived from Raoult's law (Heldman, 1974; Schwartzberg, 1976; Miles *et al.*, 1983):

$$\ln \frac{\dfrac{y_w - y_{\text{unf}} - y_{\text{ice}}}{M_w}}{\dfrac{y_w - y_{\text{unf}} - y_{\text{ice}}}{M_w} + \dfrac{y_s}{M_s}} = \frac{M_w \Delta H_f}{R}\left[\frac{1}{T} - \frac{1}{T_{f,0}}\right] \qquad (2)$$

where M_w and M_s represent, respectively, molar mass of water and dry matter and $T_{f,0}$ the freezing temperature of pure water in K.

The unfreezable water content y_{unf} (mass fraction) was taken from published literature data (Schwartzberg, 1976; Pham, 1987). Figures 9 and 10 show the influence of the solute molar mass on the ice fraction: the lower the solute molar mass, the greater the ice formation over a large temperature interval.

4.2 Diffusivity and conductivity comparison

Density and specific heat were calculated from the gel composition and from the intrinsic values of the components (ρ_i, $c_{p,i}$) taken from the literature data (Miles *et al.*, 1983; Gonnet, 1987). So, it was possible to calculate the thermal conductivities from the experimental diffusivities

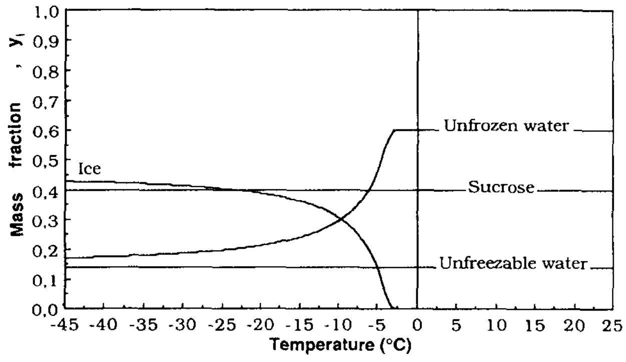

Fig. 9. Calculated gel mass composition of 40% water + sucrose gels with eqn (2).

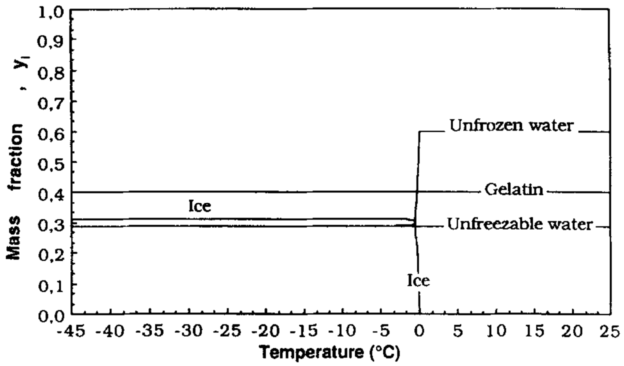

Fig. 10. Calculated gel mass composition of 40% water + gelatin gels with eqn (2).

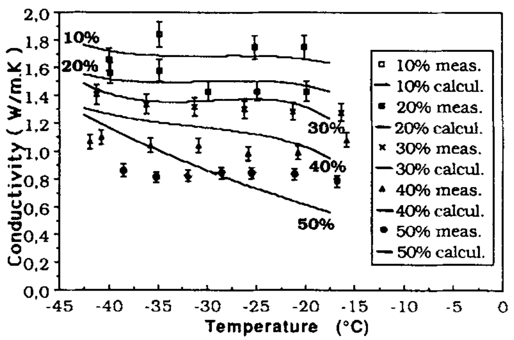

Fig. 11. Comparison between the thermal conductivity calculated from the diffusivity and the experimental conductivity for sucrose gels.

and to compare these values to the experimental conductivities obtained by the hot wire probe method. For example, Fig. 11 shows this comparison for sucrose gels. Taking into account the experimental errors of each measurement and in the estimation of the specific heat and the geometry differences for heat transfer model, the two experimental methods are in good agreement.

4.3 Heat transfer models fitting

Intrinsic thermal conductivities of the components are necessary to apply heat transfer models. Literature values were used for the ice component; for dry matter, the extrapolated experimental values from the unfrozen state were used. These values were obtained from the series model which gives the more coherent results (Gonnet, 1987; Renaud,

TABLE 2
Thermal Conductivity Values for Model

Component	*Food components conductivities* λ_s *(W/m K) = f(T(°C))*
Sucrose	$\lambda_s = 0{\cdot}304 + 9{\cdot}93 \times 10^{-4}\,T$
Starch	$\lambda_s = 0{\cdot}478 - 6{\cdot}90 \times 10^{-3}\,T$
Ovalbumin	$\lambda_s = 0{\cdot}268 - 2{\cdot}50 \times 10^{-3}\,T$
Gelatin	$\lambda_s = 0{\cdot}303 + 1{\cdot}20 \times 10^{-3}\,T - 2{\cdot}72 \times 10^{-6}\,T^2$
Water	$\lambda_w = 0{\cdot}587 + 0{\cdot}0028 \times (T - 20)$
Ice	$\lambda_{ice} = 2{\cdot}22 - 6{\cdot}25 \times 10^{-3}\,T + 1{\cdot}015 \times 10^{-4}\,T^2$

1990). For water, extrapolated experimental data which were very close to published literature data were used (Table 2). For example, at 20°C, the experimental intrinsic water conductivity for the water + gelatin system was 0·62 which is very close to literature value, namely 0·60 W/m °C (Miles *et al.*, 1983); so, using literature or extrapolated experimental data leads to no significant differences in calculated gel conductivities. The regression equations for the mean conductivity values are given in Table 2.

For these products with three components four models were used: series, parallel, Maxwell, series–parallel.

For the Maxwell's model, it was assumed that the ice is dispersed in a second phase composed of unfrozen water and dry matter; the thermal conductivity of this second phase was calculated by applying the Maxwell model with the dry matter as the continuous medium and with the unfrozen water as dispersed phase. The choice of the nature of the dispersed and the continuous phase depends on the gel structure as observed in previous works concerning modeling of frozen foodstuffs (Lentz, 1961; Barrera & Zartizky, 1983). So, for each level, the correlation becomes:

$$\lambda = \lambda_c \frac{\lambda_d + 2\lambda_c - 2\varepsilon_d(\lambda_c - \lambda_d)}{\lambda_d + 2\lambda_c + \varepsilon_d(\lambda_c - \lambda_d)} \tag{3}$$

where ε_d represents the volumic fraction of dispersed phase, λ_c and λ_d representing respectively the thermal conductivity of continuous and dispersed phase.

For the series–parallel model an adjustable parameter, *N*, which represents the parallel part was included; the corresponding relation

TABLE 3
Comparison between Theoretical and Experimental Conductivity Values
Water 90%–Sucrose 10%

T (°C)	*Experimental conductivity* λ *(W/m K)*	*Series model* λ *Calculated (W/m K)*	*Series model Error (%)*	*Parallel model* λ *Calculated (W/m K)*	*Parallel model Error (%)*	*Maxwell model* λ *Calculated (W/m K)*	*Maxwell model Error (%)*	*Series–parallel model Parallel fraction N*	*Series–parallel model* λ *Calculated (W/m K)*	*Series–parallel model Error/ average N (%)*
25·0	0·51	0·54	6·9	0·55	9·0	0·55	8·3	−3·17	—	—
22·5	0·50	0·54	6·7	0·55	8·9	0·54	8·1	−3·14	—	—
20·0	0·50	0·53	6·6	0·54	8·7	0·54	8·0	−3·10	—	—
17·5	0·49	0·53	6·4	0·54	8·5	0·53	7·8	−3·06	—	—
15·0	0·49	0·52	6·3	0·53	8·3	0·53	7·6	−3·02	—	—
12·5	0·48	0·52	6·1	0·52	8·1	0·52	7·4	−2·98	—	—
10·0	0·48	0·51	5·9	0·52	7·9	0·52	7·2	−2·94	—	—
7·5	0·48	0·50	5·8	0·51	7·7	0·51	7·1	−2·89	—	—
			6·3*		**8·4***		**7·7***	**Mean *N* −3·04**		
−10·0	1·71	1·26	−26·3	1·98	15·8	1·65	−3·3	0·62	1·64	−4·0
−12·5	1·71	1·28	−25·1	2·01	17·5	1·68	−1·8	0·59	1·67	−2·5
−15·0	1·71	1·30	−24·1	2·04	19·2	1·71	−0·4	0·56	1·69	−1·0
−17·5	1·72	1·31	−23·5	2·07	20·7	1·73	0·6	0·53	1·71	−0·4
−20·0	1·73	1·32	−23·4	2·10	21·6	1·74	1·2	0·52	1·73	0·2
−22·5	1·74	1·33	−23·7	2·13	22·0	1·76	1·1	0·52	1·75	0·8
−25·0	1·77	1·34	−24·4	2·15	21·8	1·78	0·7	0·53	1·77	0·0
−27·5	1·79	1·34	−25·2	2·18	21·6	1·79	0·0	0·54	1·79	−0·3
−30·0	1·82	1·35	−25·9	2·21	21·6	1·81	−0·4	0·55	1·81	−0·8
−32·5	1·83	1·35	−26·1	2·24	22·5	1·82	−0·1	0·54	1·82	−0·5
−35·0	1·81	1·35	−25·2	2·27	25·3	1·84	1·6	0·50	1·84	1·5
−37·5	1·75	1·36	−22·6	2·30	31·1	1·85	5·7	0·42	1·86	6·2
			−24·6*		**21·7***		**0·4***	**Mean *N* 0·53**		

*Mean value.

becoming (Renaud, 1990):

$$\lambda_{\text{series-parallel}} = \lambda_{\text{ser}}(1 - N) + \lambda_{\text{par}} N \tag{4}$$

For example, the comparison between the experimental data and the theoretical values are presented in Table 3 for each of the four models for a dry matter mass fraction of 10%.

The Maxwell's model gives maximum deviations which do not exceed 28% for frozen sucrose gel with 50% dry matter mass fraction (Fig. 12). Series and parallel models give larger deviations. The series-parallel model was used with the adjustable parameter N; the calculated conductivities with the mean N values gives a relative standard deviation of

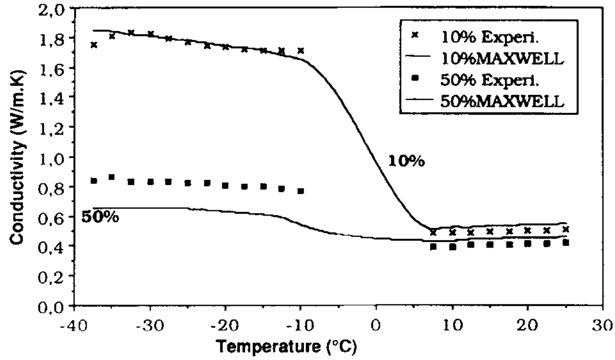

Fig. 12. Comparison of the experimental conductivity and the conductivity calculated from Maxwell's model for water + sucrose gel.

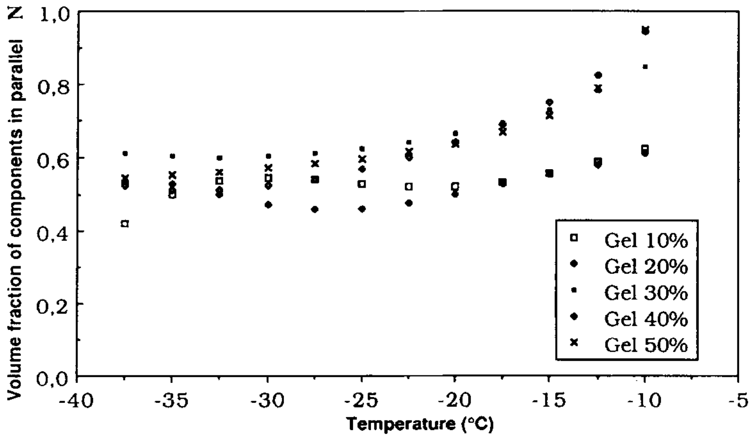

Fig. 13. Values of N parameter for water + sucrose gels.

5%; nevertheless this N value varies with each type of gel so that this model cannot be generalized for any kind of material (Figs 13–15). So, the Maxwell's model which does not need any adjustable parameter and leads to a mean relative error of 12% was preferred.

Furthermore, a parameter sensitivity study has shown that, in the frozen state, calculated conductivity values for any model are very sensitive to the ice fraction (Table 4). Consequently, it is very difficult to set up physical models which interpret accurately the whole set of experimental data without any accurate estimate or experimental determination of ice fraction.

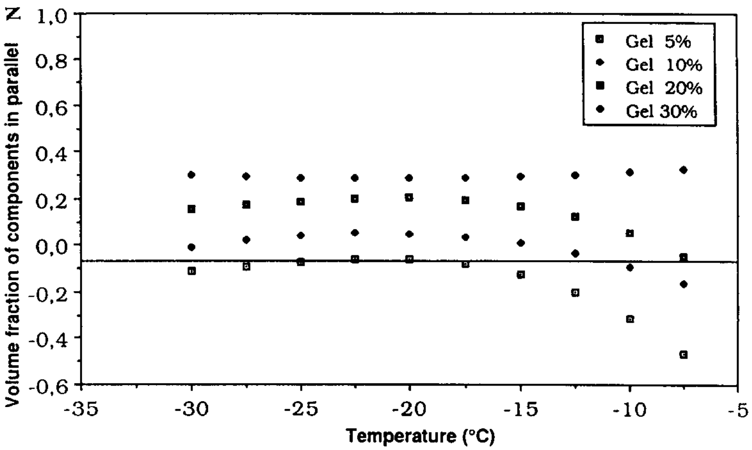

Fig. 14. Values of N parameter for water + starch gels.

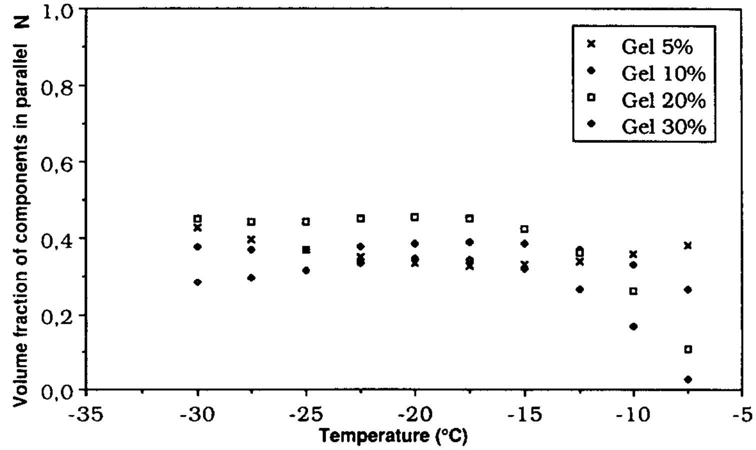

Fig. 15. Values of N parameter for water + gelatin gels.

TABLE 4

Sensitivity of Maxwell's Model in the Case of 10% Frozen Sucrose Gel (dry matter mass fraction). Sensitivity is the Variation of the Thermal Conductivity Corresponding to a Variation of + 10% for the Parameter Considered

Parameter variation	*Mass fraction ± 10%*			*Conductivity ± 10%*		
Components	Ice	Water	Sucrose	Ice	Water	Sucrose
Sensitivity	± 40%	± 2·5%	± 3·5%	± 16%	± 3%	± 2·5%

5 CONCLUSIONS

The two transient methods (hot wire probe and pulse method) in the case of model foods (gels), gives coherent results from − 40°C to + 20°C.

There is a strong correlation between the ice fraction and the thermal properties of frozen gels. Consequently, this parameter is the most important one for interpreting the experimental data as confirmed by a sensitivity study. Among the four heat transfer models selected, the Maxwell's one is the most satisfactory.

The improvement of the modeling of these data relies on an experimental validation of the ice fraction (NMR, etc.) and of the unfreezable water fraction.

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REFERENCES

Andrieu, J., Gonnet, E. & Laurent, M. (1987). Intrinsic thermal conductivities of basic food components. *High Temperature–High Pressure*, **19**, 323–30.

Barrera, N. & Zartizky, N. E. (1983). Thermal conductivity of frozen beef liver. *Journal of Food Science*, **48**, 1779–82.

Gonnet, E. (1987). Determination de la diffusivité thermique des produits alimentaires par la méthode impulsionnelle. Application aux produits pastiers. Thèse de Docteur ingénieur, Université Montpellier II.

Heldman, D. R. (1974). Predicting the relationship between unfrozen water fraction and temperature during food freezing using point depression. *Transactions of the ASAE*, **17** (1), 63–6.

Heldman, D. R. (1982). Food properties during freezing. *Food Technology*, **36** (2), 92–6.

Lentz, C. P. (1961). Thermal conductivity of meats, fats, gelatin gels and ice. *Food Technology*, **15** (5), 243–7.

Mannapperuma, J. D. & Singh, R. P. (1988). Prediction of freezing and thawing times of food using a numerical method based on enthalpy formulation. *Journal of Food Science*, **53** (2), 626–30.

Miles, C. A., Van Beek, G. & Veerkamp, C. H. (1983). Calculation of thermophysical properties of foods. *Physical Properties of Foods*, ed. R. Jowitt *et al.* Applied Science Publishers, London, Chap. 16, pp. 269–312.

Mohsenin, N. N. (1980). Thermal properties of foods and agricultural materials, ed. Gordon and Breach, London.

Pham, Q. T. (1987). Calculation of bound water in frozen foods. *Journal of Food Science*, **52** (1), 210–12.

Pham, Q. T. (1990). Prediction of thermal conductivity of meats and other animal products from composition data. In *Physical Properties and Process Control*, ed. Elsevier Applied Science, **1**, 408–24.

Pham, Q. T. & Willix, J. (1989). Thermal conductivity of fresh lamb meat, offals and fat in the range −40°C to +30°C. Measurements and correlations. *Journal of Food Science*, **54** (3), 508–9.

Renaud, T. (1990). Diffusivité et conductivité thermiques des produits alimentaires congelés. Thèse de Doctorat de l'Université de Lyon, I.

Schwartzberg, H. G. (1976). Effective heat capacities for the freezing and thawing of foods. *Journal of Food Science*, **41**, 152–6.

Sweat, V. E., Haugh, C. G. & Stadelman, W. J. (1973). Thermal conductivity of chicken meat at temperatures between 75°C and 20°C. *Journal of Food Science*, **38**, 158–60.