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MODEL CALCULATION OF THE HEAT CONTENT OF TECHNICAL SILICATE GLASSES

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ABSTRACT. Values of the heat content of technical silicate glasses, measured on samples of some flat and container glasses by the drop method on a calorimeter, are compared with values calculated from Cp-equations derived from models described in the literature. These models were developed under assumption of a ideal mixing behaviour of the oxides composing the glass, with Cp(glass) being calculated as a linear combination of the partial heat capacities of the different oxides. Calculated values show in general deviations of up to 8%.

INTRODUCTION

Accurate values of the heat content of technical silicate glasses are of great importance for calculations in glass science and technology. For its determination methods like DSC and dropcalorimetry have been normally used. Since these measurements represent a time consuming process and the required equipments are complex, several attempts have been made to develop models for its calculation. Considering that some of them were developed for calculations in geological sciences, we compare here the values we measured for two flat and four container glasses [1] with the corresponding values calculated from the models described in [2-8], in order to see how useful are the mentioned models for the description of the heat content of technical silicate glasses. These glasses show a chemical composition significantly different from that of the samples used in the development of the models mentioned in references [2-8].

BASIC PRINCIPLES

According to the models that will be treated in this paper, the heat content is calculated from the well known relation

$$\Delta H = \int C_p(\text{glass}).dt \qquad (1)$$

with C_p(glass) being calculated as a linear combination of the C_p-functions of the different oxides composing the glass. For validity of this relation, ideal behaviour of the glass components is assumed and the partial heat capacities of the oxides are considered independent of composition in the studied composition interval, even when considering a certain evidence of deviation from ideality, as reported in [8].

On the development of their model, Sharp, Ginther and Moore [2, 3] used an empirical equation proposed by Thuret [9], which describes the mean specific heat between 0 and t °C, and is given by the relation

$$C_m = \frac{at + C_0}{bt + 1} \tag{2}$$

where t is the temperature in degrees centigrade, C_0 the specific heat at 0 °C, and a and b constants. The constant a and C_0 are calculated from the factors a_i and C_{0i} of the different oxides composing the glass and respective compositions (f_i = mass fraction), using the relation

$$a = \sum f_i.a_i \qquad \text{and } C_0 = \sum f_i.C_{0i} \tag{2.1}$$

For the constant b the authors used the value obtained from measurements in vitreous silica (b = 0.00146).

Since values of the heat content are normally related to room temperature (≈ 25 °C), equation (2) was modified to express the mean specific heat between t_1 (= room temperature) and t_2 (final temperature),

$$C_{m(t_1 \rightarrow t_2)} = \frac{C_2.t_2 - C_1.t_1}{t_2 - t_1} \tag{3}$$

In equation (3), C_1 and C_2 represent the mean specific heats between 0 and t_1 and 0 and t_2 °C, respectively. For the determination of the factors (a_i and C_{0i}) of the different oxides, Sharp, Ginther and Moore transformed equation (2) to put it in the form

$$C_m.\,(b.t + 1) = a.t + C_0 \tag{4}$$

and plotted the product $C_m.(bt + 1)$ against temperature. From the resulting straight line they obtained the constants a (slope of the line) and C_0 (intercept) of a glass with a certain composition. These values of a and C_0 were used to calculate the coefficients of the different oxides according to equation (2.1). In this process they started from values of the specific heat of simple glasses (SiO_2-glass, binary glasses in the system CaO-SiO_2 and MgO-SiO_2) and used these values to determine the factors for CaO, MgO and SiO_2. These factors were then tested on glasses in the ternary system CaO-MgO-SiO_2 . After an arbitrary adjustment of the factors to reduce errors, these factors were used in the determination of further factors, by working with them on glasses with a diferent composition, for example, by applying the factors determined for CaO and SiO_2 to glasses in the system CaO-Al_2O_3-SiO_2 for the determination of the factors for aluminium oxide.

Contrary to Sharp, Ginther and Moore, models described in [4-8] propose two different equations for the solid glass and for the glass melt. Richet and Bottinga [6, 7], and Stebins et *al.* [8] use in the solid region the empiric equation proposed by Maier and Kelley [10] to describe the temperature dependence of C_p. For the glass melt they considered C_p as constant, since existing data does not reveal significant variations of C_p with temperature. For description of the dependence of the heat content of the glass with temperature, they define the partial molar heat capacity

$$\overline{C}_{p,i} = \left(\frac{\delta C_p}{\delta n_i}\right)_{T,\,n_j} = \frac{\delta^2 H}{\delta T\,\delta n} \tag{5}$$

of the various oxides composing the glass based on following relation

$$C_p(\text{glass}) = \sum x_i \cdot \bar{C}_{p,i} \qquad (6)$$

where x_i represents the mol fraction and $\bar{C}_{p,i}$ the partial molar heat capacity of a given oxide i.

Richet and Bottinga set the partial molar heat capacity of SiO_2 equal to the heat capacity of pure glassy SiO_2 and consider $\bar{C}_p(Al_2O_3)$ equal to that of corundum(α-Al_2O_3).

Under consideration of the constraints introduced for $\bar{C}_p$ (SiO_2) and $\bar{C}_p(Al_2O_3)$, $\bar{C}_{p,i}$-equations for the remaining oxides were determined using standard linear regression procedures.

Contrary to Richet and Bottinga, who used data from different sources, Stebins *et al.* [8] used data from their own measurements, obtained from dropcalorimetry and DSC for the solid region only. This was done to reduce systematic differences between results from different laboratories, that may be caused by a non-reproducibility of the quenched state attained when dropping a sample, from a temperature $T > T_{room}$, into the calorimeter, at a temperature near room temperature (T_{room}). In order to evaluate deviations from linearity they introduced non-linear terms like e.g. x_i^2 and $x_i.x_j$ (i...j) which were excluded later, since results of a statistical evaluation showed that these were non-significant.

Because of the constraints introduced by Richet and Bottinga for SiO_2 and Al_2O_3 no effort will be made to compare factors derived in [6, 7] with the ones from Stebins model, whose models are based on the same approach. Gudovich, Primenko and Galyant [4, 5] propose for C_p of the solid glass an equation of the type,

$$C_p = C_0 + a.t^{0.5} \qquad (7)$$

while for the glass melt C_p is considered independent of temperature. In equation (7) t represents the temperature, and a and C_0 coefficients determined using factors proposed in [4, 5] for the diferent oxides composing the glass and the respective mass fractions, in a similar way to that proposed by Sharp, Ginther and Moore (see equation (2.1)). Accordding to the authors, equation (7) was obtained by differentiation of measured heat contents, but no equation is given for description of variations of heat content with temperature and composition, a equation whose differentiation would apparently give equation (6).

Contrary to our dropcalorimetric measurements, carried out by the transposed-temperature drop method, with a sample being dropped from room temperature into a calorimeter at a temperature T in the region of existence of the glass melt, dropcalorimetric data used by the different authors mentioned in [2-8] were obtained by dropping a sample from a furnace at a high temperature into a calorimeter at a temperature T near room temperature. Because of the non-reproducibility of the quenched state attained in the calorimeter, an error can be introduced by this variant of the dropmethod, when measuring glass samples [2, 8]. Another potential error may occur during thermal equilibration of the sample preceding its dropping into the calorimeter. When the sample, during the phase of attainement of thermal equilibrium, is held at temperatures in the region where transformations like for example crystallization or phase separations can occur, a wrong initial thermodynamic state is being considered and consequently, through this undefined thermodynamic state, a wrong heat content will be measured [2].

Having in mind the deviation from ideality reported in [8], which reveal a dependence of partial thermodynamic properties on composition, one may ask which influence on the heat content value has the difference in chemical composition between the samples we studied (Table 1) and the ones used in the development of the different models. Last samples are, with contents up to 35 %, rich in Al_2O_3, Fe_2O_3 and TiO_2, contrary to technical silicate glasses wich show contents of the mentioned oxides lower than 2%.

RESULTS AND DISCUSSION

The experimental results discussed here represent measurements carried out on flat and container glasses, with the chemical composition given in table 1, using a dropcalorimeter HT 1500, from the Company SETARAM located in Lyon-France. For details on the experimental procedure adopted see ref. [1].

Table 1. Chemical composition of the studied glasses in weight %

Species	I	II	III	IV	V	VI
SiO_2	71.640	72.05	71.46	72.29	72.433	72.20
Na_2O	13.720	13.45	12.72	12.58	12.197	12.54
K_2O	0.183	0.21	0.45	0.511	0.768	0.720
CaO	9.360	8.55	10.36	9.753	9.779	9.852
MgO	4.030	3.75	3.43	2.806	2.733	1.996
Al_2O_3	0.696	0.66	1.23	1.510	1.555	1.892
Fe_2O_3	-	0.91	0.09	0.050	0.276	0.366
SO_3	0.237	0.51	0.15	0.449	0.184	0.143
BaO	-	0.01	0.08	0.007	0.021	0.041
TiO_2	0.048	0.005	-	0.020	0.005	0.002
MnO	-	-	-	0.006	-	0.016
NiO	-	-	-		-	0.002
Cr_2O_3	-	-	0.01	0.001	-	0.205
F^-	-	-	-	0.011	0.011	0.015
PbO	-	-	-	-	0.005	-

I-white flat glass, II-green flat glass, III-white container glass I, IV-white container glass II, V-brown container glass, VI-green container glass.

Comparison between the curve obtained from experimental results and the curves calculated from different models is shown exemplary for two of the six glasses studied in figures 1 and 2. The curves representing the experimental results (represented by the straight line) were obtained by a standard linear regression procedure, carried out on 15 to 25 values measured for each glass [1]. These figures show a good agreement between the results obtained with the models of Richet and Bottinga [6, 7], and that of Stebins [8], while results from Gudovich, Primenko and Galyant [4, 5] are more similar to those from Sharp, Ginther and Moore [2, 3] but with a much larger deviation. Table 2 shows the deviation of the calculated curves of the heat content from the experimental results, which varies between 0 and 8%.

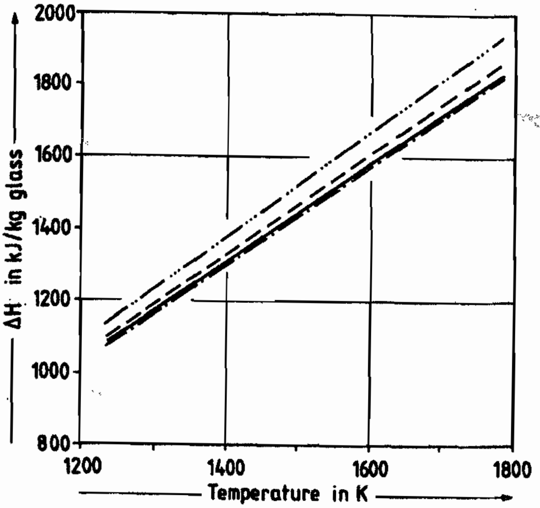

Figure 1. Calculated and experimental curves of the heat content of a white flat glass. ——— experimental; ------ Sharp, Ginther and Moore [2, 3]; -•-•-•-•- Gudovich, Primenko and Galyant [4, 5]; -• •-• • • •-• •- Richet and Bottinga [6, 7]; -• • •-• • • •-• • • •-• • •- Stebins, Carmichael and Moret [8].

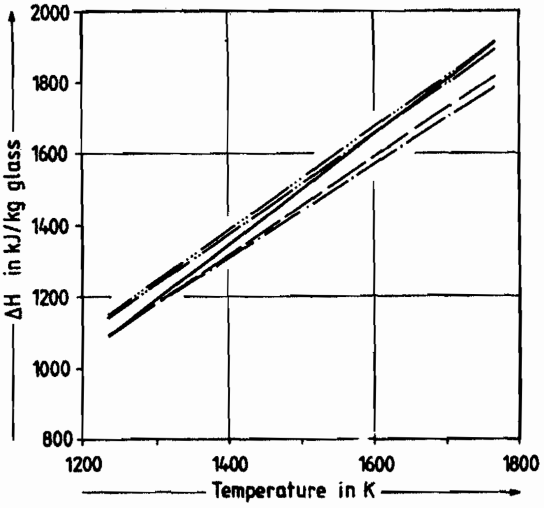

Figure 2. Calculated and experimental curves of the heat content of a white container glass. ——— experimental; ------- Sharp, Ginther and Moore [2, 3]; -•-•-•-•- Gudovich, Primenko and Galyant [4, 5]; -• •-• • • •-• •- Richet and Bottinga [6, 7]; -• • •-• • • •-• • • •-• • •- Stebins, Carmichael and Moret [8].

From this comparison one can see that the model of Stebins [8] and that of Richet and Bottinga [6, 7] give estimates slightly better than Sharp, Ghinter and Moore's procedure [2, 3], while Gudovich, Primenko and Galyant's model [4, 5] show the largest deviations. Furthermore it seems that the models developed later [4-8], about 30 years after Sharp's model and at a time where better equipments were available, do not represent any significant improvement in the calculation of the heat content of silicate glasses. This aspect must be discussed carefully since by the development of the mentioned models authors worked with samples with a chemical composition more representative for materials of a geological origin, which are rich in Al_2O_3, Fe_2O_3 and TiO_2 (with contents up to 35 %), contrary to the technical silicate glasses, which show contents of Al_2O_3, Fe_2O_3 and TiO_2 under 2%.

Considering the observed deviation from ideality, an aspect that needs further studies for its clarification, one may believe that the derivation of factors for the partial molar heat capacity from samples on one side with high contents of Al_2O_3, Fe_2O_3 and TiO_2, as done by the authors in [4-8], and on the other side with a composition similar to that of the glasses we studied, would result on values of the partial molar heat capacity to a certain extent different, what would introduce an error on the calculation of the thermal enthalpy of glasses with a chemical composition significantly different. These results seem to be more in agreement with the well known dependence of partial molar quantities on composition, and not with the assumption of the ideal behaviour of the oxides (and the assumption that partial molar heat capacities are independent of composition) as was introduced in the development of the models.

Table 2. Deviation in % of the curves of the heat content calculated from the models of Sharp, Ginther and Moore [2, 3], Gudovich, Primenko and Galyant [4,5], Richet and Bottinga [6,7] and Stebins, Carmichael and Moret [8] when compared with the experimental values measured for the studied technical silicate glasses in the temperature intervall 1200-1800 K [1].

Type of glass	Sharp	Primenko	Richet	Stebins
I	1.1 - 1.9	0.0 - 0.6	4.5 - 5.0	4.5 - 5.0
II	0.0 - 7.3	0.0 - 10.4	0.0 - 6.4	0.0 - 6.3
III	0.0 - 4.7	0.0 - 6.3	0.0 - 3.7	0.0 - 4.2
IV	0.0 - 1.9	0.0 - 2.8	2.2 - 4.7	3.0 - 4.7
V	2.7 - 6.3	4.5 - 7.8	0.0 - 2.9	0.0 - 1.8
VI	0.0 - 6.8	0.0 - 8.3	0.0 - 4.4	0.0 - 2.6

I-white flat glass, II-green flat glass, III-white container glass I, IV-white container glass II, V-brown container glass, VI-green container glass.

The question about a possible influence, on the deviation observed of the non-reproducibility of the quenched state attained in the calorimeter or the eventual crystallization of the sample, during equilibration in the furnace before dropping it, see section 2, can not be answered based on the results presented here. This aspect seems not to have a big influence since in [8] authors combined data obtained by DSC and drop-calorimetry, and C_p-data derived from dropcalorimetry are apparently as good as the ones obtained by DSC [8]. The measurements we carried out with samples of a white flat glass, on one side obtained industrially on a float process and on the other side prepared by quenching in our laboratory a glass melt sample with the same composition of the float glass produced industrially, show no significant difference. From these results it seems that the effect of the thermal history of both samples has in this case no significance on measured values. It is possible that this effect has a magnitude comparable to the experimental uncertainty and can not, for this reason, be distinctly identified.

For calculation of the heat content of glasses with a composition similar to that of the glasses studied, ΔH_{glass} , factors were derived from measured values, which enable the calculation of ΔH_{glass} in kJ/kg glass, using the following relation:

$$\Delta H_{glass}(T) = \sum m_i.a_i + (\sum m_i.b_i).T \qquad (8)$$

where m_i the content of a given oxide in the glass in mass %; T is the temperature in Kelvins; and a_i and b_i factors derived for the oxides listed in Table 3 from measured heat contents [H(T) - H(298 K)] of seven flat and container glasses [1] using standard linear regression procedure. Here, we considered the seven oxides most abundant in the glasses studied and neglected the remaining, which show contents under 0.05%.

Table 3. Factors a_i and b_i for calculation of the heat content of technical silicate glasses, ΔH, using equation (8).

Oxide	a_i	b_i
SiO_2	67.67	-0.0142
Na_2O	-133.30	0.0266
K_2O	-17.92	-0.1587
CaO	-264.00	0.1475
MgO	-224.40	0.1241
Al_2O_3	-365.10	0.2495
Fe_2O_3	-942.90	0.6263

CONCLUSIONS

The different models described in the present investigation give estimates of the thermal enthalpy with deviations of up to 8 % for some glasses. The model of Richet and Bottinga and that of Stebins show results slightly better the ones derived from Sharp, Ginther and Moore's model, while results from Gudovich, Primenko and Gallyant show the largest deviations. However, additional studies are necessary to determine the possible deviations from ideality reported in [8]. The calculation of the thermal enthalpy of glasses with a composition similar to the composition of the glasses studied here, may be better made using equation (8) and the factors shown in Table 3.

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