Configurational entropies of silicate liquids and phase diagrams

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Phase diagrams calculation is a major topic in glass science. Different methods to model liquidus temperatures have been developed, always including adjustable parameters. The goal of this work is to develop a new way to calculate this temperature without any adjustable parameter.

Using experimental data only, this work focuses on the relationship between thermodynamics and viscosity, and therefore configurational entropy. To calculate the chemical potentials, contributions from enthalpy and entropy of mixing have been separated. First, the enthalpy of mixing can be measured experimentally, derived from solution calorimetry. Secondly, the entropy of mixing is taken as purely configurational. Thus, the major part of the work is to determine the entropy of configuration in the melt. Within the framework of the Adam-Gibbs theory of structural relaxation, viscosity and heat capacity data may be combined to determine configurational entropies of silicate glasses.

The vertue of this model for predicting phase diagrams is evaluated via calculations for two eutectic diagrams (pyroxene – plagioclase) which do not show any solid solution nor any unmixing in the liquid phase. For the selected diagrams, pseudo-wollastonite – anorthite and diopside – anorthite, agreements between calculated and experimental values are excellent. It is now possible to perform liquidus temperature calculations without adjustable parameters.

Introduction

Classical models [1] [2] [3] [4] for liquidus temperatures are widely based on thermodynamics. Particularly, these models rely on the dependence of the chemical potentials with the temperature, the composition and the nature of the phase at stake. To fulfil such a calculation, a large number of adjustable parameters is introduced.

The aim of this work is to develop a different way to perform the calculation of the liquidus temperatures, and then, to eliminate any adjustable parameter. This model has been developed for the determination of liquidus temperatures at 1 atm. The fundamentals of our approach is to use the relationship between thermodynamics and viscosity through the Adam and Gibbs theory of relaxation processes to predict phase diagram surfaces.

To check the validity of such a calculation, two phase diagrams were selected. For them, no solid solution nor any unmixing in the liquid phase are observed. Moreover, these eutectic diagrams are important for igneous processes and for glass industry. These two diagrams are pseudowollastonite – anorthite, which are crystals appearing frequently during E-glass crystallization, and diopside – anorthite, which is a simplified diagram for crystallization of basalts.

Configurational entropy

Within the Adam-Gibbs [5] theory of relaxation processes in viscous liquids, the temperature dependence of the viscosity of silicate melts is determined by that of the configurational entropy. This theory thus provides a theoretical framework to model the behaviour of complex molten silicates as a function of temperature and composition.

Quantitative applications of the Adam-Gibbs theory of relaxation processes to the viscosity of silicate liquids have already been described in detail [6] [7] [8] [9]. Schematically, one considers that viscous flow takes place through configurational changes in the liquid. When the configurational entropy increases, cooperative rearrangements of the structure can take place independently in smaller and smaller domains of the liquid. Correlatively, relaxation times thus decrease when the configurational entropy (S_{Conf}) increases. Knowing that the viscosity is proportional to the structural relaxation times and from the statistical mechanical model used by Adam and Gibbs, one obtains eventually the viscosity equation :

$$\log(\eta) = A_e + B_e / TS_{Conf}(T) \tag{1}$$

where A_e is a pre-exponential term and B_e a constant proportional to the Gibbs free-energy barrier hindering the cooperative rearrangements in the liquid needed for viscous flow.

According to Eq. (1), the variation with temperature of the configurational entropy determines that of the activation energy and thus governs the extent of non-Arrhenian rheology. Between any temperature and an arbitrary reference temperature, conveniently chosen as the calorimetric glass transition temperature, T_g, this variation is given by:

$$S_{Conf}(T) = S_{Conf}(T_g) + \int_{Tg}^{T} Cp_{Conf}(T)/T \, dT \tag{2}$$

where Cp_{Conf} is the configurational heat capacity. Calorimetric determinations of Cp_{Conf} are generally determined with difficulties, but silicate liquids have the simplifying behaviour that the glass transition takes place when the heat capacity of the glass reaches the Dulong-Petit harmonic limit for the isochoric heat capacity. This allows one to write:

$$Cp_{Conf}(T) = Cp_{Liq}(T) + Cp_g(T_g) \tag{3}$$

where $Cp_{Liq}(T)$ is the heat capacity of the liquid at temperature T and $Cp_g(T_g)$ that of the glass at the glass transition temperature. For most silicates, the approximation $Cp_g(T_g) = 3nR$ with n as the medium number of atoms by oxide is correct.

Inserting Eqs. (2) and (3) in Eq. (1), one obtains a viscosity equation with only two adjustable parameters, A_e and B_e, provided the configurational entropy frozen in at the glass transition, $S_{Conf}(T_g)$, is known. For some geological compositions, configurational entropies determined by calorimetry from an entropy cycle involving the crystalline, liquid and glass phases of the material from 0 K to the congruent melting point are in excellent agreement with configurational entropies determined from viscosity measurements [10]. It justifies considering $S_{Conf}(T_g)$ as a third adjustable parameter to be determined from the viscosity data for our compositions which do not show any congruent melting.

Thermodynamic calculation

To eliminate any adjustable parameter in the calculation of the liquidus temperatures, one uses the mathematical formalism raised below, as the phase diagram do include two conditions : no solid solution and no immiscibility in the liquid.

The Gibbs energy can be written according to the chemical potentials :

$$G = \sum \mu_i N_i$$

with μ_i, the chemical potential of the component i and N_i the number of moles.

For the liquid phase, as we have a total miscibility of the phase, the chemical potentials can be divided into two contributions, one entropic and one enthalpic :

$$\mu_{iLiq} = \mu_{iLiq}* - T\Delta_m \overline{S}_i + \Delta_m \overline{H}_i \tag{4}$$

with μ_i the chemical potential of component *i* in the liquid and μ_i* the chemical potential of component *i* pure for a temperature *T* and at atmospheric pressure. $\Delta_m \overline{S}_i$ and $\Delta_m \overline{H}_i$ are respectively the molar partial entropy of mixing and the molar partial enthalpy of mixing.

The molar partial enthalpy of mixing can be derived from heats of mixing measured by dissolution calorimetry. The molar partial entropy of mixing is more complex ; contributions to the mixing can be vibrational or configurational. According to Richet et al. [11] and de Ligny et al. [12], for aluminosilicates of calcium and magnesium, the entropy of mixing is mainly configurational and, as a first approximation, the vibrational part of the entropy of mixing can be ignored.

For the solid phases, knowing that we do not have any solid solution, the chemical potential is the one of the pure phase that appears in the liquid :

$$\mu_{iC} = \mu_{iC}* \tag{5}$$

The difference between the chemical potentials for pure components is given by the relationship below :

$$\mu_{iC}* - \mu_{iLiq}* = \Delta_{C-Liq}\mu_i* = \int_T^{Tfi} \Delta_{C-Liq}Cp_i dT + T\int_T^{Tfi} \Delta_{C-Liq}Cp_i / T\, dT + (T/T_{fi} - 1)\Delta_f H_i \tag{6}$$

with T_{fi}, the melting temperature of the pure component *i*, $\Delta_{C-Liq}Cp_i$ the difference between heat capacities for component *i* between the crystal and the liquid phases, and $\Delta_f H_i$ the enthalpy of fusion of pure component *i* at T_{fi}.

At the liquidus temperature, i.e. the phase equilibrium temperature, chemical potentials of the two phases are equal. This can be written as :

$$\mu_{iC} = \mu_{iLiq} \tag{7}$$

Combining Eq. (4), (5), (6) and (7), for each composition, the liquidus temperature *T* is determined when the equation (8) is solved :

$$-T\Delta_m \overline{S}_i + \Delta_m \overline{H}_i = \int_T^{Tfi} \Delta_{C-Liq}Cp_i dT + T\int_T^{Tfi} \Delta_{C-Liq}Cp_i / T\, dT + (T/T_{fi} - 1)\Delta_f H_i \tag{8}$$

To perform such a calculation, experimental data needed are the melting temperature, the heat capacities and the melting enthalpies of the pure phases, the heat of mixing and the entropy of mixing, derived from configurational entropies. Actually, low-temperature and high-temperature viscosity measurements are to be compiled with configurational heat capacities, experimentally measured or derived from a model, to obtain the configurational entropies.

Data compilation

Diopside – Anorthite

Amongst the different experimental data, viscosity is a major property to be studied. In particular, the data set must include high-temperature measurements, i.e. low-viscosity data for temperatures above the liquidus temperature, and low-temperature measurements, i.e. high-viscosity data for temperatures around the glass transition temperature. Two data sets are available [13] [14]. The data set determined by Tauber et Arndt has been chosen because the number of available compositions and the dispersion are better. However, the viscosity range studied is smaller and so could increase the error bar on the configurational entropy. For high-temperature data, measurements performed by Scarfe et al. [15] were selected.

The fits of viscosity were realized with the Adam-Gibbs equation. The configurational heat capacities were taken according to the model developed by Jarry [16]. The behavior of the configurational entropy was studied at 1830 K, the lowest temperature at which all the diagram is liquid. According to the composition, a non-linear fit was undertaken with a regular law of mixing.

Heats of dissolution in $2PbO\bullet B_2O_3$ at 973 K and 985 K were compiled from Navrotsky et al. [17] [18]. The enthalpy of mixing was taken as a regular solution between $CaMgSi_2O_6$ et $CaAl_2Si_2O_8$.

Finally, heat capacities of the crystal phases are taken from Richet and Fiquet [19]. Heats of fusion of crystal phases are taken from Richet and Bottinga [20].

Wollastonite – Anorthite

New viscosity experiments were realized to meet the lack of high-viscosity data around the glass transition temperature. Measurements were accomplished on a creep machine with an uni-axial compression device described by Neuville and Richet [8], whereby the rate of deformation of a sample is measured as a function of the stress applied at constant temperature. All data were taken from Jarry [16].

High-temperature viscosity data are taken from Bockris et al. [21] for $CaSiO_3$, from Urbain et al. [22] for $CaSiO_3$ and $CaAl_2Si_2O_8$, and interpolations of measurements completed by Machin and Yee [23] and by Kozakovitch [24] were taken for the others compositions.

Again, the configurational heat capacities were taken according to the model developed by Jarry [16]. Fits of viscosity according to the Adam-Gibbs equation were achieved which allow us to have the variation of configurational entropy according to composition for this system. Taking the approximation that the entropy of mixing is purely configurational, one can have the molar partial entropy of mixing easily.

Heat capacities and enthalpy of melting for wollastonite were recorded from Richet et al. [25]. Heat capacities for anorthite are taken from Richet and Fiquet [19]. Heats of fusion for anorthite is taken from Richet and Bottinga [20].

Results

Results of the calculations are shown on figure 1 and 2. The agreement between experimental data and predicted temperatures is very good. The maximum derivation between experimental and calculated liquidus temperatures is around 50 K, which is acceptable as we do not include any adjustable parameter in our model.

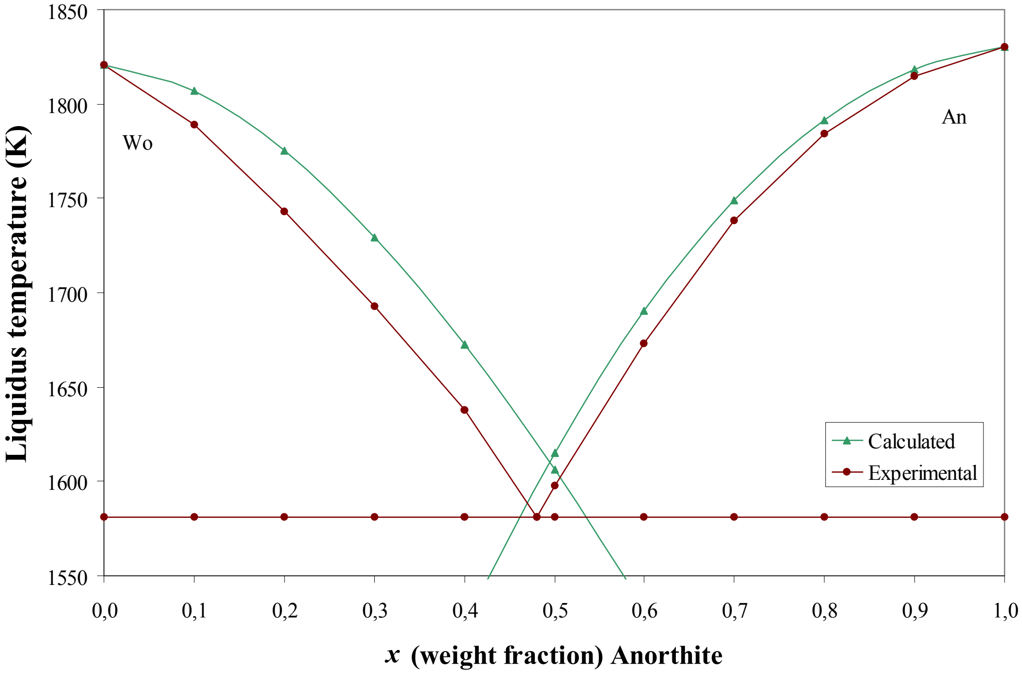

Figure 1: Phase diagram for the Pseudo-wollastonite – Anorthite system.
Circles : experimental [26]. Triangles : calculated.

Concerning the eutectic point, which is a good way to check the consistency of the model, results are given in Table 1.

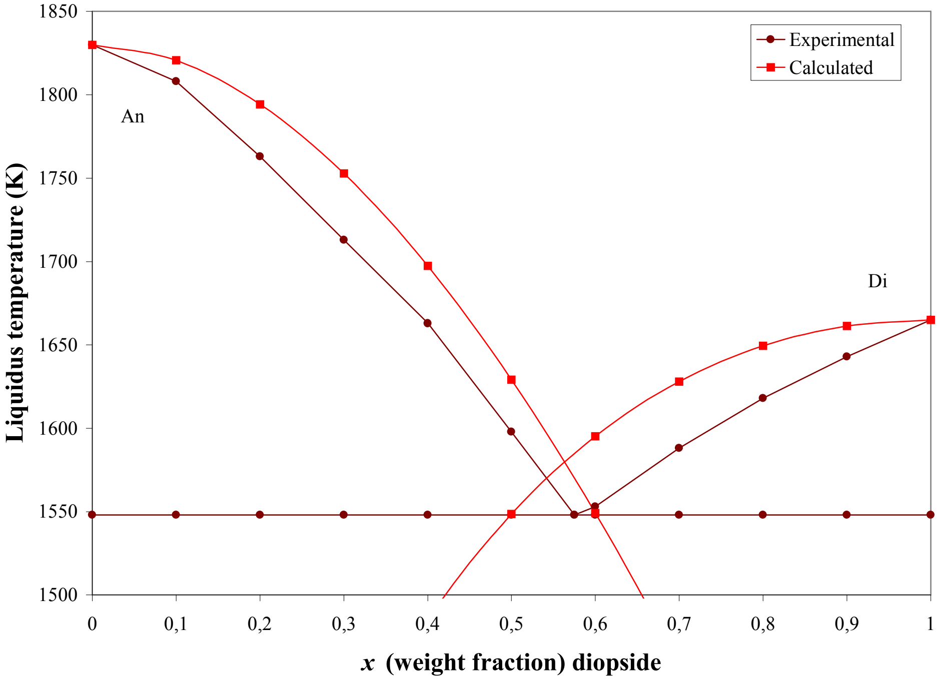

Figure 1: Phase diagram for the Diopside – Anorthite system.
Circles : experimental [26]. Squares : calculated.

The error for the pseudo-wollastonite – anorthite diagram is less than 10 K, and the error on *x*, the anorthite weight fraction, is about 0.04. About the diopside – anorthite diagram, the error on the temperature is still acceptable as it is about 30 K. On the eutectic weight fraction, the error is 0.015.

	Pseudowollastonite – Anorthite		Diopside – Anorthite	
	x (wt fraction, Anorthite)	*T* (K)	*x* (wt fraction, Diopside)	T (K)
Experimental	0.48	1581	0.575	1548
Calculated	0.52	1587	0.56	1580

Table 1: Comparison between experimental and calculated data

According to the good results shown on these diagrams, we can assume that all the hypotheses taken to perform the calculations are correct. In particular, the vibrational Dulong and Petit limit is one more time verified. Also, as a first approximation, the mixing entropy can be taken as purely configurational.

However, no error bars have been estimated, mostly because of the difficulty to assess the errors on the configurational entropy, and as a consequence the mixing entropy. Amongst the data needed for the calculation, the mixing enthalpy is another source of error, specially because of unreliable calorimetric data.

Conclusion

An excellent agreement between calculated and experimental phase diagrams is observed. Such errors on the eutectic composition and temperature are comparable to those of other liquidus temperature models.

Although rudimentary and preliminary in nature, a liquidus temperature model without any adjustable parameter can be designed. Because the use of adjustable parameters to build models is always unsatisfactory, such a work allow to show that models using only experimental data can be developed.

Herein, the use of the entropy of configuration for the calculation of the phase diagrams show that the parameter derived from the Adam-Gibbs equation has a real physical meaning and can be used for thermodynamic equations.

However, several limitations must be stressed. In particular, such calculation needs a large and accurate number of data. No error bar calculation has yet been performed and a further development of binary to ternary diagrams is to be undertaken.

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[2] FACT, Centre de Recherche en Calcul Thermochimique, Ecole Polytechnique de Montréal, http://www.crct.polymtl.ca/FACT/fact.htm.

[3] THERMOCALC, Royal Institute of Technology, Stockholm, http://met.kth.se.

[4] MTDATA, National Physical Laboratory, http://www.npl.co.uk/npl/cmmt/mtdata/mtdata.html.

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