Models for Liquidus Temperatures

Kaj H. Karlsson, Rainer Backman and Leena Hupa
Department of Chemical Engineering, Åbo Akademi University, 20500 Åbo, Finland

Modelling the relationship between liquidus temperature and glass composition can be done in two principally different ways, thermodynamic modelling and regression analysis. The former lacks still reliable data and requires also quite experienced computer skill. The latter approach has been done using two different approaces. For an *n*-component system the experimental results are either described byone polynomial giving the liquidus temperature, or by two consecutive polynomials, the first giving the primary phase region for the given composition, the second describing the liquidus within this region. In the paper the three different approaches are compared using experimental results for fifty compositions in the system Na_2O-K_2O-MgO-CaO-SrO-BaO-PbO-B_2O_3-Al_2O_3-SiO_2.

Introduction

Modelling the relationship between liquidus temperature and glass composition can be done in two principally different ways, thermodynamic modelling and regression analysis. Although the thermodynamic approach is the most attractive, necessary data are still incomplete. On the other hand phenomenological models are always restricted by the data base used in the regression analyses. In the present paper a set of fifty experimental liquidus temperatures in the system Na_2O-K_2O-MgO-CaO-SrO-BaO-PbO-Al_2O_3 -B_2O_3 -SiO_2 are compared with corresponding temperatures calculated thermodynamically and by two different polynomial models.

Experimental

Using a computer search method for minimum correlated stochastic design a set of fifty glasses in the system Na_2O-K_2O-MgO-CaO-SrO-BaO-PbO-Al_2O_3-B_2O_3-SiO_2 were chosen. The experimental setup as well as results were a part of a EURAM research program and have been reported previously[1,2,3]as have the obtained primary phases and liquidus temperatures[1,3]. A model was also derive do describe the composition dependence of the liquidus temperature. This model is fairly complex needing thirteen oxide product terms. In order to satisfactorily describe the sudden changes when crossing a phase border, fourth degree powers of oxides were needed. No model was derived to describe the compositional dependence of the primary phase.

The thermodynamic calculation was performed using the computer program ChemSage[4] and the data base FACT 2.0/98[5] as recently reported [6]. However, data for SrO, BaO and B2O3 are still not available. Thus the calculation was done on the restricted system Na_2O-K_2O-MgO-CaO-PbO-Al_2O_3-SiO_2, but so that these oxides were deleted from the experimental plan and the rest filled up to 100%. The oxide compositions as well as computed primary phases and liquidus temperatures are previously reported [6].

Using these previously reported data an attempt was made to derive a liquidus description resembling the approach used by Babcock[7]. This involved one polynomial for estimating the primary phase and another describing the liquidus temperature within the obtained primary phase. In order to describe the primary phase experiments in the wollastonite field were assigned as number 1, those in the devitrite field as number 2 and those in $Na_2O \cdot 2CaO \cdot 3SiO_2$-field by number 3. Only these three phases were represented by sufficiently many experiments to make a regression analysis possible.

Results

The best model to describe the experimentally obtained primary phase field[1] is

$$\text{P-phase} = 20.2156315 + 0.29252243 \cdot p_{K2O} + 0.210441694 \cdot p_{MgO} + 0.275951952 \cdot p_{BaO} + 0.721820772\, p^2_{B2O3} + 0.59449172 \cdot p_{SrO} + 0.493156791 \cdot p_{Na2O} + 0.119287364 \cdot p_{CaO} - 1.12851012 \cdot p_{SiO2} - 0.203847259 \cdot p_{B2O3} - 0.0607549697 \cdot p^2_{SrO} + 0.0514076352 \cdot p^2_{PbO} - 0.00691996608 \cdot p^2_{Na2O} + 0.0106422286 \cdot p^2_{SiO2} \quad (1)$$

For equation (1) the regression coefficient R^2=71.51, the residual variance = 0.242 while the F-test gave F-tot=6.95 for a significance level of 95%. When P-phase $\leq$ 1.5 the result was interpreted as describing the wollastonite field, for 1.5<P-phase<2.5 as devitrite and for 2.5$\leq$P-phase$\leq$3.5 as $Na_2O \cdot 2CaO \cdot 3SiO_2$.

Within the wollastonite field, i.e. for P-phase$\leq$1.5, the liquidus temperature in °C can be calculated by

$$\Theta_{liq} = 703.909 + 11.2471 \cdot \mathrm{pK2O} + 13.3897 \cdot p_{MgO} + 10.1381 \cdot p_{BaO} + 34.7753 \cdot p_{Al2O3} + 19.0823 \cdot p_{B2O3} + 11.8052 \cdot p_{SrO} - 112.450 \cdot p_{Na2O} + 12.3114 \cdot p_{SiO2} + 4.16628 \cdot p^2_{Na2O} + 1.19451 \cdot p^2_{CaO} \quad (2)$$

for which R^2=99.80, residual variance=12.44 and F-tot=99.0.

Within the devitrite field, i.e. for 1.5<P-phase<2.5 the liquidus temperature can be calculated by

$$\Theta_{liq} = -1176.37 + 24.8254 \cdot p_{K2O} + 42.6270 \cdot p_{MgO} + 24.1788 \cdot p_{BaO} + 36.0791 \cdot p_{Al2O3} + 28.0282 \cdot p_{SrO} + 33.7561 \cdot p_{PbO} + 45.2996 \cdot p_{CaO} + 20.0059 \cdot p_{SiO2} + 0.446271 \cdot p^2_{Na2O} \quad (3)$$

for which R^2=88.17, residual variance=1401 and F-tot=25.7. Finally, for the $Na_2O \cdot 2CaO \cdot 3SiO_2$ field, i.e. for
2.5$\leq$P-phase$\leq$3.5

Table 1: Primary phases and liquidus temperatures for 50 EURAM glasses.

No	Primary phase experimental	Primary phase by eq. (1)	Primary phase by ChemSage	T°C exp	T°C eqs (2)-(4)	T°C Euram	T°C ChemSage
1	Wollastonite	Wollastonite	Wollastonite	1060	1060	1063	1063
2	Wollastonite	Wollastonite	Wollastonite	1110	1113	1134	1081

3	Wollastonite	Wollastonite	Wollastonite	1121	1121	1131	1184
4	Wollastonite	Devitrite	Wollastonite	1114	1115	1147	1201
5	Devitrite	Devitrite	NS_2	749	783	759	732
6	1:2:3	1:2:3	1:2:3	1044	1032	1066	978
7	Devitrite	Devitrite	Wollastonite	1038	1034	1040	1116
8	Wollastonite	Wollastonite	Wollastonite	1047	1047	1072	1053
9	Wollastonite	Devitrite	Wollastonite	1110	1092	1100	1128
10	Devitrite	Wollastonite	Devitrite	855	1052	1028	975
11	Devitrite	Devitrite	Wollastonite	1048	1010	1022	1129
12	Wollastonite	Wollastonite	Wollastonite	1124	1123	1110	1148
13	Devitrite	Devitrite	Devitrite	961	929	967	880
14	Devitrite	Devitrite	Devitrite	764	704	747	775
15	Devitrite	Devitrite	N_2CS_3	953	846	958	895
16	Wollastonite	Wollastonite	Devitrite	1077	1077	1155	991
17	1:2:3	Devitrite	Wollastonite	1097	1076	1116	1039
18	Diopside	Wollastonite	Wollastonite	1168	1339	1259	1309
19	Devitrite	Devitrite	Wollastonite	990	1035	1077	1114
20	1:2:3	1:2:3	1:2:3	938	944	925	951
21	1:2:3	1:2:3	1:2:3	807	839	854	780
22	1:2:3	1:2:3	1:2:3	1018	1000	994	918
23	1:2:3	1:2:3	NCS_5	1021	1016	1106	944
24	Devitrite	Devitrite	Devitrite	725	830	821	891
25	Devitrite	Devitrite	Devitrite	905	869	914	913
26	Devitrite	Devitrite	Wollastonite	1085	1087	1086	1113
27	1:2:3	1:2:3	NM_3S_6	867	842	870	898
28	Devitrite	Devitrite	1:2:3	882	881	914	808
29	1:2:3	1:2:3	1:2:3	1068	1082	1179	1044
30	Wollastonite	Devitrite	Wollastonite	1057	1052	1132	1039
31	Wollastonite	Devitrite	1:2:3	1044	1017	1047	999
32	1:2:3	1:2:3	1:2:3	850	846	876	857
33	1:2:3	1:2:3	1:2:3	1012	1039	1090	987
34	Wollastonite	Wollastonite	Devitrite	1101	1100	1104	1009
35	Devitrite	Wollastonite	Wollastonite	1041	1186	1057	1165
36	1:2:3	Devitrite	Wollastonite	988	974	1041	1005
37	Devitrite	Devitrite	1:2:3	997	988	1014	947
38	1:2:3	Devitrite	1:2:3	1049	969	994	998
39	1:2:3	1:2:3	1:2:3	983	1018	1027	1009
40	1:2:3	Devitrite	1:2:3	1049	1052	1112	1004
41	Devitrite	Devitrite	SiO_2	881	872	872	933
42	Devitrite	Devitrite	Wollastonite	1097	1103	1095	1120
43	1:2:3	1:2:3	1:2:3	1053	1049	1055	1004
44	Devitrite	Devitrite	Devitrite	831	813	945	932
45	Wollastonite	Wollastonite	Wollastonite	1034	1035	1059	1077
46	Devitrite	Devitrite	Devitrite	697	750	713	825
47	Wollastonite	Wollastonite	Wollastonite	1082	1082	1173	1166
48	1:2:3	1:2:3	1:2:3	1036	1009	993	983
49	Devitrite	Devitrite	Wollastonite	1063	1093	1091	1084
50	1:2:3	1:2:3	1:2:3	1032	1023	1081	1042

$$\Theta_{liq} = 1847.46 + 10.4334 \cdot p_{MgO} + 19.8177 \cdot p_{Al2O3} - 151.59 \cdot p_{Na2O} + 75.7960 \cdot p_{CaO} + 4.26746 \cdot p^2_{Na2O} - 3.07671 \cdot p^2_{CaO} \qquad (4)$$

for which R^2=92.25, residual variance=837.1 and F-tot=19.8.

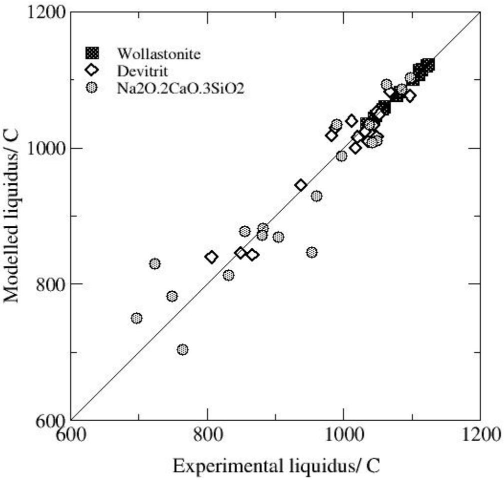

Fig. 1. Correlation between experiment and mode (eq. 1-4).

Figure 1 shows the comparison between experimentally obtained and liquidus temperatures calculated by equations (1)-(4). Figure 2 shows experimental primary phases and liquidus temperatures, figure 3 the same as obtained by equations (1)-(4).

In Table 1 the experimental primary phases[1] are compared with those predicted by equation (1) and by ChemSage[4], further the liquidus temperatures obtained by these as well as those obtained with the model original EURAM-model[1-3].

Discussion

As can be judged from figure 1 equations (1)-(4) give a good agreement between experimental and modelled liquidus temperatures for wollastonite and devitrite as primary phases. The agreement is still acceptable for $Na_2O{\cdot}2CaO{\cdot}3SiO_2$ but for two compositions.

The phase boundaries shown in figures 2a and 2b are drawn to give as few erratic points as possible. It should be noted that there were too few points to model any other phase fields than the three given in the figure. Thus the phase fields indicated for SiO_2 and Na2O·2SiO_2 have not been verified. From Table 1 it can be seen that equation (1) fails predicting 11 out of the 50 primary phases determined.

The thermodynamical calculation is not directly comparable to the experiments because the data FACT 2.0/98 lacks data for SrO, BaO and B_2O_3. Thus the calculated result is to be considered as if these oxides have no influence on the primary phase nor on the liquidus temperature. Taking this fact into account the result with 20 failed predictions is not too discouraging, cf. Table 1. The reason to nevertheless include the thermodynamical calculation is that, if the result is in reasonable agreement with experiments, this encourages more work on the data base. It is also interesting to note that the predicted liquidus temperatures are within promising agreement with experiments as is those estimated by the EURAM model. Although the phase

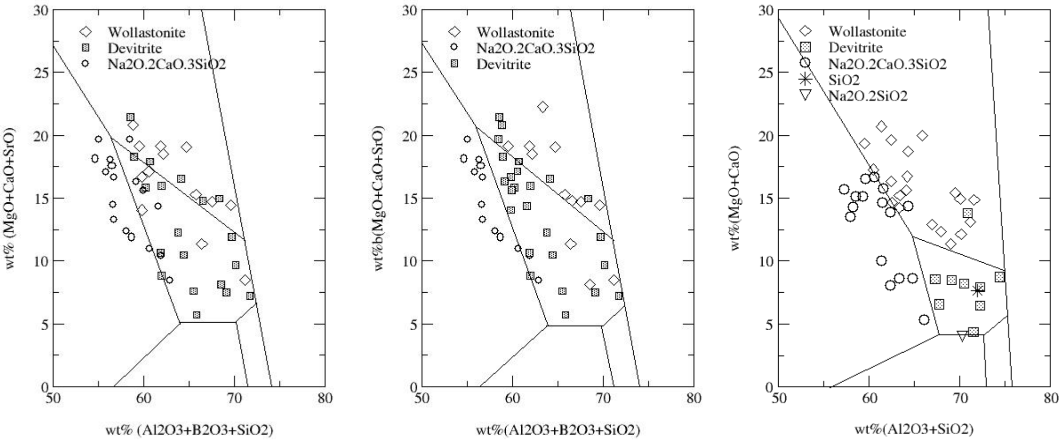

Fig.2: a) Experimental, b) modeled, c) thermodynamically calculated phase fields.

boundaries are not yet calculated it is evident from figure 2c that the thermodynamic calculation predicts the phase more systematically than the empirical methods.

Conclusion

A development of the two-stage approach suggested by Babcock 25 years ago seems quite promising for predicting the liquidus temperature of a multi-component silicate glass. It needs, however, a further refinement for accurate prediction of the primary phase. More experiments are required in particular in the phase fields for silica and disilicate.

An attempt to thermodynamically calculate the primary phase as well as liquidus temperature is promising enough to encourage further work in refining the FACT data base.

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