Original Paper

Estimation of liquidus temperatures in silicate glasses

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Two models for estimating liquidus temperature from composition are presented and compared with thermodynamically calculated temperature as well as primary phase. A simple polynomial model is given for high silica glasses, while a model covering a wide composition range and several primary phase fields is more complex. Thermodynamic calculations generally give too high liquidus temperatures in the devitrite field and too low in the primary field for $Na_2O \cdot 2\,CaO \cdot 3\,SiO_2$. In the wollastonite field the values are scattered, but in general too high.

Abschätzung der Liquidustemperaturen für Silicatgläser

Es werden zwei Modelle zur Abschätzung der Liquidustemperatur aus der Zusammensetzung vorgestellt und mit der thermodynamisch berechneten Temperatur und Primärphase verglichen. Für Gläser mit hohem SiO_2-Gehalt wird ein einfaches polynomisches Modell vorgeschlagen, während ein komplexeres Modell einen weiten Zusammensetzungsbereich und verschiedene Primärphasenfelder abdeckt. Thermodynamische Berechnungen ergeben für $Na_2O \cdot 2\,CaO \cdot 3\,SiO_2$ im allgemeinen zu hohe Liquidustemperaturen im Devitritfeld und zu geringe im Primärfeld. Im Wollastonit-Feld streuen die Werte sehr, sind meist aber zu hoch.

1. Introduction

With increasing machine speeds and corresponding changes in container glass compositions, a good estimate of the liquidus temperature becomes ever more important. Liquidus temperature can, in principle, be calculated thermodynamically [1 to 3]. However, although computer capacity no longer limits the performance of such a calculation, the necessary data bases are far from complete. Ability to determine the primary crystalline phase as well as liquidus is an important feature of the thermodynamic calculation. Solidus temperatures could also be calculated but are of little importance to glass technologists. Another method of estimating liquidus temperatures is to use a polynomial description of the relation between liquidus and glass composition. The first modeling of this kind was done by Lakatos and his coworkers [4] for the system $Na_2O-K_2O-CaO-MgO-Al_2O_3-SiO_2$, but that model was restricted to a narrow range of compositions having silica as the primary phase. Extending the composition range, however, leads to cross-ing the boundaries into other phase fields, so that liquidus is no longer a smooth function of composition and the model inevitably more complex. Separate models can of course be derived for each primary phase field, as was done by Babcock [5] but such models are of little practical interest as the primary phase is rarely obvious in a multicomponent system. A model covering a fairly large set of compositions was developed in a joint venture between Philips, Saint Gobain, and the universities of Sheffield and Åbo Akademi [6 to 8]. That model was based on fifty glasses in the system $Na_2O-K_2O-MgO-CaO-SrO-BaO-PbO-Al_2O_3-B_2O_3-SiO_2$. This paper extends the set of data used for polynomial modeling and compares estimates of liquidus temperatures obtained from those models and by thermodynamic calculation.

2. Calculations

The only sufficiently sophisticated thermodynamic model for calculating liquidus temperatures and primary phases in multicomponent oxide systems is that of Pel-

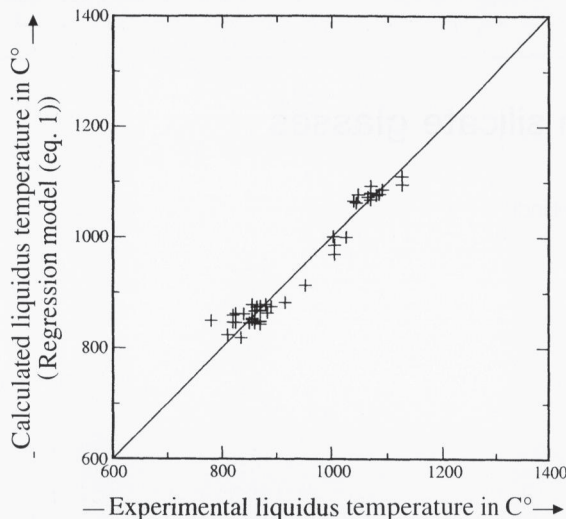Glastech. Ber. Glass Sci. Technol. 74 (2001) No. 7

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Figure 1. Correlation between modelled and experimental liquidus temperatures for 45 glasses in a seven-component system with silica contents $70 \leq SiO_2 \leq 77$ wt%.
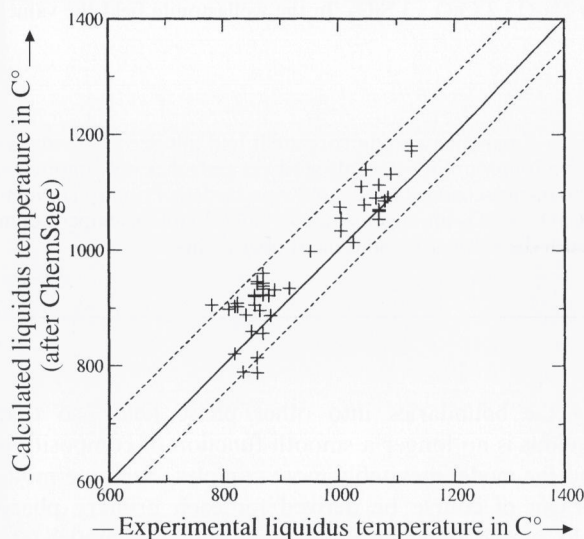

Figure 2. Correlation between thermodynamically calculated versus experimental liquidus temperatures for 45 glasses in a seven-component system with silica contents $70 \leq SiO_2 \leq 77$ wt%.

ton and Wu [3]. It requires knowledge of H, G, S and C_p values for every species in the system; the data base FACT 2.0/98 [9] and the computer program ChemSage [10] were used in the present calculations. However, that data base lacks data for SrO and BaO, so that calculations could not be made for most of the compositions in the original ten-component system. The maximum content of these two oxides was only 5 wt% (2 to 3 mol%). They were therefore ignored and the remaining oxides scaled up to make a total of 100 %. The liquidus temperatures as well as primary phases were then calcu-

lated for this new set of data and the results are given in table 1.

Calculations could also be made for this set of data using the polynomial model of Backman et al. [8] but comparison between two sets entirely of approximately calculated data was not considered as useful as desired. As the equipment to make more measurements was no longer available at Sheffield, Philips glass works in Eindhoven kindly supplied liquidus temperatures and crystalline phases for a set of 45 compositions in the system $Na_2O-K_2O-MgO-CaO-Al_2O_3-B_2O_3-SiO_2$. These all had higher silica contents than the original set. Thermodynamic calculations also showed that none of these had a primary phase occurring in the original set but either SiO_2 or $Na_2O \cdot 3\ MgO \cdot 6\ SiO_2$. The X-ray determinations dominantly gave devitrite as primary phase. However, devitrite crystals have earlier been found to be the fastest growing, even when being secondary or ternary phase [8] and, admittedly, only the fastest growing crystals are of interest to production. It should also be noted that in multicomponent glasses crystals easily form solid solutions. These are not yet implemented in the thermodynamic data base.

Before proceeding further a polynomial model was obtained for the composition dependence of liquidus for this new set of data. The model was linear in terms of the oxides in wt%.

$$\vartheta_{liq} = 4785.48 - 29.8314 \cdot p_{SiO_2} - 60.4794 \cdot p_{P_2O_5}$$
$$- 82.2195 \cdot p_{Na_2O} - 118.279 \cdot p_{K_2O}$$
$$- 43.5043 \cdot p_{MgO} - 35.0431 \cdot p_{CaO} \quad (1)$$

but the coefficients for alumina and boric oxide were insignificant. The regression coefficient $R^2 = 95.4$ % and the standard deviation of 24 K, see figure 1; this standard deviation was accepted as showing the likely agreement between experiment and any other calculations. The experimental values were then compared with those obtained by thermodynamic calculations, see figure 2, which show that the thermodynamic values are on an average about 50 °C higher than the experimental data. Note, however, that the model is valid only for glasses where $70 \leq SiO_2 \leq 77$ wt%.

To improve the usefulness of the simulated experimental data in table 1, seven randomly selected glasses from the Philips set were added to those and a regression analysis made on this set. The extension with only seven glasses is arbitrary, but was done in order not to overemphasize high silica contents, in particular as equation (1) already gives a useful approximation for this range. The regression analysis gave a polynomial description with $R^2 = 93.12$ % and a standard deviation of 34 K, i.e. had the same estimation accuracy as the original model for the ten component system [8]. The factors in the model

$$\vartheta_{liq} = \sum_{n=0}^{13} \left(B_n \prod_{i=1}^{10} p_{n,i} \right) \quad (2)$$

Table 1. Oxide composition (in wt%) for 50 glasses, their liquidus temperatures (in °C) calculated by equation (2) and thermo-dynamically calculated liquidus temperatures (in °C) as well as primary phases (N = Na_2O, M = MgO, C = CaO, S = SiO_2)

| K_2O | MgO | Al_2O_3 | PbO | Na_2O | CaO | SiO_2 | liquidus temperature acc. to | | |
							equation (2)	computer program ChemSage	primary phase
2.69	2.15	2.15	3.23	11.78	9.98	68.02	1093	1063	wollastonite
0.55	3.28	1.64	0.00	16.40	15.43	62.70	1174	1081	wollastonite
4.21	3.68	1.05	0.00	10.77	11.26	69.02	1112	1184	wollastonite
7.49	4.28	1.60	0.00	11.55	12.44	62.64	1134	1201	wollastonite
1.08	1.08	2.69	1.61	23.02	2.94	67.59	756	732	NS_2
3.68	4.74	2.63	4.74	19.06	9.54	55.61	1061	978	NC_2S_3
5.88	3.21	0.53	2.67	11.54	9.69	66.47	1050	1116	wollastonite
3.14	1.05	2.09	5.24	11.24	10.30	66.94	1097	1053	wollastonite
2.20	4.95	1.10	0.00	15.75	15.75	60.26	1123	1128	wollastonite
7.53	1.61	2.15	1.08	12.68	6.61	68.34	957	975	devitrite
1.06	4.79	0.53	0.00	12.45	10.07	71.10	1034	1129	wollastonite
3.30	1.65	0.55	0.00	11.75	13.79	68.97	1156	1148	wollastonite
1.64	1.64	3.28	2.19	18.55	6.83	65.88	920	880	devitrite
2.70	0.54	1.08	0.00	21.42	3.81	70.45	670	775	devitrite
3.70	2.65	3.17	0.00	23.96	6.20	60.32	968	895	$N4CS_3$
7.37	0.53	2.63	0.00	12.45	7.38	69.64	978	991	devitrite
3.72	5.32	2.66	0.00	17.40	14.01	56.88	1141	1039	wollastonite
4.92	3.83	3.28	0.00	9.21	16.12	62.64	1268	1309	wollastonite
7.30	3.93	3.37	0.00	12.39	8.40	64.60	1079	1141	wollastonite
6.56	0.55	2.73	5.46	17.52	7.51	59.67	902	951	NC_2S_3
4.84	2.15	2.15	0.00	23.74	3.19	63.92	768	780	NC_2S_3
0.57	1.14	2.29	4.00	24.00	8.89	59.11	988	918	NC_2S_3
4.89	2.17	3.26	0.00	24.91	5.89	58.87	988	944	NCS_5
2.67	1.07	1.07	0.00	21.47	7.47	66.26	807	891	devitrite
2.20	2.75	1.65	0.00	14.66	5.98	72.77	897	913	devitrite
4.40	5.49	3.30	3.85	13.12	9.74	60.11	1094	1131	wollastonite
7.18	3.87	0.55	2.76	15.08	3.77	66.78	780	898	NM_3S_6
1.06	4.23	3.17	3.70	23.27	4.39	60.17	920	808	NC_2S_3
7.30	2.81	2.81	0.00	16.58	13.69	56.81	1178	1044	NC_2S_3
5.41	2.70	3.24	2.16	15.24	11.95	59.30	1153	1039	wollastonite
2.69	3.76	1.61	2.15	17.80	12.00	59.99	1076	999	NC_2S_3
5.43	4.35	2.17	0.00	21.05	4.30	62.68	818	857	NC_2S_3
5.38	5.38	2.15	0.00	20.94	9.72	56.44	1045	987	NC_2S_3
0.51	0.51	2.56	0.00	14.76	13.28	68.37	1107	1009	devitrite
6.11	1.11	0.56	0.00	9.61	12.01	70.60	1141	1165	wollastonite
5.85	3.19	1.06	0.00	16.53	11.02	62.34	1026	1005	wollastonite
1.60	5.35	1.07	0.00	19.68	8.98	63.32	995	947	NC_2S_3
3.17	2.12	1.06	0.00	20.58	11.76	61.31	997	998	NC_2S_3
2.21	4.42	0.55	0.00	20.51	12.23	60.08	1031	1009	NC_2S_3
4.76	3.17	3.17	0.00	19.08	11.45	58.36	1116	1004	NC_2S_3
1.60	2.13	1.60	4.26	14.50	5.52	70.40	872	933	SiO_2
5.88	2.67	0.53	1.60	13.67	13.67	61.97	1128	1120	wollastonite
3.63	4.66	2.07	4.15	19.23	11.05	55.21	1080	1004	NC_2S_3
6.74	0.52	1.55	0.00	14.54	5.95	70.70	852	932	devitrite
4.30	3.23	0.54	1.08	14.87	12.39	63.60	1072	1077	wollastonite
2.15	1.61	0.54	0.54	23.00	4.96	67.20	717	825	devitrite
6.42	4.28	1.60	3.21	12.62	12.99	58.88	1137	1166	wollastonite
7.29	4.69	1.04	0.52	20.73	8.82	56.91	958	983	NC_2S_3
1.69	5.62	2.81	0.00	16.26	14.00	59.63	1131	1084	wollastonite
6.90	1.72	1.72	0.00	18.60	13.39	57.67	1083	1042	NC_2S_3

are given in table 2 and the relation between experiments and equation (2) in figure 3. The F-test gave a total value of 44.8, but test values for the individual terms were all safely above the elimination limit. It is interesting that the term for silica was eliminated and the remaining terms are of exactly the same forms as those in the original model [8] but the coefficients are slightly changed. Although the scatter is slightly larger, it is still within 100 K.

3. Discussion

The terms in equation (2) are quite complicated, but the fourth degree oxide products were introduced to describe the sharp change in slope when crossing a border between two phase fields. An alternative approach would be to use separate polynomials for each phase field as in the Babcock model [5]. However, then a polynomial description has to be introduced to describe the relation

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Table 2. Equation for liquidus temperatures (in °C) of complex glasses (oxides in wt%)

coefficient	value	oxide product	standard deviation	F-test
B_0	884.109			
B_1	30.284	CaO	2.75	121.0
B_2	-1.721	$Na_2O \cdot Na_2O$	0.233	54.8
B_3	2.512	$Na_2O \cdot Al_2O_3$	0.469	28.7
B_4	-1.382	$CaO \cdot SrO$	0.543	6.47
B_5	0.275	$Na_2O \cdot MgO \cdot CaO$	0.052	27.7
B_6	-0.742	$K_2O \cdot MgO \cdot Al_2O_3 \cdot B_2O_3$	0.255	8.45
B_7	0.017	$Na_2O \cdot Na_2O \cdot SrO \cdot SrO$	0.004	21.6
B_8	-0.052	$MgO \cdot MgO \cdot CaO \cdot CaO$	0.013	17.2
B_9	0.003	$Na_2O \cdot Na_2O \cdot Na_2O \cdot Na_2O$	0.0004	27.2
B_{10}	0.314	$K_2O \cdot K_2O \cdot MgO \cdot BaO$	0.079	16.0
B_{11}	-0.248	$K_2O \cdot K_2O \cdot BaO \cdot Al_2O_3$	0.097	6.58
B_{12}	-0.114	$K_2O \cdot K_2O \cdot K_2O \cdot BaO$	0.041	7.81
B_{13}	0.471	$K_2O \cdot K_2O \cdot Al_2O_3 \cdot B_2O_3$	0.114	17.0

Table 3. Prediction of primary phase by thermodynamic calculation

experimental phase	total	failed	failed predictions	
wollastonite	14	3	2 as devitrite,	1 as $Na_2O \cdot 2\,CaO \cdot 3\,SiO_2$
devitrite	19	12	7 as wollastonite,	3 as $Na_2O \cdot 2\,CaO \cdot 3\,SiO_2$
			1 as SiO_2,	1 as $Na_2O \cdot 2\,SiO_2$
$Na_2O \cdot 2\,CaO \cdot 3\,SiO_2$	17	4	3 as wollastonite,	1 as $Na_2O \cdot CaO \cdot 5\,SiO_2$
total	50	19		
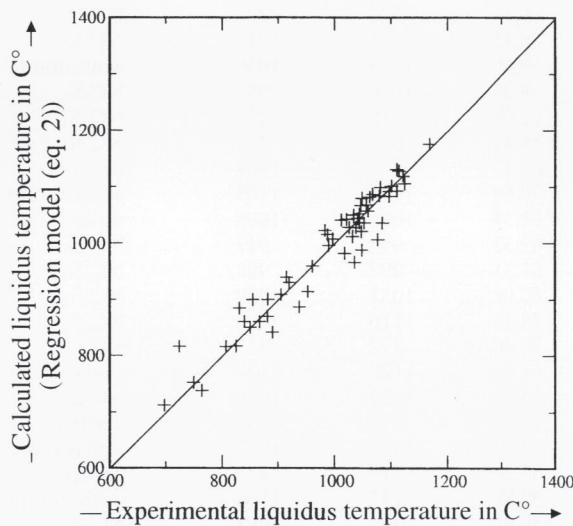
Figure 3. Correlation between polynomial model and experimental liquidus for 57 glasses in a ten-component system with silica contents $55 \le SiO_2 \le 73$ wt%.
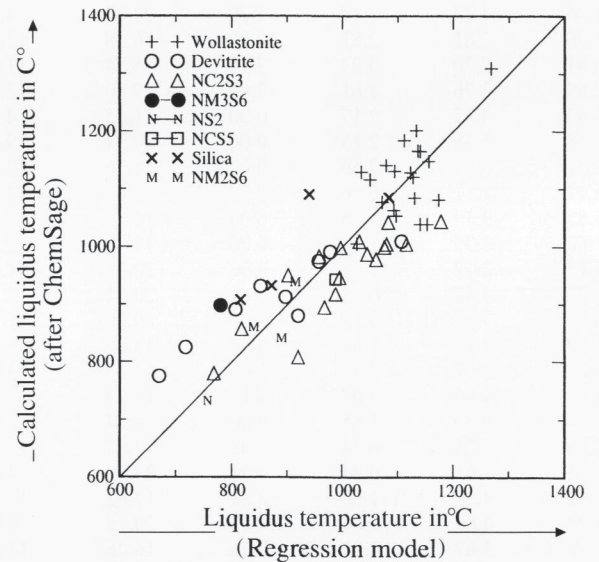
Figure 4. Correlation between thermodynamically calculated and simulated experimental liquidus temperatures for 57 glasses in an eight-component system with silica contents $55 \le SiO_2 \le 73$ wt%. N = Na_2O, M = MgO, C = CaO, S = SiO_2.

between primary phase and composition. It is doubtful whether the accuracy of the liquidus temperature estimation would be any better than with a polynomial of the type given by equation (2). Further, data available at present are not sufficient to describe all primary phase fields in the ten-component system.

The coefficients in equation (2) differ slightly from the similar equation published before [8], although the oxide terms are the same. The reason is that in deriving equation (2), the data base was extended with a few glasses so that the validity range increased from 68 to

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73 wt% silica. Further any minor component can be omitted from the composition. The equation described by Backman et al. [8] was derived assuming a minimum of 0.5 wt% of each minor components.

Figure 4 shows the relation between the liquidus values obtained using equation (2) with the thermodynamically calculated values. The thermodynamic model generally gave slightly higher values when the primary phase was devitrite, but rather lower values when it was $Na_2O \cdot 2\,CaO \cdot 3\,SiO_2$. Glasses having wollastonite as primary phase were more scattered with both higher and lower values but the difference was negligible for glasses giving disilicate. From table 3 it is seen that phase predictions failed primarily for glasses in the devitrite field (63 %). For the other two prediction failure was about 20 %. Four of the extra glasses had silica as primary phase, one of these lay on the diagonal while the thermodynamic values were too high for the others. The three having $Na_2O \cdot 2\,MgO \cdot 6\,SiO_2$ as primary phase lay on both sides of the line.

Once performed, the thermodynamic calculations yield the state variables H, S, G and C_p. However, it must be remembered that the true primary phase is sometimes obscured by faster growing secondary or ternary crystals and that the latter may thus be more important to the glass technologist.

4. Conclusions

These data indicate that the best models now available for estimation of liquidus temperature of complex glasses give a standard deviation of about 25 °C; when it is essential to have accurate result it must at present still be obtained by experiment. Good agreement between two sets of theoretical predictions does not necessarily confirm that their results are accurate but is encouraging. Further refinement of thermodynamic modeling in such complex systems is still needed.

For glasses in commercial use a polynomial model will anyway remain the quickest way of obtaining a good approximation of liquidus. However, it can be foreseen that such models will in future be able to use data obtained by thermodynamic calculations rather than laborious experiments.

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