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Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Office of River Protection

P.O. Box 450
Richland, Washington 99352

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EFFECT OF GLASS COMPOSITION ON ACTIVATION ENERGY OF VISCOSITY IN GLASS-MELTING-TEMPERATURE RANGE

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ABSTRACT

Viscosity, a key property for glass processing, is a function of glass composition and temperature. Nuclear waste glasses must be formulated to obtain a desired viscosity at the melter processing temperature for each waste composition to be vitrified. Over the past decades, a large viscosity database has been accumulated at various laboratories in the US. The database, compiled at the Pacific Northwest National Laboratory, comprises over 1300 compositions with 83 components and 6800 viscosity data. We used this database to develop a mathematical model for the viscosity-composition relationship for viscosities lower than 1000 Pa·s that are important for the melting process. In this high-temperature range, the viscosity-temperature relationship has the form of an Arrhenius function, i.e., $\ln(\eta) = A + B/T$, where η is the viscosity, T is the absolute temperature, A is a constant coefficient, and B is the activation energy. We obtained B for each data point and then fitted a first- or second-order model to B as a function of glass composition while A was kept constant for all glasses. Altogether, we have developed 12 versions of viscosity-composition relationships with a variety of first- and second-order coefficients. Two models, one first order and one second order, are presented in this paper.

I. VISCOSITY-COMPOSITION RELATIONSHIPS

Viscosity-temperature relationships are important for both glass melting and glass forming. Over the wide interval of temperatures—from the glass transition temperature to the temperature at which glass is being refined—viscosity spans 12 orders of magnitude. Many approximation functions have been suggested in the literature to model the viscosity-temperature relationship. The most popular among them are the Vogel-Fulcher-Tammann equation and the Adam-Gibbs equation,¹ the latter of which is more versatile and allows better fitting of high-temperature data.^{2,3}

As has been demonstrated with various viscosity databases, both for commercial^{4,5} and waste glasses,^{5,6} high-temperature viscosity is best fitted by an Arrhenius function,

$$\ln(\eta) = A + B/T \quad (1)$$

where η is the viscosity, T is the temperature, A is a constant coefficient, and B is the activation energy. In Equation (1), both A and B are independent of temperature. Thus, for low viscosities, $\eta < 10^3$ Pa·s, the activation energy depends on composition only. Because the melting temperatures of glass are usually below 10 Pa·s, Equation (1) fully suffices for formulating glasses to meet melt-processing constraints with respect to glass formulation as well as mathematical modeling of glass-melting furnaces.

As has been both argued⁷ and demonstrated,^{2,4-6} A is nearly independent of composition and can be treated as constant for a specific family of glasses characterized by a restricted composition region. Because of its simplicity, Equation (1) is ideally suited for glass formulation, especially for formulation of waste glasses that contain a large number of components.

The activation energy is usually expressed as a function of composition using the concept of partial properties.⁸ Thus,

$$B = \sum_{i=1}^N B_i x_i \quad (2)$$

where x_i is the i^{th} component's mass fraction, B_i is the i^{th} component's partial specific activation energy, and N is the number of components.

Partial properties are themselves functions of compositions. For narrow ranges of mass fractions, B_i s can be approximated as constants. For some highly interactive components, especially those with a wide range of mass fractions, B_i s can be approximated as linear functions of composition. Thus,

$$B_i = \sum_{j=1}^N B_{ij} x_j \quad (3)$$

where B_{ij} is the i^{th} and j^{th} components' second-order coefficient.

Over the past decades, a huge viscosity database has been accumulated at various laboratories in the US. The database compiled at the Pacific Northwest National Laboratory comprises over 1300 compositions with 83 components and nearly 6800 data for viscosities < 1000 Pa·s that are important for the melting process.⁹ Using this database and Equations (1)–(3), we have developed 12 versions of viscosity-composition relationships with a variety of first- and second-order coefficients.

II. DATA PREPARATION AND THE FIRST-ORDER MODEL

The PNNL database contains both targeted and analytical compositions. Because targeted compositions are generally more accurate (weighing of analytical-grade chemicals is an accurate operation) and analytical data were not available for a number of glasses, we chose the targeted compositions for calculations.

Out of 83 components listed in the database, oxides of various elements (As, Ce, Co, Fe, Mn, Mo, Pb, Pr, Re, Rh, Sb, Sn, Tc, Tl, and U) were listed in more than one valence state. By choosing a single valency for each of these oxides (As_2O_3 , Ce_2O_3 , CoO , Fe_2O_3 , MnO , MoO_3 , PbO , Pr_2O_3 , Re_2O_7 , Rh_2O_3 , Sb_2O_3 , SnO , Tc_2O_7 , Tl_2O , and UO_2), the number of components was decreased to 56. Then we renormalized the composition so that $\sum_{i=1}^N x_i = 1$. After sorting data by viscosity, we removed from the database all data with $\eta > 1050$ Pa·s, reducing the number of data points to 6765.

Using Equation (1), we calculated the activation energy for each data point, i.e., each (η, T) pair, as $B = T(\ln \eta - A)$. Then we fitted Equation (2) to data with the least-squares method, obtaining A and the first-order coefficients, B_i . With all 6765 data, the coefficient of determination was $R^2 = 0.9172$. This first fit resulted in unusually high B_i values for 17 components with $x_i < 0.01$ (Cs_2O , Sb_2O_3 , SeO_2 , Tl_2O ,

Tc₂O₇, Ag₂O, RuO₂, Pr₂O₃, WO₃, As₂O₃, I, PdO, Re₂O₇, Rh₂O₃, Rb₂O, Br, Nb₂O₅). We have removed these components from the composition matrix.

To meet the mass-fraction relationship, $\sum_{i=1}^N x_i = 1$, we evaluated two options: 1) renormalizing the remaining 39 components to 1, or 2) summing x_i s of the 17 removed components into a single collected component, “*Others*” (total 40 components). As expected, the coefficient of determination was slightly lower with the first option ($R^2 = 0.9172$) than with the second ($R^2 = 0.9176$) which had one extra parameter. However, the main reason for choosing the second option was that we needed the *Others* component for future use when a further reduction in the number of viscosity-affecting components appeared appropriate.

Out of the remaining components, SO₃ had an extremely high coefficient, $B_{\text{SO}_3} = 3.65 \times 10^4$ K, the highest of all B_i s. The reason we did not initially remove SO₃ from the composition matrix was its high concentration, over 2 mass %, in some glasses. Its coefficient remained high even after we deleted two glasses with > 2.0% SO₃ from the database. The impossible B_{SO_3} value was most likely caused by SO₃ segregation and evaporation from the melts, as a result of which the targeted content of SO₃ was not retained in the glass. Since replacing targeted values with analytical values did not appear practicable, we have added SO₃ to *Others*.

In the next step, we sorted the data according to the value of $\Delta^2 = (B_M - B_C)^2$, where the subscript M stands for *measured* and C for *calculated*. After repeated resorting and refitting of Equation (2) to data with $\Delta^2 > 3.3 \times 10^5$ K², the selection stabilized at 5909 data points, and we obtained preliminary values of A and B_i s. The coefficient of determination increased to $R^2 = 0.9712$.

For all data with $\eta < 1050$ Pa·s, the T span was from 752 to 1806 °C and the $\log(\eta/\text{Pa}\cdot\text{s})$ interval was (−0.85; 3.02). For data with $\Delta^2 < 3.3 \times 10^5$ K², the T span shrank to 800–1632°C and the $\log(\eta/\text{Pa}\cdot\text{s})$ interval shrank to (−0.51; 2.57).

Surprisingly, the composition region shrank little. Maximum mass fractions of only six components (SiO₂, Fe₂O₃, K₂O, CaO, MgO, and NiO) slightly decreased and the minimum mass fractions of SiO₂ slightly increased. Fig. 1 displays the data points on the (1/ T , log η) surface. It shows that out of 856 rejected data points, only a few lie outside the (1/ T , log η) region of data selected.

Fig. 1. Positions of (1/ T , log η) data with $\eta > 1050$ Pa·s and model-selected data ($\Delta^2 < 3.3 \times 10^5$ K²)

In a further attempt to eliminate components that are unlikely to influence viscosity, we sorted the components according to three criteria, $B_i - B_a$, $(B_i - B_a)x_{ia}$ and $(B_i - B_a)x_{im}$, where subscripts a and m stand for average and maximum, respectively. Components Ce₂O₃, CoO, Cr₂O₃, CuO, Eu₂O₃, Ga₂O₃, HfO₂,

MoO₃, Nd₂O₃, Sm₂O₃, SnO, ThO₂, TiO₂, UO₂, and Y₂O₃ had low values of all these criteria. After removing these components to *Others*, the number of components shrank to 24, including *Others*. Repeated fitting and Δ^2 sorting until the number of outliers stabilized at $\Delta^2 > 3.3 \times 10^5 \text{ K}^2$ resulted in the selection of 5893 data points. Both the T span and $\log(\eta/\text{Pa}\cdot\text{s})$ interval remained unaffected by removal of the noninfluential components. Likewise, the composition region remained unchanged except for the maximum mass fraction of SiO₂, which slightly decreased.

The component coefficients of the resulting first-order model, obtained by fitting Equations (1) and (2) to selected data, are listed in Table 1. The value of the A coefficient is -11.193 . The coefficient of determination, $R^2 = 0.9710$, remained high. The maximum component mass fractions, listed in Table I, represent the model validity region. The minimum component mass fraction is 0 for all components except SiO₂ (0.194) and Na₂O (0.008).

TABLE I. Component Coefficients and Maximum Component Mass Fractions

	$B_i(10^4\text{K})$	x_{im}		$B_i(10^4\text{K})$	x_{im}		$B_i(10^4\text{K})$	x_{im}
SiO ₂	2.999	0.628	Bi ₂ O ₃	1.425	0.162	Gd ₂ O ₃	1.271	0.077
Na ₂ O	-0.036	0.351	ZrO ₂	2.707	0.158	F	-0.469	0.060
Fe ₂ O ₃	1.553	0.264	MnO	0.458	0.136	V ₂ O ₅	1.396	0.060
Al ₂ O ₃	3.500	0.266	P ₂ O ₅	2.644	0.131	La ₂ O ₃	0.656	0.050
SrO	1.008	0.299	ZnO	1.034	0.099	BaO	0.662	0.047
K ₂ O	0.802	0.100	PbO	0.978	0.097	CdO	0.740	0.040
B ₂ O ₃	0.319	0.202	MgO	1.151	0.082	NiO	0.785	0.021
CaO	0.533	0.150	Li ₂ O	-3.908	0.090	<i>Others</i>	1.771	0.182

III. SECOND-ORDER MODEL

For the second-order model, we have selected 8 major components with the highest values of $(B_i - B_a)x_{ia}$. These components are SiO₂, Na₂O, Li₂O, B₂O₃, Al₂O₃, CaO, ZrO₂, and Fe₂O₃. The full second-order matrix has $N_B = (1/2)N(N + 1)$ coefficients. Thus, for $N = 8$, $N_B = 36$.

Various versions of the second-order model were subsequently developed:

Model 0. In the baseline model, the first-order terms for major components were left in the fit because does not have second-order terms for 15 minor components (SrO, K₂O, Bi₂O₃, MnO, P₂O₅, ZnO, PbO, MgO, Gd₂O₃, F, V₂O₅, La₂O₃, BaO, CdO, NiO).

Model 1. The first-order terms of SiO₂, Na₂O, Li₂O, B₂O₃, Al₂O₃, CaO, ZrO₂, and Fe₂O₃, which would be, by Equation (3), redundant in the full second-order model, were removed while keeping the list of minor components unchanged.

Model 2. To further simplify the second-order model, we removed second-order terms with $|B_i - B_a|/(B_a - S) < 1$, where B_a is the B average and S is the standard deviation.

Model 3. In another version of the second-order model, in addition to removing first-order terms of SiO₂, Na₂O, Li₂O, B₂O₃, Al₂O₃, CaO, ZrO₂, and Fe₂O₃, we also removed minor components with $|B_i - B_a|/(B_a - S) < 0.5$ (Bi₂O₃, PbO, Gd₂O₃, V₂O₅, La₂O₃, BaO, CdO, NiO) and added them to *Others*.

Model 4. Models 0 to 3 started with all 6765 data. In Models 4 to 8, we removed from the database glasses with high fractions of minor components. The number of data decreased to 5969. Without removing the first-order terms of SiO₂, Na₂O, Li₂O, B₂O₃, Al₂O₃, CaO, ZrO₂, and Fe₂O₃, we kept

removing, one-by-one, compositions in which $x_{im}/x_{ia} > 20$. Thus, glasses with high fractions of Bi_2O_3 , V_2O_5 , PbO , SrO , Gd_2O_3 , BaO , MnO , and La_2O_3 were deleted.

Model 5. Here we moved to *Others* the minor components V_2O_5 , Bi_2O_3 , Gd_2O_3 , PbO , and BaO for which $x_a|B_i - B_a|/(B_a - S) < 8.74$, a value for *Others* in Model 4.

Model 6. Continuing the component reduction, we moved to *Others* all minor components except SrO , K_2O , P_2O_5 , ZnO , MgO , and F .

Model 7. In this version of Model 6, we removed the first-order coefficients of the major components.

Model 8. With the same set of data and coefficients as in Model 6, only data with $\Delta^2 > 3.3 \times 10^4 \text{ K}^2$ (Model 8a) and $\Delta^2 > 3.3 \times 10^3 \text{ K}^2$ (Model 8b) were selected for model fitting.

The space limitation does not allow us to report details for all these model versions. Tables II and III list the component coefficients for Model 6. The number of outliers stabilized at $\Delta^2 > 3.3 \times 10^5 \text{ K}^2$ with 5867 data points, $A = -11.373$, and $R^2 = 0.9795$. The component effects are displayed in Fig. 2 (the spider plot) in terms of B versus the mass fractions of components added to the average composition of all glasses selected for model fitting. Note that the effects of B_2O_3 , CaO , and SrO are similar.

TABLE II. Model 6 Second-Order Coefficients, $10^{-4}B_{ij}(\text{K})$

	SiO_2	Na_2O	B_2O_3	Al_2O_3	Fe_2O_3	ZrO_2	Li_2O	CaO
SiO_2	0.27	-1.66	-1.28	0.88	0.62	2.29	-5.11	-0.56
Na_2O		1.99	-1.95	0.14	1.96	1.96	11.97	2.96
B_2O_3			4.33	-1.27	2.20	0.53	1.45	0.93
Al_2O_3				0.98	1.91	0.46	-8.81	-1.12
Fe_2O_3					1.43	-0.09	-1.49	1.60
ZrO_2						-1.17	-2.79	0.85
Li_2O							27.82	6.08
CaO								0.38

TABLE III. Model 6 First-Order Coefficients

	$10^{-4}B_i(\text{K})$		$10^{-4}B_i(\text{K})$		$10^{-4}B_i(\text{K})$
SiO_2	3.15	ZrO_2	1.54	P_2O_5	2.64
Na_2O	-0.22	Li_2O	-4.38	ZnO	1.59
B_2O_3	0.37	CaO	0.17	MgO	1.37
Al_2O_3	3.27	SrO	0.74	F	-0.01
Fe_2O_3	0.53	K_2O	1.03	<i>Others</i>	1.65

IV. CONCLUSIONS

The PNNL waste-glass property database is an invaluable source of data. We have evaluated data for viscosity as a function of temperature and composition and developed 12 versions of a mathematical model (two first-order models and ten second-order models) for the activation energy as a function of glass composition. Tables I through III present the component coefficients for two representative models.

Fig. 2. Spider plot: Effects of component addition to average glass composition.

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