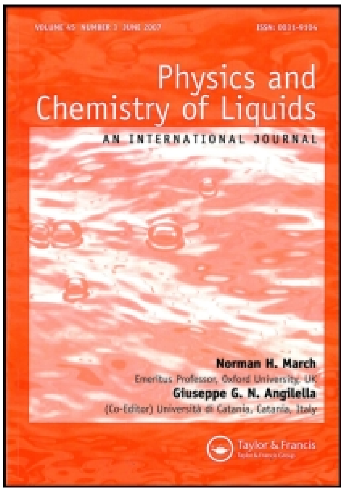

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Determination of the Excess Thermodynamic Functions in Ternary Cs_2O—SiO_2-Na_2O Melts by Knudsen Effusion Mass Spectrometry

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DETERMINATION OF THE EXCESS THERMODYNAMIC FUNCTIONS IN TERNARY $Cs_2O—SiO_2—Na_2O$ MELTS BY KNUDSEN EFFUSION MASS SPECTROMETRY

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The enthalpy and the free enthalpy of formation of the melts in the system Cs_2O–SiO_2–Na_2O are measured by mass spectrometry coupled with a Knudsen effusion cell. The measurements are performed through four quasi-binary sections at the constant SiO_2 molar fraction 0.5, 0.667, 0.75 and 0.85 in the temperature range (950–1600 K) using the intensity ratio method. Some phase limits have been determined. The thermodynamic behaviour of the melt is characterised by a slightly negative deviation from ideality and a symmetrical effect between Na and Cs regarding to SiO_2.

Keywords: Liquid silicates; mixing enthalpy; mass spectrometry; Gibbs energy

1. INTRODUCTION

For the mineralogists silicates and aluminosilicates are the main constituents of the surroundings of ore deposits and thus, have been chemically active during the differentiation process. A great part of the science in metallurgy involves the use of the physicochemical properties

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*Author for Correspondence

of these oxides in the slag–metal equilibrium. For numerous other applications of silicates, solving the problem of the elaboration requires a good knowledge of the phase diagrams and the thermochemical properties of the liquid and solid phases.

The K_2O–SiO_2–Na_2O system has already been studied in a previous work [1] and the influence of the substitution of potassium by caesium on the thermodynamic properties is analysed in the present study of the Cs_2O–SiO_2–Na_2O system.

By heating the silicate inside a Knudsen cell under vacuum, an equilibrium is established between the condensed and gaseous phases. According to several studies on silicates of potassium and sodium [1–4], the species present in the vapour phase are mainly K, Na and O_2. In our case and in the temperature range (950 K to 1600 K) Cs, Na and O_2 were the detected gaseous species.

The thermochemical tables relative to alkaline oxides [5], indicate that the decomposition in oxygen and alkaline metal in the gaseous form at average temperature T corresponds to

$$\langle\langle M_2O \rangle\rangle = 2[M] + 1/2[O_2] \tag{1}$$

The equilibrium constant of the reaction is:

$$K(T) = \frac{P_{O_2}^{1/2} P_M^2}{a_{M_2O}} \tag{2}$$

where P and a are the partial pressures and the activity respectively.

We studied four sections at constant molar fraction $X_{SiO_2} = 0.5$, 0.667, 0.75 and 0.85 and we determined the excess free energy by the intensity ratio method [6]. The measured variation with temperature yielded the corresponding enthalpy of mixing.

2. EXPERIMENTAL PROCEDURE

The apparatus used for our measurements is the Varian Mat type CH5 single focusing mass spectrometer with a magnetic sector of 90° and a deflection radius of 21 cm. The detection was carried out by a secondary electron multiplier. A molecular beam issued from the Pt Knudsen cell enters the ionization chamber through a movable shutter which separates vaporizing species from those due to the background. The energy of the ionising electrons was fixed at 14 eV to prevent the fragmentation phenomenon without minimising to much the sensibility of the apparatus. The heating of the cell was realised by electronic bombardment from a tungsten filament. The temperature was measured with a platine–platine rhodium 10% thermocouple placed at the bottom of the cell. Calibration is obtained by locating the ionic intensity plateau during the fusion of known pure substances.

Samples supplied by C.R.P.H.T were prepared from sodium and caesium carbonates for Na_2O and Cs_2O respectively and the tetraethoxysilane for SiO_2 by the sol-gel process [7].

For binary systems, the method used here needs to measure the ionic intensity ratio I_i^+/I_j^+ of the components of the alloy ij for a molar fraction x_i and this in the whole concentration range. The activity coefficient γ_i was obtained from the following relationship:

$$\ln \gamma_{i,x_i} = -\int_{X_i=1}^{X_i} X_j \, \mathrm{d} \ln \frac{I_j^+ X_i}{I_i^+ X_j} \tag{3}$$

This method avoids the determination of the sensitivity of the apparatus. The study of the variation of this ratio with the temperature leads to the molar enthalpy of formation following:

$$\Delta \bar{\mathrm{H}}_i = -R \int_{X_i=1}^{X_i} X_j \, \mathrm{d} \left[\frac{\mathrm{d} \ln \dfrac{I_j^+}{I_i^+}}{\mathrm{d}\left(\dfrac{1}{T}\right)} \right] \tag{4}$$

In the ternary system $A-B-C$, the exact differential of excess molar free energy at constant P and T is given by: $\mathrm{d}G^{XS} = G_A^{XS}\,\mathrm{d}X_A + G_B^{XS}\,\mathrm{d}X_B + G_C^{XS}\,\mathrm{d}X_C$

Since $\Sigma \mathrm{d}X_i = 0$, it follows that at constant mole fraction of component A: $(\partial G^{XS}/\partial X_B)_{X_A} = G_B^{XS} - G_C^{XS}$

Substituting activity coefficients and integration from the A–C binary to a ternary composition X_B leads to:

$$G^{XS}_{X_B} = \mathrm{RT} \int_{X_B=0}^{X_B} \ln \frac{\gamma_B}{\gamma_C}\, \mathrm{d}X_B + (G^{XS})_{A-C,X_A}$$

In terms of ion current ratio, it becomes:

$$G^{XS}_{X_B} = RT \int_{X_B=0}^{X_B} \ln \frac{I^+_B X_C}{I^+_C X_B}\, \mathrm{d}X_B + KX_B + (G^{XS})_{A-C,X_A} \tag{5}$$

The constant K, which includes calibration factors, is evaluated by carrying out integration across to the A–B binary, thus:

$$\mathrm{K} = \frac{1}{1-X_A}\left[(G^{XS})_{A-B,X_A} - (G^{XS})_{A-C,X_A} - RT \int_0^{1-X_A} \ln \frac{I^+_B X_C}{I^+_C X_B}\, dX_B\right]$$

where I^+_B and I^+_C are the ionic intensities of the B and C species at constant X_A, respectively.

3. RESULTS

3.1. Definition of Temperature Range of Measurements

At room temperature the samples are in the glassy state. From the experimental results of Shelby [8], the glass transition should be below 950 K. To apply the method described above in the best conditions, it is necessary to know the range of stability of the liquid phase. However, in the case of the Cs_2O–SiO_2–Na_2O system, very few is known on the phase diagram. The Figure 1 shows the variation of the logarithm of the pressures (P_i is proportional to I_iT) of sodium and caesium as a function of $1/T$ for the composition $X_{SiO_2} = 0.5$ and $x_{Cs_2O} = 0.1$. The breaks in the slope (arrows A and B) correspond to the crossing of the two-phase ranges and indicate the lowest temperature from which the measurements have to be performed. On the figure, the points belonging to the liquid phase and collected for the

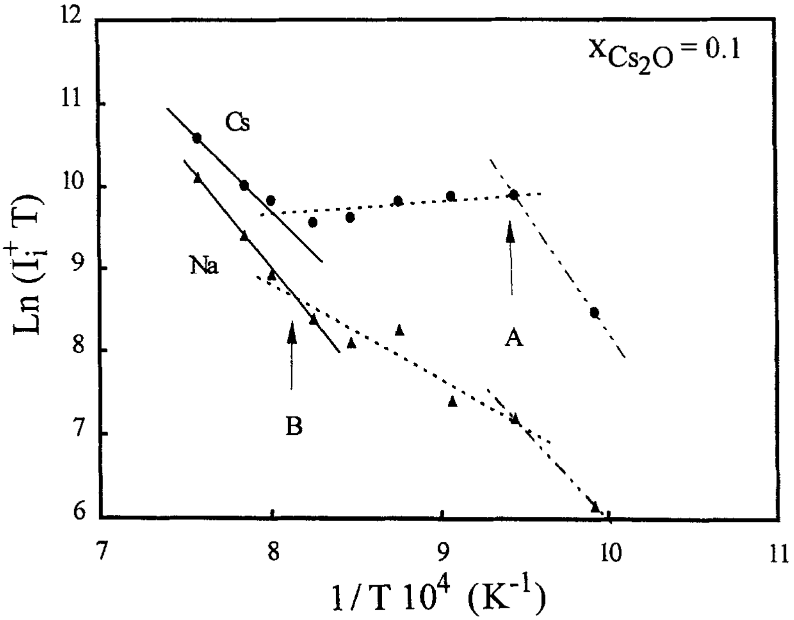

FIGURE 1 Variation of the logarithm of the (I_i^+T) vs. the inverse temperature for $x_{Cs_2O} = 0.5$.

determination of the excess free energy are shown by the full line. The temperature range is also limited towards high temperatures (for example, $T > 1400$ K for the section $X_{SiO_2} = 0.5$) since for too high pressure values the conditions of application of the Knudsen law are no more fulfilled. The Figures 2 to 5 present the curves of $\ln(I^+_{Cs}/I^+_{Na}) = f(1/T)$ for four quasi-binaries ($X_{SiO_2} = 0.5$, 0.667, 0.75 and 0.85). The measurements are carried out on heating.

3.2. Excess Free Enthalpy in Ternary Silicates

The initial results obtained by Knudsen effusion of the liquid samples can be treated by two different ways:

Considering the following equilibrium:

$$n\text{SiO}_2 + \text{Na}_2\text{O} \Leftrightarrow 2\text{NaSi}_{n/2}\text{O}_{(2n+1)/2} \qquad \text{(a)}$$

$$n\text{SiO}_2 + \text{Cs}_2\text{O} \Leftrightarrow 2\text{CsSi}_{n/2}\text{O}_{(2n+1)/2} \qquad \text{(b)}$$

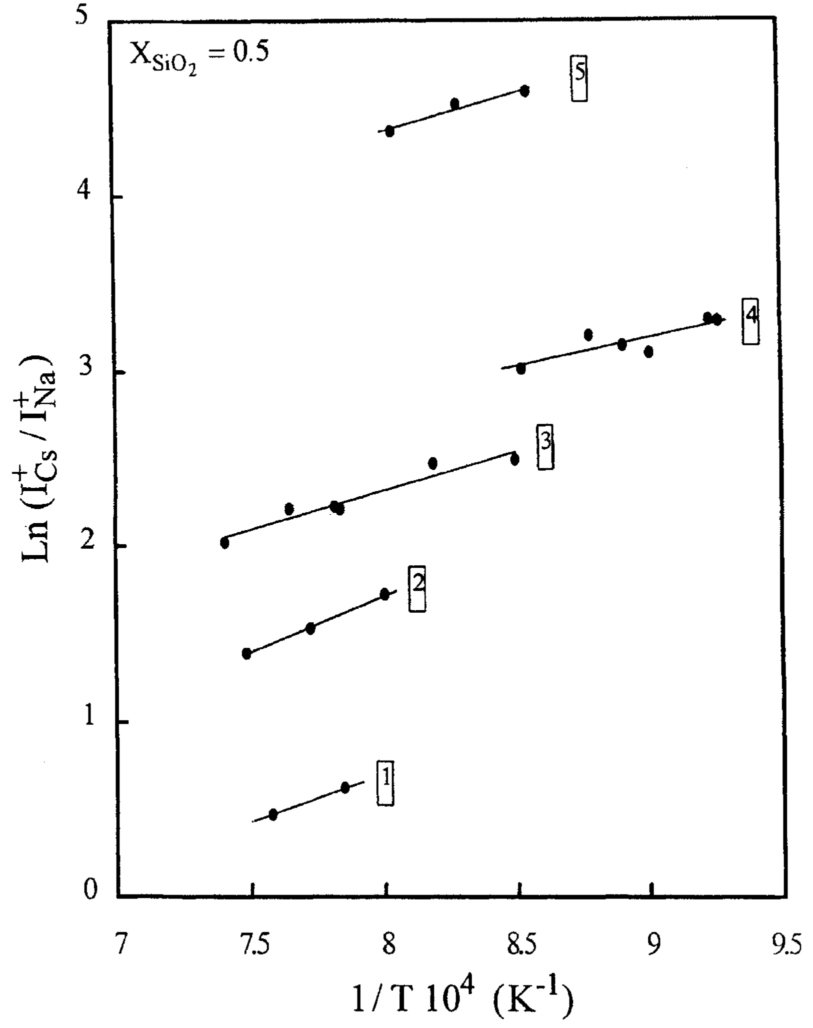

FIGURE 2 Logarithm of the ratio of the ionic intensities of ^{133}Cs and ^{23}Na plotted against the reciprocal temperature for the different mole fractions x_{Cs_2O} in: $0.5\ SiO_2 + 0.5\ [(1-x)_{Na_2O} + x_{Cs_2O}]$.
1: $x_{Cs_2O} = 0.1$, 2: $x_{Cs_2O} = 0.3$, 3: $x_{Cs_2O} = 0.5$, 4: $x_{Cs_2O} = 0.7$, 5: $x_{Cs_2O} = 0.9$.

The equilibrium constant is written in each case:

$$K_a = \frac{a^2_{NaSi_{n/2}O_{(2n+1)/2}}}{a_{Na_2O} \cdot a^n_{SiO_2}} \quad \text{and} \quad K_b = \frac{a^2_{CsSi_{n/2}O_{(2n+1)/2}}}{a_{Cs_2O} \cdot a^n_{SiO_2}}$$

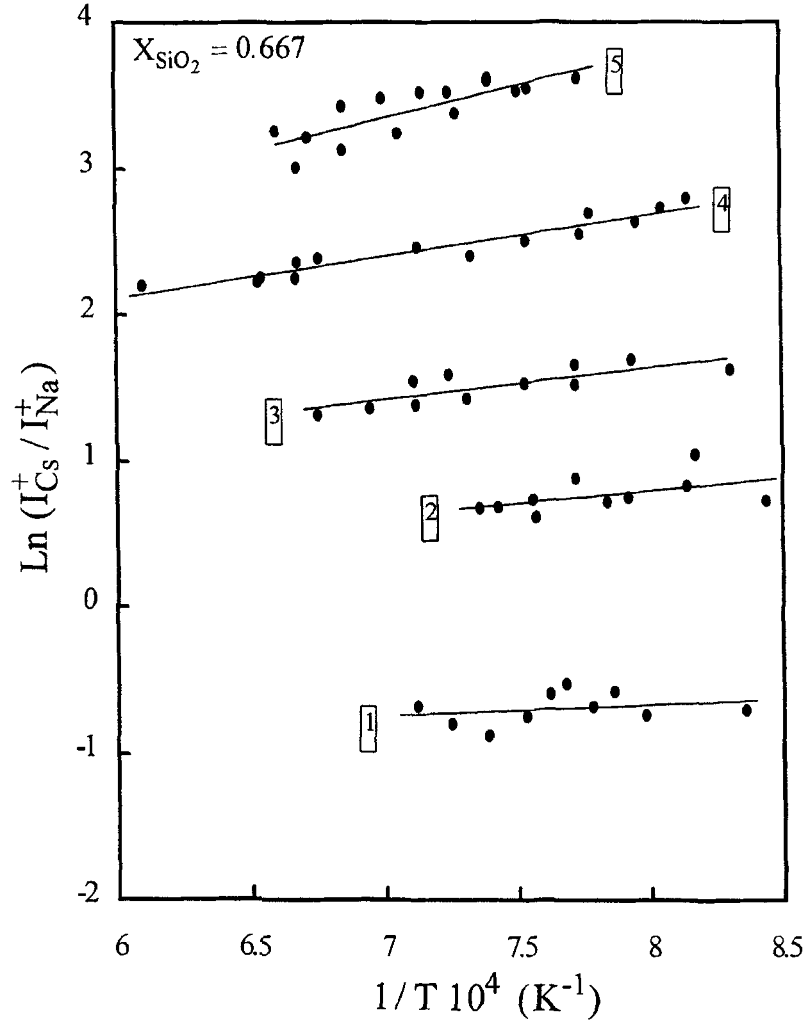

FIGURE 3 Logarithm of the ratio of the ionic intensities of ^{133}Cs and ^{23}Na plotted against the reciprocal temperature for the different mole fractions x_{Cs_2O} in:
$0.667\ SiO_2 + 0.333\ [(1-x)_{Na_2O} + x_{Cs_2O}]$.
1: $x_{Cs_2O} = 0.1$, 2: $x_{Cs_2O} = 0.3$, 3: $x_{Cs_2O} = 0.5$, 4: $x_{Cs_2O} = 0.7$, 5: $x_{Cs_2O} = 0.9$.

Assuming that the mixing properties are due to the alkaline oxide, we obtained one simple relation between the activities of the components $NaSi_{n/2}O_{(2n+1)/2}$ and $CsSi_{n/2}\ O_{(2n+1)/2}$:

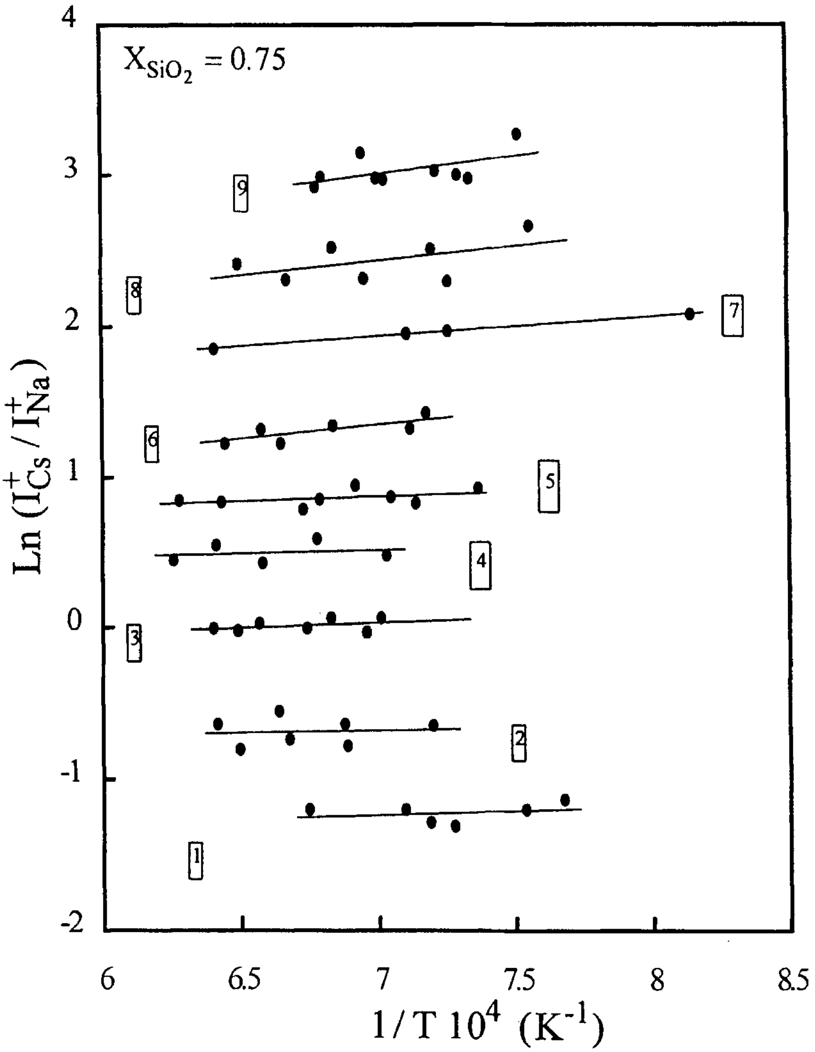

FIGURE 4 Logarithm of the ratio of the ionic intensities of ^{133}Cs and ^{23}Na plotted against the reciprocal temperature for the different mole fractions x_{Cs_2O} in: $0.75\ SiO_2 + 0.25\ [(1-x)_{Na_2O} + x_{Cs_2O}]$.
1: $x_{Cs_2O} = 0.1$, **2**: $x_{Cs_2O} = 0.2$, **3**: $x_{Cs_2O} = 0.3$, **4**: $x_{Cs_2O} = 0.4$, **5**: $x_{Cs_2O} = 0.5$, **6**: $x_{Cs_2O} = 0.6$, **7**: $x_{Cs_2O} = 0.7$, **8**: $x_{Cs_2O} = 0.8$, **9**: $x_{Cs_2O} = 0.9$.

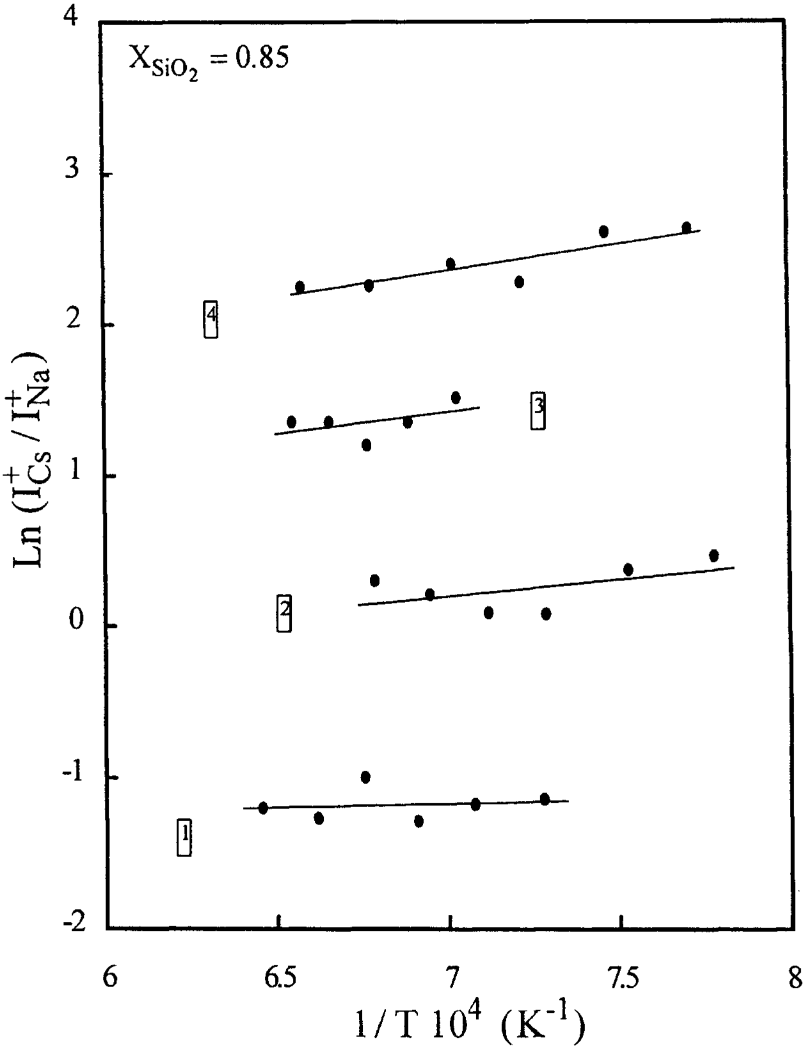

FIGURE 5 Logarithm of the ratio of the ionic intensities of ^{133}Cs and ^{23}Na plotted against the reciprocal temperature for the different mole fractions x_{Cs_2O} in:
$0.85\ SiO_2 + 0.15\ [(1-x)_{Na_2O} + x_{Cs_2O}]$.
1: $x_{Cs_2O} = 0.1$, **2**: $x_{Cs_2O} = 0.3$, **3**: $x_{Cs_2O} = 0.5$, **4**: $x_{Cs_2O} = 0.7$,

$$K = \frac{K_a}{K_b} = \frac{a^2_{\mathrm{NaSi}_{n/2}\mathrm{O}_{(2n+1)/2}}}{a^2_{\mathrm{CsSi}_{n/2}\mathrm{O}_{(2n+1)/2}}} \frac{a_{\mathrm{Cs_2O}}}{a_{\mathrm{Na_2O}}} \quad \text{and} \quad \frac{a_{\mathrm{NaSi}_{n/2}\mathrm{O}_{(2n+1)/2}}}{a_{\mathrm{CsSi}_{n/2}\mathrm{O}_{(2n+1)/2}}} = \left(K\frac{a_{\mathrm{Na_2O}}}{a_{\mathrm{Cs_2O}}}\right)^{1/2}$$

Using the Gibbs Duhem equation, we obtain the expression for the activities of the two components against their molar fraction and the alkaline oxide activities ratio, let:

$$\mathrm{d}\ln a_{\mathrm{CsSi}_{n/2}\mathrm{O}_{(2n+1)/2}} = -X_{\mathrm{NaSi}_{n/2}\mathrm{O}_{(2n+1)/2}}\,\mathrm{d}\ln\left(\frac{a_{\mathrm{Na_2O}}}{a_{\mathrm{Cs_2O}}}\right)^{1/2}$$

$$\ln a_{\mathrm{CsSi}_{n/2}\mathrm{O}_{(2n+1)/2}} = -\int_0^{X_{\mathrm{NaSi}_{n/2}\mathrm{O}_{(2n+1)/2}}} X_{\mathrm{NaSi}_{n/2}\mathrm{O}_{(2n+1)/2}}\,\mathrm{d}\ln\left(\frac{a_{\mathrm{Na_2O}}}{a_{\mathrm{Cs_2O}}}\right)^{1/2}$$

As the alkaline oxide activities are proportional to the square of the alkaline intensities, this relation becomes:

$$\ln a_{\mathrm{CsSi}_{n/2}\mathrm{O}_{(2n+1)/2}} = -\int_0^{X_{\mathrm{NaSi}_{n/2}\mathrm{O}_{(2n+1)/2}}} X_{\mathrm{NaSi}_{n/2}\mathrm{O}_{(2n+1)/2}}\,\mathrm{d}\ln\left(\frac{I^+_{\mathrm{Na}}}{I^+_{\mathrm{Cs}}}\right) \qquad (6)$$

by considering this as a reference state $\mathrm{NaSi}_{n/2}\mathrm{O}_{(2n+1)/2}$ and $\mathrm{CsSi}_{n/2}$ $\mathrm{O}_{(2n+1)/2}$ (monomer hypothesis).

If the treatment is effected by considering the case where the reference state is $\mathrm{Na_2Si}_n\mathrm{O}_{(2n+1)}$ and $\mathrm{Cs_2\ Si}_n\mathrm{O}_{(2n+1)}$ (dimer hypothesis), equation (6) is written:

$$\ln a_{\mathrm{Cs_2Si}_n\mathrm{O}_{(2n+1)}} = -\int_0^{X_{\mathrm{Na_2Si}_n\mathrm{O}_{(2n+1)}}} X_{\mathrm{Na_2Si}_n\mathrm{O}_{(2n+1)}}\,\mathrm{d}\ln\left(\frac{I^+_{\mathrm{Na}}}{I^+_{\mathrm{Cs}}}\right)^2$$

Our results on the mixing of $\{(1-X_2-X_3)\,\mathrm{SiO_2}, X_2\mathrm{Cs_2O}, X_3\mathrm{Na_2O}\}$ are calculated by assuming the second reference state that means that the oxide activities are related to the square of the ionic intensities.

On the Figure 6 is shown the curve of ln $(I^2_{\mathrm{Cs}}\,X_{\mathrm{Na_2O}}/I^2_{\mathrm{Na}}\,X_{\mathrm{Cs_2O}})$ against $x_{\mathrm{Cs_2O}}$, at 1573 K for the four paths studied in this paper. Within experimental uncertainty, our results can be treated as straight lines according to the equation:

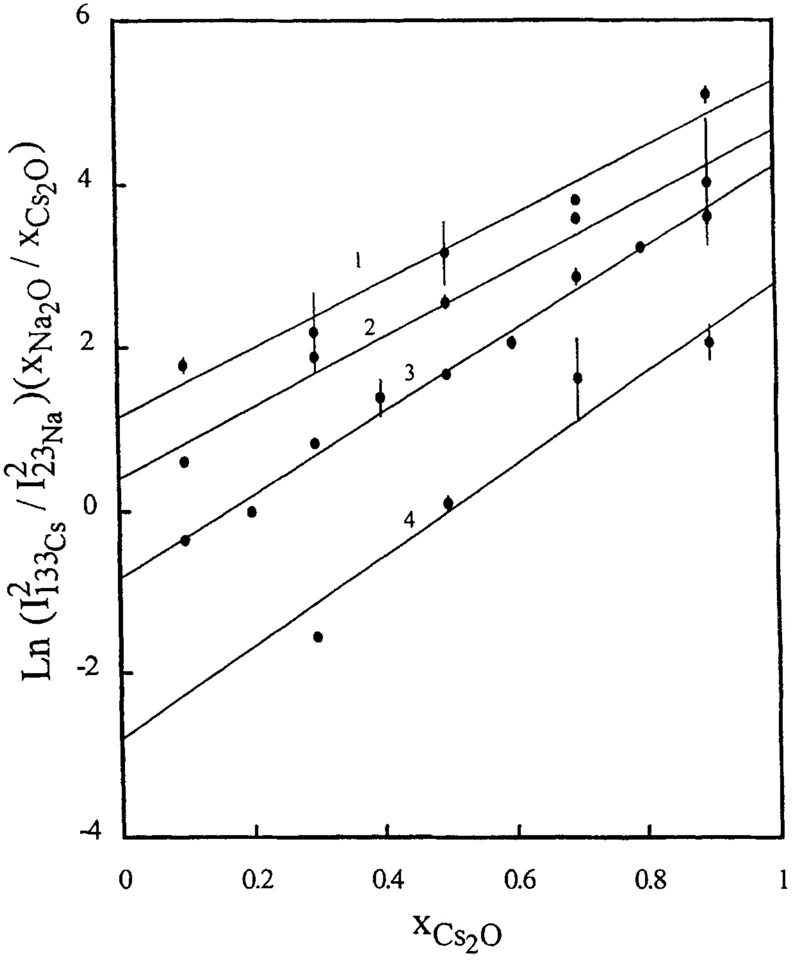

FIGURE 6 Variation of the logarithm of the ratio: Ln $(I^2_{133_{Cs}}/I^2_{23_{Na}})$ (x_{Na_2O}/x_{Cs_2O}) vs. the mole fraction x_{Cs_2O} at 1573 K for different silica mole fractions: $X_{SiO_2}=0.5$ (1), $X_{SiO_2}=0.667$, (2), $X_{SiO_2}=0.75$ (3) and $X_{SiO_2}=0.85$ (4).

$\ln(I^2_{Cs}\,X_{Na_2O}/I^2_{Na}\,X_{Cs_2O})=A+B\,x_{Cs_2O}$ of which coefficients A and B are given in the Table II.

The activities of Cs_2O and Na_2O $(Cs_2Si_nO_{(2n+1)}, Na_2Si_nO_{(2n+1)})$, a_{Cs_2O} and a_{Na_2O}, in the four quasi-binaries at constant $X_{SiO_2}=0.5$, 0.667, 0.75 and 0.85 and at $T=1573$ K are plotted vs. x_{Cs_2O} in Figure 7. Our results show negative deviations from the ideality defined above.

TABLE I Experimental values of the logarithm of the ionic intensity ratios of Cs and Na at 1573 K and of the slopes vs. the inverse temperature at four different silica mole fractions

X_{Cs_2O}	$\ln(I_{^{133}Cs}/I_{^{23}Na})$	$\partial\ln(I_{^{133}Cs}/I_{^{23}Na})/\partial(1/T)$
(a) $X_{SiO_2}=0.5$:		
0.1	−0.21	5555
0.3	0.67	6346
0.5	1.58	4484
0.7	2.33	3274
0.9	3.64	4399
(b) $X_{SiO_2}=0.667$:		
0.1	−0.79	753
0.3	0.51	1711
0.5	1.28	2155
0.7	2.21	2871
0.9	3.11	4041
(c) $X_{SiO_2}=0.75$:		
0.1	−1.27	581
0.2	−0.69	318
0.3	−0.01	682
0.4	0.49	452
0.5	0.83	647
0.6	1.23	1893
0.7	1.86	1317
0.8	2.31	1954
0.9	2.90	2218
(d) $X_{SiO_2}=0.85$:		
0.3	−1.21	534
0.5	0.05	2310
0.7	1.24	2930
0.9	2.13	3533

TABLE II Coefficients A and B of the straightlines $\ln(I^2_{^{133}Cs}/x_{Na_2O}/I^2_{^{23}Na}x_{Cs_2O} = A + Bx_{Cs_2O}$ for four different values of X_{SiO_2}.

X_{SiO_2}	A	B
0.5	1.1	4.12
0.667	0.39	4.27
0.75	−0.82	5.05
0.85	−2.80	5.60

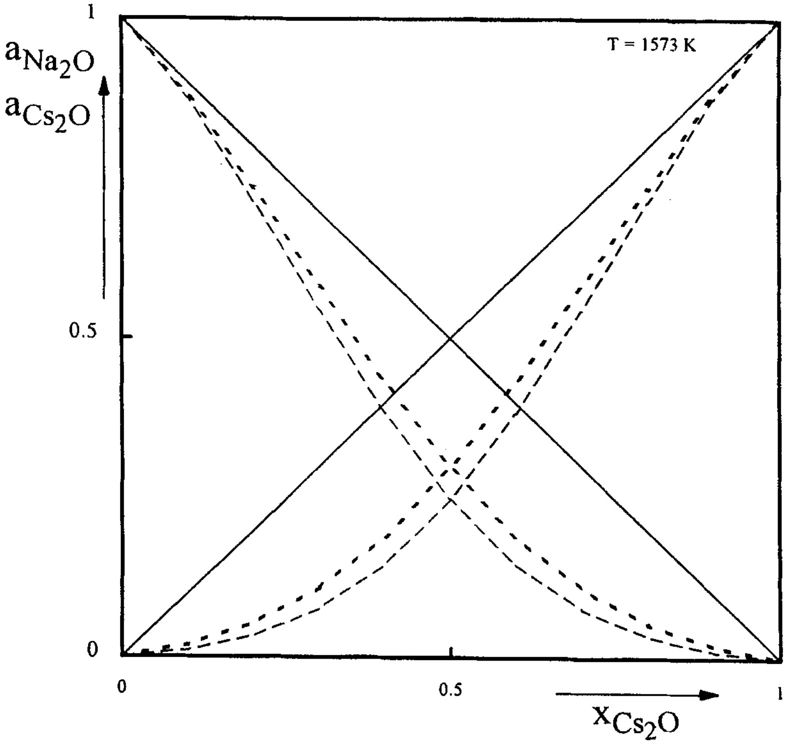

FIGURE 7 Variation of the activities of the components in: $X_{SiO_2}+(1-X)[(1-x)_{Na_2O}+x_{Cs_2O}]$ vs. the mole fraction x_{Cs_2O}. at 1573 K:------X = 0.85; ---X = 0.5.

The values of the excess free enthalpies in the quasi-binaries are listed in Table III, while Figure 8 shows their mole fraction dependence. The temperature of 1573 K is choosed because of the data of the limiting quasi-binaries available in the literature are at 1573 K.

According to the equation (5), the knowledge of the thermodynamic data of the two constituent binaries Na_2O–SiO_2 and Cs_2O–SiO_2 at the mole fractions corresponding to the studied paths, is necessary to obtain the excess free enthalpies in the ternary system, with molecular mixing of SiO_2, Na_2O and Cs_2O. A mean value for these excess free enthalpies has been obtained from the measurements of Rego *et al.* [9], Shult's *et al.* [10] and the tabulated values [5] for the binary Na_2O—SiO_2 and from Knacke *et al.* [11] for the binary Cs_2O—SiO_2 both at 1573 K. The other values were obtained by extrapolation

TABLE III Excess molar free enthalpies in the quasi-binary, G^E_{QB}, in the ternary system, ΔG^E_T, and in the ternary system referred to ideal mixing following the additivity of the limiting binaries at constant mole fractions of SiO_2, X_1.

X_{Cs_2O}	X_2	X_3	$-G^E_{QB}$ (kJ.mol^{-1})	$-(\Delta G^E_T - \sum_i X_i G^E_i)$ (kJ.mol^{-1})	$-\Delta G^E_T$ (kJ.mol^{-1})
(a) $X_1 = X_{SiO_2} = 0.5$					
0	0	0.50	0	0	101.54
0.1	0.05	0.45	2.42	1.21	104.40
0.2	0.10	0.40	4.30	2.16	107.00
0.3	0.15	0.35	5.66	2.83	109.33
0.4	0.20	0.30	6.46	3.23	111.39
0.5	0.25	0.25	6.74	3.37	113.18
0.6	0.30	0.20	6.46	3.23	114.70
0.7	0.35	0.15	5.66	2.83	115.95
0.8	0.40	0.10	4.30	2.16	116.93
0.9	0.45	0.05	2.42	1.21	117.64
1.0	0.50	0	0	0	118.08
(b) $X_1 = X_{SiO_2} = 0.667$					
0	0	0.333	0	0	75.47
0.1	0.033	0.300	2.52	0.84	76.42
0.2	0.067	0.266	4.44	1.48	77.18
0.3	0.100	0.233	5.85	1.95	77.75
0.4	0.133	0.200	6.69	2.23	78.14
0.5	0.166	0.166	6.96	2.32	78.35
0.6	0.200	0.133	6.69	2.23	78.36
0.7	0.233	0.100	5.85	1.95	78.20
0.8	0.266	0.067	4.44	1.48	77.84
0.9	0.300	0.033	2.52	0.84	77.30
1.0	0.333	0	0	0	76.57
(c) $X_1 = X_{SiO_2} = 0.75$					
0	0	0.25	0	0	58.00
0.1	0.025	0.225	2.96	0.74	58.91
0.2	0.050	0.200	5.28	1.32	59.65
0.3	0.075	0.175	6.92	1.73	60.23
0.4	0.100	0.150	7.92	1.98	60.64
0.5	0.125	0.125	8.24	2.06	60.88
0.6	0.150	0.100	7.92	1.98	60.97
0.7	0.175	0.075	6.92	1.73	60.88
0.8	0.200	0.050	5.28	1.32	60.64
0.9	0.225	0.025	2.96	0.74	60.23
1.0	0.25	0	0	0	59.64
1.0	0.15	0	0	0	36.00
(d) $X_1 = X_{SiO_2} = 0.85$					
0	0	0.15	0	0	33.30
0.1	0.015	0.135	4.26	0.64	34.20
0.2	0.030	0.120	6.53	0.98	34.81
0.3	0.045	0.105	8.00	1.20	35.30
0.4	0.060	0.090	8.80	1.32	35.69
0.5	0.075	0.075	9.06	1.36	36.00
0.6	0.090	0.060	8.80	1.32	36.23
0.7	0.105	0.045	8.00	1.20	36.38
0.8	0.120	0.030	6.53	0.98	36.43
0.9	0.135	0.015	4.26	0.64	36.35
1.0	0.15	0	0	0	36.00

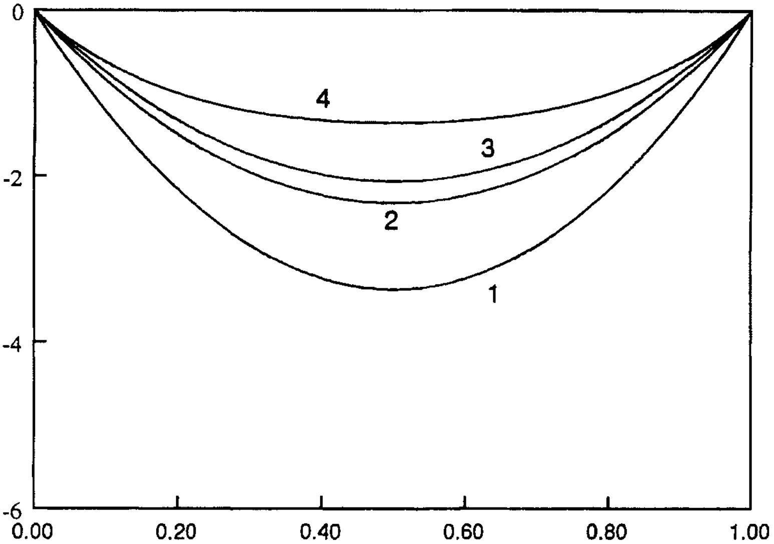

FIGURE 8 Variation of the integral excess free enthalpy in the ternary system: $X_{SiO_2}+(1-X)[(1-x)_{Na_2O}+x_{Cs_2O}]$ vs x_{Cs_2O}. with reference to the limiting binaries (Na_2O–SiO_2 and Cs_2O–SiO_2) for $X_{SiO_2}=0.5$. (1); 0.667 (2); 0.75 (3) and 0.85 (4) at 1573 K.

based on a model described by [12]. These values are shown in the following.

Binary	*Ref*	*G^E/ kJ. mol^{-1} at X_{SiO_2}*			
		0.5	0.667	0.75	0.85
Na_2O—SiO_2	5,9,10	(−101.5)	−75.47	−58	(−33.3)
Cs_2O—SiO_2	11	−118.08	−76.57	(−59.6)	(−36)

( ) calculed from the model [12].

The calculated values of the excess free enthalpies for the ternary system are reported in the Table III.

The excess free enthalpies in the ternary system are negative, the minima being located at $x_{Cs_2O}=x_{Na_2O}=0.5$ and amount to -3.37 ± 0.3 kJ.mol^{-1} for the metasilicates, -2.32 ± 0.3 kJ. mol^{-1} for the disilicates, -2.06 ± 0.3 kJ.mol^{-1} for $X_{SiO_2}=0.75$ and -1.36 ± 0.3 kJ.mol^{-1} for $X_{SiO_2}=0.85$. This deviation with respect to the ideality shows that the system presents either interactions in the liquid state or important excess entropy. The comparison with the ternary system K_2O–SiO_2–Na_2O indicates a similar behaviour [1].

3.3. Enthalpies in Ternary Silicates

The slopes of the straight lines

$$\partial \ln\left(\frac{I^+_{Cs}}{I^+_{Na}}\right)/\partial(1/T)$$

against the molar fraction shown in the Figures 2 to 5 are listed in the Table I and graphically represented in the Figure 9 for three different sections. For the section $X_{SiO_2}=0.5$, the measurements at high temperature have not been performed because of the difficulties encountered in this temperature range (important volatility of cations). The curves obtained at the other sections can be treated as straight lines

$$\frac{d\ln\left(\frac{I^+_{Cs}}{I^+_{Na}}\right)}{d(1/T)}=A+Bx_{Cs_2O}$$

of which coefficients A and B are given in the following table.

X_{SiO_2}	A	B
0.667	372.66	3867 ± 400
0.75	-61.97	2360 ± 750
0.85	-558.94	4810 ± 1500

Multiplying these values by 2, we can deduce the enthalpies of mixing according to equation (4). Figure 9 shows the variation of the values of the slopes versus x_{Cs_2O}; the integration yields partial and integral heats of mixing in quasi-binary sections. The enthalpies of mixing values are consistent with a regular solution behaviour for $X_{SiO_2}=0.667$, 0.75 and 0.85. The results are given in Table IV and shown in the Figure 10. The mixing enthalpies are negative with a minimum of -2.67 ± 0.4 kJ for the disilicate, -1.22 ± 0.4 kJ for $X_{SiO_2}=0.75$ and -1.49 ± 0.4 for $X_{SiO_2}=0.85$.

In order to deduce the enthalpies of mixing referred to pure oxides, the data corresponding to the limiting binaries are obtained from the

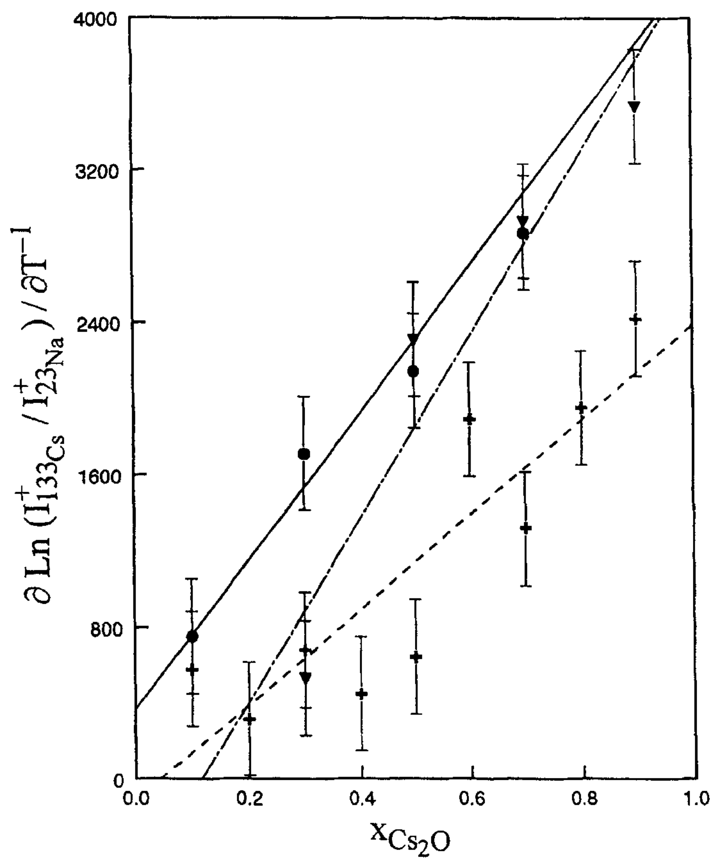

FIGURE 9 Variation of the slopes vs. the mole fraction x_{Cs_2O}, for different silica mole fractions:—— $X_{SiO_2} = 0.667$; ---- $X_{SiO_2} = 0.75$ (2) and —·—— $X_{SiO_2} = 0.85$ (3).

literature. For the Na_2O–SiO_2 and Cs_2O–SiO_2 binary system, the enthalpies of formation of liquid disilicate, at $X_{SiO_2} = 0.75$ and $X_{SiO_2} = 0.85$ are given in the following table.

Binary	*Ref*	H^f / kJ. mol^{-1} at X_{SiO_2}		
		0.667	0.75	0.85
Na_2O–SiO_2	5	−80.27	(−53.57)	(−32.16)
Cs_2O–SiO_2	11	−83.62	(−58.08)	(−34.85)

( ) calculed from the model [12].

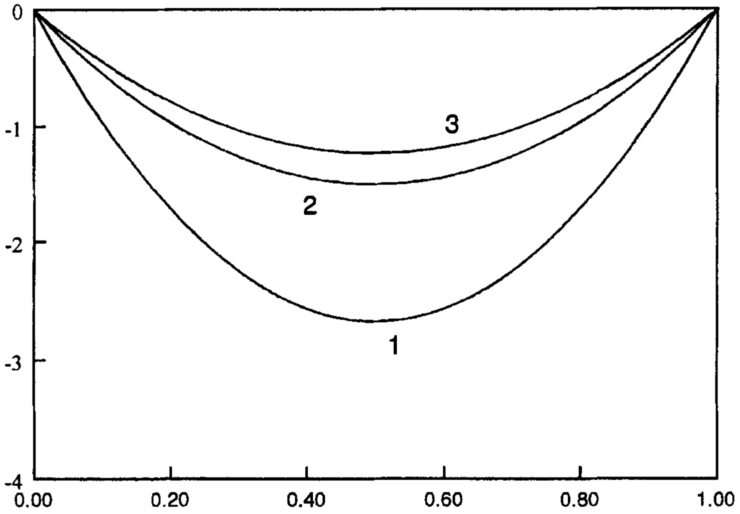

FIGURE 10 Variation of the integral enthalpy in the ternary system: $X_{SiO_2} + (1 - X)[(1 - x)_{Na_2O} + x_{Cs_2O}]$ vs x_{Cs_2O}, with reference to the limiting binaries (Na_2O–SiO_2 and Cs_2O–SiO_2) for 0.667 (1); 0.75 (2) and 0.85 (3) at 1573 K.

The corresponding enthalpies of formation referred to pure oxides are given in Table IV.

4. CONCLUSION

The experimental study of the variation of the activity of Na_2O and Cs_2O in the liquid ternary silicate (at several values of SiO_2) carried out by Knudsen cell mass spectrometry allowed us to determine the free energy of formation of these melts. We show that the free energies of formation of melts along the quasi-binary sections present a small negative deviation with respect to the ideal mixing of the SiO_2, Na_2O or SiO_2, Cs_2O oxides. We notice an excess negative term during the formation of the ternary solution from the mixing of two binaries. Comparison with the previous results on the K_2O–SiO_2–Na_2O system [1], shows a similar behaviour of the two systems with a symmetrical aspect between Na and Cs regarding to SiO_2.

Finally, this study shows the potentiality of the Knudsen cell mass spectrometry method which allows in the same time the determination

TABLE IV Molar enthalpies in the quasi-binary, H_{QB}, and in the ternary system, ΔH_T, referred to ideal mixing following the additivity of the limiting binaries at three paths of constant mole fractions of SiO_2, X_1.

X_{Cs_2O}	X_2	X_3	$-H_{QB}$ ($kJ.mol^{-1}$)	$-(\Delta H_T - \sum_i X_i H_i)$ ($kJ.mol^{-1}$)	$-\Delta H_T$ ($kJ.mol^{-1}$)
(a) $X_1 = X_{SiO_2} = 0.667$					
0	0	0.333	0	0	80.27
0.1	0.033	0.300	2.88	0.96	81.56
0.2	0.067	0.266	5.13	1.71	82.65
0.3	0.100	0.233	6.75	2.25	83.52
0.4	0.133	0.200	7.72	2.57	84.18
0.5	0.166	0.166	8.02	2.67	84.62
0.6	0.200	0.133	7.72	2.57	84.84
0.7	0.233	0.100	6.75	2.25	84.86
0.8	0.266	0.067	5.13	1.71	84.66
0.9	0.300	0.033	2.88	0.96	84.25
1.0	0.333	0	0	0	83.62
(b) $X_1 = X_{SiO_2} = 0.75$					
0	0	0.25	0	0	53.58
0.1	0.025	0.225	1.76	0.44	54.47
0.2	0.050	0.200	3.12	0.78	55.26
0.3	0.075	0.175	4.12	1.03	55.96
0.4	0.100	0.150	4.72	1.18	56.55
0.5	0.125	0.125	4.88	1.22	57.06
0.6	0.150	0.100	4.72	1.18	57.46
0.7	0.175	0.075	4.12	1.03	57.76
0.8	0.200	0.050	3.12	0.78	57.96
0.9	0.225	0.025	1.76	0.44	58.07
1.0	0.25	0	0	0	58.08
(c) $X_1 = X_{SiO_2} = 0.85$					
0	0	0.15	0	0	32.16
0.1	0.015	0.135	3.60	0.54	32.97
0.2	0.030	0.120	6.40	0.96	33.66
0.3	0.045	0.105	8.40	1.26	34.23
0.4	0.060	0.090	9.60	1.44	34.68
0.5	0.075	0.075	10.00	1.50	35.00
0.6	0.090	0.060	9.60	1.44	35.22
0.7	0.105	0.045	8.40	1.26	35.30
0.8	0.120	0.030	6.40	0.96	35.28
0.9	0.135	0.015	3.60	0.54	35.13
1.0	0.15	0	0	0	34.85

of enthalpy values in cases where the classical calorimetry technique is difficult to apply.

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References

[1] Chastel, R., Bergman, C., Rogez, J. and Mathieu, J. C. (1987). *J. Chem. Geol.*, **62**, 19.
[2] Piacente, V. and Matousek, J. (1973). *Silikaty (Moscow)*, **17**, 269.
[3] Plante, E. R. (1979). *Natl. Bur. Stand. Spec. Publ.*, **561**, 265.
[4] Altemose, V. O., Tong, S. S. C. (1980). *J. Non-Cryst. Solids*, **38/39**, 587.
[5] Stull et H. Prophet, D. R. (1989). *JANAF Thermochemical Tables. (Natl. Bur. Stand.*, U.S. Dept. Commerce, Washington, D. C.
[6] Belton, G. R. and Fruehan, R. J. (1967). *J. Phys. Chem.*, **71**, 1403.
[7] Douy, A., Canale, P. and Coutures, J. P. (1992). *J. Europ. Ceram. Soc.*, **9**, 373.
[8] Shelby, J. E. (1976). *J. Res. Natl. Bur. Stand.*, **57**, 97.
[9] Rego, D. N., Sigworth, G. K. and Philbrook, W. O. (1985). *Met. Trans.*, **16B**, 313.
[10] Shult's, M. M., Stoyorova, V. L. and Ivanov, G. G. (1987). *Zh. Fiz. Khim. Stekla.*, **13**, 168.
[11] Knacke, O., Kubaschewski, O. and Hessemann, L., *Thermochemical Properties of Inorganic Substances* (Springer-Verlag, Berlin, 1991), 2nd ed.
[12] Bennour, F. (1995). *Contribution à l'étude Thermodynamique des Silicates Liquides. Système* $Cs_2O-SiO_2-Na_2O$. Thèse Doct. Univ. Aix-Marseille I, Marseille, France.