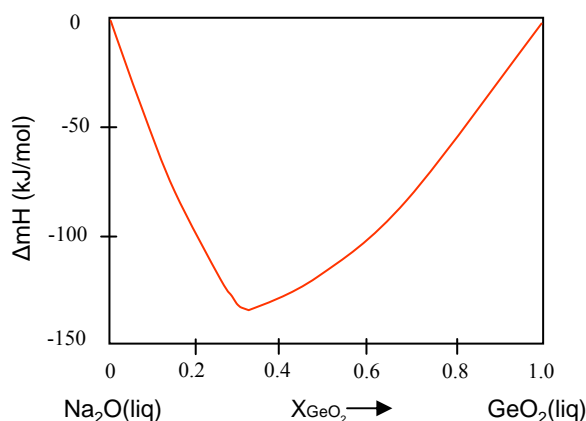


## Thermochemistry and structure of the liquid Na<sub>2</sub>O-GeO<sub>2</sub> system

**Reference:** Thermochemistry and structure of the liquid Na<sub>2</sub>O-GeO<sub>2</sub> system M. Fan, F. Müller and W. Wilsmann *Thermochimica Acta*, 224 (1993) 19-32

**Introduction:** The main objective of the present investigation is the completion of the thermochemical data base for the Na<sub>2</sub>O- GeO<sub>2</sub> system as well as the provision of systematic experimental data on the thermochemical behavior of oxide liquids.



Integral molar enthalpy of mixing  $\Delta_m H$  of the liquid mixture Na<sub>2</sub>O + GeO<sub>2</sub> as a function of composition expressed by the mole fraction  $x$  of GeO<sub>2</sub>; standard states : Na<sub>2</sub>O(liq), GeO<sub>2</sub>(liq)

### Experimental

Calorimetric measurements were made by the drop-mixing method using a differential high-temperature integrated heat-flux calorimeter.

Samples containing well-defined mechanical mixtures of pure Na<sub>2</sub>O and hexagonal GeO<sub>2</sub> or of pure Na<sub>2</sub>O and vitreous GeO<sub>2</sub> at room temperature were dropped into the calorimeter operating at 1400 K and the enthalpic effects associated with the reactions occurring in the calorimeter were measured.

**Instrument :**  
High-Temperature Calorimeter  
Multi HTC 96 with  
"drop-calorimetry" detector



### Results

The integral molar enthalpy of mixing of the liquid mixture Na<sub>2</sub>O-GeO<sub>2</sub> was measured in the composition range from 15 to 100 mol.% GeO<sub>2</sub> at 1400K.

The partial molar enthalpies of mixing of the component oxides were obtained by the method of intercepts. The enthalpies of mixing are exothermic at all compositions. Near  $x_{\text{GeO}_2} \approx 0.33$ , the integral enthalpy shows a minimum value ( $\Delta_m H = -134 \text{ kJ} \cdot \text{mol}^{-1}$ ), and the partial enthalpies display a sharp dependence on composition. The strong energetic asymmetry of the considered system is attributed to the energy associated with the breakdown of the network structure of liquid GeO<sub>2</sub>. The relationship between these structural changes and the thermochemical properties of the liquid mixture is discussed, employing a simple electrostatic model and using the information reported on the structures of sodium germanate glasses and melts in the literature.

For more details ask for the publication B0879.