

VAPORIZATION OF SIMULATED NUCLEAR WASTE GLASS

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Industrial development of glass-forming processes for nuclear waste disposal, particularly borosilicate glasses, requires basic data on glass vaporization thermodynamics. Using special high-temperature mass-spectrometric methods, species partial pressure data have been obtained for a non-radioactive borosilicate process glass containing simulated nuclear waste isotopes. Alkali metaborates were observed to be dominant vapor species and their partial pressures indicate significant transport under likely process conditions. The relative order of significance of vapor transport of radionuclides was found to be $Cs \geq Re (\sim Tc) > Ru \gg Sr$.

Significant losses by vaporization can also occur during the initial glass-forming process. Decomposition and hydrolysis of the cesium formate starting material appear to be the significant reactions. Detailed thermal decomposition studies indicate that the degradation of cesium formate to yield cesium carbonate involves a complex stepwise pathway. The resultant carbonate releases $Cs(g)$ at a rate up to an order of magnitude higher than for the pure carbonate due to reduction interactions with the carbon produced by formate decomposition.

1. Experimental techniques

The mass spectrometric methods of Knudsen effusion mass spectrometry (KMS), gas inlet Knudsen mass spectrometry (GKMS), and transpiration mass spectrometry (TMS) were used to obtain molecular-specific data regarding the vapor species concentrations and modes of vaporization of simulated nuclear waste glass and related precursors. As much of the existing literature relates to total vapor transport, a high temperature Knudsen cell Thermogravimetric Analysis (KTGA) apparatus was also used to identify regions of interest. The mass spectrometric techniques used have been described in the literature previously (KMS ref. [1]; TMS ref. [2]).

1.1. Knudsen effusion mass spectrometry (KMS and GKMS)

Ion currents obtained by the now classical KMS method are converted to pressure using the expression:

$$P_i = kI_iT,$$

where the partial pressure P_i of species i is related to the observed ion signal I_i at temperature T by a calibration constant k . The gas inlet KMS system (GKMS) also utilizes platinum Knudsen cells, similar to KMS but with the

cell modified to allow the introduction of small quantities of gas into the cell. Special care was taken in the design to minimize non-equilibrium flow of the added gas, a potential source of error. Both methods use modulated beam detection to minimize error from scatterable gases such as O₂, CO, etc.

1.2. Transpiration mass spectrometry (TMS)

The relatively modern TMS technique normally uses a platinum transpiration cell, operating at 0.1–1 atm total pressure. A small orifice (~ 0.08 mm diam.) at the end of the cell serves as a sonic nozzle, producing a “frozen-equilibrium” molecular beam which is directed toward a quadrupole mass spectrometer in a specially designed high-pumping-speed vacuum system. The differentially pumped molecular beam is modulated to isolate the beam components from background or scattered gas. The high-pressure inlet system provides control of foaming, which can be a problem with KMS experiments. This technique also allows for control of reactions using gas mixtures. Also, due to the much longer gas residence time (s vs ms for the KMS measurements), TMS provides a means for measuring vapor pressures of minor glass constituents and at higher pressures than is possible with the KMS technique. Vapor pressures can be related to ion currents using the carrier gas as a reference, or by comparison of integrated ion currents [3] with measured mass losses to determine absolute instrument sensitivities.

2. Simulated nuclear waste glass measurements

The mass spectrometric and thermogravimetric techniques were applied to a simulated nuclear waste borosilicate glass (SNG-1) prepared by Dupont–Savannah River [4], using non-radioactive isotopes. The composition of this glass is given in table 1. No previous literature mass-spectrometric vaporization data exist for a glass of this type. However, there are indications from vapor transport measurements of metaborate glasses [5,6] that alkali

Table 1
Simulated nuclear waste (SNG-1) glass composition [4]

Compound	Nominal wt. %	Analytical wt. %	Compound	Nominal wt. %	Analytical wt. %
SiO ₂	52.00	53.76	CaO	1.59	1.01
Fe ₂ O ₃	12.96	11.49	MgO	0.68	0.54
Al ₂ O ₃	4.86	4.75	ZrO ₂	0.70	3.79
B ₂ O ₃	7.29	6.49	SrO	0.09	0.05
Li ₂ O	5.10	3.96	Cs ₂ O	0.10	0.07
Na ₂ O	10.13	8.59	RuO ₂	0.09	0.11
MnO ₂	3.25	3.57	Re ₂ O ₇	0.10	0.02
NiO	1.05	1.80			

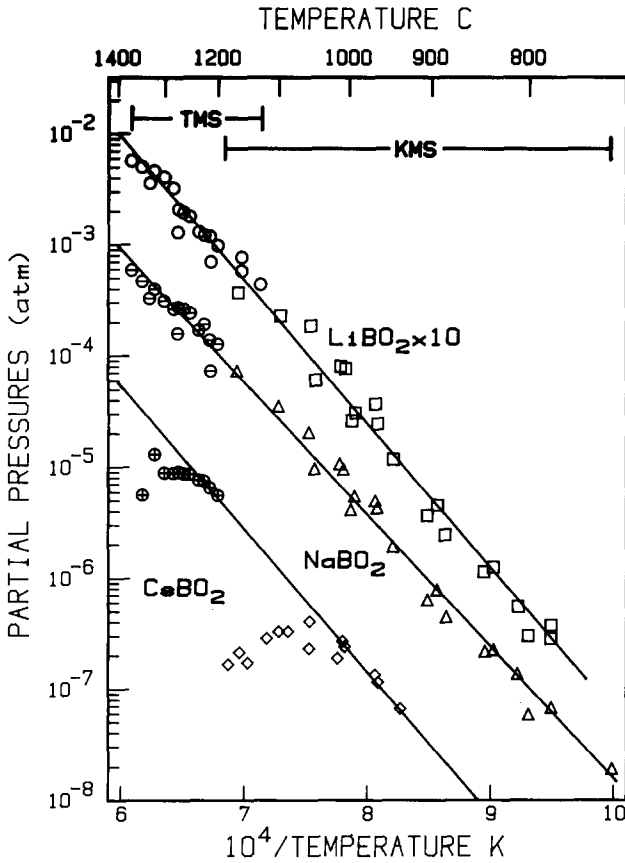


Fig. 1. Alkali metaborate pressure/temperature behavior from SNG-1 simulated nuclear waste glass. Open symbol data at lower temperatures were obtained via Knudsen effusion mass spectrometry in vacuum; circle data at higher temperatures were obtained by transpiration mass spectrometry at ~ 0.3 atm inert atmosphere. Solid lines represent least-square fits to equilibrium portions of both data sets.

metaborates and metaboric acid are likely vapor species. The principal mass-spectrometric results from the present study are given in fig. 1, based on the data interpretation given below.

2.1. Glass vapor species

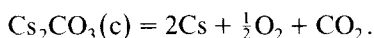
In the temperature range 1075 to 1425 K (800 to 1150°C) with 30 eV ionizing energy and neutral or vacuum conditions, both the TMS and KMS observations indicated the key mass spectral ions: Na^+ (23 amu), NaBO_2^+ (66), Li^+ (7), LiBO_2^+ (50), Cs^+ (133), O_2^+ (32), and the associated isotopic species. For vaporization from the bulk glass, the Li^+ and Na^+ ions were identified as arising from fragmentation of precursor metaborate gas species.

This assignment is supported both by the observation that the ratios M^+/MBO_2^+ are invariant with temperature, and that the observed appearance potentials for Li^+ and Na^+ were (10 ± 0.5) and (9.0 ± 0.5) eV respectively, compared to 5.4 and 5.1 eV for ionization from the elements.

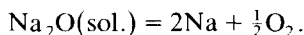
The Cs-containing species were present at too low a concentration in the glass and its vapor, to permit reliable appearance potential measurements. Also, neither the KMS nor TMS experiments detected the $CsBO_2^+$ ion. Gorokov et al. [7] have reported the $Cs^+/CsBO_2^+$ ratio to be 32.7 at 70 eV. Therefore, at the low Cs^+ ion intensities available before Cs exhaustion from the glass, we would not have expected to observe the molecular ion, even if the 30 eV ion ratios were somewhat more favorable than at 70 eV. By analogy with the electron impact behavior of the sodium and lithium metaborates, we have assigned the Cs^+ ion as a fragment of the precursor $CsBO_2$. The other possibilities for the source of Cs^+ include $Cs(c)$, $Cs_2CO_3(c)$, $CsOH(c)$, and $Cs_2O(c)$. The observed oxygen partial pressure/temperature behavior was not consistent with the presence of metallic Cs. The possibility of oxide or carbonate decomposition, or hydroxide fragmentation contributing to the Cs^+ signal was examined by measurements of pure Cs_2O and $CsOH$, and was considered to be negligible by analogy with the Na- and Li-metaborates.

2.2. Alkali transport mechanisms

Although our independent measurements of pure Cs_2CO_3 noted high CO_2 partial pressures typical of the carbonate decomposition reaction,



CO_2 evolution from the SNG-1 glass via this mechanism was not consistent with the bulk behavior. However, during the initial glass vaporization, the TMS technique noted high CO_2 pressures and an abnormally high sodium pressure. Both observations were typical of the presence of carbonate impurities. After cycling the temperature to above 1600 K, the CO_2 pressure fell dramatically, and it was possible to infer a minor contribution to Na transport from residual oxide decomposition via



This secondary mechanism appeared to account for much less than 20% of the bulk sodium transport mechanism at any temperature. No analogous process was identified for Li. It is possible, but not established, that a carbonate or oxide decomposition process could also be responsible for the mass spectroscopic observation of low Cs inclusion in the SNG-1 glass.

It is clear from fig. 1 that metaborate volatilization is the chief transport mechanism of alkali from SNG-1. The non-linearity of the cesium metaborate data is due to exhaustion of cesium in the glass by the vaporization process, because the glass contained only a few hundred ppm of alkali. This interpretation is supported by the agreement between the Cs-content, obtained by time

integration of the metaborate ion signals, and the analyzed composition of table 1. The different exhaustion point temperatures for the KMS and TMS CsBO₂ data agree well with the large difference in gas residence times for the two techniques. It should be noted that both techniques were necessary to obtain reasonable measurements of the temperature dependence of cesium evolution.

Assuming CsBO₂(l) is the predominant Cs species in the glass, the mass-spectrometrically derived activity coefficient of CsBO₂(l) in the SNG-1 glass in the 100–1000 ppm concentration regime is 0.01.

2.3. Other radionuclide simulant species

At processing temperatures below 1500 K, thermodynamic predictions indicating the most volatile species of strontium (SrO) and ruthenium (RuO₃) are at, or below, the mass spectrometer detection limits (SrO < 10⁻¹⁵ atm, RuO₃ < 10⁻⁸ atm at 1100°C). NaReO₄ is expected to be the most volatile Re-containing species [8,9]. For the predominant oxide gas molecule, Re₂O₇, to be important, rhenium oxides would have to be nearly ideally mixed in the glass, and the Re(s) reduction product of vaporization would have to dissolve in SNG-1 with low activity.

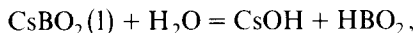
A search for Ru⁺, RuO⁺, RuO₃⁺, RuO₄⁺, and Re⁺, ReO⁺, ReO₂⁺, ReO₃⁺, Re₂O₇⁺ via the KMS technique was made up to 1800 K without success. It is possible that rhenium loss could occur through NaReO₄ (or LiReO₄) without observation. The NaReO₄ species fragments extensively on electron impact to form Na⁺ with only a small fraction of parent ion production. Thus the alkali metaborate signals could mask Re transport if Re-containing positive ions are not produced. Both gravimetric and detailed Li- and Na-ion analysis limit this mode of transport to less than 10% of the metaborate transport. The failure to observe any Re-containing ions also suggests that alkali perrhenate vaporization is not a major transport mechanism below the 200 ppm level but could be responsible for low Re incorporation (see table 1).

2.4. Vaporization in off-gas atmosphere

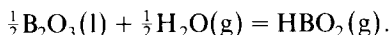
In nuclear waste glass processing, the atmosphere is potentially quite reactive as it contains a high concentration of water vapor. Thermodynamic models predict additional transport of radionuclides from the glass as hydroxides. TMS experiments were carried out in an atmosphere consisting of N₂ (0.67 mole fraction), O₂ (0.18), CO₂ (0.15), and H₂O (0.1). This composition approximates the equilibrium value of the non-equilibrium off-gas composition: H₂O (0.86 mole fraction), N₂ (0.09), O₂ (0.02), CO (0.008), H₂ (0.008), CO₂ (0.01), and minor N- and S-containing species. GKMS studies, with inlet H₂O pressures up to 1 × 10⁻⁴ atm, were also carried out.

Within the experimental limits of the GKMS and TMS techniques, the presence of additional H₂O or O₂ had no effect on the SNG-1 glass vaporiza-

tion. Neither species distributions nor gravimetrically observed total mass transport were affected, a result which is not expected from thermodynamic calculations. In the case of the alkali metaborates, our calculations using experimental activities indicate reactions, such as



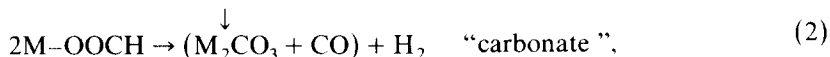
would be of comparable importance to the metaborates in alkali transport. Neither HBO_2 nor alkali hydroxides were observed under off-gas conditions with either TMS or KMS. Our measurements over pure hydroxides indicate that the parent alkali hydroxide ion is a major ion. Also, experiments with variable H_2O pressure over $\text{B}_2\text{O}_3(\text{c})$ [3] showed an essentially equilibrium production of HBO_2 according to the reaction:



Thus the failure to observe hydroxide transport is apparently due to a kinetic inability for glass-water systems to form hydroxides. This is a problem noted for other glasses [10], and indeed may be a relatively general phenomenon.

3. Cesium formate

Processing of high-level nuclear waste prior to incorporation into glass results in conversion of alkalies to their formates. Thus, the incorporation of Cs into the glass requires an understanding of the thermochemical behavior of CsOOCH at high temperatures. Meisel et al. [12] report studies of alkali metal formates using thermogravimetric analysis (TGA). The two main reactions are



and the reactions may proceed stepwise. In continuous heating experiments, Meisel et al. [12] report oxalate intermediates only for sodium and potassium with cesium formate converting directly to the carbonate (via 2), and independent of heating rate, atmosphere or container (glass vs platinum).

Our KTGA experiments in vacuum show that the two reactions can be separated if the temperature is changed stepwise. At 210°C , (1) can go to completion, although the reaction is slow (time scale is ~ 2 h). On raising the temperature to 325°C no further weight loss occurs. At 425°C , (2) commences and can be driven to completion at 475°C .

Both the KMS and TMS mass spectrometer results clearly confirm reaction (1) with the evolution of H_2 but not CO (or CO_2). It is interesting to note that Cs^+ is present during this stage and the signal disappears as the H_2 emission falls at the end of (1). Current evidence suggests the ion arises from $\text{Cs}(\text{g})$. Our interpretation is that the high H_2 pressure causes a reduction side-reaction which enhances the Cs emission, perhaps by as much as 4% of the Cs. During

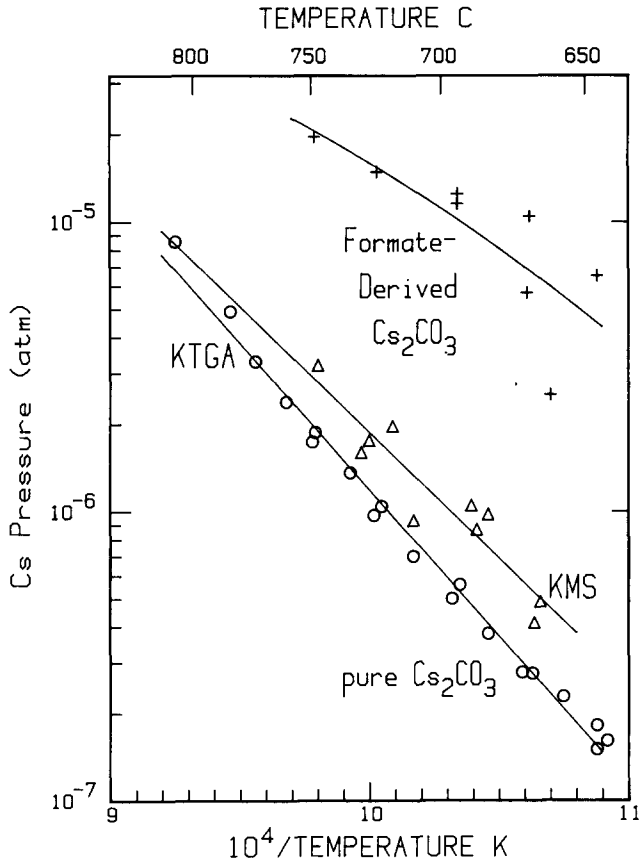


Fig. 2. Circle data are from Knudsen thermogravimetric analysis (KTGA), and triangle data are from Knudsen effusion mass spectrometry (KMS) measurements of Cs pressure over pure Cs_2CO_3 . The + data points are KTGA-determined pressures of Cs from the end-product Cs_2CO_3 as obtained from the decomposition of CsOOCH .

the second step, (2), CO emission is evident, and the final product is predominantly $\text{Cs}_2\text{CO}_3(\text{c})$. In fact, this product contains a small amount of elemental C(c), which strongly scavenges O_2 . With the O_2 partial pressure lower by several orders of magnitude (below the $\sim 10^{-8}$ atm detection limits of KMS), the environment is reducing and the resulting partial pressure of Cs over formate-derived Cs_2CO_3 is roughly an order of magnitude greater than that observed from reagent-grade Cs_2CO_3 (see fig. 2).

4. Summary

Direct observation of a simulated nuclear waste glass has shown major alkali losses to occur by alkali metaborate vaporization. No evidence was

found for an enhanced alkali vapor transport in the high H₂O environments typical of process off-gas conditions. This observation suggests a kinetic hindrance of the thermodynamically favored hydroxide forming process. Vaporization of other radionuclide simulants was not observed, although a possible mode for Re (Tc simulant) loss via LiReO₄ and NaReO₄ could exist at partial pressures of up to a few percent of the main alkali metaborate values, roughly comparable to CsBO₂ transport.

Cesium formate, a glass precursor feed stock for nuclear waste inclusion, undergoes a two-step thermal conversion through the oxalate to form Cs₂CO₃, although the oxalate step is slow, and is expected to be only an intermediate at processing temperatures. However, a side reaction apparently involving a reduction step has been observed, which persists into the carbonate vaporization stage and appears to be responsible for up to an order-of-magnitude increase in Cs transport from formate-derived Cs₂CO₃.

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