

On-line gas chromatographic studies of Rf, Zr, and Hf bromides

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Summary. The Heavy Element Volatility Instrument (HEVI), an on-line isothermal gas chromatography system, has been used to separate the volatile bromide compounds of the group 4 elements Zr and Hf and the transactinide Rf according to their volatilities, and to provide data on the gas phase chemical properties of very short-lived isotopes in amounts as low as a few atoms. For these studies ²⁶¹Rf was produced via the ²⁴⁸Cm(¹⁸O, 5n) reaction. ^{165–167}Hf was produced via the reaction ^{nat}Eu(¹⁹F, xn), and ⁸⁵Zr was produced via the ^{nat}Cu(²⁸Si, 3p3n) reaction. The half-life for ²⁶¹Rf was measured to be 75 ± 7 seconds.

A Monte Carlo code was used to deduce the enthalpy of adsorption (ΔH_a) from the observed volatility and parameters of the chromatography system. The resulting adsorption enthalpies for the Zr, Hf, and Rf tetrabromides are: $-108 \pm 5 \text{ kJ} \cdot \text{mol}^{-1}$, $-113 \pm 5 \text{ kJ} \cdot \text{mol}^{-1}$ and $-87 \pm 7 \text{ kJ} \cdot \text{mol}^{-1}$, respectively.

Volatilities of the group 4 bromides support the conclusion from previous results for the group 4 chlorides that Rf deviates from the trend expected by simple extrapolation of the properties of its lighter homologs in the periodic table. The group 4 bromides are also observed to be less volatile than their respective chlorides, as predicted by relativistic calculations.

1. Introduction

At the upper end of the periodic table relativistic effects play an important role in determining the chemical properties of the heaviest elements and their compounds. Due to the large nuclear charge of very heavy atoms, electrons in orbitals with a high probability density near the nucleus are moving with relativistic velocities. As a consequence, the $s_{1/2}$ and $p_{1/2}$ orbital radii contract and the binding energies increase. As a secondary effect, the d and f orbitals expand spatially and are energetically destabilized due to the increased screening of the nuclear charge by the $s_{1/2}$ and $p_{1/2}$ orbitals. Fricke and Greiner first discussed the possible in-

fluence of relativistic effects on the properties of the atom in 1969 [1]. Pitzer was also responsible for some of the early theoretical work on relativistic effects, and even predicted they might cause elements 112 and 114 to behave as pseudo-noble gases rather than like the other group 12 and 14 elements [2]. Pyykkö [3–5] and others [6–10] have studied the theoretical limits of relativistic contractions on the electrons in the other shells (p, d, f), and have calculated the effects caused by the contraction of the inner shell electrons on the outer shell electrons. More recently, theorists such as Pershina and others [11–20] have studied the specific effects of changes in the electronic structure on the molecular orbitals formed in transactinide compounds and on the gas phase properties of the group 4, 5, and 6 halides and oxyhalides. For example Pershina *et al.* [12] predicted that 105Br_5 should be more volatile than its lighter homolog TaBr_5 . Similarly RfCl_4 should be more volatile than HfCl_4 [18]. Since volatility is one of the few properties that can be investigated experimentally even when working with only single atoms or molecules, these predictions can be verified experimentally.

Studies of the gas phase properties of transactinides and their compounds began in the late 1960s and early 1970s. Zvara *et al.* [21, 22] at the Joint Institute of Nuclear Research in Dubna developed an extremely fast on-line isothermal chromatographic method to study the volatility of Rf-chlorides on various column surfaces (stainless steel, teflon, glass). These experiments were designed to chemically identify an isotope of Rf decaying by spontaneous fission (SF) with a half-life of 0.3 s that was previously reported by a team of physicists at the same laboratory [23], and thus confirm the discovery of element 104. The existence of an isotope of Rf decaying by SF with a half-life of 0.3 s could not be confirmed, however [24]. If, indeed, Rf-chlorides were chemically isolated, the recorded SF events must be attributed to the longer-lived ²⁵⁹Rf ($T_{1/2} = 3.1 \text{ s}$). Thus, Zvara *et al.* [22] developed a thermochromatographic method suitable for isolating nuclides with half-lives of a few seconds and longer. In contrast to isothermal chromatography (or frontal chromatography) where a constant column temperature is maintained, in thermochromatography a linearly decreasing temperature profile is established over the length of the column in order to retain the

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volatile halide species at a specific position on the column which is then related to its volatility. Thermochromatography has been applied to the study of the volatile halides and oxyhalides of Rf, 105, and Sg [25–28]. The thermochromatographic method has, up until now, suffered two serious drawbacks in comparison to isothermal chromatography. Detection and identification was based on tracks left on silica plates and only SF decays were registered. Furthermore all information about the half-life of the investigated nuclide is lost. However, by coupling on-line isothermal chromatography to a detection system the unambiguous identification of the separated nuclides became possible. This development began around 1980 when Dinkelage *et al.* [29] constructed an on-line isothermal gas chromatography apparatus and used α -particle spectroscopy to identify short-lived neutron-deficient Hf nuclides separated as volatile HfCl_4 . An attempt to identify the nuclide ^{261}Rf failed due to the destruction of the employed surface barrier detectors by the prolonged exposure to residual Cl_2 gas. A similar apparatus was constructed by Gäggeler *et al.* [30] and used to investigate the behavior of short-lived Po isotopes on various surfaces. This apparatus was called OLGA I (On-line Gas Chromatography Apparatus). In both systems, the volatile atoms or molecules exiting the hot chromatography column were condensed on cooled surfaces of a rotating wheel, which then moved the collected samples to α -particle detectors. Common to both approaches, the reaction products were transported from the target to the chromatography instrument by an aerosol gas-jet transport system. The first unambiguous identification of ^{261}Rf after gas-phase chemical separation as a volatile tetrachloride was accomplished by Türler *et al.* [31] using OLGA II [32]. Instead of condensing the separated molecules on a rotating wheel, they were reattached to new aerosol particles directly at the exit of the column and then rapidly transported to the MG (Merry Go round) detection system described by Hoffman *et al.* [33]. The aerosols were deposited on thin foils mounted on the circumference of a rotating wheel. Periodically, the collected samples were moved between pairs of chemically inert PIPS detectors. Thus, the detection efficiency was twice that of earlier setups. By registering the data in an event-by-event mode the characteristic decay chain of ^{261}Rf and its daughter ^{257}No could be detected. Further experiments by Türler *et al.* [31] found that RfBr_4 exhibited a lower volatility than RfCl_4 . The OLGA II system was then also applied to study the volatility of group 5 bromides [31, 34]. A similar chromatographic system (HEVI, the Heavy Element Volatility Instrument) with a much improved temperature profile was developed by Kadkhodayan *et al.* [35]. This system was used to investigate the relative volatility of Zr, Hf, and Rf tetrachlorides [36]. As predicted by relativistic calculations [18], RfCl_4 was more volatile than HfCl_4 and similar in volatility to ZrCl_4 . This result was confirmed in an independent experiment by Türler *et al.* [37] using the OLGA III system, where Hf and Rf were produced simultaneously and investigated under identical conditions.

In the current work, HEVI was used to study the relative volatility of the group 4 tetrabromides ZrBr_4 , HfBr_4 , and RfBr_4 and to compare the results to our previous studies of the tetrachlorides.

2. Experimental

All of the targets used in these experiments, with the exception of the ^{nat}Cu target, were prepared by electrochemical deposition from a solution of isopropanol [38–40] as a 6 mm diameter circle on a 2.75 mg/cm^2 Be foil $10 \text{ mm} \times 10 \text{ mm}$ in size. This method produces adherent targets which have a quite uniform thickness. The ^{nat}Cu target consisted of a thin (1.14 mg/cm^2) foil of copper purchased from Braun-Knecht-Weimann Co. (San Francisco) mounted on a HAVAR backing.

All irradiations were performed at the Lawrence Berkeley National Laboratory 88-Inch Cyclotron. ^{85}Zr was produced by the $^{nat}\text{Cu}(^{28}\text{Si}, 3p3n)$ reaction. Beam energy out of the cyclotron (laboratory system) was 143 MeV. After passing through a 2.75 mg/cm^2 Be vacuum window, 0.2 mg/cm^2 N_2 cooling gas, and the 1.8 mg/cm^2 HAVAR backing, the final beam energy on target was 86 MeV.

$^{165-167}\text{Hf}$ was produced via $^{nat}\text{Eu}(^{19}\text{F}, xn)$ reactions. Initial beam energy was 116 MeV (laboratory system). The beam energy was degraded by passing through a 2.75 mg/cm^2 Be vacuum window, 0.2 mg/cm^2 N_2 cooling gas, and the 2.75 mg/cm^2 Be target backing and final beam energy (on target) was 96 MeV. The target consisted of 0.86 mg/cm^2 ^{nat}Eu in the form Eu_2O_3 . Typical beam currents of 0.1 particle μA ($\text{p}\mu\text{A}$) were used.

The $^{248}\text{Cm}(^{18}\text{O}, 5n)$ reaction was used to produce the 75-s ^{261}Rf . Initial beam energy (laboratory system) was 117 MeV, and final beam energy on target (after energy degradation through window, cooling gas, and backing) was 99 MeV. Typical beam currents of $0.5 \text{ p}\mu\text{A}$ were used throughout the experiment. The thickness of the ^{248}Cm target was 0.8 mg/cm^2 in the form of Cm_2O_3 (96.5% ^{248}Cm , 3.5% ^{246}Cm).

All nuclear reaction products were transported from the production chamber to the gas chromatography system using either a MoO_3 or KBr aerosol gas jet transport system. The reaction products recoiling out of the target are attached to these aerosols suspended in He gas and are transported through a 3-mm Teflon capillary to the entrance of HEVI [35]. Transport yields were 60–80%. This gas jet system has been used extensively in the past with different aerosol materials [41–43]. Previous experiments used both KCl and MoO_3 in attempts to find a material with a low vaporization point which would not affect the formation of the group 4-halides within the chromatography system or coat the quartz column surface. MoO_3 was found to be superior to KCl in the latter respect and was used initially for the experiments with ^{261}Rf . In further experiments it was observed that KBr did not coat the column surface to the same extent as KCl . KBr was thus chosen as the aerosol material for the homolog-bromide experiments due to this fact and the absence of oxygen in the structure, which might in the case of MoO_3 contribute to the production of oxyhalides rather than the pure tetrahalides.

After transport to the entrance to HEVI the aerosols are collected on a plug of quartz wool kept at 900°C . The high temperature of this section of the quartz column vaporizes the aerosol particles leaving the reaction products on the quartz wool plug. A second gas stream consisting of HBr (100 ml/min) is introduced into the column, where it bromi-

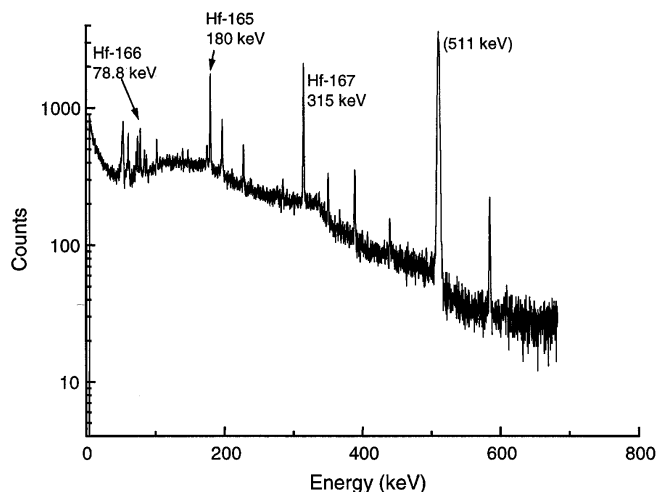


Fig. 1. γ -Spectrum of yield check collection for the $^{nat}\text{Eu}(^{19}\text{F}^{5+}, \text{xn})$ $^{165,166}\text{Hf}$ reaction.

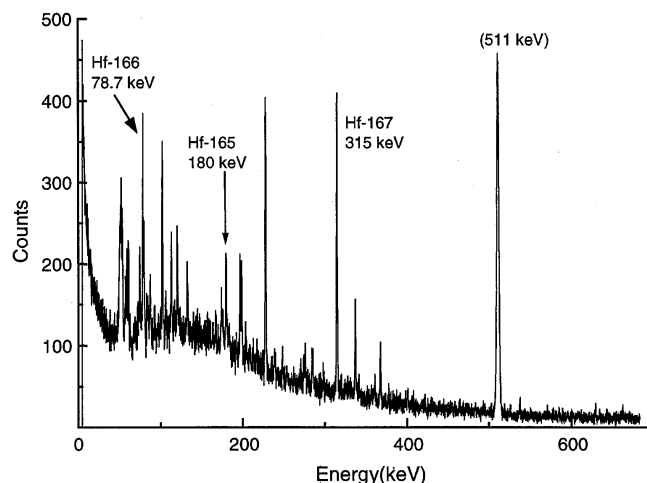


Fig. 2. γ -Spectrum of gas chromatography collection for the $^{nat}\text{Eu}(^{19}\text{F}^{5+}, \text{xn})$ $^{165,166}\text{Hf}$ reaction. Isothermal temperature = 500°C.

rates the reaction products. These volatile bromide compounds enter the remaining isothermal section of the quartz chromatographic column, which is kept at a series of lower temperatures between 50° and 650°C during successive experiments. At column temperatures where the group 4 bromides become volatile they will travel through the column essentially without delay, while less volatile compounds are retained. Most of the nuclides interfering with detection form less volatile trihalides that are retained at all the experimental temperatures (<700°C) and decay in the column.

The fraction of molecules that are detected at the exit thus depends primarily on the retention time of the molecule on the column surface and the half-life of the nuclide, and will not be limited by production of interfering activities. By measuring the yields at different temperatures the retention times in the column can be determined using the half-life of the investigated nuclide as an internal clock, with a 50% chromatography yield observed for a retention time equal to the half-life of the decaying nuclei. By applying the laws of ideal isothermal chromatography [34] or a more sophisticated microscopic model based on a Monte Carlo approach [44], the enthalpy of adsorption on the column surface (ΔH_a) can be determined.

At the exit of the chromatography column the separated molecules enter the recluster chamber, where the gas stream is cooled via adiabatic expansion and where they are reattached to new aerosol particles of the same type and transported in a He carrier gas to an appropriate collection/detection site.

At each temperature the relative yield of the volatile halide of the isotope under study is measured. First, a *yield check* measurement is made by routing the He aerosol containing the isotopes under study directly to the detection apparatus. Two *gas chromatography* measurements are then taken in the normal manner. Another yield check is taken, and the relative yield for that temperature is calculated based on the ratio of the activity measured after the gas chromatography system to the activity measured in the yield checks, taking into account the variations in beam current, time of collection, and flow rate of the gas jet.

By performing a series of experiments at different temperatures, a graph of the yield of a particular species vs. temperature may be constructed, showing the volatility of the species. The volatility is reported here as a *volatility temperature*, which is defined as the temperature at which the yield of the compound is 50% of the maximum yield observed.

In the case of the Zr and Hf compounds, detection of the products was achieved by the observation of characteristic gamma rays. The gamma detection system consisted of a teflon collection site in front of an EG&G Ortec intrinsic germanium γ -ray detector. Data collection was performed using the ORTEC Ace 4-K system with a PC and consisted of a 4096 channel spectrum for each collection.

Activity entered the collection site via the aerosol gas-jet transport system and was collected on a glass fiber filter, while the helium gas passes through. This collection site sits directly in front of the face of the detector and counting of the sample takes place as the activity is collected on the glass fiber filter. This filter is replaced after each collection. The resulting gamma spectra are analyzed using the SAMPO code [45] for peak fitting, energy and efficiency calibration as well as deconvolution of multiple peaks. The calculation of yield was based on the most intense photopeak of each isotope seen in the spectrum, and was corrected for variations in the beam current and the dead time of the ADC. Typical gamma spectra for the experiments with the homologous element Hf are shown in Figs. 1 and 2. Fig. 1 shows the gamma spectrum for the yield check collection from the $^{nat}\text{Eu}(^{19}\text{F}, \text{xn})$ $^{165-167}\text{Hf}$ reaction taken immediately prior to the gas chromatography collections at 500°C. Fig. 2 shows the gamma spectrum for the first gas chromatography collection at 500° for the same experiment.

Detection of ^{261}Rf was accomplished via α spectroscopy using the Merry-Go-Around (MG) system [33]. The separated molecules, which were sorbed on the surface of the recluster aerosol, are then continuously transported through a thin capillary from the recluster chamber to the MG system. There they are deposited successively on 80 thin (0.040 ± 0.01 mg/cm²) polypropylene foils, arranged around the periphery of a 51-cm diameter wheel. The wheel

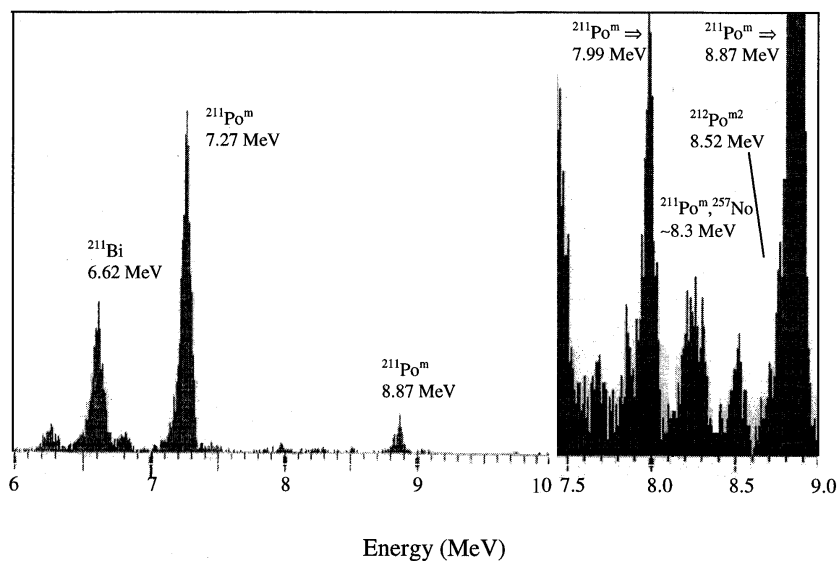


Fig. 3. α -spectra from gas chromatography collection from the $^{248}\text{Cm}(^{18}\text{O}, 5n)^{261}\text{Rf}$ reaction. Left: 6.0 MeV to 10.0 MeV region. Right: 7.5 MeV to 9.0 MeV region with increased vertical scale.

is rotated at preset intervals between 6 pairs of Passivated Ion Implanted Planar Silicon (PIPS) detectors, each pair arranged with one detector above and one detector below the wheel, allowing a solid angle detection efficiency of approximately 60% for α - and spontaneous fission (SF) decay. The entire apparatus is kept under vacuum, and the He gas stream is evacuated through a chemically inert vacuum pump and the exhaust neutralized in a scrubber system. The stepping rate of the wheel is varied depending on the half-life of the isotope under study. For the ^{261}Rf experiment, the wheel was stepped at 1-min intervals. After two complete rotations, each wheel is replaced with a new wheel containing clean foils in order to minimize the buildup of long-lived activities and the aerosol clustering material.

The Realtime Data Acquisition System (RAGS) [46] was used to record the data. Signals from the α - and SF events are amplified and digitized using an ORTEC AE811 analog to digital converter (ADC). Each event is then stored in list mode with the time of the event, detector identity, and channel number. Fig. 3 shows the sum of the α -spectra between 6 and 10 MeV for all gas chromatography collections for the first 3 minutes of counting. The measured yield of ^{261}Rf was corrected for variations in the beam current throughout the run as well as the presence of α -events within the expected energy range (8.12–8.38 MeV) which were due to the presence of reaction products of Pb impurities in the target, mainly $^{211}\text{Po}^m$.

3. Results and discussion

A microscopic model developed by Zvara which uses a Monte Carlo simulation [44] was used to determine adsorption enthalpy values for all compounds based on their observed volatilities. The Monte Carlo model simulates the passage of molecules along the quartz column, taking into account the characteristics of the molecule and the gas chromatographic column to calculate an expected yield curve of the % of molecules passing through the column before they decay, as a function of temperature. The best fit of the calculated curves to all experimental points presented as observed yield as a function of temperature gives

the best estimate for the value of adsorption enthalpy. The uncertainties reported for the adsorption enthalpy values are based on a combination of uncertainty in the observed yield, true volume flow rate, density of the expected compound, and in the case of ^{261}Rf , half-life.

Unexpectedly high yields were observed at low isothermal temperatures for a variety of compounds both in these studies as well as in previous studies using HEVI [35, 36, 47, 48]. During some of the same experiments, a high yield of radionuclides expected to form nonvolatile compounds, such as ^{94}Sr , were simultaneously observed at isothermal temperatures of 50°C to ~200°C. Yields of these nonvolatile compounds were observed to drop off to 0% yield at temperatures of ~200°C or more. This yield of nonvolatile compounds indicated that some mechanism other than gas phase chromatography was responsible for transport through the column at low temperatures, possibly incomplete destruction of the transport aerosols. Relative yields for Zr, Hf, and Rf (Figs. 4, 5, and 7) are thus shown only for isothermal temperatures $\geq 150^\circ\text{C}$ where this effect is minimized.

Zirconium bromides

Fig. 4 shows the relative yield curve for 7.9-min ^{85}Zr . From these data a volatility temperature of 250°C and a calculated adsorption enthalpy of -108 ± 5 kJ/mol is obtained for $^{85}\text{ZrBr}_4$, somewhat less than the results for $^{98}\text{ZrBr}_4$ of -91 ± 6 kJ/mol reported by Kadkhodayan [35]. The current studies used KBr rather than MoO_3 as was used for Kadkhodayan's work, but showed no indication that the column was coated with the aerosol salt. Kadkhodayan reported his results as preliminary, and observed very low yields at all temperatures.

Our current volatility measurement for $^{85}\text{ZrBr}_4$ agrees with results of similar experiments performed with OLGA III [49] on ZrCl_4 . Türler *et al.* report volatility temperatures for ^{99}Zr with different chlorinating agents to be between 250°C and 400°C. The lowest volatility temperatures of ZrCl_4 are observed with the chlorinating agent HCl, which

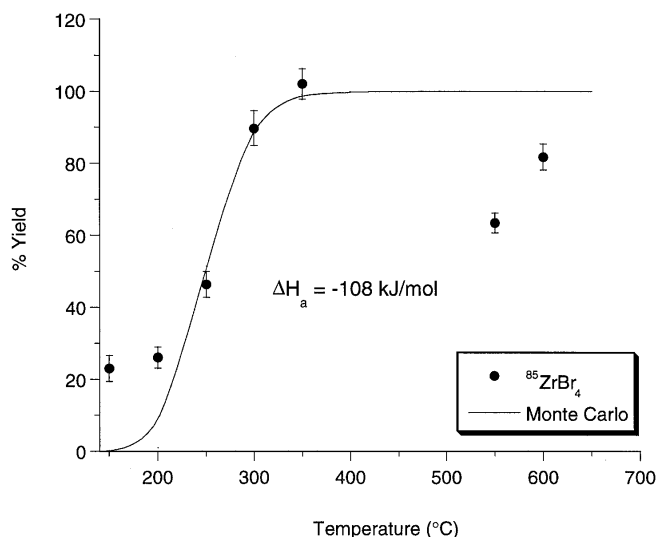


Fig. 4. Normalized volatility (% yield) as a function of isothermal temperature, and the adsorption enthalpy curve obtained from the Monte Carlo analysis with $\Delta H_a = -108 \text{ kJ} \cdot \text{mol}^{-1}$ for $^{85}\text{ZrBr}_4$, from the reaction $^{\text{nat}}\text{Cu}(^{28}\text{Si}, 3\text{p}3\text{n}) ^{85}\text{Zr}$.

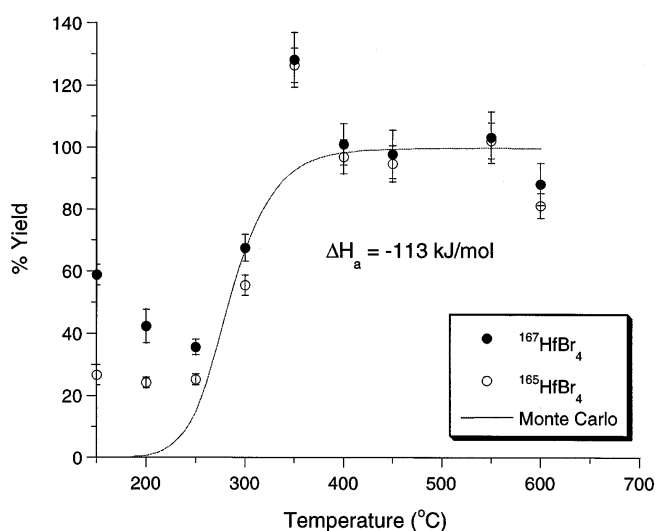


Fig. 5. Normalized volatility (% yield) as a function of isothermal temperature, and the adsorption enthalpy curve obtained from the Monte Carlo analysis with $\Delta H_a = -113 \text{ kJ} \cdot \text{mol}^{-1}$ for $^{165,167}\text{HfBr}_4$, from the reaction $^{\text{nat}}\text{Eu}(^{19}\text{F}^{5+}, \text{xn}) ^{165-167}\text{Hf}$.

is analogous to the brominating agent HBr used in these experiments.

Hafnium bromides

Both 1.26-min ^{165}Hf and 2.0-min ^{167}Hf were produced in the reaction $^{\text{nat}}\text{Eu}(^{19}\text{F}^{5+}, \text{xn})$, and the results are shown in Fig. 5. The observed volatility temperature for both $^{165}\text{HfBr}_4$ and $^{167}\text{HfBr}_4$ was 280°C , and the calculated adsorption enthalpy for HfBr_4 based on these results was $-113 \pm 5 \text{ kJ/mol}$ for both isotopes.

Rutherfordium bromides

^{261}Rf was produced in the reaction $^{248}\text{Cm}(^{18}\text{O}, 5\text{n})$ and a half-life of 74^{+7}_{-6} s was calculated after a multi-component

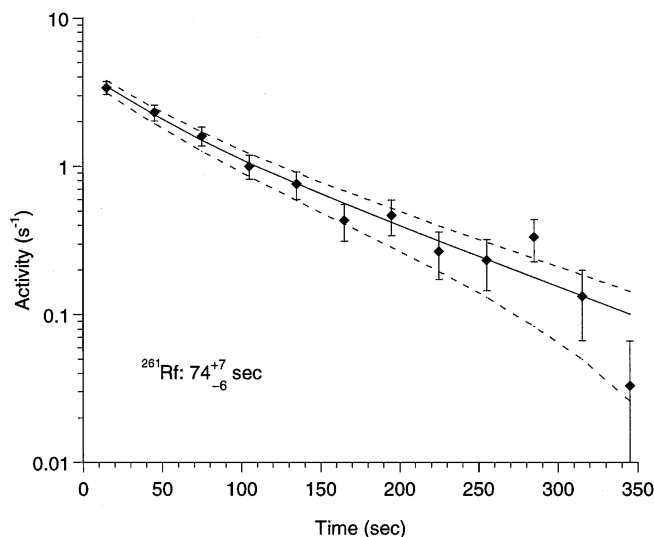


Fig. 6. α -decay data for energy region 8.12–8.38 MeV. A maximum likelihood decay (MLDS) fit was used to fit the half-life of ^{261}Rf , assuming the presence of the daughter (^{257}No) and a single interfering component ($^{211}\text{Po}^{\text{m}}$). The solid line gives the best fit to the data for a half-life of ^{261}Rf of 74 s, while the dashed lines represent the upper and lower 68% confidence limits given by the statistical standard deviation of the measured count rates (81 s and 68 s, respectively).

decay analysis was performed on events in the 8.12–8.38 MeV region. This region contains activities from ^{261}Rf and its ^{257}No daughter, and the unrelated interfering component $^{211}\text{Po}^{\text{m}}$. For half-life analysis, both the half-life and initial activity of ^{261}Rf were allowed to vary. The half-life of the daughter ^{257}No was held constant at 26 s while the initial activity was allowed to vary. For the unrelated $^{211}\text{Po}^{\text{m}}$, the half-life was fixed at 25.2 s, and its initial activity was fixed at 0.25% of the activity of the major $^{211}\text{Po}^{\text{m}}$ peak measured between 7.10 and 7.36 MeV. The data and best fit are shown in Fig. 6.

This result is in excellent agreement with the value of 78^{+11}_{-6} s previously measured by Kadkhodayan *et al.* [36]. Both values are expected to be better than the early value of 65 ± 10 seconds measured by Ghiorso *et al.* [50] due to the ability of HEVI to separate out nonvolatile interfering activities prior to counting. Based on our experiment and the previous experiment of Kadkhodayan, a weighted average value of $75.5 \pm 6.6 \text{ s}$ for ^{261}Rf was calculated. The recommended best value is $75 \pm 7 \text{ s}$.

The yield dependence vs. temperature for ^{261}Rf tetrabromide is shown in Fig. 7. The volatility temperature of $^{261}\text{RfBr}_4$ was determined to be 175°C , and a corresponding adsorption enthalpy of $-87 \pm 7 \text{ kJ/mol}$ was determined from the Monte Carlo best fit to the data.

4. Conclusions

The lighter group 4 compound (ZrBr_4) was found to be slightly more volatile and have a larger adsorption enthalpy than HfBr_4 . Were this trend to continue down the group, RfBr_4 would be expected to be less volatile than HfBr_4 . The reverse has been observed, and the volatility for the group 4 bromides has been established to decrease in the order: $\text{RfBr}_4 > \text{ZrBr}_4 \geq \text{HfBr}_4$. Table 1 gives the results of these experiments.

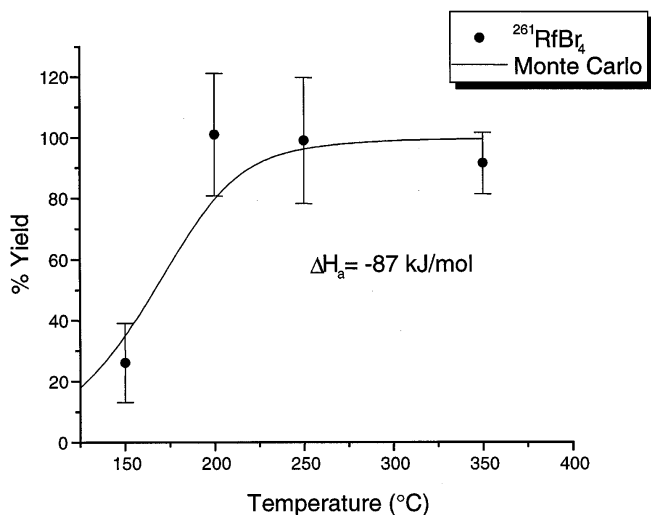


Fig. 7. Normalized volatility (% yield) as a function of isothermal temperature, and the adsorption enthalpy obtained from the Monte Carlo analysis is with $\Delta H_a = -87 \pm 7 \text{ kJ} \cdot \text{mol}^{-1}$ for $^{261}\text{RfBr}_4$, from the reaction $^{248}\text{Cm}(^{18}\text{O}, 5n)^{261}\text{Rf}$.

Table 1. Volatility Temperatures and adsorption enthalpy values for the group 4 tetrabromides obtained in this work. All experiments were performed with HBr as the brominating agent and KBr as the transport aerosol material.

Compound	Volatility Temp. (°C)	ΔH_a^0 (kJ/mol)
$^{85}\text{ZrBr}_4$	250	-108 ± 5
$^{165}\text{HfBr}_4$	280	-113 ± 5
$^{167}\text{HfBr}_4$	280	-113 ± 5
$^{261}\text{RfBr}_4$	175	-87 ± 7

For the chlorides, Kadkhodayan *et al.* observed that ZrCl_4 was more volatile than RfCl_4 [36, 47]. The volatility temperatures and adsorption enthalpies reported for Zr and Rf were extremely close, 175°C for both ZrCl_4 and RfCl_4 , resulting in adsorption enthalpy values of $-74 \pm 5 \text{ kJ/mol}$ and $-77 \pm 6 \text{ kJ/mol}$, respectively. The difference in assigned volatility order between the chlorides ($\text{Zr} \geq \text{Rf} > \text{Hf}$) and the bromides ($\text{Rf} > \text{Zr} \geq \text{Hf}$) may be a result of overlapping errors rather than a true difference in chemical behavior; theoretical predictions indicate $\text{Rf} > \text{Zr} > \text{Hf}$. Fig. 8 shows the results of the experiments presented in this work and Kadkhodayan's work with the chlorides [36, 47]. The reversal of the periodic trend is evident in the comparatively low adsorption enthalpy values (high volatilities) for the Rf-halides.

All of the bromide species studied were observed to be slightly less volatile than their corresponding chloride species (MCl_4). This is in good agreement with physicochemical data for macroscopic amounts [49, 51] as well as with previous experimental work [31] using OLGA II. Recent experimental results comparing the volatilities of the group 4 oxychlorides (MOCl_2) with those of the tetrachlorides also support the conclusion that the compounds observed in this research were the tetrabromides. Türlér *et al.* [37] have observed $^{165}\text{HfOCl}_2$ and $^{261}\text{RfOCl}_2$ to be volatile only

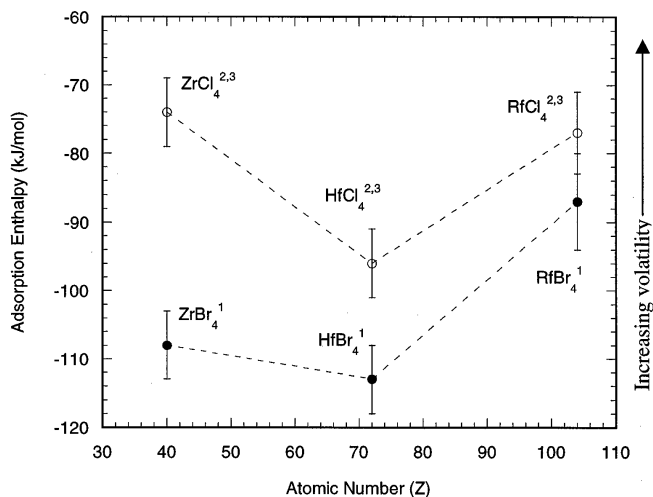


Fig. 8. Adsorption enthalpy values for the group 4 bromides and chlorides. ● = Bromides, ○ = Chlorides. References given are: ¹this work, ²[36], ³[47].

at temperatures in excess of 350°C , and the volatilities of the species observed here are well below this temperature.

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