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Journal of Alloys and Compounds 271–273 (1998) 316–321

Journal of ALLOYS AND COMPOUNDS

Thermochromatography of heavy actinides adsorption of No-259 on Ti, V, Nb, Ta and Mo

Steffen Taut[a,*], S. Hübener[a], B. Eichler[b], A. Türler[b], H.W. Gäggeler[b,c], S.N. Timokhin[d], I. Zvara[d]

[a]*Forschungszentrum Rossendorf e. V., Institut für Radiochemie, P.O. Box 510119, D-01314 Dresden, Germany*
[b]*PSI Villigen, Labor für Radio- und Umweltchemie, Villigen, Switzerland*
[c]*Universität Bern, Departement für Chemie und Biochemie, Bern, Switzerland*
[d]*JINR Dubna, Flerov Laboratory of Nuclear Reactions, Dubna, Russia*

Abstract

The adsorption of elemental No on Ti, V, Nb, Ta and Mo was studied in comparison to Cf, Es and Fm by thermochromatography. The adsorption enthalpy values of No show the predicted metallic divalency of this element. This is confirmed by calculations with two semiempirical models developed by Eichler [1] and Miedema [2]. Using the experimentally proved correlation between adsorption and sublimation enthalpies, we calculated the No sublimation enthalpy to be 134±15 kJ mol^{-1}. © 1998 Elsevier Science S.A.

Keywords: Thermochromatography; ^{259}No; Adsorption; Sublimation enthalpy

1. Introduction

In contrast to the lighter actinides up to Fm, for the heaviest actinides there is no possibility to measure metallic properties directly. The standard method, vaporization experiments with the Knudsen effusion technique, was used successfully up to Fm [3]. It requires at least picogram quantities [4] which are not available for No.

Adsorption studies are suitable to measure such properties indirectly [5]. A characteristic feature of the thermochromatographic method is the possibility to simultaneously investigate several elements in one experiment, even if these elements are available in amounts of only a few atoms [6–9]. In the present work, we investigated the adsorption of ^{259}No (half life: 1 h) onto Ti, V, Nb, Ta and Mo.

2. Experimental

2.1. Production of No-259

The experiments were carried out at the U-400 cyclotron of the Flerov Laboratory of Nuclear Reactions, Dubna (FLNR) and at the Philips cyclotron at Paul Scherrer Institut, Villigen (PSI) in both cases using the PSI target chamber equipment [10].

Targets of 1.01 mg cm^{-2} (FLNR) and 0.65 mg cm^{-2} (PSI) ^{248}Cm were irradiated for 4 h with ^{18}O. The beam energy on target was 99 MeV, the beam intensities were 3×10^{12} (FLNR) and 1×10^{12} (PSI) particles per second. Under these conditions, ^{259}No is produced in the ^{248}Cm (^{18}O, α3n) ^{259}No reaction with a cross-section of about 30 nb [11,12]. Cf, Es and Fm nuclides are produced as transfer products with cross-sections in the μb range [12].

Five μm Ti catcher foils were mounted at a short distance behind the target in order to collect the nuclear reaction products. Ti was chosen because diffusion experiments with rare earth elements in Ti [13] indicated a fast vaporization kinetic. We confirmed this by evaporation studies of Sr as model substance for divalent elements. Another important property of Ti is its ability to form very stable solid solutions with oxygen. Thus, Ti is a strongly reducing substance. As shown in [14], actinides are desorbed from Ta backings covered with Ti as atoms, not as oxides. Therefore, the Ti catcher foils were used as thermochromatographic samples without any further time-consuming preparations.

2.2. Thermochromatographic experiments

The thermochromatographic setup is similar to the one described in detail elsewhere [9]. We chose for the No

*Corresponding author. Tel.: 49 351 2602895; fax: 49 351 2603553; e-mail: taut@fz-rossendorf.de

PII S0925-8388(98)00079-6

Table 1
Experimental parameters

Column	Start temperature (K)	Temperature gradient (K cm^{-1})	Normalized column area (cm^2 per cm column length)	Carrier gas flow (cm^3 min^{-1})
Ti	1480	42.4	1.35	230
V	1480	24.4	1.35	230
Nb	1480	42.4	1.35	230
Ta	1480	42.4	1.35	230
Mo	1480	24.4	1.35	230

experiments column support tubes made from quartz glass instead of tantalum because the adsorption temperatures of Cf, Es and Fm, even on Mo, are below the melting point of quartz. The inside of these quartz glass tubes were lined with thin tantalum foils in order to absorb the oxygen emitted from the quartz at high temperatures. Table 1 lists the experimental parameters of the thermochromatographic experiments.

After 20 min thermochromatography time the columns were cut into 1 cm pieces which were counted off-line in an α-spectrometer with PIPS detectors for at least 4 h in intervals of 30 min. The whole procedure, from the end of bombardment until the start of spectroscopy, lasted about 1 h.

2.3. Alpha spectra analysis

All alpha spectra were analyzed manually with the commercially available Microcal™ Origin™ Peak Fitting Module, which we customized for alpha spectroscopic purposes.

The analysis of the ^{259}No spectra is somewhat difficult because its α branch exhibits a multiplet of five lines that is spread in the broad energy range from 7.455 to 7.685 MeV [15]. As expected, we did not observe distinguishable peaks from the few α events from ^{259}No that were detected (see Section 3). Fortunately, there are only two interferences with α active nuclides: ^{250}Fm which has a strong line at 7.430 MeV and there is an activity at 7.69 MeV (^{214}Po?), which is too intensive for the ^{259}No peak at 7.685 MeV compared to the other peaks of the ^{259}No multiplet. Other possible interfering nuclides decayed within the experimental time. In fact, some of them may be produced as daughters of longer lived nuclides. However, all these mother nuclides are separated from the divalent actinides in the thermochromatographic process.

Taking into account both the FWHM of the α spectra (20–25 keV) and the α interferences at 7.43 and 7.69 MeV, events between 7.460 and 7.655 MeV were considered to originate from ^{259}No. The activity observed in this energy range always disappeared within the first 2 h of α spectroscopy which is in agreement with the 1 h half life of ^{259}No. Fig. 1 shows the sum of the spectra where ^{259}No was observed on the Nb column.

2.4. Calculation of adsorption enthalpies

The adsorption temperatures are correlated to the adsorption position on the thermochromatographic column. To calculate the corresponding enthalpies, we used the algorithms from [16,17].

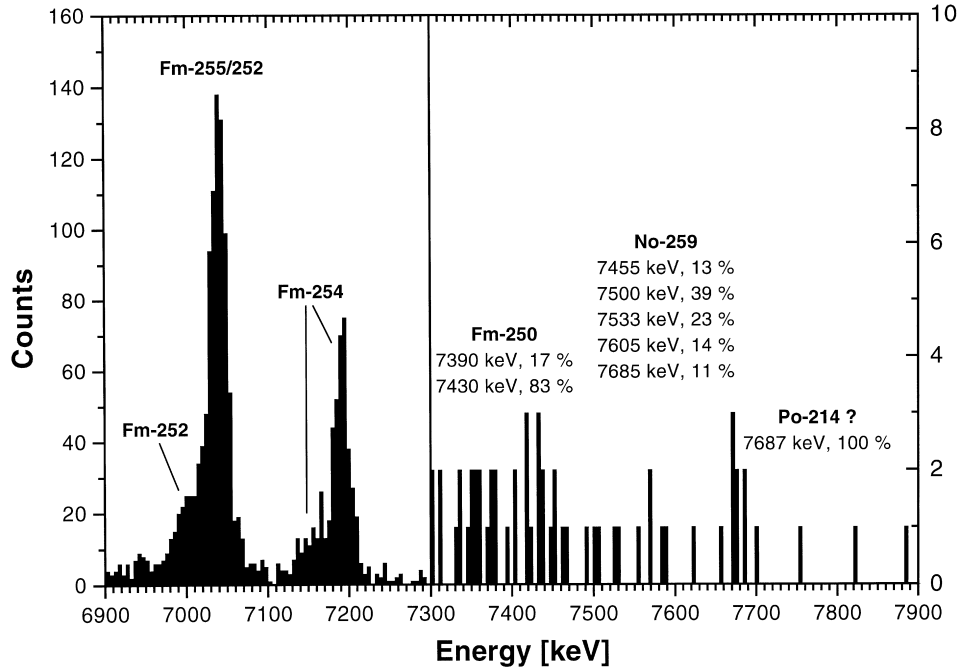

Fig. 1. ^{259}No α spectrum on a Nb column.

3. Results and discussion

Fig. 2 shows the distribution of Cf, Es, Fm and No on a Nb column obtained at FLNR. All elements shown were simultaneously investigated in a single thermochromatographic experiment.

In the Nb experiment we observed a total of 16 ^{259}No events. An estimation of the ^{259}No activity to be expected after the chromatographic experiment results in about ten ^{259}No α events in the first hour of spectroscopy, taking the FLNR irradiation conditions into account and using as input data a cross-section of 30 nb [11,12], a catching efficiency of 80%, a chemistry efficiency of 15%, 1 h between end of bombardment and start of spectroscopy, and a counting efficiency of 25%. This is in rather good agreement with our observation, considering the uncertainty of the chemistry efficiency.

3.1. The Eichler and Miedema models

It is presently impossible to calculate adsorption enthalpies of actinides ab initio. Therefore, a quantitative discussion of the adsorption enthalpies is only possible using semiempirical approaches. Eichler [1] and Miedema [2] developed similar models for describing adsorption of (metal) atoms on metallic substrates. Both have the common idea of the adsorption enthalpy as a sum of the desublimation enthalpy and a net adsorption enthalpy term:

$$\Delta H_{\text{ads A on B}} = -\Delta H_{\text{subl A}} + \Delta H_{\text{ads A on B, netto}} \quad (1)$$

$\Delta H_{\text{ads A on B}}$ – enthalpy of adsorption of adatom A on adsorbent metal B, $\Delta H_{\text{subl A}}$ – sublimation enthalpy of A, $\Delta H_{\text{ads A on B, netto}}$ – netto adsorption enthalpy term.

The Eichler model describes the adsorption onto the surface layer of B as:

$$\Delta H_{\text{ads A on B, netto}} = 0.6(\Delta H_{\text{sol, A in B}} - V_{\text{A in B}}/V_{\text{B}}\,\Delta H_{\text{VVF}}). \quad (2)$$

$\Delta H_{\text{sol, A in B}}$ – enthalpy of solution of A in B, $V_{\text{A in B}}$ – molar volume of A soluted in B, ΔH_{VVF} – volume vacancy formation enthalpy.

This is true for $\Delta H_{\text{sol, A in B}} > 50$ kJ mol^{-1}. If $\Delta H_{\text{sol, A in B}}$ is smaller, A will be adsorbed into the surface layer of B:

$$\Delta H_{\text{ads A on B, netto}} = 0.9(\Delta H_{\text{sol, A in B}} - V_{\text{A in B}}/V_{\text{B}}\,\Delta H_{\text{VVF}}) + V_{\text{A in B}}/V_{\text{B}}\,\Delta H_{\text{SVF}}. \quad (3)$$

ΔH_{SVF} – surface vacancy formation enthalpy.

In the Miedema approach the netto adsorption term is mainly a function of the surface energies γ^0_{A} and γ^0_{B} [18] of both adsorpt and adsorbent metal:

$$\Delta H_{\text{ads A on B, netto}} = F\gamma^0_{\text{B}}S_{\text{A}} + (1-F)\gamma^0_{\text{A}}S_{\text{A}} + F\,\Delta H_{\text{sol, A in B}}. \quad (4)$$

F – normalized surface area of A atoms in contact with B, $0 \le F \le 1$, γ^0_{X} – surface energy of metal X at zero temperature, S_{X} – molar surface area of metal X with F being the normalized contact area between A and B.

The unknown values of the actinides $\Delta H_{\text{sol, A in B}}$ and γ^0_{A}, which are necessary for the model calculations, can be estimated as described in detail in [19,20] and [18], respectively.

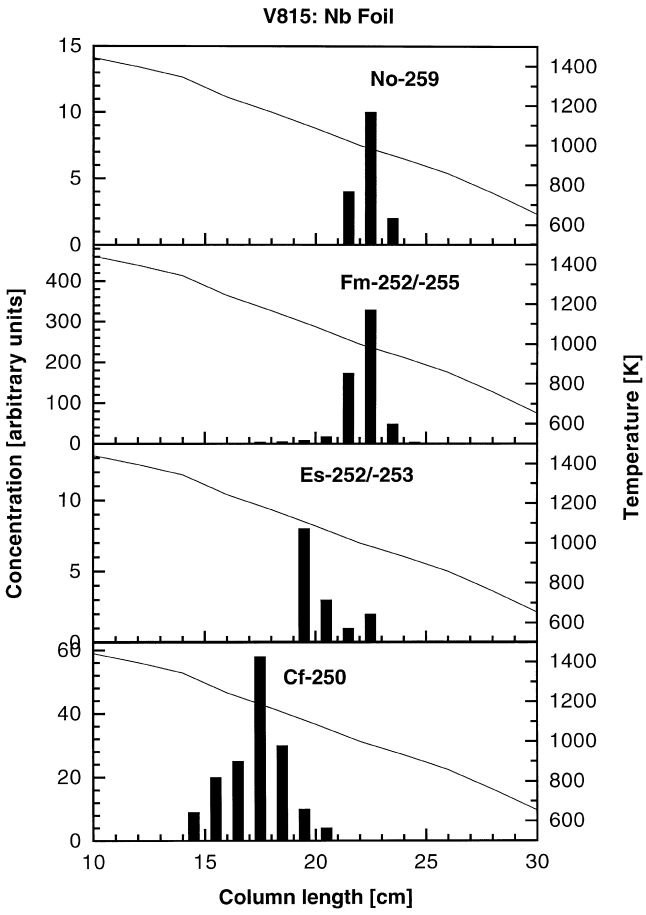

Fig. 2. Thermochromatogram of Cf, Es, Fm and No on a Nb column.

3.2. Adsorption behavior

Table 2 lists the adsorption data measured in comparison with literature data and the results of both Eichler and Miedema model calculations. The experimental data are consistent with the models. Furthermore, the calculations reproduce the experimental correlation between adsorption and sublimation enthalpies.

The adsorption behavior of Cf, Es, Fm and No on V, Nb, Ta and Mo is rather similar. The Eichler model clearly predicts an adsorption of Es, Fm and No in the divalent state onto the surface of these adsorbent metals. Also assuming that the adsorption of Cf is onto the surface, the Eichler model calculation agrees with the experimental

Table 2
Experimental adsorption data compared to Eichler [1] and Miedema model [2] calculations

Element	Column	Adsorption enthalpy (kJ mol^{-1})			
		Experimental	Eichler model, ads. onto surf. [1]	Miedema model [2]	F
Cf	Ti	−201 [9]	−285 (divalent)	−219 (divalent)	0.27
			−308 (trivalent)	−349 (trivalent)	0.27
	V	−296 [9], −302 [9]	−341 (divalent)	−294 (divalent)	0.15
	Nb	−290 [9], −288 [9]	−297 (divalent)	−297 (divalent)	0.15
	Ta	−309 [9]	−361 (divalent)	−325 (divalent)	0.10
	Mo	−326 [9], −305 [9]	−339 (divalent)	−330 (divalent)	0.10
Es	Ti	−220 [8], −189 [9]	−241	−176	0.27
	V	−284 [9], −276 [9]	−293	−252	0.15
	Nb	−290 [8], −268 [9], −269 [9]	−250	−254	0.15
	Ta	−284 [9]	−310	−283	0.10
	Mo	−314 [9], −291 [9]	−291	−288	0.10
Fm	Ti	−210 [8], −182 [9]	−212	−159	0.27
	V	−271 [9], −262 [9]	−260	−229	0.15
	Nb	−270 [8], −241 [9], −250 [9]	−221	−231	0.15
	Ta	−280 [8], −267 [9]	−277	−258	0.10
	Mo	−290 [8], −284 [9], −279 [9]	−257	−262	0.10
No	Ti	−177	−221	−171	0.27
	V	−258	−268	−248	0.15
	Nb	−241	−231	−250	0.15
	Ta[a]	−258	−289	−279	0.10
	Mo[a]	−277	−264	−284	0.10

F – normalized surface area of A atoms in contact with B, $0 \leq F \leq 1$.
[a] Only 1 α event of ^{259}No detected.

adsorption enthalpy, regardless of the valency of Cf in the adsorbed stated being di- or trivalent.

The Miedema model shows good agreement with the experimental data if the contact surface F between the actinide atoms and the adsorbent is about 10 to 15%. This confirms the Eichler model result of an onto surface adsorption.

The experimental adsorption enthalpies on Ti are in

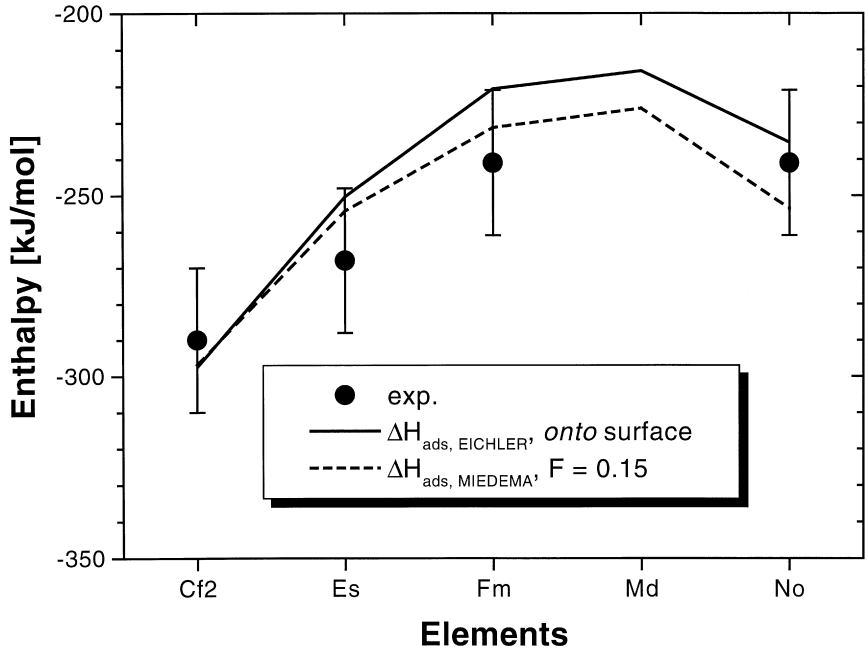

Fig. 3. Adsorption enthalpies on Nb.

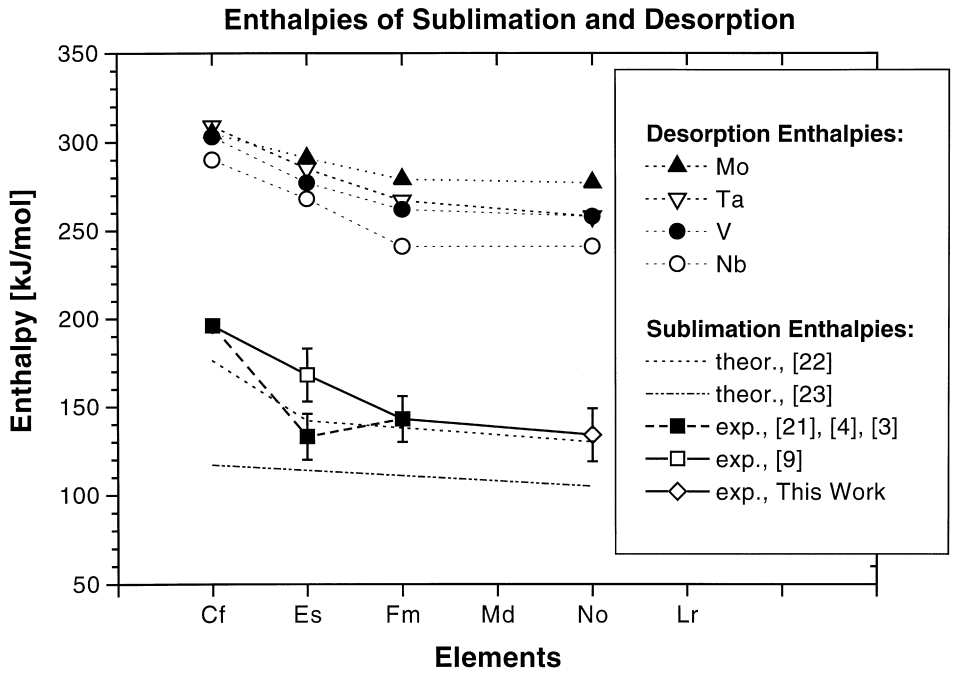

Fig. 4. Desorption enthalpies compared with experimental and theoretical sublimation enthalpies of heavy actinides; experimental sublimation enthalpies from: Cf [21], Es [4,9], Fm [3]; theoretical calculations from [22,23].

good agreement with the Miedema approach if $F = 0.27$. This indicates a deeper adsorption in comparison to V, Nb, Ta and Mo.

As an example, Fig. 3 shows the experimental adsorption enthalpies on Nb together with the Eichler and Miedema model curves.

3.3. The sublimation enthalpy of No

No is always adsorbed at only slightly lower temperatures than Fm. The model calculations showed that $\Delta H_{\text{ads A on B, netto}}$ for Fm and No has similar values. No should have, therefore, a sublimation enthalpy similar to Fm (see Eq. (1)).

We calculated this value using the experimentally proved correlation between adsorption and sublimation enthalpies as shown in [9]. As input data for the regression calculations we chose the following sublimation enthalpy values for Cf, Es and Fm: 196.4 kJ mol^{-1} [21], 167 kJ mol^{-1} [9] and 141.5 kJ mol^{-1} [3], respectively. The resulting value of ΔH_{subl} of No is 134 ± 15 kJ mol^{-1}. This is in good agreement with both experimental sublimation enthalpies of the lighter actinides and theoretical calculations as shown in Fig. 4.

Acknowledgements

The authors gratefully acknowledge the continuous interest of Prof. H. Nitsche. This work was supported by both DFG, contract No. Hu642/1-1 and BMBF, contract No. 06DR666I(4)/1.

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