

Predictions of adsorption temperature of element 112 on gold for gas-phase chromatography experiments

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Investigations of chemical properties of element 112 discovered by the GSI laboratory, Darmstadt, are to be conducted by an international collaboration of several experimental groups [1,2]. Element 112, the heaviest man-made transition d-element, is expected to exhibit an unusual chemical behaviour due to the maximum of relativistic effects on the 7s orbital shell in the 7th row of the Periodic Table: Due to the very strong relativistic contraction and stabilization of the 7s electrons and its closed shell ground state configuration, 7s²6d¹⁰, element 112 is expected to be almost as inert as a noble gas and, therefore, volatile.

In view of coming experiments, predictions of adsorption of element 112 on metal surfaces based on quantum-chemical calculations are highly desirable. As a first step in such a study, bonding in the dimers MHg and M112, where M=Pd, Cu, Ag and Au, has been determined using the four-component relativistic density-functional theory method (RDFT) [3]. First calculations of the interaction of Hg and element 112 with small clusters of the above mentioned metals have also meanwhile been reported by our groups [4]. In the present work, a way is suggested to predict the adsorption temperature of an element (in this case of element 112) using thermodynamic equations for the adsorption equilibrium.

In the isothermal chromatography an adsorption temperature, T_{ads} , of a heaviest element (B) in relation to that of its lighter homolog (A) at the established adsorption-desorption equilibrium (the peak of the temperature distribution curve) is usually measured. This corresponds to the condition when $K_A(T_A) = K_B(T_B)$, or using statistical thermodynamics

$$e^{-\Delta E_A / RT_A} \frac{Q_A^s}{Q_A^g} = e^{-\Delta E_B / RT_B} \frac{Q_B^s}{Q_B^g}, \quad (1)$$

where ΔE is the adsorption energy of a species A or B, and Q is their partition function. Due to a model of localized adsorption, where an atom is considered to be bound to the surface and the contribution of the configurational entropy should be taken into account, the equilibrium constant is

$$K = \frac{Q_{\text{conf}}^s Q_{\text{vibr}}^s}{Q_{\text{trans}}^g Q_{\text{rot}}^g} \quad (2)$$

Since experiments for the heaviest elements and their homologs are conducted in the same set up under the same conditions and often simultaneously, any parameter on the left- and right-hand sides of eq. (1) connected with specific experimental conditions cancel, so that the final equation depends only on properties of the adsorbate and on its interaction with the adsorbent, i.e.

$$\begin{aligned} e^{-\Delta E_A / RT_A} \left(\frac{\pi IR_A^2}{d^2} - 1 \right) \frac{T_A^{3/2}}{v_A^3 r_A^3 m_A^{3/2}} &= \\ = e^{-\Delta E_B / RT_B} \left(\frac{\pi IR_B^2}{d^2} - 1 \right) \frac{T_B^{3/2}}{v_B^3 r_B^3 m_B^{3/2}} & \end{aligned} \quad (3)$$

Here m is the mass of a species, IR its ionic radius upon an interaction with the surface, r is atomic radius of the gaseous species, d is the distance between atoms in a metal lattice of the adsorbent, and v is a vibration frequency of the adsorption bond. Using eq. (3), either adsorption temperature of a species can be defined on the basis of the knowledge of its interaction with the surface, or its sublimation enthalpy can be determined from its adsorption temperature, provided T_{ads} and ΔH_{ads} are known for a homologous one. The r values for Hg and element 112 have been, and those for IR can be calculated using the atomic relativistic Dirac-Fock method [5] (Table 1).

Table 1. Properties of Hg and element 112 used for the calculations of T_{ads} of element 112

Property	Hg	112	Comment
$r_{A/B}$, Å	1.815	1.711	$r_{\text{Hg}} - \Delta r_{\text{max}}(\text{Hg}/112)$
$IR(\text{Hg}/112\text{-ads.})$, Å	1.36	1.41	from calc. R_c [3]
$m_{\text{Hg}/112}$, g/at	186	283	used in experiments
$v_0 \cdot 10^{-12}$, s ⁻¹	2.99	2.21	calculated [3]

To give $T_{\text{ads}}(112)$ relative to the experimental $T_{\text{ads}}(\text{Hg})$, $\Delta E_{\text{ads}}(112)$ is taken as “experimental” $\Delta H_{\text{ads}}(\text{Hg})$ (deduced using the Monte-Carlo simulation from an experimental T_A , e.g., of 155 °C [2]) minus the calculated difference in the binding energies of 21.7 kJ/mol between the dimers HgAu and 112Au. The solution of eq. (3) with parameters of Table 1 gives a difference in T_{ads} between Hg and element 112 of 96 degrees. Thus, results of our DFT calculations for the dimers suggest that element 112 should form metal-metal bonding and should be adsorbed at a much higher temperature than that of Rn. This should, however, take place at ideal circumstances (for which the calculations were performed): any deviation from an ideal surface/lattice would result in the formation of the van der Waals bond and a shift of T_{ads} of element 112 in the area of T_{ads} of Rn.

References

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