Prediction of adsorption enthalpies of the SHE 112 and 114 on transition metals

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An empirical adsorption model for the adsorption interaction of light noble gases on metal surfaces is given by Miedema et al. [1]. It assumes a proportionality between the adsorption enthalpy (ΔH^o_{ads}) and the energy of adhesion ($\Delta\gamma_{ad}(A,B)$). The energy of adhesion can be calculated using the surface energies (γ^o) of the elements A (adsorbate) and B (surface) at 0 K[1] (see eqns.1 and 2).

$$\Delta\gamma^{ad}(A,B) = -2\,\Phi\,(\gamma^0(A)\,\gamma^0(B))^{1/2} \qquad (1)$$

$$\Delta H^o_{ads} = -0.71{*}10^9\,F\,\Phi\,V_A^{2/3}\,(\gamma^0(A)\,\gamma^0(B))^{1/2} \qquad (2)$$

Φ ... dissimilarity parameter (calculated) [1]
F ... geometrical factor (empirically 0.31) [1]
V_A ... Volume of the spherical, adsorbed atom

A comparison of a large number of experimentally determined adsorption enthalpies for the light noble gases with such a calculation suggests [1], to calculate the adsorption enthalpies of the light noble gas elements Ne, Ar, and Kr by multiplying known adsorption enthalpies of Xe with empirical constant factors ($C_x(Z,Xe)$); see eqn. 3. Recommended factors are compiled in the upper part of Table 1 for Ne, Ar, Kr and Xe.

$$\Delta H^o_{ads}(Z) = C_x(Z,Xe)\cdot\Delta H^o_{ads}(Xe) \qquad (3)$$

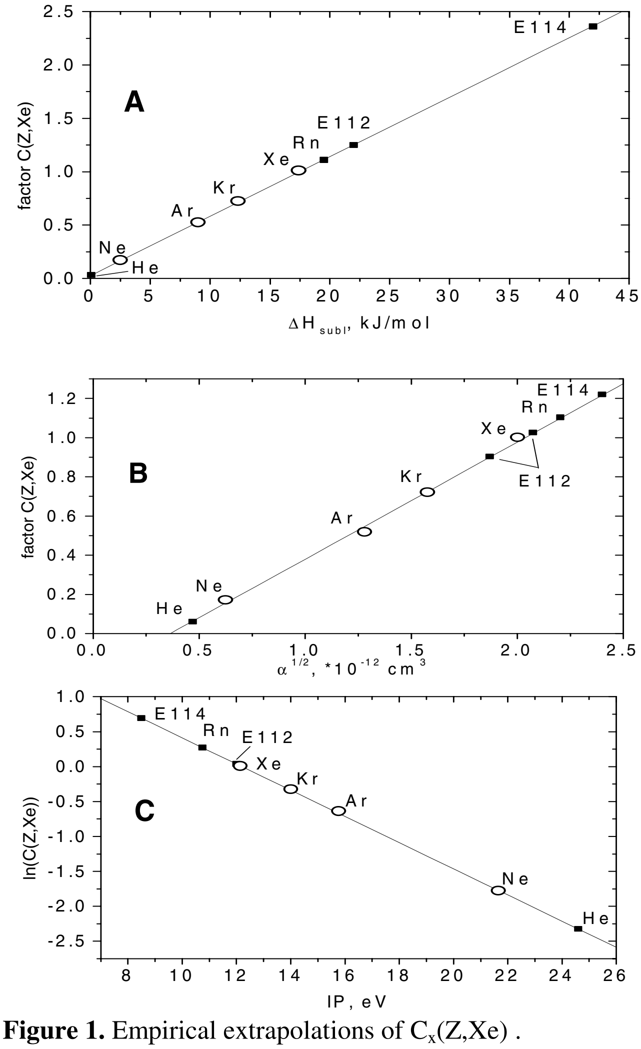

Figure 1. Empirical extrapolations of $C_x(Z,Xe)$.

Three different empirical correlations of $C_x(Z,Xe)$ have been obtained from known properties of adsorbate atoms (circles in Figure 1, A-C): the enthalpy of sublimation (ΔH_{subl}), the polarizability (α), and the ionization potential (IP). The factors extrapolated for the noble gases He and Rn and for the hypothetical noble gas elements 112 and 114 (squares in Figure 1 A-C) are listed in the lower part of Table 1.

Table 1. Empirical factors $C_x(Z,Xe)$ that connect the heat of adsorption of a closed shell atom, **Z,** with the known heat of adsorption of Xe on the same metallic substrate.

Element	$C_A(Z,Xe)$	$C_B(Z,Xe)$	$C_C(Z,Xe)$
Ne	0.17	0.17	0.17
Ar	0.52	0.52	0.52
Kr	0.72	0.72	0.72
Xe	1	1	1
He	0.032	0.12	0.098
Rn	1.11	1.11	1.31
E112	1.25	0.91 1.04	1.04
E114	2.36	1.2	2.00

As a test, adsorption enthalpies of Rn on different transition metals have been calculated with eqn. 3. They agree well with the experimental results from [2]; see Table 2. Even the trend in the adsorption interactions of Rn on the metals Ag<Au<Pd≤Ni is well reproduced. The deviation of Cu is object of further investigations.

Table 2. Comparison of experimental [2] and calculated data for the adsorption of Rn on transition metal surfaces [2]

Metal	$-\Delta H^o_{ads\,(Exp)}$ / kJ/mol	$-\Delta H^o_{ads\,(calc)}$ / kJ/mol
Ag	21±3	26±2
Au	31±3	33±2
Pd	39±3	35±2
Ni	41±3	37±2
Cu	38±3	25±2

Assuming a fictitious noble gas behavior of the elements 112 and 114, we predict adsorption enthalpies on the transition metals Cu, Ag, Au, Pd, and Ni; see Figure 2.

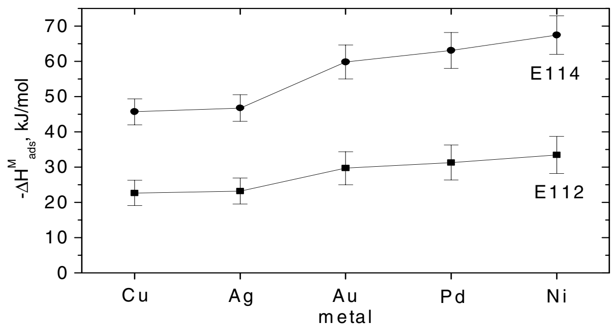

Figure 2. Predicted standard adsorption enthalpies of the hypothetical noble gas elements 112 and 114.

References

[1] A.R. Miedema et al., *Surf. Sci. 104*, 491 (1981).
[2] R. Eichler et al., this GSI report, and *J.Phys.Chem B,* submitted 2001.