Experimental and Predicted Bond Energies of Gaseous Rare-earth Aurides

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Summary The experimental dissociation energies for the diatomic molecules LaAu, CeAu, PrAu, and NdAu are presented and compared with the values that were calculated on the basis of the Pauling concept of a polar bond.

THE available information on gaseous diatomic intermetallic compounds has recently been reviewed by Drowart[1] and by Cheetham and Barrow.[2] Of particular interest is the general high stability of a number of gaseous intermetallic molecules in which gold is a constituent atom, *e.g.* UAu,[3] AlAu,[4,5] SnAu,[6] CrAu,[7] NiAu,[8] CeAu[9] and others.[1,2,10] The high stability of these compounds has in several cases been explained[1,3,5,8] in terms of a polar bond according to a Pauling model.[11] Due to the large electronegativity difference between gold and the rare-earth metals a significant ionic contribution to the bond energy in rare earth aurides could be expected. This expectation has been borne out in the preliminary results for CeAu.[9] The present work contributes to the further testing and possible refinement of the Pauling model of a polar bond and the related electronegativity concept.

The gaseous equilibria LnAu + Au $\rightleftharpoons$ Ln + Au_2, where Ln is either La, Ce, Pr, or Nd, have been studied by means of Knudsen-effusion high-temperature mass spectrometry, using both second- and third-law methods.† The molecules LaAu, PrAu, and NdAu were identified in the gas phase over the same condensed system and using the same experimental conditions as for the molecule CeAu.[9] Their observation was possible because of the lanthanum, praseodymium, and neodymium impurities that were present in the cerium and cerium sulphide used as starting materials.

The free energy functions needed in the third-law evaluations[9] were taken from the literature for La, Ce, Pr, Nd, and Au.[12,13] For the diatomic species they were calculated from standard formulae using the following estimated molecular parameters for LaAu, CeAu, PrAu, and NdAu, respectively: ω_e = 132, 145, 152, and 144 cm.$^{-1}$; r_e = 2·91, 2·86, 2·88, and 2·86 Å; the electronic partition function was assumed to be g = 1, 2, 3, and 4. The resulting $-(G^0_{2000} - H^0_0)/T$ values, are 74·34, 75·50, 76·26, and 76·96 e.u.

The second-law reaction enthalpies, ΔH^0_T, were obtained from the relation: $\Delta H^0_T = -\boldsymbol{R}\mathrm{d}\ln K'/\mathrm{d}(1/T)$ and corrected to the reference temperature in degrees absolute. The equilibria LnAu(g) + Au(g) $\rightleftharpoons$ Ln(g) + Au_2(g) were studied over the temperature ranges 2085—2270° K for Ln = La, 1860—2270° K for Ln = Ce, 2025—2115° K for Ln = Pr, and 1980—2100° K for Ln = Nd. In Table 1 the second- and third-law reaction enthalpies, ΔH^0_0, are summarized, together with the values for the dissociation energies, D^0_0(LnAu) that were obtained with $D^0_0(Au_2)$ = 52 kcal. mol^{-1}.[14] The error term given for the latter includes the estimated overall uncertainties. The LnAu molecules in Table 1 have, together with UAu and AlAu, the highest bond energies between two metal atoms presently known from thermal equilibrium measurements.

The value D^0_0(CeAu) = 75·0 ± 4 kcal. mol.$^{-1}$ is based on somewhat different free energy functions and on a larger number of measurements as compared with the value of 71 ± 5 kcal. mol.$^{-1}$ that was previously reported.[9] As a consequence the previously reported value for $D^0_0(Ce_2)$,[15] becomes 48 ± 6 kcal. mol.$^{-1}$.

The experimentally measured values for the Ln–Au bond energies listed in Table 1 may be interpreted in terms of the

TABLE 1. *Enthalpies of reaction for* LnAu(g) + Au(g) = Ln(g) + Au_2(g)

Reaction and number of data sets evaluated		Method	ΔH^0_0 kcal. mol.$^{-1}$	D^0_0 (LnAu)[a] kcal. mol.$^{-1}$
LaAu(g) + Au(g) $\rightleftharpoons$ La(g) + Au_2(g)	6	3rd law	29·6 ± 0·8	81·6 ± 7
CeAu(g) + Au(g) $\rightleftharpoons$ Ce(g) + Au_2(g)	18	2nd law	22·6 ± 1·2	
		3rd law	23·4 ± 0·4	75·0 ± 4
PrAu(g) + Au(g) $\rightleftharpoons$ Pr(g) + Au_2(g)	6	3rd law	20·3 ± 0·5	72·3 ± 7
NdAu(g) + Au(g) $\rightleftharpoons$ Nd(g) + Au_2(g)	4	3rd law	16·4 ± 1·4	68·4 ± 7

[a] Based on selected values for ΔH^0_0 and on $D^0_0(Au_2)$ = 52 kcal. mol.$^{-1}$, B. Siegel, *Quart. Rev.*, 1965, **19**, 77.

† The mass spectrometric experiments were performed at the Columbus Laboratories of Battelle Memorial Institute.

Pauling model of a polar bond[11] by using the relation: $D(\text{Ln–Au}) = 1/2[D(\text{Ln–Ln}) + D(\text{Au–Au})] + 23[X(\text{Au}) - X(\text{Ln})]^2$ with the slightly higher electronegativity, $X = 1{\cdot}3$, for the rare-earth metals instead of Pauling's values of 1·1 or 1·2.[11]

Using this latter formula, the dissociation energies of all rare-earth aurides have been calculated and are presented in Table 2. They agree well with the experimental data where the latter are available. The covalent single bond energies, $D(\text{Ln–Ln})$, of Sc_2 and Y_2, were taken from Drowart.[1] For La_2 a value was used[16] which was 10 kcal. mol.$^{-1}$ lower than that given by Drowart.[1] The dissociation energies of the lanthanide dimers Pr_2—Lu_2 were estimated in a similar way to that used previously,[15] by assuming a constant α-parameter of 2·34 ± 0·4 that has been based on the experimental D_0^0 values for Sc_2, Y_2, La_2, and Ce_2 and the heats of sublimation, $\Delta H^0_{\text{v},0}$, for the rare-earth metals.[17]

TABLE 2. *Predicted and experimental bond energies of the rare-earth aurides using Pauling model (in* ev)

M	D(M–M)	1/2[D(M–M) + D(Au–Au)]	Calc. D(M–Au)	Expl. D(M–Au)
Sc	1·6	1·9	3·1	
Y	1·6	1·9	3·1	
La	2·1	2·2	3·4	3·5
Ce	2·1	2·2	3·4	3·3
Pr	1·6	1·9	3·1	3·2
Nd	1·4	1·8	3·0	3·0
Sm	0·9	1·6	2·8	
Eu	0·8	1·5	2·7	
Gd	1·8	2·0	3·2	
Tb	1·7	2·0	3·2	
Dy	1·3	1·8	3·0	
Ho	1·3	1·8	3·0	
Er	1·4	1·8	3·0	
Tm	1·0	1·7	2·9	
Yb	0·7	1·5	2·7	
Lu	1·9	2·1	3·3	

The calculated values for the bond energies of the rare-earth aurides are all rather high and vary between 2·7 and 3·4 ev. The estimated uncertainty for ScAu and YAu was ± 0·3 ev. The uncertainty in the values for the estimated bond energies of the gaseous lanthanides aurides yet unobserved is larger, in view of the rather large uncertainties in the estimated dissociation energies for the diatomic symmetric lanthanide molecules and in the electronegativities used. Particularly noteworthy are the high predicted bond energies for EuAu, YbAu, and SmAu. In these molecules the relative ionic contribution to the bonding would, according to the Pauling model, be strongest.

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