Mass-spectrometric Determination of the Dissociation Energy of the Molecule Ce₂ and Predicted Stability of Diatomic Rare-earth Metals

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THE dissociation energies of gaseous, diatomic metals have previously been reviewed.[1,2] The molecule Ce_2, for which we report the dissociation energy is the first diatomic symmetric molecule of an inner-transition element with a partially filled f-shell for which this property has been measured.

The Ce_2-molecule was identified in the gas phase by the use of a mass spectrometer, with the same condensed system and experimental conditions were used for the molecule CeAu.[3] The dissociation energy, D_0°, of the molecule Ce_2 was derived from the third-law enthalpy, ΔH_0°, of the isomolecular reactions

$$Au_2(g) + Ce_2(g) = 2CeAu(g) \qquad (1)$$

and

$$CeAu(g) + Ce(g) = Ce_2(g) + Au(g) \qquad (2)$$
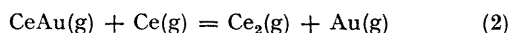
by using the same relation for the calculation of ΔH_0° and the same simplified assumptions in the determination of K_p as were used previously.[3] The same free-energy functions as previously[3] were also used for Au(g), Ce(g), $Au_2(g)$, and CeAu(g) The numerical values, in e.u., for the free-energy functions, $-(G_T - H_0^\circ)/T$, of the Ce_2-molecule were calculated from the estimated molecular parameters w_e

$= 119$ cm.$^{-1}$, $r_e = 3\cdot29$ Å, and an assumed electronic multiplicity of 3 for the ground-state. They are 75·14, 75·98, and 76·75 for 2000, 2200, and 2400° K, respectively.

From the data listed in the Table an average enthalpy of

Enthalpy change for the isomolecular reactions (1) *and* (2)

$T(^\circ K)$	Reaction	$\log K_p$	$-\Delta[(G_T^\circ - H_0)/T]$ (cal. deg.$^{-1}$mole^{-1})	ΔH_0° (kcal./mole)
2217	(1)	5·972	4·67	−48·3
2212	(1)	5·844	4·67	−48·8
2086	(1)	6·037	4·67	−48·0
2127	(2)	−3·724	−3·17	29·5
2212	(2)	−3·561	−3·28	28·8
2086	(2)	−3·662	−3·12	28·5

$\Delta H_0^\circ = -48\cdot4 \pm 0\cdot4$ kcal./mole is obtained for reaction (1) and $\Delta H_0^\circ = 28\cdot9 \pm 0\cdot6$ kcal./mole for reaction (2). With the known dissociation energies for $D_0^\circ(Au_2) = 52$ kcal./mole[1] and $D_0^\circ(CeAu) = 71$ kcal./mole[3] one obtains for $D_0^\circ(Ce_2)$ a value of 41·6 kcal./mole from reaction (1) and 42·1 kcal./mole from reaction (2). A value of $41\cdot8 \pm 6$ kcal./mole is selected for the dissociation energy of $D_0^\circ(Ce_2)$, where the error term gives the estimated accuracy.

With a value for the heat of vaporization of cerium,

$\Delta H_V(Ce) = 97$ kcal./mole[4] one obtains the dimensionless parameter $\alpha = \Delta H_V(Ce)/D_0^\circ(Ce_2) = 2\cdot32$. It has been shown[5] that for elements with a similar electronic configuration the values for the α-parameter are constant. By assuming this relation holds for the rare-earth metals, which have a partially filled $4f$-shell and a $5s^2 5p^6 6s^2$ configuration, one may predict the dissociation energies of the yet unknown diatomic metals. The necessary heats of vaporization of the corresponding metals were taken from ref. 4.

The calculated values, $D_0^\circ(M_2)$ are: Pr, 37; Nd, 33; Sm, 21; Eu, 18; Tb, 38; Dy, 27; Ho, 32; Er, 33; and Tm, 25 kcal. mole. The highest dissociation energies are expected for Pr_2 and Tb_2, the lowest for Sm_2 and Eu_2. It seems important to obtain experimental data on these diatomic molecules in order to investigate the effect of f-electrons on bond energies. The predicted values for the dissociation energies are only approximate but should be accurate enough for the definement of the optimum experimental conditions under which the detection and measurement of these molecules will be possible.

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[5] G. Verhaegen, F. E. Stafford, P. Goldfinger, and M. Ackerman, *Trans. Faraday Soc.*, 1962, **58**, 1926.