

The Dissociation Energy of the Molecule PdGe

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The dissociation energy of the molecule PdGe was determined by the mass spectrometric Knudsen cell method: $D_0^0(\text{PdGe}) = 256.6 \pm 12 \text{ kJ mol}^{-1}$ ($61.4 \pm 3 \text{ kcal mol}^{-1}$).

This laboratory has reported earlier dissociation energies of borides^{1, 2}, carbides^{1, 3} and silicides^{2, 4} of transition metals, which proved to be quite high. In extension to these investigations, the gaseous molecule PdGe was identified and its dissociation energy determined from the measurement of the equilibrium con-

Table 1. Enthalpy change for the reaction $\text{Pd}(\text{g}) + \text{Ge}_2(\text{g}) = \text{PdGe}(\text{g}) + \text{Ge}(\text{g})$, in kJ mol^{-1} .

T (K)	$\log K^a$	$-R \ln K$	$-\Delta(G_T^0 - H_0)/T$	ΔH_0^0
2013	0.33 ^b	-6.34	11.64	10.7
2102	0.37	-7.05	11.67	9.7
2110	0.31	-5.90	11.68	12.2
2163	0.34	-6.51	11.72	11.3
2180	0.32	-6.07	11.73	12.4
2193	0.35	-6.60	11.74	11.3
2202	0.35	-6.60	11.75	11.3
2217	0.37	-7.01	11.75	10.5
2256	0.36	-6.97	11.74	10.8
2302	0.37	-7.03	11.74	10.8
2316	0.39	-7.45	11.73	9.9
2351	0.35	-6.64	11.71	11.9
Average:				11.1 ± 1.0

^a The variation of $\log K$ with reciprocal temperature is given by $\log K = -(6.096 \pm 3.036) \times 10^2/T + (0.626 \pm 0.138)$.

^b Typical intensity ratios are $I(\text{Pd}) : I(\text{Ge}_2) : I(\text{PdGe}) : I(\text{Ge}) = 190 : 6.5 : 1 : 3000$.

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¹ N. S. McINTYRE, A. V. AUWERA-MAHIEU, and J. DROWART, *Trans. Faraday Soc.* **64**, 3006 [1968].

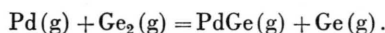
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³ A. V. AUWERA-MAHIEU and J. DROWART, *Chem. Phys. Letters* **1**, 311 [1967].

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⁵ J. DROWART and P. GOLDFINGER, *Angew. Chem. Internat. Edn.* **6**, 581 [1967].

stant of the reaction



The principle of the method and the experimental procedure have been described previously⁵. In this work, the sample, a mixture of palladium and germanium was placed in a graphite Knudsen cell. The measurements were performed with 70 eV ionizing electrons.

The equilibrium constant at each temperature (Table 1) was set equal to the product of the relative ion intensities, i. e. it was assumed that the relative ionization cross sections and multiplier yields compensate one another. The reaction enthalpy (Table 1) was calculated both by the second and third law methods.

The necessary thermodynamic functions for Pd(g) and Ge(g) were taken from the literature⁶, while those for Ge₂ and PdGe were calculated with the usual statistical mechanical formulae. The interatomic distance, $r = 244 \text{ pm}$, the vibration frequency, $\omega = 37 \text{ cm}^{-1}$ and the electronic state, $^3\Sigma$, were estimated previously for Ge₂⁷. For PdGe, $r = 250 \text{ pm}$ was deduced from the covalent radii⁸, $\omega = 25 \text{ cm}^{-1}$ was assumed to be equal to that of AuGe⁹ while, by analogy with PdSi², a $^1\Sigma$ ground state was postulated.

The numerical values of the free energy function are $-(G^0 - H_0^0)/T = 286.4, 288.2, 289.9, 291.5, 293.1$ for Ge₂ and $290.4, 292.2, 293.9, 295.5, 297.1 \text{ JK}^{-1} \text{ mol}^{-1}$ for PdGe at 2000, 2100, 2200, 2300 and 2400 K respectively.

The average of the reaction enthalpy derived by the second law, $\Delta H_0^0 = 11.3 \pm 6$ and by the third law, $\Delta H_0^0 = 11.1 \pm 8 \text{ kJ mol}^{-1}$, yields, combined with $D_0^0(\text{Ge}_2) = 267.8 \pm 9 \text{ kJ mol}^{-1}$ (see^{7, 10}), the dissociation energy of the molecule PdGe, $D_0^0(\text{PdGe}) = 256.6 \pm 12 \text{ kJ mol}^{-1}$ ($61.4 \text{ kcal mol}^{-1}$).

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