

The Dissociation Energy of the Molecule PdGe

R. PEETERS, A. M. VANDER AUWERA-MAHIEU
and J. DROWART

Laboratory for Molecular Physical Chemistry,
Free University of Brussels, Belgium

(Z. Naturforsch. 26 a, 327 [1971]; received 31 December 1970)

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)	$\log K^a$	$-R \ln K$	$-\Delta(GT^0 - H_0)/T$	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 $\log K = -(6.096 \pm 3.036) \times 10^3/T + (0.626 \pm 0.138)$.

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

Reprint requestments to Prof. Dr. J. DROWART, Laboratory for Molecular Physical Chemistry, Free University of Brussels, Belgium, B-1050 Brüssel, Belgien.

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

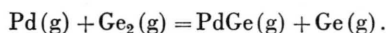
² A. V. AUWERA-MAHIEU, R. PEETERS, N. S. MCINTYRE, and J. DROWART, *Trans. Faraday Soc.* **66**, 809, [1970].

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

⁴ A. V. AUWERA-MAHIEU, N. S. MCINTYRE, and J. DROWART, *Chem. Phys. Letters* **4**, 198 [1969].

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, $\omega = 37 \text{ mm}^{-1}$ and the electronic state, $^3\Sigma$, were estimated previously for Ge₂⁷. For PdGe, $r = 250 \text{ pm}$ was deduced from the covalent radii⁸, $\omega = 25 \text{ mm}^{-1}$ 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, $D_0^0(\text{PdGe}) = 256.6 \pm 12 \text{ kJ mol}^{-1}$ ($61.4 \text{ kcal mol}^{-1}$).

The authors gratefully acknowledge support from the Fund for Collective Fundamental Research, Belgium.

⁶ D. R. STULL and G. C. SINKE, *Thermodynamic Properties of the Elements*, Adv. Chem. Series. **18**, American Chemical Society, Washington D. C. 1956.

⁷ J. DROWART and R. E. HONIG, *J. Phys. Chem.* **61**, 980 [1957]. — J. DROWART, G. DE MARIA, A. J. H. BOERBOOM, and M. G. INGRAM, *J. Chem. Phys.* **30**, 308 [1959].

⁸ L. PAULING, *Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York 1960.

⁹ R. F. BARROW, W. J. M. GISSANE, and D. N. TRAVIS, *Nature London* **201**, 603 [1964].

¹⁰ A. KANT, *J. Chem. Phys.* **44**, 2450 [1966].



Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.