Thermodynamic Functions of Hydrogen Selenide

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Ideal gas thermodynamic functions of H_2Se were calculated at 298.15° to 6000° K., considering the effects of anharmonicity and vibration-rotation interaction.

THERMODYNAMIC data for H_2Se are required in the analysis of high-temperature processes incorporating selenium, including combustion of various oxygen-deficient systems.

Values for the observed vibrational fundamentals σ_i, the rotational constants A_{000}, B_{000}, C_{000}, the anharmonicity terms X_{11}, X_{33}, and X_{ij}, and the vibration-rotation interaction terms $\alpha_i^{A,B,C}$ have been determined by Hill and Edwards (*5*). Alternate values for the α_i (together with the same values of σ_i) were given by Palik (*6*), but were not used here. It is necessary to estimate a value for the anharmonic term $-X_{22}$; Hill and Edwards prefer 5.0 cm.$^{-1}$ or less. The $-X_{22}$ of H_2S is 5.72 according to Allen and Plyler (*1*), and the author adopts a conservative value of 4.0. The molecular constants used for this calculation are in Table I.

Thermodynamic functions (Table II) were computed over the temperature range 298.15° to 6000° K. for an ideal gas of H_2Se molecules at 1 atm., using the program described previously (*2, 3, 4*). In these calculations, R is 1.98717 calorie per mole degree, hc./k. is 1.4388, and the Sackur-Tetrode constant K_6 is −7.2832.

Data are tabulated to five significant figures for reason of internal consistency and ease of polynomial curve fitting, although absolute data accuracy in the absence of firm rotational stretching information and neglect of resonance between $2\sigma_3$ and $2\sigma_1$ probably does not warrant more than four figures. The computing procedure flow chart and program statements for the thermodynamic functions of triatomic gases are given in detail by Gordon *et al.* (*4*).

Table I. Molecular Constants of H_2Se (Cm.$^{-1}$)

σ_1	2344.5	α_1^A	0.082
σ_2	1034.21	α_2^A	−0.271
σ_3	2357.8	α_3^A	0.127
A_{000}	8.1730	α_1^B	0.142
B_{000}	7.7271	α_2^B	−0.142
C_{000}	3.9019	α_3^B	0.11
$-X_{11}$	21.43	α_1^C	0.054
$-X_{22}$	4.0 (estimated)	α_2^C	0.043
$-X_{33}$	21.71	α_3^C	0.047
$-X_{12}$	17.69		
$-X_{23}$	20.2		
$-X_{13}$	84.9		

Molecular weight = 80.976
Heat of formation $\Delta H_{f_0}^\circ$ = 8.05 Kcal./mole (*7*)
Ground state statistical weight, $g_0 = 1$
Symmetry No. $\sigma = 2$

Table II. Thermodynamic Functions for H_2Se (g.)[a]

T., ° K.	$-(G^\circ - H_0^\circ)/T$	$(H^\circ - H_0^\circ)/T$	S°	C_p°, Cal. Mole^{-1} Deg.$^{-1}$	$H_T^\circ - H_{298}^\circ$, Kcal. Mole^{-1}
298.15	44.325	8.022	52.347	8.306	0.0
500	48.533	8.306	56.839	9.178	1.762
1000	54.593	9.318	63.911	11.372	6.927
1500	58.553	10.241	68.794	12.661	12.970
2000	61.600	10.941	72.541	13.354	19.490

[a] The author invites written requests for the complete table of data at 100° K. intervals to 6000° K.

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