PALLADIUM AND PLATINUM SULPHIDES. THERMODYNAMIC PROPERTIES

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The investigation of the dependence between the numerical values of the thermodynamic properties and equilibrium parameters of the system is the main target of the physical-chemical analysis. The requirements to the theoretical validity o the models created on the basis of employed thermodynamic values of components, are to be put in the forefront. Theoretical research without adequately precise information on the thermodynamic values of elements, compounds, ions, etc. is virtually unfeasible; otherwise, obtained results are wide of the mark. It is caused by the fact that the thermodynamic values of minerals, chemical compounds and elements are either missing or show an essential scatter of values in numerous reference and scientific publications [1-10]. The analysis of the published data on the thermodynamic values of Pd and Pt sulphides is represented in Table 1, which displays the essential scatter of all the values given. Hence, employment of these data for the theoretical model investigation is impossible due to the probable origination of imperfectly correct results. In this connection, there is a need for revision of the available data in the reference sources and for employment of possible ways of establishing true values of the thermodynamic properties and values of the compounds given.

Table 1. Reference data on Pd and Pl sulphides

Sulphides	V^0_{298}, J/bar	S^0_{298}, J/mole·K	$-\Delta H^0_{298}$, kJ/mole	$-\Delta G^0_{298}$, kJ/mole
PdS	1,4218 – 2,0635	46,00 – 70,60	70,7096 – 76,9886	66,9440 – 73,0819
PdS_2	3,00 – 3,16	78,69 – 106,90	78,2408 – 86,6088	74,0568 – 74,5000
PtS	2,215 – 2,2489	55,061 – 84,517	81,5880 – 87,0272	76,1000 – 90,3744
PtS_2	2,91 – 3,34	72,954 – 74,684	108,7840 – 116,3152	99,5792 – 114,2232

The paper focuses on the estimation of the possible ways of getting more correct thermodynamic values and volume characteristics of Pd and Pt sulphides. The analysis of the every possible existing methods of theoretical prediction of the thermodynamic and volume values has shown a need for attracting any constant parameters of the elements under study and chemical compounds for the purpose of revealing correlation dependence with their contribution. During the investigation, a correlation analysis has been carried out for distinguishing a variation mechanism of standard values of Gibbs free energy (ΔG^o_{298}), enthalpy (ΔH^o_{298}), entropy (S^0_{298}), heat capacity (Cp^0_{298}), and molecular volume (V^0_{298}) of Pd and Pt sulphides from the values of their molecular weight (M), molecular weight logarithm (lgM), and order number (N) in the periodic table.

The method of comparative calculation allows defining properties of a substance on the basis of data on other substances, which are close in composition and structure [11]. This method makes it also possible to correct thermodynamic properties with a relatively high precision. These possibilities of the method were used to clarify the thermodynamic values available in the published sources. The volume of the primary reference information was found quite enough to use successfully the method of comparative calculation. The determination of high-temperature heat capacity values has been carried out using standard entropy and melting (decomposition) temperature [12].

Table 2. Research results for the thermodynamic parameters of Pd and Pt sulphides

	V^0_{298}, J/bar	S^0_{298}, J/mole ·K	$-\Delta H^0_{298}$, kJ/mole	$-\Delta G^0_{298}$, kJ/mole	$Cp = a + в\cdot T\cdot 10^{-3} + c\cdot T^{-2}\cdot 10^5$			
					a	в	- c	T K
PdS	2,0635	57,6171	74,2650	70,7110	44,514	14,799	0,352	1243
PdS_2	3,2482	78,6310	80,8475	74,1077	66,541	21,797	0,637	1245
PtS	2,2150	54,8654	83,5367	78,0376	44,935	13,185	0,612	1448
PtS_2	3,5534	74,1736	110,4227	101,2293	67,180	18,750	1.172	1500

The estimation of calculated values of enthalpy, Gibbs free energy, entropy, heat capacity and volume have been checked by multiple simple regression coefficients obtained using a least-squares method. The thermodynamic values of Pd and Pt sulphides are given in Table 2.

The error of the thermodynamic properties and volume characteristics of Pd and Pt sulphides varies within ±1% of the average reference data, and that allows considering them as rather correct.

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