ISSN 0016-7029, Geochemistry International, 2007, Vol. 45, No. 9, pp. 931–937. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © V.K. Karzhavin, 2007, published in Geokhimiya, 2007, No. 9, pp. 1014–1021.

SHORT COMMUNICATIONS

Sulfides, Selenides, and Tellurides of Platinum and Palladium: Estimation of Thermodynamic Properties

V. K. Karzhavin

Geological Institute, Kola Scientific Center, Russian Academy of Sciences, ul. Fersmana 14, Apatity, Murmansk oblast, 184209 Russia

e-mail: karzhavin@geoksc.apatity.ru

Received February 28, 2006

DOI: 10.1134/S0016702907090078

Investigations in physical chemistry, geochemistry, and other disciplines require the knowledge of the thermodynamic properties of many minerals, chemical compounds, and elements. The plausibility of predictive models obtained in such investigations relies on the accuracy of these data. Unfortunately, necessary thermodynamic data are often absent or show a large scatter in numerous handbooks and research papers [1–17]. The empirical and semiempirical methods of thermodynamic calculations yield considerable uncertainties [2, 17, 18]. Moreover, it was noted that the experimental methods of the determination of thermodynamic values may also be unreliable [19]. Theoretical studies are impossible without sufficiently accurate thermodynamic data for elements, compounds, and ions. Otherwise, the obtained data may be implausible. The main requirements to thermodynamic values are their reliability, mutual consistency, etc. [19]. In our theoretical study, thermodynamic values are derived by various computational methods using the available reference data and their correlation relationships and functions.

The available thermodynamic data for individual elements, as well as sulfides, selenides, and tellurides of palladium and platinum, were compiled in Table 1. The wide scatter observed in almost all the thermodynamic properties of platinum and palladium compounds can be related to difficulties in calorimetric experiments, specific properties of the compounds, their insufficient purity, and other factors. As a result, fairly wide ranges were obtained, for example, for some volume parameters [13]. The standard entropy of sulfide (PtS) is higher than that of disulfide [15]. Significantly overestimated (by up to 80%) values of standard entropy were recently reported for PdS and PdS_2 by Moiseev and Vatolin [16]. The computational methods employed by these authors may be implausible for many compounds. In addition, identical coefficients were published for the heat capacity equations of platinum and palladium sulfides [10]. All of these facts indicate that the thermodynamic data on sulfides, selenides, and tellurides of platinum and palladium taken from different sources (Table 1) must be treated with great caution. The use of these Gibbs free energy (ΔG^0_{298}), formation enthalpy (ΔH^0_{298}), standard entropy (S^0_{298}), heat capacity (Cp_{298}), and molar volume (V^0_{298}) data for the theoretical studies of both simple chemical reactions and complex homogeneous and heterogeneous systems may lead to insufficiently reliable results. In this paper, we attempted to refine the available thermodynamic values and volume characteristics of sulfides, selenides, and tellurides of platinum and palladium and to estimate the missing thermodynamic properties in the simplest modification of the Pt–Pd–S–Se–Te system, using various methods.

Calculation methods are the main sources of thermodynamic data for elements, chemical compounds, and minerals [2, 17, 20–26]. Among a great number of phenomenological procedures and approaches used for the theoretical estimation of physicochemical properties of various classes of materials, the method of comparative calculation is of special interest [2, 17]. Many empirical relations obtained from the dimensional rule of linear approximation allowed the authors to refine known properties and calculate yet unknown thermodynamic parameters with an accuracy comparable with that of experimental measurements. This method is as follows. If no direct data are available to determine the thermodynamic properties of a substance, the required parameters can be obtained from the data for other substances of similar composition and structure, provided that the properties of substances are correlated. Comparative calculations are based on the chemical similarity of the compounds and employ numerous techniques, including the additivity principle, comparison on the basis of similar materials and similar series of compounds, etc. The following schemes can be applied for a direct comparison of similar materials, similar series of compounds, and similar reactions (after Karapet'yants [17]):

(1) comparison of a given property in two similar series of similar compounds under identical conditions

Table 1. Reference thermodynamic data for sulfur, selenium, tellurium, palladium, platinum, and their sulfides, selenides, and tellurides

Compound	V^0_{298}, J/bar	$-\Delta H^0_{f,298}$, kJ/mol	$-\Delta G^0_{f,298}$, kJ/mol	S^0_{298}, J/mol K	Cp_{298}, J/mol K
S	1.5269–1.553 [1–3, 4, 6, 12]	0	0	31.77–31.923 [1–3, 8, 10–12, 14, 15]	22.60–22.72 [2, 3, 8, 12, 14]
Se	1.642–1.647 [1, 3, 6, 12]	0	0	42.09–42.84 [1–3, 8, 10–12, 14, 15]	25.06–25.363 [2, 3, 8, 12, 14]
Te	2.041–2.058 [1,3, 4, 6, 12]	0	0	49.45–49.706 [1–3, 8, 10–12, 14, 15]	25.60–25.773 [2, 3, 8, 12, 14]
Pd	0.879–0.8867 [6, 7, 9, 12]	0	0	37.202–37.907 [2, 4, 7–12, 14, 15]	25.857–25.983 [2, 4, 8, 11, 12]
Pt	0.9074–0.9095 [1, 3, 6, 7, 9, 12]	0	0	41.547–41.84 [1, 2, 4, 7–12, 14, 15]	25.81–26.57 [2, 4, 8, 11, 12]
PdS	1.422–2.270 [4, 7, 9, 13]	70.7096–76.9886 [4, 5,10, 11, 14, 16]	66.9440–73.0819 [4, 10, 11, 14]	46.00–70.60 [4, 5, 10, 11, 14]	43.388 [10, 11]
PdS_2	3.00–3.16 [13]	78.2408–86.6088 [4, 5, 10, 11, 14]	74.0568–74.5000 [4, 10, 11]	78.69–106.90 [4, 5, 10, 11, 16]	65.898 [5, 10, 11]
PdSe	–	50.208 [5, 11]	48.116 [11]	72.988–73.220 [3–5, 11, 14]	–
$PdSe_2$	3.6658 [13]	58.576 [5, 11]	58.9944 [11]	123.428 [5, 11]	–
PdTe	1.970–2.5492 [4, 9, 13]	37.656–37.660 [5, 10, 11]	38.360–38.4928 [10, 11]	89.538–89.6213 [3–5, 10, 11, 14]	51.17 [3, 4, 10, 14]
$PdTe_2$	4.3558–4.3619 [4, 9, 13]	54.392–54.400 [3–5, 10, 11]	51.300–51.4632 [5, 10, 11]	126.566–126.775 [3–5, 10, 11]	76.609 [3, 5, 10]
PtS	2.215–2.2489 [1, 4, 8, 9, 13, 15]	81.5880–87.0272 [1–8, 10–12, 14, 15]	76.1000–90.3744 [1–4, 6–8, 10–12, 14, 15]	55.061–84.517 [1–12, 14, 15]	43.388 [2–5, 8, 10–12, 14]
PtS_2	2.91–3.34 [13]	108.7840–116.3152 [3–7, 10, 11, 14, 15]	99.5792–114.2232 [3–7, 10, 11, 14, 15]	72.954–74.684 [2–6, 10, 11, 14, 15]	65.898 [2–5, 10, 11, 14]
PtSe	1.892 [13]	48.500–48.5344 [10, 11]	46.024–46.100 [10, 11]	66.916–67.534 [10, 11]	42.33 [5]
$PtSe_2$	3.6392–3.6657 [13]	79.496 [5, 11]	72.3832 [11]	102.508 [5, 11]	–
PtTe	–	41.840 [5, 10, 11]	38.9112 [10, 11]	51.923–81.211 [3–5, 10, 11, 14]	49.915 [3–5, 14]
$PtTe_2$	4.3973–4.4319 [4, 9, 13]	58.576 [5, 10, 11]	52.7184 [10, 11]	120.918–121.001 [3–5, 10, 11, 14]	75.438 [3–5]

(for example, a comparison of the heat capacity of alkali halogenides at identical temperature–pressure conditions);

(2) comparison of two properties in a series of similar compounds at fixed conditions (for example, heat capacity and entropy of alkali halogenides at the same temperature);

(3) comparison of a given property in a series of similar compounds at two different sets of parameter (for example, heat capacities of sodium halogenides at 298 and 1000 K);

(4) comparison of a given property of two substances under the same conditions (for example, saturated vapor pressure for two liquids at identical temperatures);

(5) comparison of two properties of a given substance under variable conditions (for example, viscosity and saturated vapor pressure of liquid at different temperatures);

(6) comparison of a given property of one substance at two values of a state parameter under variable conditions with respect to another parameter (for example, at two temperatures and variable pressure).

Using the potential of this method, we refined the available reference data and determined missing thermodynamic parameters for the sulfides, selenides, and tellurides of palladium and platinum. The amount of available reference data appeared to be sufficient for the successful application of the method.

As can be inferred from the above-described variants of theoretical prediction (estimation) of the ther-

modynamic and volume properties of elements and chemical compounds, there are no possible forms of direct comparison of similar substances and series of substances for the sulfides, selenides, and tellurides of palladium and platinum. Therefore, some constant characteristics and certain parameters of these elements and their chemical compounds should be used. During our study, we tested different ways for the comparison of the thermodynamic and volume properties of the sulfides, selenides, and tellurides of palladium and platinum. The results were checked by means of graphical constructions. It was established that the use of all published thermodynamic data for each compound led to a sharp decrease in correlation coefficients. Therefore, the thermodynamic values that showed the largest deviation from average values were sequentially excluded from calculations.

The calculated values of formation enthalpy, Gibbs free energy, standard entropy, heat capacity, and volume were controlled by the coefficients of multiple regression equations obtained by the least-squares method.

The molar volumes of sulfides, selenides, and tellurides of platinum and palladium. Various computational procedures were used for the estimation of the molar volumes of the compounds. It was found that the most optimal values can be obtained of the basis of a linear dependency between the molar volumes of sulfides, selenides, and tellurides of palladium and platinum and their molecular weights (Fig. 1). The calculations and diagrams showed that the light (palladium) and heavy (platinum) compounds are characterized by distinctly different volume dependencies. A relatively distinct linear dependency was observed between constant and variable parameters. It can be described by the following equations:

(a) PdS, PdSe, PdTe: V^0_{298}, J/bar = 0.005084 × M + 1.3594

with a correlation coefficient of 0.906;

(b) PtS, PtSe, PtTe: V^0_{298}, J/bar = –0.00689 × M + 3.7796

with a correlation coefficient of 0.996;

(c) PdS_2, $PdSe_2$, $PdTe_2$: V^0_{298}, J/bar = 0.0062585 × M + 2.0926

with a correlation coefficient of 0.995;

(d) PtS_2, $PtSe_2$, $PtTe_2$: V^0_{298}, J/bar = 0.007876 × M + 0.88539

with a correlation coefficient of 0.968.

Similar separate dependencies were obtained for the thermodynamic properties and volume characteristics of the light (palladium) and heavy (platinum) elements [27, 28]. The difference between the light and heavy PGE is clearly seen from the covariations of their standard entropies and heat capacities [29, 30].

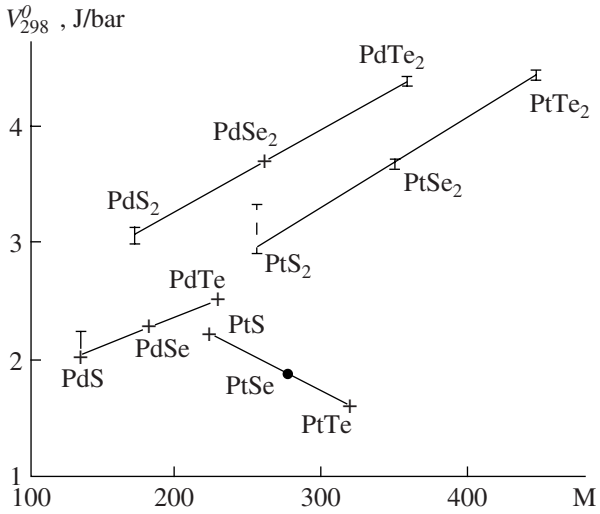

Fig. 1. Correlation between the molar volume and molecular weight of sulfides, selenides, and tellurides of palladium and platinum.

The standard entropy of sulfides, selenides, and tellurides of platinum and palladium. Since entropy is a characteristic function, different variants of certain constant values of the chemical compounds were used for the estimation of linear correlations with a given parameter. A distinct linear correlation was observed between the standard entropy and molecular weight of sulfides, selenides, and tellurides of platinum and palladium (Figs. 2, 3). As follows from the obtained data, the standard entropy of light (palladium) sulfides, selenides, and tellurides is linearly correlated with their molecular weight (M), whereas the standard entropy of heavy (platinum) ones is linear with their reciprocal molecular weight. Given the distinct correlation between constant and variable parameters, the following dependencies were obtained:

(1) PdS, PdSe, PdTe: S^0_{298}, J/mol K = 0.3338 × M + 11.3992

with a correlation coefficient of 0.999;

(b) PtS, PtSe, PtTe: S^0_{298}, J/mol K = 0.2747 × M – 7.5339

with a correlation coefficient of 0.992;

(c) PdS_2, $PdSe_2$, $PdTe_2$: S^0_{298}, J/mol K = 169.2023 – 15382.38/M

with a correlation coefficient of 0.989;

(d) PtS_2, $PtSe_2$, $PtTe_2$: S^0_{298}, J/mol K = 183.84 – 28320.1/M

with a correlation coefficient 0.999.

The high correlation coefficients indicate a close relation between the values of standard entropy and molecular weights for the chemical compounds under study.

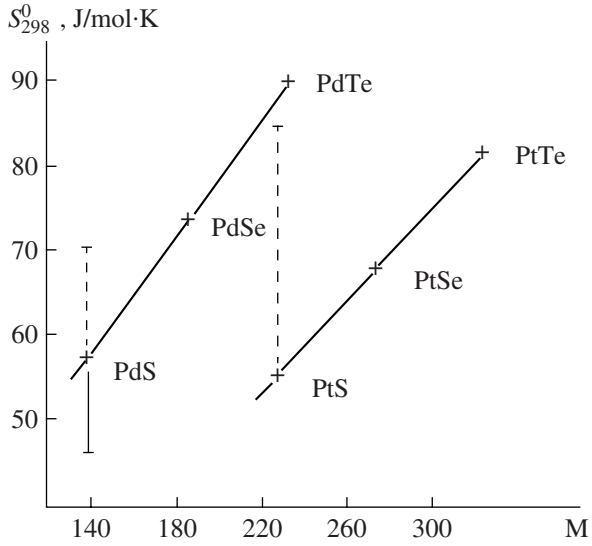

Fig. 2. Correlation between the standard entropy and molecular weight of sulfides, selenides, and tellurides of palladium and platinum.

The formation enthalpy of sulfides, selenides, and tellurides of palladium and platinum. The standard enthalpy of formation of elements, chemical compounds, minerals, etc. is typically determined by experimental (calorimetric) methods. The accuracy of experimental results depends on the purity of the material and some other factors [31]. The main requirement to theoretical investigations is that regular relations must be established, which allow the determination of required values using available data for other substances [2, 17]. At the current stage of the study, we tested different ways to determine possible regular relations between various parameters and the formation enthalpies of sulfides, selenides, and tellurides of palladium and platinum. Many properties of chemical compounds are sometimes represented as sums of contributions of constituent molecules and elements. Based on the additivity principle, the entropies were determined by summing the previously calculated standard entropies of platinum and palladium and the standard entropies of sulfur, selenium, and tellurium, which were taken from IVTANTERMO [14].

Figure 4 presents covariations of the formation enthalpies of compounds and the sums of standard entropies of their constituents. The distribution of points in the diagram suggests the existence of a linear correlation between these parameters. This dependence is interpolated by the following equations:

(a) PdS, PdSe, PdTe: $-\Delta H^0_{298}$, kJ/mol = 2.26218 × $\Sigma S^0_{298,\,elem}$ – 233.7131

with a correlation coefficient of 0.994;

(b) PtS, PtSe, PtTe: $-\Delta H^0_{298}$, kJ/mol = 2.60951 × $\Sigma S^0_{298,\,elem}$ – 273.7090

with a correlation coefficient of 0.961;

(c) PdS_2, $PdSe_2$, $PdTe_2$.: $-\Delta H^0_{298}$, kJ/mol = 0.85135 $\Sigma S^0_{298,\,elem}$ – 166.9069

with a correlation coefficient of 0.959;

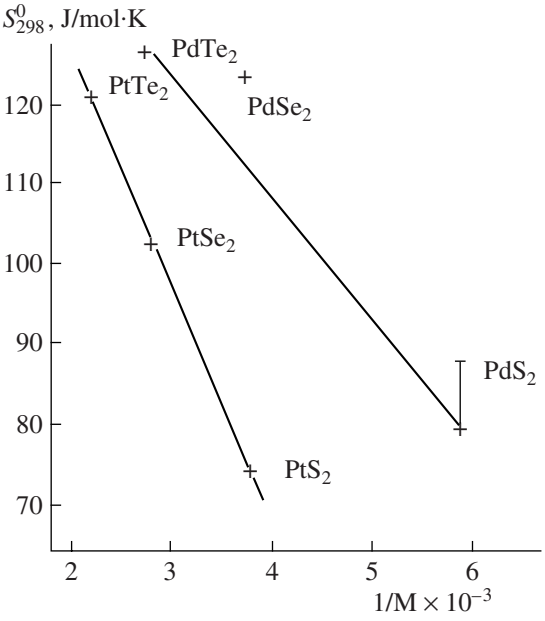

Fig. 3. Correlation between the standard entropy and reciprocal molecular weight of disulfides, diselenides, and ditellurides of palladium and platinum.

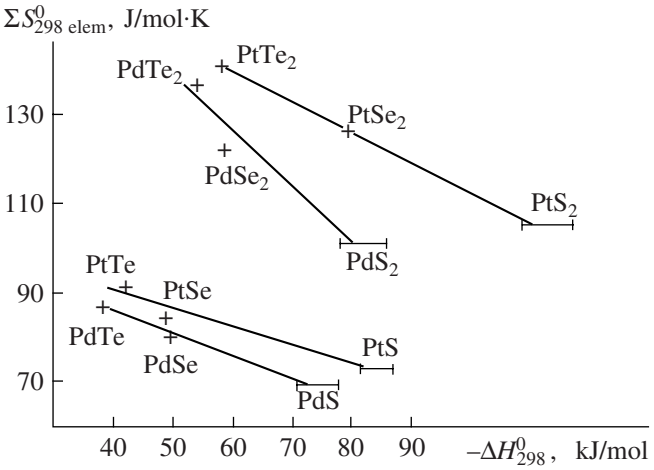

Fig. 4. Correlation between the sum of the standard entropies of elements and formation enthalpy of sulfides, selenides, and tellurides of palladium and platinum.

(d) PtS_2, $PtSe_2$, $PtTe_2$: $-\Delta H^0_{298}$, kJ/mol = $1.51726\,\Sigma S^0_{298,\,elem} - 271.5478$

with a correlation coefficient of 0.999.

The results of numerous studies revealed [17, p. 280] "a relation between the heat of formation (standard enthalpy) and standard isobaric–isothermal potential of formation" for various types of chemical compounds and for different dimensions as a distinct linear correlation. Figure 5 shows the dependence $-\Delta G^0_{298} = f(-\Delta H^0_{298})$, which was obtained on the basis of all published thermodynamic data for PGE sulfides, selenides, and tellurides (Table 1). The boxes shown in the diagram denote the ranges of ΔG^0_{298} and ΔH^0_{298} values from all available literature sources. Since the data points define fairly distinct (taking into account variations in the parameters) and almost linear dependence, the Gibbs free energies of sulfides, selenides, and tellurides of platinum and palladium were determined using the Gibbs equation. For these purposes, we used the calculated values of formation enthalpy, standard entropy, and sum of the standard entropies of constituent elements:

$$\Delta G^0_{298}, \text{kJ/mol} = \Delta H^0_{298} - 298.15(S^0_{298,\,comp} - \Sigma S^0_{298,\,elem}).$$

This equation was then used to obtain the desired consistent thermodynamic properties of sulfides, selenides, and tellurides of palladium and platinum (Table 2).

The heat capacity of sulfides, selenides, and tellurides of palladium and platinum. The heat capacities of sulfides, selenides, and tellurides of platinum and palladium were approximated within a wide temperature range by a power series with empirical coefficients using Landia's [20] method, which yields satisfactory results with a relatively high accuracy. This author developed a calculation procedure for the high-temperature heat capacity of various types of crystalline inorganic compounds. The method allows the calculation of coefficients of heat capacity equations for chemical compounds, using their standard entropies and temperatures of melting or decomposition. The heat capacities of sulfides, selenides, and tellurides of palladium and

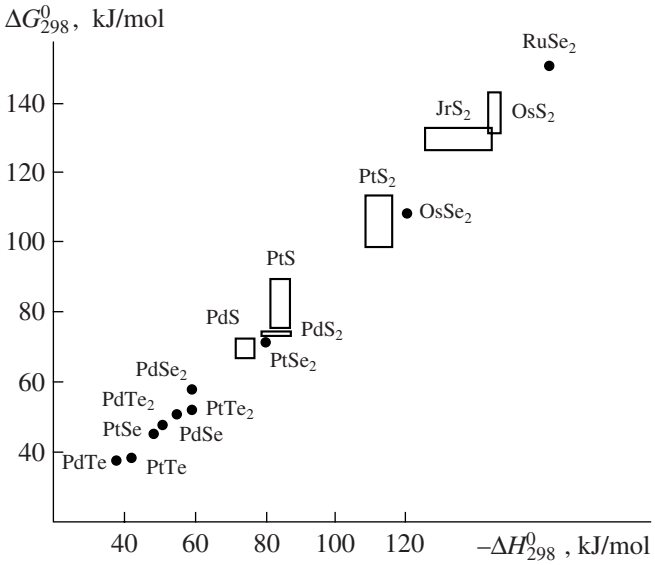

Fig. 5. Correlation between the Gibbs free energy and formation enthalpy of selenides and tellurides of some PGE.

Table 2. Calculated thermodynamic parameters of sulfides, selenides, and tellurides of palladium and platinum

Compound	Molecular weight	ρ, g/cm^3	V^0_{298}, J/bar	$-\Delta H^0_{f,\,298}$, kJ/mol	$-\Delta G^0_{f,\,298}$, kJ/mol	S^0_{298}, J/mol K	Cp_{298}, J/mol K	$Cp = a + bT \times 10^{-3} + cT^{-2} \times 10^5$			Temperature range, K
								a	*b*	*–c*	
PdS	138.486	6.7120	2.0635	75.8680	72.2498	57.63	48.66	44.583	14.904	0.320	1243
PdS_2	170.552	5.3972	3.1599	80.3037	73.5450	79.02	72.36	66.571	21.809	0.630	1245
PtS	227.146	10.2508	2.2146	81.7879	76.2222	54.87	48.17	44.933	13.187	0.612	1448
PtS_2	259.212	8.8568	2.9267	111.4957	102.2923	74.59	71.49	67.200	18.780	1.163	1500
PdSe	185.380	8.0533	2.3019	52.7833	50.7881	73.28	49.89	45.075	16.019	–0.037	1200
$PdSe_2$	264.340	7.0549	3.7409	62.9282	59.6215	111.01	74.88	67.603	24.128	–0.077	1200
PtSe	274.040	14.4879	1.8915	55.1587	50.3901	67.75	49.53	44.792	15.909	0.004	1200
$PtSe_2$	353.000	9.6301	3.6656	80.5295	73.8937	103.62	74.76	66.679	26.314	–0.215	1050
PdTe	234.020	9.1801	2.5492	36.1317	36.7809	89.51	51.18	44.858	19.067	–0.569	993
$PdTe_2$	361.620	8.3020	4.3558	50.3949	47.3644	126.67	76.30	67.196	27.946	–0.691	1013
PtTe	322.680	20.7338	1.5563	35.9504	32.9695	81.11	50.12	45.515	16.190	0.193	1193
$PtTe_2$	450.280	10.1602	4.4318	58.1928	52.3331	120.949	75.09	68.618	21.875	0.039	1398

platinum were calculated using a procedure developed for binary oxygen-free compounds. Heat capacity values for the given type of crystalline compounds (for several temperatures) were calculated using the following expression within the interval 298°C – T melt:

$$Cp = n\left[6.6 - \frac{a}{b + K(T - b)}\right.$$

$$\left. + \frac{1.24}{T\,\text{melt}}\left(6.6 - \frac{a}{298}\right)^2 T^{3/2} 10^{-3}\right],$$

where n is the number of atoms in the compound, $a = 2200/S^{at}$, $S^{at} = S^0_{298}/n$, $b = a/0.87$, and T is the temperature for which heat capacity is calculated.

The coefficients of the heat capacity equation were determined on the basis of a system of equations obtained for different temperatures. The estimated values of the standard entropy of sulfides, selenides, and tellurides of palladium and platinum were used in heat capacity calculations. According to the data of Landia [20], the errors of heat capacity values calculated for the given type of crystalline compounds are lower than 5%.

CONCLUSIONS

New relations were established for variations in molar volume and thermodynamic properties, and coefficients of high-temperature heat capacity equations were determined for the sulfides, selenides, and tellurides of palladium and platinum. A numerical method was used to derive unknown parameters and refine known values (Table 2).

The examination of the obtained data indicates that the significant deviations of the calculated volumes of some sulfides (PdS, PtS_2) and kotulskite (PdTe) from the parameters reported in handbooks are related to the inaccuracy of the latter values, as was expected. The other volumes were calculated with a high accuracy within ±3%. The obtained values of entropy appeared to be close to those from the IVTANTERMO database [14] with an average error of ±2%. However, some aforementioned entropy values from the literature showed significantly higher errors. A similar conclusion can be drawn from the calculated values of formation enthalpy and Gibbs free energy. The observed high correlation coefficients indicate a close relation between the formation enthalpy, Gibbs free energy, standard entropy of chemical compounds, and corresponding parameters.

In general, the difference between the calculated thermodynamic properties of sulfides, selenides, and tellurides of palladium and platinum and average values from the literature is within ±3%, which indicates the correctness of our estimates. The results of our theoretical study can be used to determine the thermodynamic parameters of reactions and describe systems with the participation of chemical compounds addressed here.

REFERENCES

1. *A Handbook of Physical Constants*, Ed. by S. P. Clark (Geol. Soc. Am., New York, 1966; Mir, Moscow, 1969).
2. V. A. Kireev, *Methods of Practical Calculations in the Thermodynamics of Chemical Reactions* (Khimiya, Moscow, 1970) [in Russian].
3. G. B. Naumov, B. N. Ryzhenko, and I. L. Khodakovsky, *A Handbook of Thermodynamic Data (for Geologists)* (Atomizdat, Moscow, 1971; US Geol. Surv., 1974).
4. *Thermal Constants of Matters*, Ed. by V. P. Glushko (VINITI, Moscow, 1972), Issue 6, Pt. 1 [in Russian].
5. K. C. Mills, *Thermodynamic Data for Inorganic Sulfides, Selenides and Tellurides* (Butterworths, London, 1974).
6. *Chemistry. A Reference Book* (Khimiya, Leningrad, 1975) [in Russian].
7. S.E. Livingstone, *The Chemistry of Ruthenium, Rhodium, Palladium, Osmium, Iridium, and Platinum* (Pergamon, Oxford, 1973; Mir, Moscow, 1978) [in Russian].
8. A. G. Bulakh and K. G. Bulakh, *Physicochemical Properties of Minerals and Components of Hydrothermal Solutions* (Nedra, Leningrad, 1978) [in Russian].
9. *Platinum-Group Elements: Mineralogy, Geology, Recovery*, Ed by L. J. Cabri (CIM Spec., Ontario, 1981).
10. H. Yokokawa, "Tables of Thermodynamic Properties of Inorganic Components," J. Nat. Chem. Lab. Ind. (Spec. Iss.) **83**, 27–121 (1988).
11. B. W. Mountain and S. A. Wood, "Chemical Control on the Solubility, Transport and Deposition of Platinum and Palladium in Hydrothermal Solution: A Thermodynamic Approach," Econ. Geol. **83**, 492–510 (1988).
12. R. A. Robie and B. S. Hemingway, "Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 bar (10^5 Pascals) Pressure and at Higher Temperature," US Geol. Surv. Bull. **2131** (1995).
13. *The Geology, Geochemistry, Mineralogy and Mineral Beneficiation of Platinum-Group Elements*, Ed. by L. J. Cabri (CIM Spec., Ontario, 2002).
14. IVTANTERMO, 2004. http://www.chem.msu.su/cgi-bin/tkv2.pl.
15. R. M. Garrels and Ch. L. Christ, *Solutions, Minerals, and Equilibria* (Harper & Row, New York, 1965; Mir, Moscow, 1968).
16. G. K. Moiseev and N. A. Vatolin, *Some Relations and Methods of Calculation of the Thermochemical Properties of Inorganic Compounds* (Inst. Metallurg. UO RAN, Yekaterinburg, 2001) [in Russian].
17. M. Kh. Karapet'yants, *Methods of Comparative Calculation of Physicochemical Properties* (Nauka, Moscow, 1965) [in Russian].
18. F. A. Letnikov, *Isobaric Potentials of Mineral Formation (Chemical Affinity) and Their Application in Geochemistry* (Nedra, Moscow, 1965) [in Russian].
19. I. K. Karpov, S. A. Kashik, and V. D. Pampura, *Constants of Matters for Thermodynamic Calculations in Geochemistry and Petrology* (Nauka, Moscow, 1968) [in Russian].
20. N. A. Landiya, *Calculation of High-Temperature Heat Capacity of Solid Inorganic Matters Using Standard Entropy* (AN GSSR, Tbilisi, 1962) [in Russian].

21. H. C. Helgeson, J. M. Delany, H. W. Nesbitt, and D. K. Bird, "Summary and Critique of the Thermodynamics Properties of Rock-Forming Mineral," Am. J. Sci. **278A**, 1–229 (1978).

22. N. V. Vilor, L. A. Kaz'min, V. V. Lashkevich, and A. Sh. Mintsis, *Fluid Postmagmatic Systems* (Nauka, Novosibirsk, 1983) [in Russian].

23. R. G. Berman and T. H. Brown, "Heat Capacity of Minerals in the System Na_2O–K_2O–CaO–MgO–FeO–Fe_2O_3–Al_2O_3–SiO_2–TiO_2–H_2O–CO_2: Representation, Estimation and High Temperature Extrapolation," Contrib. Mineral. Petrol. **89**, 168–183 (1985).

24. Ph. Viellard and V. Tardy, "Estimation of Enthalpies of Formation of Minerals Based on Their Refined Crystal Structures," Am. J. Sci. **288**, 997–1040 (1988).

25. T. J. B. Holland, "The Dependence of Entropy on Volume for Silicate and Oxide Minerals: A Review and a Predictive Model," Am. Mineral. **74**, 5–13 (1989).

26. T. J. B. Holland and R. Powell, "An Enlarged and Updated Internally Consistent Thermodynamic Dataset with Uncertainties and Correlations: K_2O–Na_2O–CaO–MgO–MnO–FeO–Fe_2O_3–Al_2O_3–TiO_2–SiO_2–C–H_2–O_2," J. Metamorph. Geol. **8**, 89–124 (1990).

27. V. K. Karzhavin, "Platinum Group Elements. Thermodynamic Properties," in *Annual Seminar on Experimental Mineralogy, Petrology, and Geochemistry, 2003)* (GEOKhI, Moscow, 2003), p. 25 [in Russian].

28. V. K. Karzhavin, "Platinum Group Elements (PGE): Thermodynamic Properties," Vestn. Otd. Nauk Zemle, No. 1 (21), 2003. http://www.scgis.ru/russian/cp1251/h_dgggms/1-2003/informbul-1_2003.htm#1.1.

29. A. A. Marakushev, N. M. Gavrilov, and S. A. Marakushev, "Thermodynamic Basis for the Geochemical Systematics of Elements," Dokl. Akad. Nauk **387A**, 811–816 (2002) [Dokl. Earth Sci. **387**, 1104–1109 (2002)].

30. A. A. Marakushev, N. M. Gavrilov, and S. A. Marakushev, "Periodicity in Variation of Thermodynamic, Physical, and Biogeochemical Properties of Elements," Dokl. Akad. Nauk **393**, 241–247 (2003) [Dokl. Earth Sci. **393**, 1185–1191 (2003)].

31. W. W. Wendlandt, *Thermal Methods of Analysis* (Wiley, New York, 1974; Mir, Moscow, 1978).