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Enthalpies of formation of tellurides of palladies from elements

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Palladium as other platinum metals belongs to the group of transitive metals of the VIII-th group of the periodic system. Their electronic structure is rather complicated, mainly due to the closeness of d and s-energetic levels. Thus, a transition from one level to another is easily realized there. According to the type of interaction with the other elements of the periodic system platinum metals are divided into three groups: – Ru, Os, II–Ir, Rh, III–P, Pd is characterized by the largest reaction capacity, especially Pd due to a specific structure of its electronic levels. In contrast to Pt and other platinum metals Pd has three electronic levels (4s, 4p an 4d) filled, but two (5s and 5p) are free, what explains its increased reaction capacity.

In nature tellurides of platinum and palladium are most widely spread. They usually contain bismuth, however, no pure binary compounds are found.

Tellurides of platinum and palladium are typical for ores of complex copper-nickel deposits. It is very important to reveal geochemical factors of separation of platinum and palladium in the processes of depth mineral formation what is impossible without knowledge of thermodynamic properties most widely-spread on the deposits of compounds (minerals).

Due to the above – mentioned facts the researchers of the laboratory of thermodynamics of minerals of IEM, Russian Academy of Sciences have thermochemical investigations of the compounds of platinum metals with halcogenites. The object of this study are tellurides of palladium.

Two stable compounds PdTe and $PdTe_2$ [*Groeneveld*, 1955] are found in the palladium–tellurium system.

Both tellurides are easily obtained while heating stochiometric mixtures. The latter are placed into the capsules made from melted quartz, pumped to pressure 10^{-4} mm, sealed in the flame of the oxygen burner and heated at T=800°C.

It was determined by the preliminary investigations that the synthesis of tellurides took place completely under the above-described conditions for 5–6 min. The X-ray analysis of the synthesis products confirmed the presence of substances of only given composition there. Calorimetric definitions were performed at a high-temperature vacuum-block calorimeter, made in the laboratory of thermodynamics of minerals, IEM, Rus. Acad. Sci. and described earlier [*Soboleva and Vasil'ev*, 1962, *Fleisher and Stolyarova*, 1978]. The capsule with the charge processed as above was put into the furnace of the calorimetric bomb which was then filled by argon: pressure 5 atm. The calorimetric bomb was put into the vessel; the latter was pumped to the remnant pressure 10^{-2} mm. The temperature of the isothermic cover was 25±0,02°C. The electric energy was measured with the accuracy to 0.02 %.

Temperature rise during the run was measured by a copper resistance thermometer (-865 Om at T=25°C), located along the calorimetric bomb. The calorimeter was calibrated by the electric energy.The accuracy of determination of the thermal value was 0.02%. The reactions of synthesis in the calorimeter took place completely during the first heating, the second heating gave no additonal effect what confirmed our conclusion on a total reaction during the first heating.

The X-ray phase analysis of products of calorimetric runs confirmed the presence of only given substances PdTe and $PdTe_2$ there, respectively. The results of the calorimetric definitions are given in Tables 1 and 2.

The average square error was calculated at the level of valuability of 95% [*Nalimov,* 1960].

The following values were obtained:

For PdTe $\Delta_f H^o_{298.15}$ = -51.93±0.49 кJ/mol

For $PdTe_2$ $\Delta_f H^o_{298.15}$ = -75.75±0.68 кJ/mol

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Таблица 1. Enthalpy of formation from elements of palladium tellurides PdTe (MM 234,02 g·mol^{-1})

		Characteristics of heater work							Heat number in the run, Q/J			
Runs	Charge, g	t, sec	V, V	J, A in switchig on	$\int_{t_н}^{t_к} Jdt$ on device, A·sec	$\int_{t_н}^{t_к} Jdt$ in the run, A·sec	Speed cooling, 10^{-5}, K·min^{-1}	ΔR + δ, Om [*]	Total	on the heater	in the run	$-\Delta H^{o}_{реак} f_{298.15}$ kJ/mol in unique run
1	1.8200	360.472	35.478	3.079	1118.576	1119.665	38	6.1148	40123.6	39723.5	400.1	51.44
2	2.0550	361.716	35.481	3.074	1119.364	1121.201	36	6.1336	40246.8	39781.3	465.5	53.01
3	2.9020	361.649	35.501	3.070	1122.579	1124.207	40	6.1796	40548.7	39910.5	638.2	51.46
4	2.1200	360.690	35.596	3.078	1117.308	1119. 067	40	6.1418	40300.7	39843.3	466.4	51.48
5	2.7205	360.298	35.518	3.072	1117.709	1118.262	41	6.1667	40329.0	39718.4	610.6	52.52
6	2.0252	360.516	35.524	3.073	1112.882	1114.105	37	6.1193	40019.0	39577.5	441.5	51.02
7	2.5109	360.087	35.624	3.083	1118.411	1118.314	40	6.1767	40394.4	39834.3	466.4	51.48
8	2.0449	361.154	35.657	3.080	1119.518	1119.626	35	6.1749	40382.6	39922.5	460.1	52.68
Result												51.93±0.49

Note:

Thermal value of calorimeter in the runs 1–4 W=6561.7±2 J/Om; in runs 5–8 W=6539.8±2 J/Om

[*] (ΔR + δ) – A change of thermometer resistence with the correction for thermal exchange

Таблица 2. Enthalpy of formation from elements of palladium ditellurides from elements (MM 361,627 g·mol^{-1})

		Characteristics of heater work							Heat number in the run, Q/J			
Runs	Charge, g	t, sec	V, V	J, A in switchig on	$\int_{t_н}^{t_к} Jdt$ on device, A·sec	$\int_{t_н}^{t_к} Jdt$ in the run, A·sec	Speed cooling, 10^{-5}, K·min^{-1}	ΔR + δ, Om [*]	Total	on the heater	in the run	$-\Delta H^{o}_{peak} f_{298.15}$ kJ/mol in unique run
1	3.6057	360.500	35.719	3.086	1117.870	1119.049	33	6.1934	40722.0	39971.3	751.1	-75.37
2	3.1576	360.938	35.751	3.087_5	1120.262	1122.795	37	6.2051	40799.8	40141.0	658.8	-75.45
3	1.3959	360.983	35.485	3.077	1116.747	1119.409	41	6.0827	40021.7	39722.2	299.5	-77.59
4	1.4080	360.957	35.517	3.072_5	1115.240	1117.817	39	6.0791	39998.0	39701.5	296.5	-76.15
5	3.1636	361.618	35.473	3.062	1118.237	1119.766	35	6.1379	40384.9	39721.4	663.5	-75.84
6	1.4910	361.283	35.510	3.072_5	1115.470	1115.975	37	6.0703	39940.1	39628.3	311.8	-75.62
7	1.5041	360.671	35.497	3.073	1111.554	1113.253	34	6.0533	39828.3	39517.1	311.2	-74.82
8	1.4982	361.627	35.518	3.0765	1116.768	1116.851	36	6.0733	39979.6	39668.3	311.3	-75.14
Result												75.75 ±0.68

Note: In the runs 1–2 – – thermal value of the calorimeter – W = 6575.2±2 J·Om^{-1}; In the runs 3–8 – W = 6579.6 ±2 J·Om^{-1} .
[*] (ΔR+δ) - change of thermometer with the correction for thermal exchange