ENTHALPY OF FORMATION OF DIARSENIDES OF RUTHENIUM AND URIDIUM

Stolyarova T.A. (IEM RAS, Chernogolovka)

Key-words: enthalpy, thermochemical investigations

Similarity of metals referring to one group- platinoid group-is emphasisized in geochemistry. Ruthenium and iridium, referring to one group really behave differently, for example, iridium and ruthenium together with osmium in contrast to platinum and palladium refer to high-melting metals. Thermodynamically high-melting metals differ by considerably lower values of free energy of formation of their disulfides.

Study of geochemical behavior of elements of this group is very important to understand processes of depth mineral for mation where they are concentrated in sulfide nickel-copper and sulfide – chromite ores. Sulfide ore formation is extremely various in geochemical specifics; on the one hand, it is determined by participatio0n of selenium and tellurium there, on the other hand – by that of antimony and arsenic. Thermochemical investigations of sulfides and arsenides of platinum metals have been studied for several years already in the laboratory of thermodynamics of minerals.

This work is devoted to determination of enthalpies of formation of diarsenides of ruthenium and iridium. There are no thermodynamic data on these compounds in literature. It has been determined by preliminary investigations that diarsenides of ruthenium and iridium are easily obtained from their stoichiometric mixtures of the given composition in the capsules pumped to the vacuum of 10 mm from melted quartz at heating up to 1000°C during several minutes.

These reactions were used for a thermochemical study of diarsenides of ruthenium and iridium.

The investigations were done at the high-temperature vacuum-blocking calorimeter {I}.To prepare stoichiometric mixtures powders of metals of ruthenium and iridium of 99,9% purity and metallic arsenic of SP grade were used. The capsule with the charge of stoichiometric mixture was placed into the furnace, which was in the calorimetric bomb, filled by argon (5 atm). The space of the vessel where the calorimetric bomb was put into, was pumped to the vacuum of 10 mm. The temperature of the isometric cover was 25±0,004°C. The electric energy was measured the accuracy of 0.02%. The temperature rise during the run was determined by the copper thermometer of resistance of 865 Om at 25°C, located along the calorimetric bomb. The calorimeter was preliminarily calibrated with the help of the electric energy. The accuracy of determination of the thermal value was 0,005%.

Synthesis reaction completely took place during the first heating. The second heating, performed for control, did not give any effect, what confirms our conclusion: synthesis takes place during the first heating.

The x-ray analysis of the run products showed the presence of only arsenides of the given composition there. The results of the calorimetric determinations are given in tables 1 and 2. The average square errors were calculated on the level of magnitude of 95%. [2].

The following values are obtained: for $RuAs_2$: $-\Delta H^0{}_{f298.15} = 153.2\pm0.6$ kJ/mol;
for $IrAs_2$: $-\Delta H^0{}_{f298.15} = 148.7\pm1.4$ kJ/mol.

The values of enthalpies of formation of diarsenides of ruthenium and iridium are first obtained.

References

1. *Soboleva M.S., Vasil'ev Ya.V.* Enthalpy of formation of Ni telluride // Vesti. Leningrad Univ. 1962. Ser. Phys. and Chem. V. 16. P.153.
2. *Nalimov V.V.* Use of mathematics statistics at substance analysis. 1960. Moscow.

Electronic Scientific Information Journal "Herald of the Department of Earth Sciences RAS" № 1(24)'2006
ISSN 1819 – 6586
Informational Bulletin of the Annual Seminar of Experimental Mineralogy, Petrology and Geochemistry – 2006
URL: http://www.scgis.ru/russian/cp1251/h_dgggms/1-2006/informbul-1_2006/mineral-8e.pdf

Table 1 Enthalpy of formation of their elements $IrAs_2$ (MM=3420.6 g·мol^{-1})

		Characteristics of heater work							Heat quantity in the run, Q, J			
№ run	Charge, g	t, sek	V, B	J A At the moment of switching	$\int_{t_н}^{t_k} Jdt$ on device, A·sek	$\int_{t_н}^{t_k} Jdt$ in the run, A·sek	K, min^{-1}	ΔR + δ, Om	total	On heater	In run	$-\Delta H^0 f_{298.15}$ kJ/mol
1.	3.3886	311.43222	46.844	4.0085	1259.471	1260.888	50	9.2269	60537.7	59065.1	1472.6	148.65
2.	3.9949	309.35709	46.855	4.0295	1256.846	1257.972	46	9.2534	60711.5	58942.3	1769.3	151.49
3.	3.6357	311.02831	47.027	4.046	1268.737	1268.536	45	9.2762	61223.1	59655.4	1567.7	147.49
4.	3.8453	311.51742	47.105	4.0215	1269.812	1271.578	45	9.3248	61543.7	59897.7	1646.0	146.42
5.	1.9694	312.11342	46.882	4.040	1271.644	1271.786	50	9.1630	60475.8	59623.9	851.9	147.96
6.	1.7800	311.99545	47.351	4.069	1284.486	1288.221	48	9.3593	61771.4	60998.6	772.8	148.51
7.	1.8256	312.07360	46.670	4.019	1265.385	1265.069	47	9.0691	59856.3	59054.5	801.8	150.23
8.	1.7800	311.63497	46.560	3.969	1255.211	1257.416	43	8.9871	59314.7	58545.3	769.4	147.86
9.	1.3879	311.70072	46.889	4.0315	1264.564	1264.564	51	9.0945	60024.0	59411.8	612.2	150.88

Thermal values of calorimeter: **run 1-2:** W=6561.0+2J/Om; **3-9:** W=66600+2J/Om; K – temp. of cooling of calorimeter 10^{-5} min^{-1} ; ΔR+δ - changer of resistance with heating correction. $-\Delta H^0 f_{298.15}$=-148.7+1.4 kJ/g·mol

Table 2 Enthalpy of formation of their elements $RuAs_2$ (MM=250.916 g·mol^{-1})

		Characteristics of heater work							Heat quantity in the run, Q, J			
№ run	Charge, g	t, sek	V, B	J A At the moment of switching	$\int_{t_н}^{t_k} Jdt$ on device, A·sek	$\int_{t_н}^{t_k} Jdt$ in the run, A·sek	K, min^{-1}	ΔR + δ, Om	total	On heater	In run	$-\Delta H^0 f_{298.15}$ kJ/mol
1	2.4500	311.73898	46.664	4.367	1379.817	1382.728	48	9.9612	66022.8	64523.7	1499.1	153.5
2	2.5910	311.19237	46.640	4.384	1381.632	1382.160	45	9.9630	66034.8	64463.9	1570.9	152.1
3	2.6510	311.17261	46.643	4.3305	1367.505	1367.937	45	9.8751	65452.2	63804.7	1647.5	155.9
4	2.6100	312.35777	46.622	4.396	1394.215	1395.472	49	10.0558	66649.7	65059.7	1590.0	152.8
5	2.6469	311.700	46.683	4.3545	1375.680	1378.413	46	9.9804	65990.4	64348.5	1641.9	155.6
6	2.8100	311.00893	46.672	4.423	1396.340	1396.064	42	10.1117	66858.4	65157.1	1701.5	151.9
7	2.6181	312.06421	46.734	4.426	1401.210	1401.178	42	10.1443	67074.1	65482.7	1592.4	152.5
8	2.0860	311.27130	46.645	4.3805	1381.084	1381.857	46	9.9382	65711.4	64456.7	1254.7	150.9

1 -4 runs - thermal values of calorimeter: W=6628 ± 2 J/Om; 5-8 W=6612± 2 J/Om. $-\Delta H^0 f_{298.15}$=153.2±0.6 kJ/mol