PLATINUM GROUP ELEMENTS (PGE). THERMODYNAMIC PROPERTIES

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Thermodynamic modelling of complex reactive chemical systems has found an application for various scientific and engineering fields. However, the reliability of the results obtained depends mostly on the accuracy of thermodynamic properties. Thus, when designing the theoretical investigations, it is essential to use more precise information on thermodynamic properties of minerals, chemical compounds and elements, which are often missed or display a considerable scatter in the values as one can learn from available publications [1-12]. The thermodynamic modelling of natural processes allows estimating possible formation conditions (P-T parameters and fluid regime), for example, for layered intrusions containing PGE compounds. The data obtained, when computing such a complex natural system, would, however, be defined by the accuracy of used thermodynamic properties of chemical elements and compounds. In the studying process, the published data on PGE thermodynamic properties were analyzed (Table 1). The table displays the considerable scatter of all the PGE values. It is known though that the correct selection of thermodynamic values is of principal significance for implementing applied and fundamental investigations, excepting the probability of getting false conclusions.

Table 1

Some reference data on platinum group elements

Elements	V^0_{298}, J/bar	S^0_{298}, J/mol·K	Cp^0_{298}, J/mol·K
Ru	0,81181 – 0,82844	28,53 – 28,8696	24,0 – 24,267
Rh	0,823 – 0,82988	31,5055 – 31,7984	24,95 – 25,104
Pd	0,879 – 0,88667	37,202 – 37,907	25,857 – 25,983
Os	0,84123 – 0,846	32,60 – 32,65	23,86 – 24,71
Ir	0,84857 – 0,85812	35,45 – 36,4008	24,93 -25,522
Pt	0,9074 – 0,90951	41,5471 – 41,84	25,81 – 26,57

In offered operation the attempt by a calculated way define more precise values of thermodynamic properties and volumetric characteristics of platinum group elements is undertaken. The analysis of existing every possible methods of the theoretical prognosis of thermodynamic and volumetric values has shown necessity of application of any stationary values of parameters of researched elements and chemical components with the purpose of an establishment of possible correlation dependence with their participation. For a basis of investigation the attempt of an establishment of possible regularity of a alteration of standard values of an entropy (S^0_{298}), heat capacity (Cp^0_{298}) and molecular volume (V^0_{298}) of platinum group elements from values of their molecular weight (M), logarithm of a molecular weight (lgM), and also serial number (N) in a periodic system of elements is undertaken.

The method of the comparative calculation using the explained approaches, allows with a relatively split-hair precision to determine and (or) to correct thermodynamic values of elements and chemical components [3,5]. The given method employing the stated approaches makes it also possible to correct thermodynamic properties to a relatively high accuracy. Such advantages of the method were used in specifying the published thermodynamic values for PGE. The volume of the source information used turned out to be quite sufficient for successful application of the comparative computing method. The estimation of the calculated entropy, heat and volume values was checked by factors of multiple linear regression equations obtained through the technique of least squares. The investigation has found out that the above-listed rules however take place as distinctive linear dependences. It was reflected in their separate description both for light (Ru, Rh, Pd) and heavy (Os, Ir, Pt) PGE. Equations such as V^0_{298} = 0,21270 / (2,26746 - lgM) at a coefficient of correlation equal 0,99484, S^0_{298} = M·1,74030 - 147,32945 at a coefficient of correlation equal 0,99997 and Cp^0_{298} = lgM·79,88573 - 135,93305 at a coefficient of correlation equal 0,98597 reflect a clear linear dependence between the indicated parameters with participation only of light elements of platinum group. Equations such as V^0_{298} = 0,12245 / (2,42541 - lgM) at a coefficient of correlation equal 0,98687, S^0_{298} = M·1,82970 - 315,34570 at a coefficient of correlation equal 0,99996 and Cp^0_{298} =

lgM·137,95276 - 289,90937 at a coefficient of correlation equal 0,99456 reflect a clear linear dependence between the indicated parameters for heavy elements of platinum group. The results of a solution of the presentation equations are submitted in the table 2.

It has allowed, at presence of an explicit coherence between stationary values and variable parameters, to receive the relevant interpolation equations as for light, and heavy of platinum group elements. The results of the research and solutions of the given equations are represented in Table 2 as suggested entropy, thermal capacity and molecular values.

Table 2

Results of computing the values of PGE thermodynamic properties and volumetric characteristics

Elements	V^0_{298}, J/bar	S^0_{298}, J/mol·K	Cp^0_{298}, J/mol·K
Ru	0,80925	28,5627	24,2075
Rh	0,83406	31,7561	24,8322
Pd	0,88445	37,8385	25,9905
Os	0,83760	32,6632	24,5139
Ir	0,86440	36,3592	25,1402
Pt	0,90590	41,6105	26,0356

Variation of values of errors of thermodynamic properties and volumetric characteristics of platinum group elements are in limits from -0,43 % up to +0,76 %. The comparison of the values given in Table 2 and published (Table 1) ones allows the adduced equations to be considered as quite correct.

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