THERMODYNAMIC PROPERTIES OF CHALCOGENES ON PLATINUM AND PALLADIUM

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For theoretical methods of research the basic condition is the establishment of natural connections which enable to determine necessary sizes on the basis of the available data for other substances. The analysis of existing every possible methods of the theoretical forecast of thermodynamic and volumetric sizes has shown necessity of attraction for realization of the given research of any constants, concrete parameters of elements and chemical compounds. For the given purpose sizes of molecular weight of connections (M), a serial number of elements (N) in periodic system were used, their logarithmic expression (lgM, lgN), and also the sums entropy the elements making connection etc. For an establishment of any laws in change of properties of the specified connections, depending on various factors, parameters, were used their known data in numerous reference books of thermodynamic properties. As a result of the carried out work some laws of change of values of free Gibbs energy, enthalpy formations, standard entropy, thermal capacities and molecular volume of sulfides, selenides, tellurides of a palladium and platinum from the specified parameters were established.

During studying the listed dependences the control with application of graphic constructions was carried out. An estimation of the designed sizes was supervised by factors of the equations of the plural linear regress received by a method of the least squares. It is necessary to note, that thermodynamic properties and volumetric characteristics of the specified connections appeared separate, as before at platinum group of elements [1,2], on easy (palladium) and heavy (platinum) sulfides, selenides and tellurides.

The carried out research, from use of various variants of calculation, it was established, that the found out law of change has the common character, and the optimal appeared dependences of molecular volumes of researched connections on molecular weight of sulfur, selenium and tellurium. At presence of an obvious coordination rather precise linear dependence between constants and variable parameters which can be described by the following equations is established:

а) *PdS, PdSe, PdTe*: V^o_{298}, J/bar = 0.005084 x M + 1.3594
at the factor of correlation equal 0.9059;
б) *PtS, PtSe, PtTe*: V^o_{298}, J/bar = -0.00689 x M + 3.7796
at the factor of correlation equal 0.9955;
в) PdS_2, $PdSe_2$, $PdTe_2$: V^o_{298}, J/bar = 0.0062585 x M + 2.0926
at the factor of correlation equal 0.9954;
г) PtS_2, $PtSe_2$, $PtTe_2$: V^o_{298}, J/bar = 0.007876 x M + 0.88539
at the factor of correlation equal 0.9682.

Rather precise linear dependence is established between standard sizes entropy sulfides, selenides, tellurides of palladium and platinum and their molecular weight. As follows from the received settlement material, standard entropy easy (palladium) sulfides, selenides, tellurides have linear connection with their molecular weight (M), and heavy (platinum) - from return size in M. At presence of an obvious coordination between constants and variable parameters the following types of dependences are established:

а) *PdS, PdSe, PdTe*: S^o_{298}, J/mol x T^o = 0.3338 x M + 11.3992
at the factor of correlation equal 0.9996.
б) *PtS, PtSe, PtTe*: S^o_{298}, J/mol x T^o = 0.2747 x M - 7.5339
at the factor of correlation equal 0.9918.
в) PdS_2, $PdSe_2$, $PdTe_2$: S^o_{298}, J/mol x T^o = 169.2023 - 15382.38/M
at the factor of correlation equal 0.9897.
г) PtS_2, $PtSe_2$, $PtTe_2$: S^o_{298}, J/mol x T^o = 183.84 - 28320.1/M
at the factor of correlation equal 0.9998.

At the given investigation phase, after approbation of various variants for an establishment of possible natural connections, the principle of additivity was taken for a basis. Many properties of chemical compounds can be presented as the sum of contributions of molecules making them. In our case the sum entropy elements which was determined by addition standard entropy platinum and a palla-

dium, designed by us earlier, and standard sizes sulfur, selenium and tellurium from IVTANTERMO [3] was used.

The graphic analysis of position of values enthalpies depending on the sum standard entropies elements of their components has shown formations that position of points on the diagram allows counting valid presence of linear dependence between the specified parameters. The given dependence is described by the following separate for researched chemical compounds interpolation the equations:

а) *PdS, PdSe, PdTe*: - ΔH^o_{298}, kJ/mol = 2.26218 x Σ S^o_{298}, *elem.*-233.7131
at the factor of correlation equal 0.9937;
б) *PtS, PtSe, PtTe*: - ΔH^o_{298}, kJ/mol = 2.60951 x Σ S^o_{298}, *elem.*-273.7090
at the factor of correlation equal 0.9614;
в) PdS_2, $PdSe_2$, $PdTe_2$: - ΔH^o_{298}, kJ/mol = 0.85135 x Σ S^o_{298}, *elem.*-166.9069
at the factor of correlation equal 0.9596;
г) PtS_2, $PtSe_2$, $PtTe_2$: - ΔH^o_{298}, kJ/mol = 1.51726 x Σ S^o_{298}, *elem*. - 271.5478
at the factor of correlation equal 0.9995.

For definition of size of free energy of sulfides, selenides, tellurides of a palladium and platinum equation Gibbs, and also the sizes designed by us enthalpy formations, standard entropy and the sums standard entropy the elements making these connections was used:

$$- \Delta Go298, \text{ кДж/моль} = - \Delta H^o_{298} - 298.15 \text{ x } (S^o_{298,}\, comb. - \Sigma\, S^o_{298,}\, elem.).$$

The given equation has allowed specifying and receiving the coordinated required thermodynamic sizes of sulfides, selenides, tellurides of a palladium and platinum. From known in limits ±3.0 %.

For definition of sizes of a thermal capacity of sulfides, selenides, tellurides of a palladium and platinum in rather wide interval of temperatures by means of power numbers with empirical factors Landia method [4] which yields quite satisfactory results with rather high accuracy was used.

As a result of the carried out research new laws of change of sizes of molecular volume, the thermodynamic data of sizes, and also factors of the equation of a thermal capacity for definition of values of a high-temperature thermal capacity of sulfides, selenides, tellurides of a palladium and platinum are established.

The received values of thermodynamic properties and variation of sizes of mistakes for sulfides, selenides, tellurides of a palladium and platinum is in limits ±3 % from average literary values that allows to count them correct enough. The submitted results of theoretical research can be used as for definition of thermodynamic parameters of reactions, and systems with participation of the chemical compounds submitted by the given work.

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