THERMODYNAMIC STUDY OF MOLECULAR OXYGEN DISSOCIATION PROCESSES IN VAPOR OVER OXIDES AND THEIR COMPOUNDS

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The study of evaporation and condensation processes of substance has attracted considerable interest for the solution of different theoretic and practical tasks. In particular this interest derives from the importance of this data for understanding of the problems relating to the chemical evolution of protoplanet substance in the process of successive condensation of incandescent gases at forming space objects as physicochemical systems.

The process of successive condensation of any matter is assumed to be characterized by temperature dependencies of the total pressure of the gas phase over the compounds [1]. Recently in the investigation of regularities of evaporation processes of CaO-MgO-Al_2O_3-SiO_2 compounds [2] we observed the linear dependence of logarithm of vapor total pressure over the compounds *vs.* the molecular oxygen content in vapor (or the degree of its dissociation). It points to the fact that there is a relationship between the red-ox reactions in the gaseous substance and the condensation processes. In this connection it seems to be useful to consider the observed regularities on example of another oxide compounds.

In the present study the composition and partial pressures of 305 vapor species along with the total pressures over 162 most investigated oxides and 36 oxide compounds were calculated in terms of thermodynamic approach for the temperature range 1700-2200 K using the own experimental and reference data on the constants of gas-phase and heterogeneous equilibriums and the oxide activities in oxide compounds [3-8]. The choice of the study temperature range was caused by the condensation temperatures of most important compounds formed at cooling of substance in the solar nebula. The total vapor pressure over oxides and its compounds were calculated by summing over the proper partial pressures of the vapor species taken for the case of chemically neutral conditions. It should be pointed out that such data are not numerous and it hasn't been used earlier for the thermodynamic calculations.

On examination of the obtained temperature dependences of vapor species partial pressures over oxides and their compounds some regularities between partial pressures of atomic and molecular oxygen and the total vapor pressure have engaged our attention.

The calculated values of vapor total pressure over investigated compounds *vs.* the molecular oxygen content (*a*) and the ratio of partial pressures of atomic and molecular oxygen (*b*) at 2000 K showed in the Figures. According to calculations the significant difference is observed in the values of the total vapor pressures over oxides and their compounds, in particular, the values of $p_{tot}(X_iO_j)$ lie in the range from 10^{-10} (for HfO_2 and Tb_2O_3) to 10^{10} (for RhO_2) atm at 2000 K. The same Figures demonstrate the curve (1), which corresponds to oxygen itself. It can be noticed that in the temperature interval 1700-2200 K no sufficient change in point location relative to each other was observed.

According to the Figures one can subdivide oxides and their compounds into two main groups with respect to the dissociation degree of the molecular oxygen in the gas phase. The significant dissociation of the molecular oxygen in the gas phase ($x(O_2) < 1$ mole %) is typical for the first group (B_2O_3, BaO, CrO, EuO, GeO, H_2O, MoO_i, NbO, NbO_2, Nd_2O_3, P_4O_{10}, Pu_iO_j, Re_iO_j, Rh_iO_j, RuO_2, SO_3, SeO_2, SnO, ThO_2, Ti_iO_j, U_iO_j, V_iO_j, WO_i), which denoted (2) in the Figures.

Another one denoted (3-6) in the Figures is characterized by the different content of molecular oxygen in vapor and the atomic-to-molecular oxygen ratio being the same as in the case of pure oxygen. The minimal molecular oxygen content in vapor possess Am_iO_j, BeO, Ce_iO_j, Dy_2O_3, Er_2O_3, Gd_2O_3, HfO_2, Ho_2O_3, La_2O_3, Lu_2O_3, Pr_2O_3, PrO_2, Sc_2O_3, Sm_2O_3, Ta_2O_5, Tb_iO_j, ThO_2, Tm_2O_3, Y_2O_3, Yb_2O_3 and ZrO_2 denoted (3) in the Figures.

A number of the latter group oxides and their compounds (Al_2O_3, CaO, CoO, Eu_2O_3, Fe_iO_j, Ga_2O_3, MgO, Mn_iO_j, Nb_2O_3, Pr_6O_{11}, Pr_7O_{12}, SiO_2, SrO_i) denoted (4) in Figures are of a special interest since they possess the minimal total vapor pressure values at maximal percentage of molecular oxygen in the gas phase. We should also emphasize the linear relationship between the mole fraction of the molecular oxygen in the gas phase and the total vapor pressure value. As may be seen from the Figure *b*

the very low values of vapor total pressures (in respect to other oxides of this group) are observed for CaO_2, OsO_2 and OsO_4 denoted (5) in the Figures.

The suggested oxide classification based on the molecular oxygen dissociation degree gives an opportunity to make some conclusions on the general features of the condensation processes and provides rather accurate estimations of the total vapor pressures over oxides and oxide compounds.
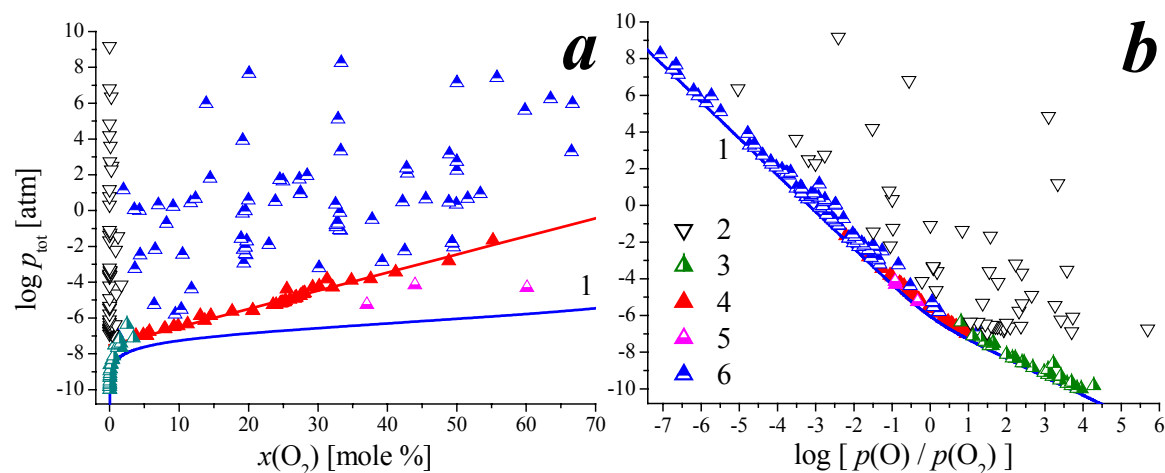

Fig. The dependences of total vapor pressure over oxides and its compounds *vs.* content (*a*) and ratio of partial pressures of atomic and molecular oxygen (*b*) at 2000 K. Table of symbols: 1 – the curve, which corresponds to oxygen; 2-6 – the point, which corresponds to different group of oxides and its compounds (see text for explanation).

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