

A THERMODYNAMIC REGULARITIES OF EVAPORATION PROCESSES OF CMAS COMPOUNDS.

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Introduction: The chemical evolution of proto-planet substances and the problems relating to the condensation and the cooling of substance in the solar nebula have attracted considerable interest of scientists for a long time [1, 2]. This interest derives from the importance of the process of successive condensation of incandescent gases at forming space objects as physico-chemical systems. Firstly the condensation of the hot gas of solar composition was investigated quantitatively by Larimer [3] and then by him together with Grossman [4]. It's necessary to notice that the results of further theoretical investigation didn't give rise to any substantial review of their important conclusions about the sequence of protoplanet substance condensation [5]. At the same time the theoretical calculations require of experimental confirmation.

The oxide system under study, CaO-MgO-Al₂O₃-SiO₂ (CMAS) is a part of the system CaO-FeO-MgO-Al₂O₃-SiO₂ (CFMAS) which is one of the most important ones to understand the above-mentioned cosmo-chemical problem. More than 30 compounds were found to exist in the CMAS system [6]. However the information about the evaporation processes and thermodynamic properties of CMAS compounds and their melts at high temperatures (more than 1800 K) is poor and contradictory in comparison with the one for oxides [7].

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 [3, 4]. However at the determination of the total pressure of the gas phase over the substance the researcher runs into a number of problems rising at the proper experiment. These problems are caused by both some peculiarity of physico-chemical properties of the system under study and the necessity to take into consideration the shift in the chemical equilibrium brought on by the high temperature chemical interaction of the melt with the container material [8]. In this connection the information obtained by the high-temperature Knudsen effusion method [9] is of great interest. This method combines the data about the equilibrium constants of the reactions in the gas phase and the activity of oxides in compounds. It should be pointed out that such data haven't been used earlier for the thermodynamic calculations.

Experimental: The study of the evaporation of CMAS compounds from molybdenum effusion cells

was carried out using MI 1201 mass spectrometer with the ion source modified for the high-temperature investigations [9]. One of the unique characteristics of this source is the possibility of heating of the effusion cell up to 3000 K at the background pressure less than 10⁻¹⁰ atm.

Calculations: In this investigation we took into account all the equilibriums in the gas phase with the participation of the following atoms and molecules: Al, AlO, AlO₂, AlSiO, Al₂, Al₂O, Al₂O₂, Al₂O₃, Ca, CaO, CaSiO₃, Mg, MgO, MgAlO, O, O₂, O₃, Si, SiO, SiO₂, Si₂, Si₂O₂, Si₃, Si₃O₃ [7, 10-13]. The activities of oxides for CMAS compounds were obtained experimentally. Their short resume is given in [6]. The temperature dependence of the total vapour pressure over CMAS compounds were calculated by summing over the proper partial pressures of the vapour species taken for the case of chemically neutral conditions within 1700-2200 K.

Results and Discussion: The obtained data are summarized in the Table and Fig. 1 and 2.

As may be seen from the Fig. 1 the dependence of the total vapour pressure over CMAS compounds are not at variance with the condensation sequence of compounds which was calculated by Larimer and Grossman [4]. The values of the total vapour pressure over corundum (Al₂O₃), hibonite (CaAl₁₂O₁₉), CaAl₄O₇ and CaAl₂O₄ are practically identical. The values of the total vapour pressure over lime (CaO), Ca₃Al₂O₆ and mayenite (Ca₁₂Al₁₄O₃₃) are also close each other. The maximum value of the total vapour pressure belongs to the one of silica (SiO₂).

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

As one can see from Table and Fig. 2 the value of the total vapour pressure over CMAS compounds depends on the content of molecular (atomic) oxygen in vapour: the more molecular oxygen in vapour, the more other vapour species, and the higher the total vapour pressure.

Fig. 2 shows the linear dependence of the logarithm of the total vapour pressure over CMAS compounds on the contents of molecular oxygen in vapour (or the degree of its dissociation). It points to the fact that there is a relationship between the red-ox reactions

in the protoplanet gaseous substance and the processes of condensation and formation of space objects.

The considered thermodynamic regularities of evaporation of CMAS compounds are likely to be obeyed for the other oxide compounds and to have more general character. Our further work will be devoted to these questions.

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Table: The calculated total vapour pressures and vapour content over CMAS compounds for the case of chemically neutral conditions at 2000 K.

№	Compound	p_{tot} , atm	$x(\text{O})$, mole %	$x(\text{O}_2)$, mole %	Vapour species	$x(i)$, mole %
1	A	$1.05 \cdot 10^{-7}$	47.6	5.3	AlO	18.3
2	CA ₆	$1.06 \cdot 10^{-7}$	47.3	5.3	AlO	17.9
3	CA ₂	$1.03 \cdot 10^{-7}$	47.0	5.1	AlO	16.7
4	CA	$1.14 \cdot 10^{-7}$	43.5	4.8	Ca	36.1
5	C ₅ A ₃	$2.44 \cdot 10^{-7}$	37.9	7.9	Ca	52.8
6	C ₁₂ A ₇	$2.50 \cdot 10^{-7}$	37.7	8.0	Ca	53.0
7	C	$3.19 \cdot 10^{-7}$	36.0	9.3	Ca	54.4
8	C ₃ A	$3.20 \cdot 10^{-7}$	35.9	9.3	Ca	54.1
9	C ₃ S	$3.56 \cdot 10^{-7}$	35.1	9.9	Ca	31.4
10	C ₂ S	$4.60 \cdot 10^{-7}$	32.9	11.2	SiO	41.4
11	C ₂ AS	$7.16 \cdot 10^{-7}$	29.2	13.7	SiO	49.7
12	C ₃ S ₂	$2.55 \cdot 10^{-6}$	18.9	20.6	SiO	59.9
13	MA	$2.69 \cdot 10^{-6}$	18.5	20.7	Mg	59.6
14	M	$5.57 \cdot 10^{-6}$	13.7	23.6	Mg	60.8
15	C ₃ AS ₃	$5.60 \cdot 10^{-6}$	13.8	24.0	SiO	61.4
16	CAS	$6.79 \cdot 10^{-6}$	12.7	24.6	SiO	61.9
17	M ₂ A ₂ S	$7.02 \cdot 10^{-6}$	12.5	24.8	SiO	47.4
18	MAS	$7.02 \cdot 10^{-6}$	12.5	24.8	SiO	47.4
19	CS	$7.45 \cdot 10^{-6}$	12.2	24.9	SiO	62.1
20	CMS ₂	$7.89 \cdot 10^{-6}$	11.9	25.2	SiO	61.7
21	A ₃ S ₂	$1.13 \cdot 10^{-5}$	10.2	26.2	SiO	62.4
22	M ₂ A ₂ S ₅	$1.27 \cdot 10^{-5}$	9.7	26.6	SiO	59.7
23	M ₂ S	$1.35 \cdot 10^{-5}$	9.4	26.7	SiO	59.3
24	CAS ₂	$1.42 \cdot 10^{-5}$	9.2	26.9	SiO	62.8
25	MS	$1.77 \cdot 10^{-5}$	8.3	27.5	SiO	61.4
26	S	$2.73 \cdot 10^{-5}$	6.8	28.3	SiO	63.1

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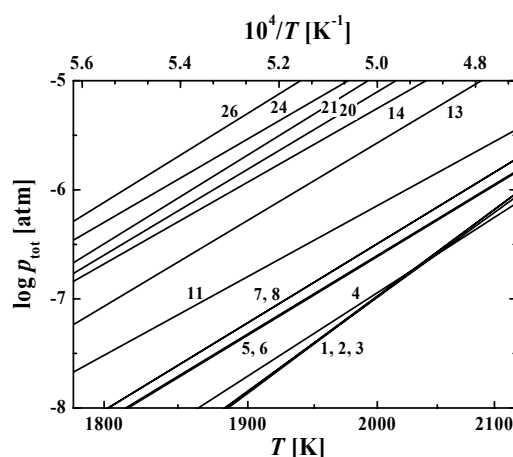


Figure 1: Temperature dependencies of the total vapour pressure over some CMAS compounds.

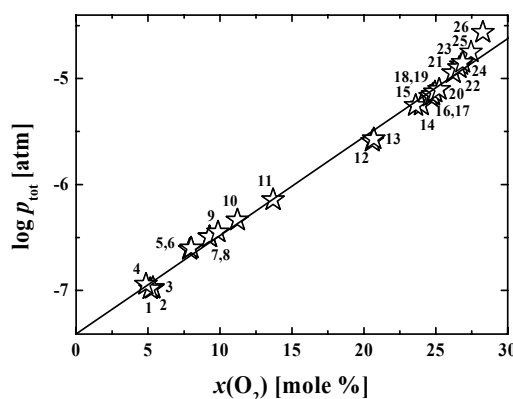


Figure 2: The total vapour pressure over CMAS compounds vs molecular oxygen content.