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REGULAR ARTICLE

Thermodynamic Analysis of the Equilibrium Vapor Phase Composition of the Cd-I_2 System

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The thermodynamic analysis of the composition of the vapor phase of the Cd-I_2 system in the temperature range of 298-2000 K at the values of the total pressure in the system from 0.1 kPa to 100 kPa was assessed. The calculations assumed that the Cd-I_2 system in the vapor phase contains the following components: I, I_2, Cd, CdI, and CdI_2. The results show that the dominant component of the vapor phase is cadmium diiodide (CdI_2). In the temperature range of 298-950 K, Cd, and I_2 predominate among the dissociation products, and the equilibrium in the vapor phase is described by the reaction $CdI_2(g) \leftrightarrow Cd(g) + I_2(g)$. The optimal temperature conditions for growing cadmium diiodide crystals from the vapor phase are proposed. Single crystals of CdI_2 have been grown at the temperature of the source zone – 890-900 K, and crystallization zone – 500-530 K.

Keywords: Cadmium diiodide, Thermodynamic analysis, Equilibrium constant, Partial pressure, Vapor phase.

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1. INTRODUCTION

Layered wide band gap ($E_g \approx 3.8$ eV [1]) cadmium diiodide crystals attract the attention of researchers due to the possibility of their use as scintillation detectors, ultraviolet photochromic materials, phosphors, materials for memory elements, photography, electroplating, and lithography [2, 3]. Interest in the thermochemical properties of cadmium diiodide is due to the possibility of CdI_2 formation in nuclear reactors during emergency conditions [4-6]. At high temperatures, iodine is a very aggressive substance and can react with various components of a nuclear reactor. Cadmium or its alloys with silver and indium are used in control rods as neutron absorbers. Therefore, it is important to predict the quantitative and qualitative composition of vapors when heating iodides for modeling chemical interactions in reactors at different temperatures and pressures.

The CdI_2 layer package consists of three monolayers of I-Cd-I atoms, which are connected by a strong ionic-covalent bond. There are weak van der Waals forces between the layer packets. More than 250 polytypes of cadmium diiodide have been identified [7], which differ in the method of packaging layered packages. With various growing methods, the 4H-polytype CdI_2 is most often obtained, which is the most stable at room and high temperatures.

CdI_2 crystals are most often obtained by crystallization from a melt [3, 8, 9], from solutions [9, 10], from the vapor phase [8, 11-13], as well as by chemical deposition of thin films on a substrate [14]. The synthesis of two-dimensional layered cadmium diiodide nanoplates using a vapor transport and deposition approach is reported in [15]. Crystallization from the vapor phase is a promising method of obtaining single crystals of cadmium diiodide. The high structural perfection of crystals grown from the vapor phase is because they have more degrees of freedom during crystallization than crystals obtained from the melt or thin films deposited on a substrate. However, the process of crystallization of CdI_2 from the vapor phase has not been sufficiently studied, in particular, there is no information on the thermodynamic analysis of the equilibrium composition of the vapor phase of the Cd-I_2 system.

The analysis of the equilibrium composition of the vapor phase allows to optimization of the experimental process of growing crystals. The temperature dependence of the equilibrium composition of the vapor and condensed phases determines the mechanism of mass transfer in the system and the quality of the grown crystals. The purpose of the work is the thermodynamic analysis of the equilibrium composition of the vapor phase of the Cd-I_2 system in the temperature range of 298-2000 K at total pressure values of 0.1-100 kPa and establishing the optimal conditions for the growth of single crystals of cadmium diiodide.

2. CALCULATION OF REACTION EQUILIBRIUM CONSTANTS AND PARTIAL PRESSURES OF VAPOR PHASE COMPONENTS

The use of thermodynamic methods for the study of chemical reactions makes it possible to establish which of the chemical reactions in the system at given temperatures, pressures, and concentrations of components can proceed spontaneously. Also, thermodynamic methods help to establish the limit of the spontaneous flow of reactions and how the parameters need to be changed so

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that the process proceeds in the right direction and to the right extent.

Calculations of the equilibrium composition of the vapor phase for the conditions of growing crystals in a closed system were carried out according to the known method: 1) formation of a system of equations of independent chemical reactions; 2) calculation of equilibrium constants of independent reactions in the temperature range of 298-2000 K; 3) calculation of the temperature dependence of the partial pressures of the vapor phase components at a given total pressure.

Experimental studies of the composition of the vapor phase over CdI_2 were carried out in works [4, 6, 16]. In [4] the vapor composition above CdI_2 system was studied by the Knudsen effusion mass spectrometry. In mass spectrum of vapor above CdI_2 the ions Cd^+, CdI^+, CdI_2^+ were detected in the temperature range 500-750 K. As the temperature rises to 750 K, I^+ and I_2^+ ions additionally appeared in the vapor mass spectrum. As a result of the study of the absorption spectrum and emission spectrum of gaseous CdI_2, it was established that iodine bands are detected at 1323 K, and dissociation into Cd, I_2 and CdI occurs at 1273-1573 K [16].

Taking into account the results of previous experimental studies, during calculations it was assumed that in the Cd-I_2 system (similar to the Pb-I_2 system [17]) there are five types of molecules in the vapor phase: I, I_2, Cd, CdI, and CdI_2, which consist of two independent chemical elements.

Chemical interaction in the vapor phase is described by three independent reactions:

$$I_2(g) \leftrightarrow 2I(g) \quad (1)$$

$$CdI_2(g) \leftrightarrow CdI(g) + I(g) \quad (2)$$

$$CdI_2(g) \leftrightarrow Cd(g) + I_2(g) \quad (3)$$

Each chemical reaction is directed to an equilibrium state in which the composition of the system (concentration or partial pressures of starting substances and products) does not change over time. The equilibrium state of a chemical reaction is characterized by the equilibrium constant. Chemical equilibrium depends on temperature and can shift when the temperature changes, that is, it is dynamic, which is expressed in a change in the constant of chemical equilibrium. Knowledge of the equilibrium constant is very important from a practical point of view, as it makes it possible to determine the optimal parameters of the technological process.

Using standard thermodynamic data [18] of substances included in reactions (1)-(3), the temperature dependences of reaction equilibrium constants were calculated. From the equations of chemical reactions (1)-(3), three equations of the relationship between the partial pressures of the components of the vapor phase can be obtained. Entering the notation $p_1 = p(\mathrm{I})$, $p_2 = p(\mathrm{I}_2)$, $p_3 = p(\mathrm{Cd})$, $p_4 = p(\mathrm{CdI})$, $p_5 = p(\mathrm{CdI}_2)$, we obtain

$$K_1 = \frac{p_1^2}{p_2} \quad (4)$$

$$K_2 = \frac{(p_1 \cdot p_4)}{p_5} \quad (5)$$

$$K_3 = \frac{(p_2 \cdot p_3)}{p_5} \quad (6)$$

Two more equations are needed to describe the equilibrium in the vapor phase, which contains five components.

Let's write the equation for the stoichiometry of the vapor phase (the number of iodine atoms per unit volume is twice as large as the number of cadmium atoms):

$$p_1 + 2p_2 + p_4 + 2p_5 + = 2(p_3 + p_4 + p_5) \quad (7)$$

Having introduced the designation of the known total pressure in the system – p, we write down Dalton's law for the pressure of a mixture of gases:

$$p = p_1 + p_2 + p_3 + p_4 + p_5 \quad (8).$$

From the system of non-linear equations (4)-(8) the equation of the fourth power with respect to p_1 was obtained. After solving the equation and finding the pressure p_1, the pressures p_2, p_3, p_4, and p_5 were determined.

3. RESULTS AND DISCUSSION

Fig.1 shows the calculated temperature dependencies of the logarithm of the equilibrium constants of reactions (1)-(3). From the obtained results, it can be seen that in the temperature range of 298-1400 K, the values of the logarithms of the reactions equilibrium constants are negative, which indicates that the reactions equilibrium is shifted towards the formation of starting substances. The values of the equilibrium constants and their logarithms testify to the high efficiency of these reactions in the temperature range of 300-1000 K.

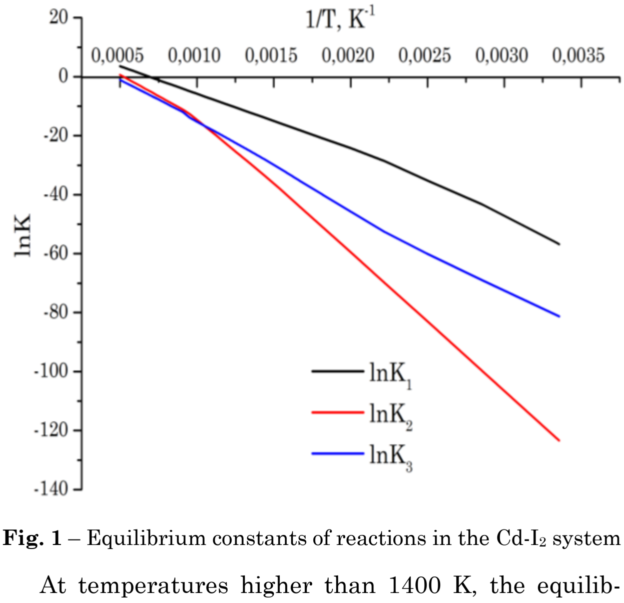

Fig. 1 – Equilibrium constants of reactions in the Cd-I_2 system

At temperatures higher than 1400 K, the equilibrium of reaction (1) shifts towards the formation of atomic iodine I, since the logarithm of the reaction equilibrium constant becomes positive (Fig. 1). The equilibrium of reaction (2) shifts towards the formation of cadmium monoiodide CdI and atomic iodine I at temperatures higher than 1900 K.

The results of calculations of the temperature dependence of the partial pressures of the vapor phase components of the Cd-I_2 system for total pressures of 0.1 kPa, 1 kPa, 10 kPa, and 100 kPa are presented in Fig. 2 (*a*-*d*).

The following conclusions can be made from the obtained results:

1) In the temperature range of 298-2000 K for the total pressure range of 0.1-100 kPa, the main component of the vapor phase is cadmium diiodide (CdI_2).

2) In the temperature range of 298-950 K, Cd and I_2 predominate among the dissociation products. At temperatures above 1000 K, the partial pressure of cadmium monoiodide CdI and atomic iodine I increases. The dissociation of CdI_2 into individual components (I, I_2, Cd, CdI) is significant at temperatures above 1500 K.

3) In the temperature range of 298-1000 K, the pressure of cadmium diiodide is 4 orders of magnitude higher than the partial pressures of the dissociation products. Under the temperature conditions that are most often realized when growing cadmium diiodide, the vapor phase can consist almost entirely of CdI_2 molecules.

4) In the first approximation, the equilibrium in the vapor phase of the Cd-I_2 system in the temperature range of 298-950 K is described by one reaction (3).

The obtained results are consistent with the experimental studies presented in works [4] and [16]. According to the absorption spectrum and emission spectrum of gaseous CdI_2 in work [16], it was established that at a temperature of 1069 K and a pressure of 100 kPa, the following are in equilibrium with CdI_2: CdI – $p \sim 0.25$ Pa, I – $p \sim 0.25$ Pa, I_2 – $p \sim 0.063$ Pa and Cd – $p \sim 0.126$ Pa. The appearance energies of ions and temperature dependences of ion current in [4] allow to conclude that vapor above cadmium iodide consists from CdI_2 molecules only.

The analysis of the temperature dependence of the partial pressures of the vapor phase components of the Cd-I_2 system allows us to make the following conclusions regarding the conditions for obtaining cadmium diiodide crystals from the vapor phase. Since a temperature gradient of 100-400 K is sufficient for substance transport during crystallization from the vapor phase, and the temperature of the crystallization zone should not exceed 661 K (the melting temperature of CdI_2), then the maximum temperature of the source zone should be considered 850-950 K. In the temperature range of 850-950 K at a total pressure of 0.1-100 kPa in the Cd-I_2 system, the predominant component of the vapor phase is CdI_2, the pressure of the dissociation products does not exceed 0.1 %. Precipitation of crystals, as a rule, occurs at temperatures lower than the melting temperature, so the temperature of the crystallization zone should be 500-600 K.

CdI_2 single crystals were grown by us from the vapor phase in a closed system (vacuum ampoules) at the temperature of the source zone – 890-900 K, the crystallization zone – 500-530 K and the duration of the growing process was 4.5 hours. Cadmium diiodide synthesis and crystal growth were carried out according to the method described in detail in works [19, 20]. Cadmium diiodide, previously synthesized from individual components, was used as a source of evaporation. As a result of crystallization from the vapor phase, transparent colorless plate-shaped crystals of CdI_2 with a diameter of up to 1 cm^2, a thickness of ~ 0.1 mm, and a 4H-polytype were obtained.

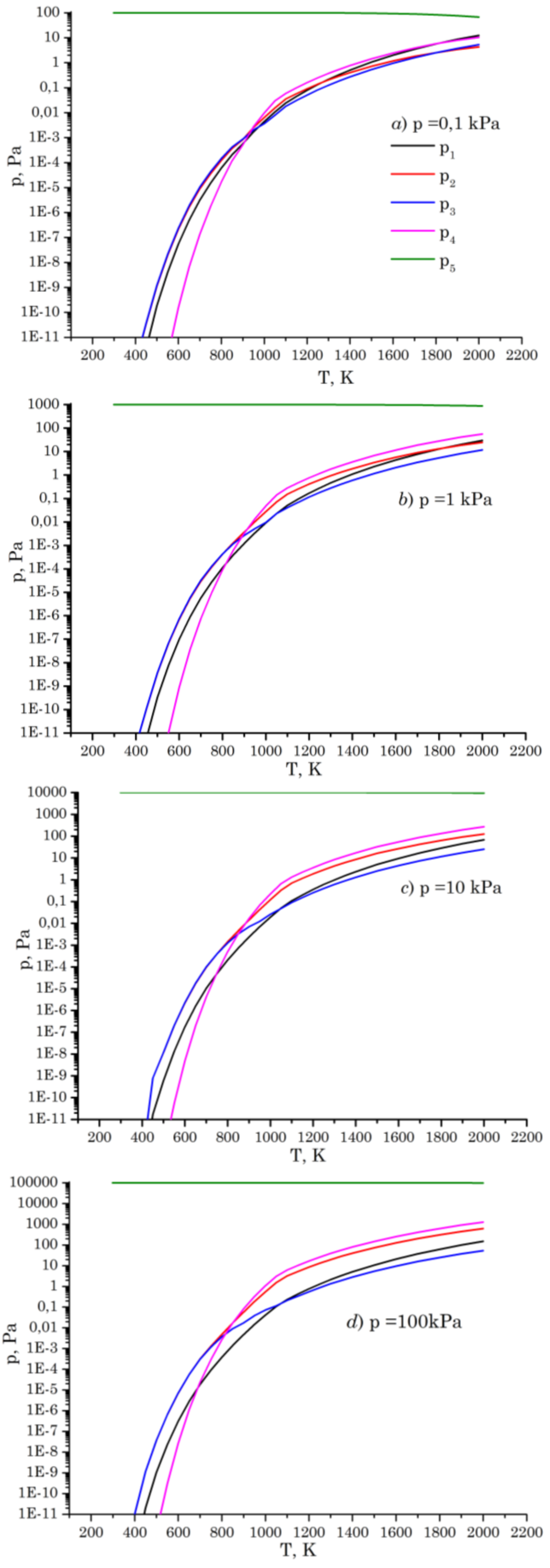

Fig. 2 – Partial pressures in the Cd-I_2 system at total pressures of (*a*) 0.1 kPa, (*b*) 1 kPa, (*c*)10 kPa, and (*d*) 100 kPa

In [11], single crystals of cadmium diodide were grown from the vapor phase in vacuumed ampoules at the temperature of the source zone of 663-693 K and the crystallization zone of 593-663 K with the duration of the growing process being 20-24 hours. Dendritic single crystals of cadmium iodide were grown from vapor growth technique in a flow system in [13] at temperature of source zone near 773 K and the temperature of the growth region was between 553-583 K, during the growing time of 6-7 hours. All CdI_2 crystals grown from the vapor phase were of the 4H-polytype [13]. Having analyzed the results of previous works on the growth of cadmium diiodide crystals from the vapor phase, it can be concluded that the technological regimes proposed based on the results of thermodynamic analysis are optimal from the point of view of the duration of the growing process and the quality of the obtained crystals.

4. CONCLUSIONS

To determine the optimal technological conditions for growing CdI_2 single crystals from the vapor phase, a thermodynamic analysis of the equilibrium composition of the vapor phase of the $Cd-I_2$ system in the temperature range of 298-2000 K was carried out. It was established that the main component of the vapor phase at total pressures in the system of 0.1 kPa, 1 kPa, 10 kPa, and 100 kPa is cadmium diiodide, the partial pressure of which is 4 orders of magnitude higher than the pressure of the dissociation products. Based on the thermodynamic calculations, the optimal temperature regimes for growing single crystals of cadmium diiodide from the vapor phase in a closed system are proposed: the temperature of the source zone T = 850-950 K, the temperature of the crystallization zone T = 500-600 K.

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Термодинамічний аналіз рівноважного складу парової фази системи $Cd-I_2$

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Проведено термодинамічний аналіз складу парової фази системи $Cd-I_2$ в інтервалі температур 298-2000 К при значеннях сумарного тиску в системі від 0,1 кПа до 100 кПа. При розрахунках вважали, що система $Cd-I_2$ у паровій фазі містить такі компоненти: I, I_2, Cd, CdI та CdI_2. У результаті розрахунків встановлено, що домінуючим компонентом парової фази є дийодид кадмію (CdI_2). В інтервалі температур 298-950 К серед продуктів дисоціації переважають Cd і I_2, а рівновага в паровій фазі описується реакцією $CdI_2(g) \leftrightarrow Cd(g) + I_2(g)$. Запропоновано оптимальні температурні умови для вирощування кристалів дийодиду кадмію з парової фази. Вирощені монокристали CdI_2 за температури зони джерела – 890-900 К, зони кристалізації – 500-530 К.

Ключові слова: Дийодид кадмію, Термодинамічний аналіз, Константа рівноваги, Парціальний тиск, Парова фаза.