Specific features of sodium iodide (NaJ·2H$_2$O) dehydration in vacuum

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Sodium iodide dehydration in vacuum has been studied by baric analysis and spectrophotometry. The decomposition process of NaJ·2H$_2$O has been shown to be possible at room temperature. During the subsequent heating, water has bben found to be eliminated within 180 to 280°C and 280 to 450°C ranges.

Проведено исследование обезвоживания йодида натрия в вакууме методами барического и спектрометрического анализа. Показано, что процесс разложения кристаллогидрата NaJ·2H$_2$O может протекать при комнатной температуре. В ходе последующего термического нагрева обнаружено выделение воды в диапазонах 180−280°С и 280−450°С.

Thermal dehydration of the hygroscopic substances is associated with solution of at least two problems: definition of decomposition parameters of crystal hydrate and prevention of hydrolysis. For sodium iodide which used widely in scintillation engineering, the existence region of crystalline dihydrate at normal pressure is within the temperature interval from −13.5 up to +68°C [1]. Accordingly, thermal dehydration of NaJ·2H$_2$O at normal pressure should be carried out at 68 to 70°C. Thus, the dehydration process parameters should be selected taking into account not only the condition of hydrolysis prevention, but also interaction of sodium iodide with oxygen-containing air components [2, 3]. The most suitable way to prevent hydrolysis and interactions with air components is dehydration in vacuum. The first publication concerning features of sodium iodide vacuum dehydration was appeared relatively recently [3]. Accordingly to [3], the use of weight analysis allows to conclude that decomposition of sodium iodide dihydrate in vacuum occurs at room temperatures. The baric analysis responses were registered at the temperatures 130−350°C. The latter were also interpreted as a result of dehydration.

In this work, an attempt is made to identify the baric analysis responses.

The dehydration of samples was studied in vacuum using a setup presented schematically in Fig. 1. To realize the measurements, a special experimental setup (Fig. 1) combining two measuring circuits, namely, a circuit for quantitative estimation of thermal desorption products on the basis of pressure measurement in a stream [3], and a circuit for identification of products thermal desorption by recording of oscillatory absorption spectra [4]. The setup consists of a quartz ampoule (3) where the sample to be studied was placed (the sample mass was varied from 1 up to 150 g) connected to a vacuum system. The vacuum system includes roughing-down (1) and diffusion (9) pumps, the pressure gauge tube (4) and a spectrometric analysis circuit consisting of a submillimeter spectrometer (6), 2 m long absorption cell (5) and the detector (7). The ampoule is placed in an oven (2) with a
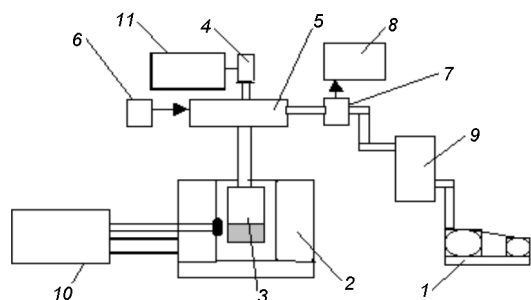
Fig. 1. Schematic view of the setup to measure the pressure change in vacuum system during the exhausting: *1* – vacuum pump; *2* – heating oven; *3* – ampoule with the salt sample to be studied; *4* – pressure gauge tube; *5* – absorption cell; *6* – submillimeter spectrometer; *7* – detector; *8* – computer; *9* – diffusion pump; *10* – temperature control block; *11* – ionization-thermocouple vacuum gauge.

Fig. 2. Pressure change dynamics in the system during exhausting of NaJ samples at room temperature: special purity grade sodium iodide, sample mass 2.3 g, water content in the sample 0.6 % (*1*); NaJ·2H$_2$O, sample mass 3.5 g, water content in the sample 20.6 % (*2*).

temperature controlling and measuring instrument (10). The setup includes a thermocouple, a vacuum gauge (11), and a computer (8).

The function of the baric analysis circuit was reduced to recording of pressure variations in vacuum system under continuous exhausting [3]. Prior to experiments, the setup was calibrated at the limiting residual pressure value in the vacuum system with an empty ampoule. The limiting vacuum value is a characteristic quantity for a specific vacuum system that depends on the system design and also on the vacuum pump operation. The limiting residual pressure value was defined as a value that has been established in the system and showed no variations within 30 min at continuous exhausting.

The function of the spectrometric analysis circuit was reduced to recording of intensity variations of the water molecule absorption spectrum. The radiation of a submillimeter range synthesizer of electromagnetic spectrum (6) was tuned in frequency at about 10 kHz steps near to 325152.82 MHz frequency [5] (water absorption line) by the personal computer and after passage through absorption cell was registered by the detector (7). The detector signal was processed by computer and displayed (8). Since the spectrometer uses frequency modulation of probing radiation to record the absorption lines of gases under study, the displayed image was not the absorption line but its derivative. Besides, it is to note that, as the pressure in the system during the spectrum recording
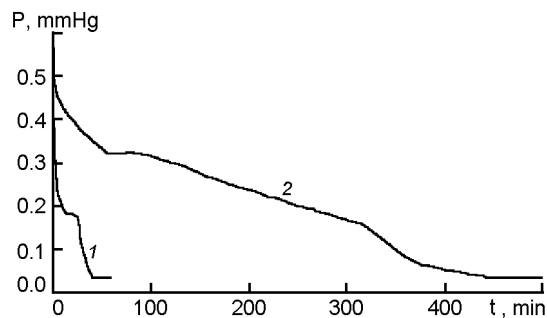
amounted (1.0 to 1.5)·10^{-2} Torr, the widening character of the water spectral line has a complex character and is very similar to the Doppler type. In this case, the spectral line width changes insignificantly but it is just its intensity that is subjected to changes mainly.

The absorption frequencies in the oscillatory molecular spectra lay in infra-red spectral region (frequency from about 50 up to 10000 cm^{-1}). These frequencies are approximately described by the formula [6] $\nu = 2B(J + 1)$, where J is the quantum number of the momentum forof the lower state ($J1$); B, rotary constant. The selection rule consists in that $J_2 = J_1 + 1$ or $\Delta J = \pm 1$. Knowing a rotary constant it is possible to calculate frequency of any transition. For water, such constant $B = 4347 \cdot 10^2$ MHz; for OH$^-$ group, $B = 5658 \cdot 10^2$ MHz. Since oscillatory spectra of all molecules, as it was mentioned above, are in infrared region, influence of spectra of other molecules is possible to affect the spectral line shape. In this case, however, such influence is not observed. The oven temperature in the furnace was raised at a rate from 10 to 200°C/h or in step-by-step manner at steps of 6 to 8°C with exposure at least 3 min at each temperature. The temperature was measured at an accuracy of ±2°C. As initial samples, special purity grade sodium iodide was used (suitable to single crystal growing) containing 0.2–0.5 % water as well as NaJ·2H$_2$O synthesized on its basis. The crystalline dihydrate was obtained by crystallization from its solution acidified with hydroiodic acid.
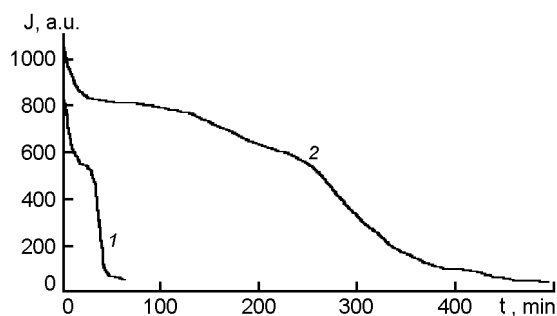
Fig. 3. Intensity change of water absorption spectral lines during exhausting at room temperature. Curves are numbered as in Fig. 2.

In Fig. 2, presented is the dependence of pressure change in the vacuum system under exhausting the sodium iodide samples at room temperature. As follows from the presented dependences, the character of pressure variation in the system under exhaust is the same for exhausting of samples with low water content (0.2 to 0.5 %), and with high one (dihydrate samples). The vacuum in system is improved up to limiting value, and then the pressure in system remains unchanged. In the case of dihydrate samples (Fig. 2, curve 2), the course of pressure-time dependence has a prolonged character as compared to sodium iodide sample with low water content (Fig. 2, curve 1) that is connected with large water amount to be exhausted. Spectroscopic intensity measurements of water absorption spectral lines (Fig. 3) confirm the fact of water release into gas phase during the exhausting of samples. The intensity curve of the spectral line reproduces essentially accurately the pressure change in the vacuum system. The time to attaining the limiting vacuum value and to the termination of water release (as measured by the absorption spectrum line intensity) are the same. Thus, we can state that during the exhausting, the decomposition of the dihydrate crystal in vacuum at room temperature occurs according to the total reaction scheme: $NaJ \cdot 2H_2O \rightarrow NaJ_s + 2H_2O_g$.

To estimate the sample dehydration efficiency at room temperature, the samples dehydrated were exposed to heat treatment under recording the pressure changes in the system (Fig. 4) and intensity of water absorption spectral lines (Fig. 5). As has been revealed at the subsequent heat treatment, for NaJ samples of special purity grade which initially contained 0.2 to 0.5 % of water, two peaks are observed in the pressure-temperature curve within the 180 to 280°C range
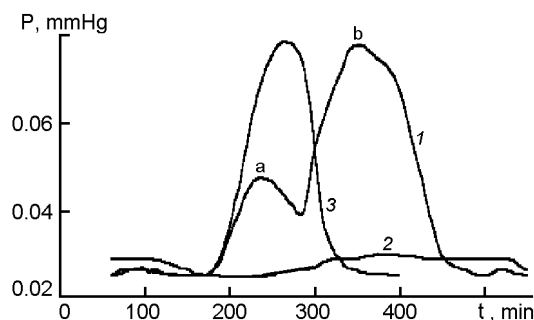

Fig. 4. Pressure change in the system under heat treatment, heating rate 200°C/h: special purity grade sodium iodide, sample mass 8.5 g (1); $NaJ \cdot 2H_2O$ samples preliminary dehydrated at room temperature, mass 3.5 g (2); data from [3] (3).
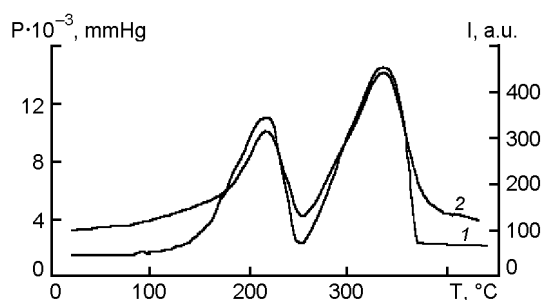

Fig. 5. Change of pressure in vacuum system (1) and lines in water absorption spectrum (2) at the heat treatment of sodium iodide samples. Heating rate 50°C/h.

with a maximum at 230°C (peak a) and in 280 to 400°C one with a maximum at 340°C (peak b). According to the spectroscopic measurement data (Fig. 5), the observed baric analysis responses answer to water release into gas phase. The relative mass change, W, due to the heat treatment (determined as $W = [(\mu_a - \mu_b)/ \mu_a] \cdot 100$ %, where μ_a is the sample mass before the heat treatment, g; μ_b, that after heat treatment, g; makes about 0.01 to 0.03 mass %.

At the heat treatment of $NaJ \cdot 2H_2O$ samples preliminary dehydrated at room temperature (Fig. 4, curve 2), no water release into gas phase is observed. This can evidence that the crystal dihydrate is completely dehydrated at room temperature under formation of anhydrous salt. In [3], one peak in the 127 to 347°C range with a maximum at 240°C is described (Fig. 4, curve 3). It has been interpreted as decomposition of a high-temperature compound of sodium iodide with water. However, the small amount of water released at heat treatment (0.01 to 0.03 mass %) indicates

more likely the presence of an impurity phase which structure includes water molecules. Besides, if the peaks mentioned would be connected with crystal hydrate, their occurrence would to be expected first of all at heat treatment of the crystal hydrate samples. As experimental data show, at heat treatment of the crystal hydrate samples no water (as well as other substances) are released under heating. Therefore, it may be assumed that the high-temperature release of water is not connected to the crystal hydrate decomposition. Thus, the initial raw material may contain a phase which decomposition results in release of water, its decomposition proceeding within a wide temperature range (180 to 450°C).

Basing on the experimental data presented, the following conclusions can be drawn. The observed responses of baric analysis at sodium iodide dehydration and $NaJ \cdot 2H_2O$ correspond to water release into the gas phase. The high-temperature release of water within the 180 to 450°C range during heat treatment of sodium iodide is probably connected to the presence of an impurity phases in sodium iodide.

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Особливості зневоднювання йодиду натрію (NaJ·2H₂O) у вакуумі

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Проведено дослідження зневоднювання йодиду натрію у вакуумі методами баричного та спектрометричного аналізу. Показано, що процес розкладання NaJ·2H₂O може протікати при кімнатній температурі. У ході наступного термічного нагріву виявлено виділення води у діапазонах 180−280°C та 280−450°C.