

# Synthesis of the dihydride phase of vanadium

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## Abstract

There are two constituents that determine success in synthesizing vanadium hydride: activation and supply of hydrogen to vanadium at an appropriate pressure.

The most efficient activation has been found to occur, depending on the vacuum produced in a facility, in temperature ranges between 550 and 750 K or above 850 K.

Dependencies of equilibrium sorption pressures of protium and deuterium over respective dihydride phases of vanadium are provided. At an atomic ratio of  $0.85 \leq X/V \leq 1.5$  (X is protium or deuterium), they take the following form, respectively,  $\log P(\text{Pa}) = -2160/T + 12.8$  and  $\log P(\text{Pa}) = -2480/T + 13.6$ . At higher hydrogen concentrations, coefficients in the Van't Hoff equation are observed to depend on the hydrogen content.

Based on the obtained experimental data on equilibrium sorption pressures and available literature data on isotopic effects, the same dependence of sorption pressure has been calculated for vanadium ditritide. For  $T/V = 0.85$ , it is expressed as:  $\log P(\text{Pa}) = -2490/T + 13.4$ .

Dependencies of equilibrium sorption pressures for all the three hydrogen isotopes at temperatures between 273 and 323 K and ratios of  $0.85 \leq (H, D \text{ or } X)/V \leq 1.9$  are presented in the form of diagrams.

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## 1. Introduction

Thermal desorption hydrogen isotope sources based on vanadium hydride have found wide application for studying nuclear fusion reactions at pressures up to 160 MPa [1–3]. By now there have been developed and are in use sources with a working pressure up to 500 MPa [4].

The highest pressures of hydrogen isotopes (HIs) can be achieved by the decomposition of corresponding dihydride phases of vanadium  $VX_2$ , where X is H, D or T. However, data on the conditions that allow such phases to be produced are lacking. This made it necessary to carry out the corresponding research.

## 2. Materials

The study used electrolytic vanadium VEL-2. According to the manufacturer, the maximum content of controlled

impurities in the vanadium was: Al, 0.01; Fe, 0.1; Si, 0.01; Ni, 0.04; S, 0.005; C, 0.01;  $N_2$ , 0.04 and  $O_2$ , 0.1%. No entry assay of metal batches in terms of impurities was conducted.

The HIs used were purified by passing through a palladium membrane.

## 3. Activation of vanadium

A simple and commonly used method to activate a metal and to remove volatile impurities from it is to heat the metal in vacuum under evacuation. Metals of Group V, including vanadium, are activated at temperatures from 573 to 1273 K in vacuum with  $D < 1.3 \times 10^{-4}$  to 1 Pa [5–7].

We studied the correlation between the vacuum produced in a facility during activation and the temperature of the most efficient activation. Samples were activated for 0.5–3 h. The quality of activation was evaluated based on the averaged composition of the hydride that formed 5 min after deuterium was supplied. This composition can be assumed to be proportionate to the rate of interaction between the metal and the gas.

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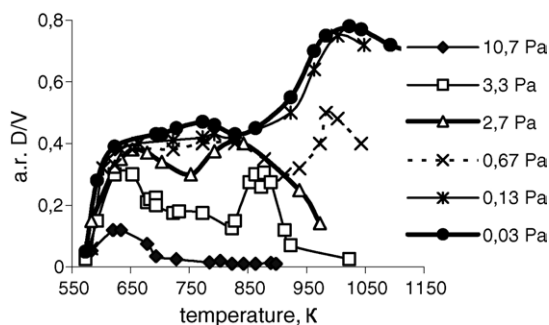


Fig. 1. Composition of deuteride produced vs. activation temperature.

While interacting with the gas, the samples were at 273.2 K. The initial pressure of the gas supplied was  $9.5 \times 10^4$  Pa. The maximum pressure variation in the facility due to gas absorption was  $\sim 1.5 \times 10^4$  Pa.

The samples were activated at several temperatures at different levels of vacuum. The rates of vanadium–deuterium interaction after hour activation at different temperatures and levels of vacuum in the facility are shown in Fig. 1.

Fig. 1 shows that the curves obtained have one or two peaks. The number of peaks depends on the level of vacuum in the facility. At a low vacuum (for example, at a pressure of 10.7 Pa in Fig. 1), activation can be implemented effectively only at a temperature between 570 and 750 K (low-temperature range). At higher activation temperatures, the rate of vanadium–gas interaction slows down. This can be attributed to the oxidation of the sample when heated in low vacuum. Reducing the pressure of the residual gas (to  $\sim 3.3$  Pa in Fig. 1) allows activation to run at temperatures above  $\sim 800$  K (high-temperature activation range). The upper temperature limit of this range was not achieved within this study.

According to Fig. 1, the efficiency of activation in the high-temperature range increases with the improvement of vacuum. Based on the plotted curves of hydride formation rate as a function of vacuum level in the facility, at pressures equal or higher than 4.1 Pa, optimal activation temperatures were found to lie in a range from 550 to 750 K, depending on the pressure. At pressures below 4.1 Pa, optimal activation temperatures range was found between 850 and 1100 K.

The non-monotonic function obtained can be explained qualitatively by use of data on the thermal desorption of gases from vanadium (Fig. 2). The rate of sample heating was 0.5 K/s. The gases released were determined using an quadruple mass spectrometer (MX-7304).

Fig. 2 shows that, when heated, vanadium releases gaseous impurities with a charge-to-mass ratio of  $m/e = 2, 18, 28$  and 44.

According to literature, raw commercial metals of Group V, including vanadium, are usually strongly contaminated with interstitial impurities of light elements, such as H, C, N and O. Such impurities can be comparatively easily removed by heating in vacuum [6]. Based on the composition of impurities contained in the starting vanadium, one can assume that

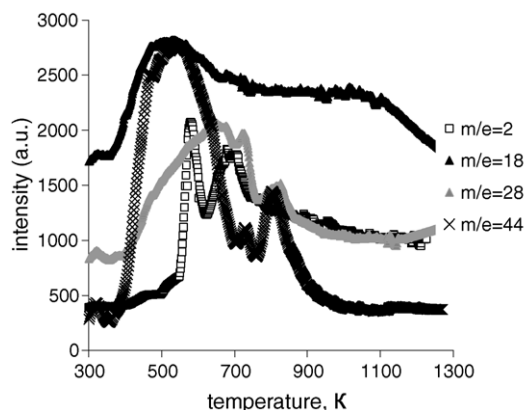


Fig. 2. Temperature dependence of thermodesorption spectra of vanadium.

gases having the above mass-to-charge ratio  $m/e$  are  $H_2$ ,  $H_2O$  ( $CO/N_2$  or their mixture) and  $CO_2$ , correspondingly.

As can be seen in Fig. 2, when heated to temperatures between 400 and 850 K (low-temperature range), the sample releases all the above gases. One can say that heating to this temperature range purifies the metal from interstitial impurities of light elements by their thermal desorption. Further heating, to the high-temperature range, can be observed to cause the release of  $H_2$  and  $H_2O$  only (according to Fig. 2, the temperature, at which the latter is released most actively, is  $\sim 1050$  K). Most probably, the release of  $H_2O$  in this temperature range is caused by the reduction on the sample surface of one of vanadium oxides by the hydrogen released.

Thus, the non-monotonic dependence of the rate of vanadium–hydrogen interaction on the activation temperature can be attributed to the mechanism of metal purification from H, C, N and O impurities by thermal desorption.

Measurements of temperatures providing the highest rates of interaction with hydrogen (peak temperatures in Fig. 1) after activation at 0.03 Pa for 0.5–3 h revealed no dependence of these on the activation time. After activation for 0.5, 1, 2 and 3 h, activation temperatures corresponding to the maximum rates of interaction agreed within the experimental spread ( $\pm 10$  K for the low-temperature and  $\pm 15$  K for the high-temperature peaks). Apparently, this can be explained by the fact that in order to completely remove gaseous impurities, it would suffice to heat vanadium for about half an hour.

#### 4. HIs pressures to synthesize vanadium hydride

Good activation is only one of the factors that provide success in synthesizing metal hydrides. Of no smaller significance is the pressure of hydrogen during synthesis.

Dependencies of equilibrium sorption pressures of protium and deuterium over respective dihydride phases of vanadium have been studied in Ref. [8]. The dihydride phase (pressure “plateau” in isotherms) at temperatures close to the room temperature was found to form in a sample containing hydrogen in a quantity corresponding to atomic ratios H/V

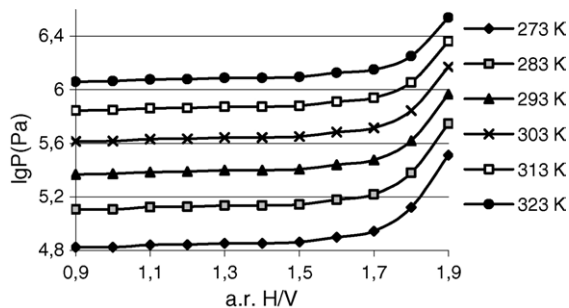


Fig. 3. P–T–C dependencies for hydrogen sorption.

$\approx 0.85$  and  $D/V \approx 0.8$ . Isotherms given in Ref. [1] indicate that the boundary between the mono- and the dihydride phases is also observed at the atomic ratio of  $T/V \approx 0.8$ . Thus, one can say that at  $X/V \geq 0.85$ , the dihydride phase forms for all of the hydrogen isotopes.

The functions of equilibrium sorption pressures of protium and deuterium versus temperature at the atomic ratio of  $0.85 \leq (H, D)/V \leq 1.5$  take the following form, respectively,  $\log P(\text{Pa}) = -2160/T + 12.8$  and  $\log P(\text{Pa}) = -2480/T + 13.6$  [8]. In the range of HI concentrations of  $(H, D)/V > 1.5$ , coefficients in the Van't Hoff equation are observed to depend on the hydrogen content; therefore, it is difficult to express the temperature dependence of equilibrium sorption pressures as an equation. Based on the isotherms given in Ref. [8], we have plotted P–T–C curves for the sorption process of hydrogen (Fig. 3) and deuterium (Fig. 4) in the ranges of atomic ratios of  $0.85 \leq (H, D)/V \leq 1.9$  and temperatures of 273–323 K.

References provide no data on the pressures necessary for the synthesis of vanadium tritide. However, these can be estimated based on the equilibrium sorption pressures for protium or deuterium and available data on the isotopic effects for vanadium hydride.

In the  $\alpha - \beta$  transition region (on the pressure “plateau”), the separation factor can be determined using the equation:

$$\alpha_{A-B} = \left( \frac{P_A}{P_B} \right)^{1/2},$$

where  $P_A$  and  $P_B$  are equilibrium sorption pressures of respective hydrogen isotopes in the two-phase region [9].

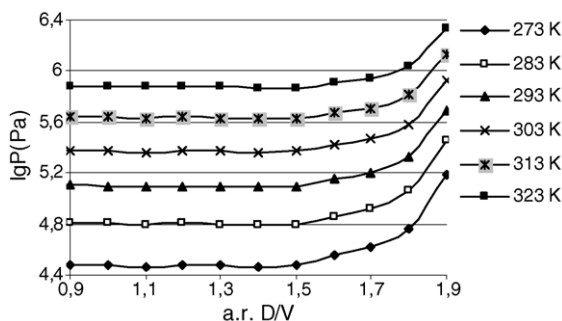


Fig. 4. P–T–C dependencies for deuterium sorption.

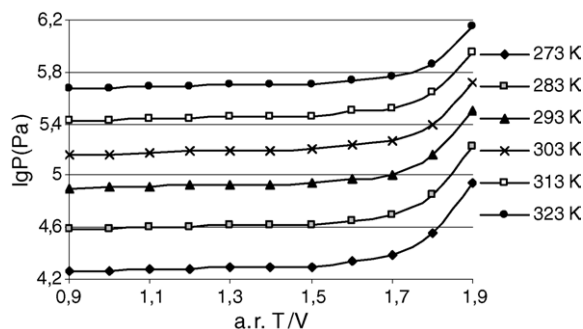


Fig. 5. P–T–C dependencies for tritium sorption.

The temperature dependence of the separation factor  $\alpha_{H-T}$  for the vanadium–protium–tritium system plotted based on the data provided in Ref. [10] for the dihydride phase of vanadium takes the following form:  $\log \alpha_{H-T} = 154.3/T - 0.284$ .

Using the temperature dependence  $\alpha_{H-T}$  obtained and the P–T–C dependencies for protium sorption shown in Fig. 3, one can calculate the same dependencies for tritium. For example, the function of equilibrium sorption pressure versus temperature at the atomic ratio of  $T/V = 0.85$  was found to be:  $\log P(\text{Pa}) = -2490/T + 13.4$ .

The P–T–C curves for tritium sorption are shown in Fig. 5.

Using the dependencies shown in Figs. 1–5, one can estimate pressures that need to be produced in a facility to synthesize the dihydride phases of vanadium of prescribed composition containing any of the hydrogen isotopes, if the sample's temperature lies in the range from 273 to 323 K.

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