

*Equilibrium Pressure Measurements  
in the Beta Region of Palladium Protide  
and Palladium Deuteride*

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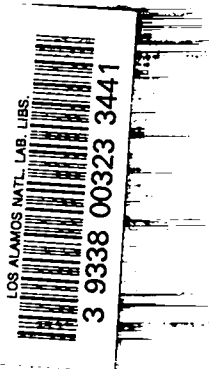
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*Equilibrium Pressure Measurements  
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*Dean H. W. Carstens  
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# EQUILIBRIUM PRESSURE MEASUREMENTS IN THE BETA REGION OF PALLADIUM PROTIDE AND PALLADIUM DEUTERIDE

by

Dean H. W. Carstens and W. Roy David

## ABSTRACT

We have measured the pressure-composition isotherms of the palladium-deuterium and palladium-protium systems in the beta region of both and the plateau region of the protide. For these two systems, data were measured at pressures up to about 3.5 MPa (500 psi) and at temperatures from 173 to 473 K. This study extends to a greater pressure and temperature regime the work on palladium hydrides reported previously by other authors.

We also report results of an empirical analytical fit to the data for these two isotope systems. For completeness, we have applied our analysis to previously reported data for the tritide. The data were fit to an equation of the form

$$P = \exp\{A + 2\ln[R/(1 - R)] - (B - CR)/T\} + \exp[D + E/T],$$

where R is the hydrogen-to-metal atomic ratio, P is the pressure, and T is the temperature. A, B, C, D, and E are empirically determined parameters and differ for absorbing and desorbing systems of each isotope. This equation gives a good fit to the data in the beta region of the absorption curves but a poorer fit in the alpha plus beta (plateau) region.

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## INTRODUCTION

The equilibrium overpressure of all three isotopes of hydrogen over palladium hydride has attracted much interest over the years.<sup>1-15</sup> Isotherms for the palladium protide system, for example, have been reported up to 100 MPa and 477 K by Levine and Weale.<sup>8</sup> Our objective in this report was to provide a large body of data for the protide and deuteride to be used with the tritide data of Talcott et al.<sup>9</sup> in developing an analytical fit to describe the behavior of the data in the beta region of the absorption isotherms.

As will be shown in a later section, our data do not agree well with previously reported work. This we now believe to be due to a systematic error or to lack of equilibrium, the latter particularly at low temperatures. Despite the error, we report the protide and deuteride data for two reasons. First, it helps to extend the known body of data to a larger temperature regime and, in the case of the deuteride, to a higher pressure regime. Second, it provides a body of data for testing our analytical fit, described later.

Also, we performed a smaller series of experiments using a carefully calibrated volume and large amounts of protium added in a single increment. These experiments were designed to minimize any systematic errors, and better agreement with the literature data was obtained. However, the data shown in later sections of this report were not corrected to reflect these one-addition experiments.

At the start of this decade, Semiltov and others<sup>11-13</sup> reported the existence of a third phase of palladium protide, the gamma phase, at hydrogen-to-metal ratios above 1.0. Another of our objectives in this work was to look for this phase, but we saw no evidence of such a phase.

## EXPERIMENTAL DETAILS

Palladium (99.9% pure) for the experiments was purchased from Englehard (# A-4573, lot F01161). Usual sample size was 2 g, and the powder particles were 2-50 m and had a specific surface area ranging from 0.734 to 0.797 m<sup>2</sup>/g. Protium and deuterium gas were used as they came from the cylinder with no further purification. Before measurements, the palladium metal was treated using a two-step protium absorption and desorption procedure. After this procedure, reproducible isotherms were obtained.

A typical, all-metal Sieverts' apparatus was used for the measurements. It consisted of a stainless steel furnace (volume 16 cc), which contained the metal, connected to a measuring volume (20 cc) and a pressure transducer. The temperatures of the measuring volume and the furnace were both measured with thermocouples to permit accurate determinations of hydrogen-to-metal ratios. The temperatures of each, although different, were maintained constant by a suitable heater (for the furnace) and insulation (for both). The interconnecting volume was small (4 cc), to minimize errors. During the experimental runs, the system was automated so that an HP85 computer controlled the temperature and took data measurements. The experimental apparatus was constructed for pressures only up to 3.5 MPa (500 psi), and the transducer had a similar range. It was designed for relatively larger amounts of gas and metal than was the apparatus described in our previous report,<sup>9</sup> which helped to minimize measurement errors arising from temperature differences at various points of the apparatus.

The experimental procedure for this series of experiments was as follows. To obtain a series of data points, a measured quantity of protium or deuterium (to give a hydrogen-to-metal ratio of about 0.7) was added to the metal and the temperature was cycled up and down at approximately constant composition between the two temperature extremes (173 and 473 K) while data were

taken continuously. Each up and down cycle took about 24 hours with half-hour pauses at each extreme to allow equilibration.

For each run, the cycles were repeated at least three times to check for reproducibility. Data points were taken every minute and stored on tape for later analysis. Following a given run, a measured amount of gas was removed from the system and the process repeated to give a new series of data points. These removals and measuring processes were repeated until the pressures dropped to the plateau region.

The data were then transferred to a larger desk-top computer (HP 9845) for plotting and data analysis. For the protide and deuteride, the data for each run were plotted on the CRT screen and digitized every ten degrees. The digitized data (an average of the several runs) were then used for plotting and analysis and were fit to an analytical form (discussed later) by a nonlinear least squares method based on the algorithm of Marquardt.

## RESULTS AND DISCUSSION

In the following six figures we present the data for the protide (Figs. 1 and 2), the deuteride (Figs. 3 and 4), and the tritide (Figs. 5 and 6). In all three cases, the first figure is for the system absorbing gas, the second, for desorbing gas. In all plots, isotherms for the higher temperatures are shown on the left, with temperature decreasing as the isotherms progress to the right. Actual data points are represented by either closed or open circles. To aid the reader in identifying isotherms, the open points and dashed lines show temperatures at 50-degree intervals.

The lines through the points shown on the six figures represent our mathematical model of the data, which is discussed in more detail later.

On comparing the protide and deuteride data with the tritide data, we noted a significant discrepancy in the results obtained for the beta region. Examining the plots for the three isotope systems in the beta region of the curves reveals that although the curves shift to the right on going from the tritide to the deuteride to the hydride, the first shift is appreciably less than the second. This is not what has been reported by other authors. Lasser and Klatt,<sup>1</sup> for example, found the shift from the tritide to the deuteride only slightly smaller than that from the deuteride to the hydride for the rising curves in the beta region.

The difference is made more obvious when our data are compared with those in the literature. (Most of the data reported by previous authors have been summarized by Santandrea and Behrens<sup>2</sup> in their review article on palladium hydrides.) Comparing data from different studies is difficult because in general, authors tend to present plots rather than actual data points. Thus, our discussion will concentrate on the data of Perminov,<sup>13</sup> Wicke and Nernst,<sup>14</sup> and Lasser and Klatt,<sup>1</sup> all of whom either presented tables of data or gave an empirical analytical formula that facilitates comparison. These three studies also appear to represent the bulk of the reported data.

For the most part, the three reported data sets agreed to within a few percentage points. An error envelope of 1-3% is reasonable agreement based on expected random experimental errors. And although our tritide data agreed with those of Lasser and Klatt to this limit, the deuteride data were somewhat lower (by about 4%) and the hydride data even lower (by 5-6%). In at least one case, that of the hydride data of Perminov at 373 K, a good agreement with our data was seen. This appeared to be an isolated case, however.

Thus, there appears to be a meaningful systematic error in our measurement for the protide and the deuteride. Analyzing conceivable sources of error suggests several possibilities: (1) hysteresis effects or a lack of equilibrium in the samples, (2) differences in the form of the palladium used, (3) an improperly prepared sample or admission of oxygen to the gas supply, or (4) a systematic error caused by a faulty volume calibration or by a sum of small systematic errors in the gas additions.

Because the data points were taken from both sides of equilibrium, we do not suspect lack of equilibrium as a major source of error. However, the magnitude of the difference tends to increase as the temperature decreases, suggesting that subtle equilibrium effects may be influencing the measured values.

For a second possible source of error, evidence in the literature indicates that apparently the form of the palladium sample (black, powder, or massive) does not affect the curves in the beta regions. A third possibility, oxidation of the sample is always conceivable and would displace the curves in the correct direction. However, because we took pains to pretreat our samples by at least two hydriding and dehydriding cycles, we do not believe oxidation to be a source. Of course, even a very small leak during the experiment could appreciably contaminate the sample.

Thus, we now believe the last possibility (a volume calibration error or a sum of small volumetric errors) to be the most plausible explanation of the total shift in the data. Because the error increases at lower temperatures, lack of equilibrium may be affecting the data. Unfortunately, the apparatus had been dismantled by the time we realized the magnitude of the error, making it impossible to check out the volume calibrations. We did do a series of "one-addition" experiments with the protide, using a new and carefully recalibrated system. For these experiments, a large amount of gas was added to a pretreated palladium sample such that the final equilibrium point would lie on some part of the beta region of the curve. Several data points were measured, with the sample being decomposed between each measurement. These points were essentially within the error envelope defined above (lying about 2% below Lasser and Klatt's data points).

We measured plateau pressures only for the protide. Applying a least squares fit to the protide data (for  $H/M = 0.3$  to  $0.4$ ) led to the following equations for the plateau:

$$\ln P \text{ (MPa)} = -4390/T + 8.33 \text{ (desorbing data),} \quad (1)$$

$$P(\text{MPa}) = -4760/T + 8.99 \text{ (absorbing data).} \quad (2)$$

As a comparison, we calculated standard desorbing and absorbing heats of formation of the protide from the first coefficient, obtaining -8730 cal/mole H<sub>2</sub> and -9470 cal/mole H<sub>2</sub> for the two cases, respectively. The values compare well with the value of -8860 cal/mole H<sub>2</sub> calculated by Gillespie and Hall<sup>7</sup> from their p-c-t data. Similarly, Lasser and Klatt<sup>1</sup> found values of -9320 and -8940 cal/mole H<sub>2</sub> for the palladium protide system desorbing and absorbing gas. The agreement is about as expected considering the inaccuracies in the data measurements.

Several authors have attempted to fit the curves in the beta regions of palladium hydrides to their data. Perminov<sup>13</sup> was the first. Noting that the plots of log *P* versus concentration were linear at high pressures, he used an equation of the form

$$\ln P = a + bR, \quad (3)$$

where *R* is the hydrogen-to-metal ratio. His data were for the protide at pressures up to 1700 atm. Later, Wicke and Nernst<sup>14</sup> fit the protide and deuteride data, and Sicking,<sup>15</sup> the tritide data, with an equation of the form

$$\ln P = A + 2\ln[R/(1 - R)] - (B - CR)/T, \quad (4)$$

where *A*, *B*, and *C* are empirically determined parameters differing for each isotope system, *R* is the gas-to-metal composition ratio, *P* is the pressure, and *T* the temperature. We attempted this fit using the nonlinear regression analysis discussed in the experimental section. Note that for this analytical fit, as well as for those discussed later in this section, we used the entire data set for each individual isotope system, whether absorption or desorption data, a total of six fits for each of the six cases.

The Sicking fit was not successful for two reasons. First, as should be obvious from the analytical form of the equation, it returns to zero too rapidly and cannot begin to account for the plateau region of the experimental curve. Second, and more important in this case, the analytical curves were not wide enough to account for the data. That is, the data at high temperatures were too far to the left of the curves, while the data at low temperatures were too far to the right of the curves. Our second, more-successful attempt at the fit used an equation of the form

$$P = \exp(\text{Sicking}) + \exp[D + E/T], \quad (5)$$

where *D* and *E* are two more empirical parameters and "Sicking" is the right-hand side of Eq. (2) above. Note that this is just the Sicking equation with an added term to account for the constant plateau region of the experimental data.



Figures 1-6 show the fits to this equation. The fits agree very well in the beta regions over the temperature extremes, but the fitted curves fall somewhat below the data in the plateau regions.

In the table below we have included the values of the six parameters for all six cases for reference. These parameters are for the pressure, as measured in MPa, and the temperature, in degrees Kelvin. The numbers in parentheses represent the statistical 90% confidence limit on the parameters.

Semiletov and coworkers<sup>10-12</sup> have reported the preparation and crystal structure of a new, higher phase of palladium protide (the gamma phase), with a composition of PdH<sub>1.2-1.3</sub>. They believed they had prepared this phase by either heating the palladium to 873 K in an atmosphere of protium followed by rapid cooling or by bombarding the metal with protium ions. The phase had a tetragonal structure, as determined by electron diffraction.

As mentioned in the Introduction, one of our objectives was to form this phase. We had hoped that applying higher pressures would force the palladium to absorb more gas and to approach this second phase. However, our absorption diagrams show no evidence of this phase in the curves.

Semiletov reported that the new protide was decomposed only by heating under vacuum to temperatures above 1073 K. If true, this implies that the gamma phase is more stable than the beta, which does not seem reasonable. It also implies that the plateau equilibrium pressure, if a plateau is observed in the phase diagram as the gamma phase is formed, would be lower than that for the beta. Thus, if one could form the gamma phase by increasing the pressure, one would expect a break in the p-c-t curves as the gamma phase formed.

Parameters for the Fit to Eq. (2) for the Three Hydrides

	A	B	C	D	E	
Tritide Absorbing	10.23 (0.03)	10770 (20)	10370 (20)	11.93 (0.19)	-5270 (90)	
Tritide Desorbing	10.30 (0.25)	10870 (350)	10460 (380)	12.50 (2.1)	-5550 (920)	
Deuteride Absorbing	7.93 (0.54)	9050 (680)	9070 (760)	9.86 (1.23)	-4540 (570)	
Deuteride Desorbing	9.58 (0.55)	10510 (690)	10260 (760)	9.81 (0.89)	-4620 (420)	
Protide Absorbing	8.61 (0.23)	10110 (200)	9780 (330)	9.11 (0.88)	-4710 (400)	
Protide Desorbing	8.66 (0.39)	10050 (240)	9540 (270)	11.87 (1.1)	-6060 (510)	

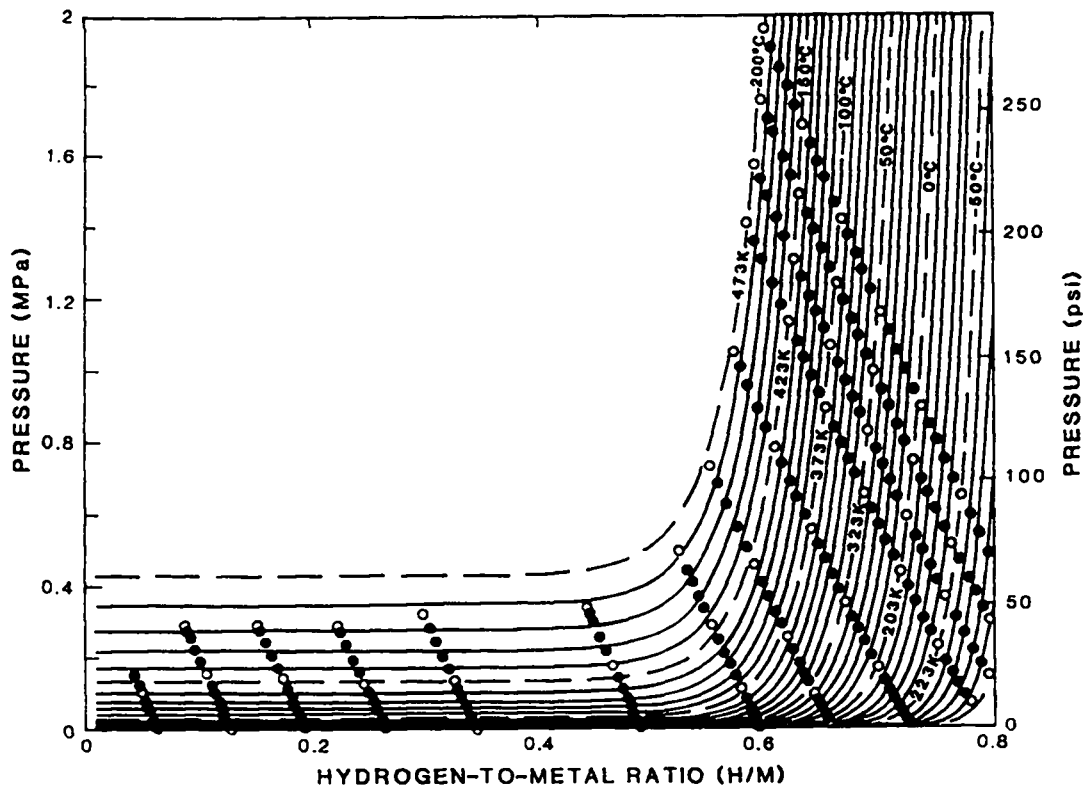


Fig. 1. Isotherms (absorbing) for this palladium-protium system.

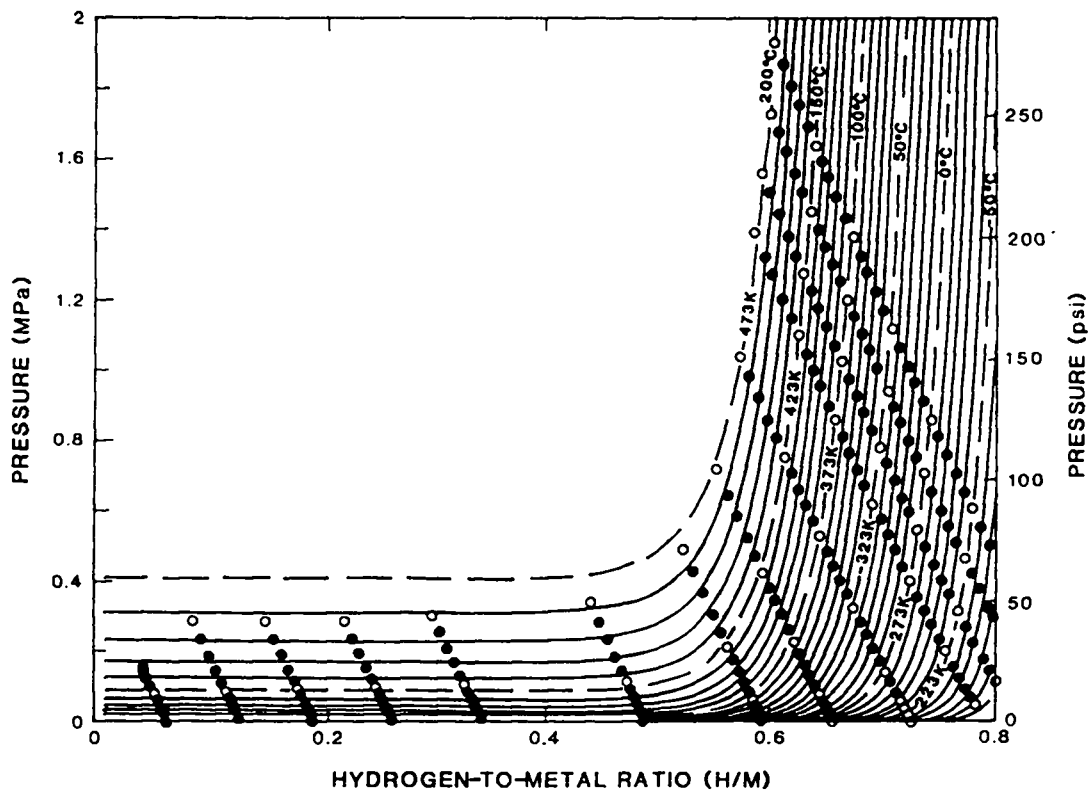


Fig. 2. Isotherms (desorbing) for this palladium-protium system.

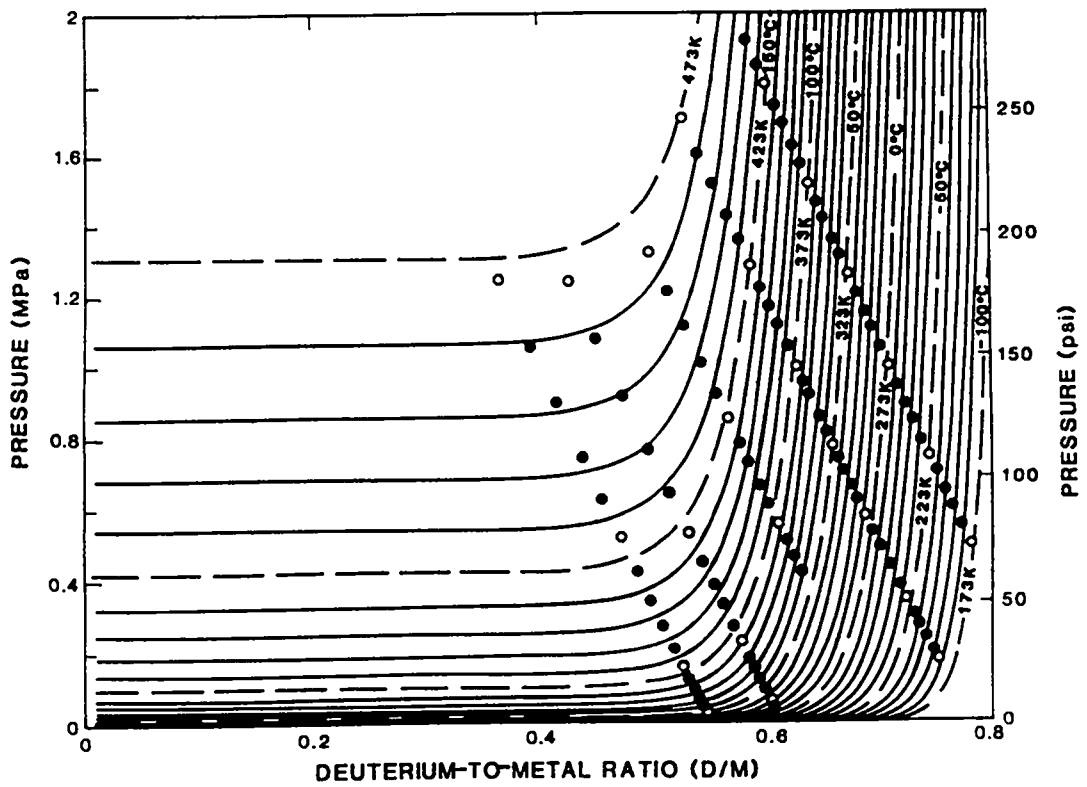


Fig. 3. Isotherms (absorbing) for the palladium-deuterium system.

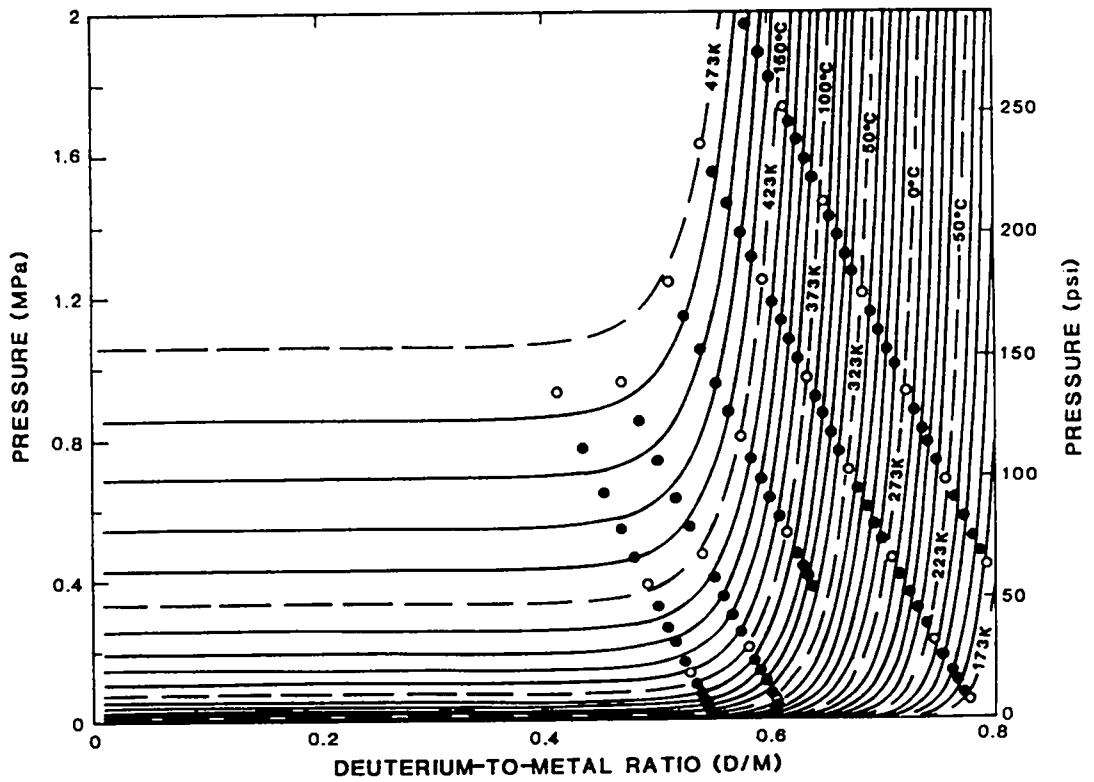


Fig. 4. Isotherms (desorbing) for the palladium-deuterium system.

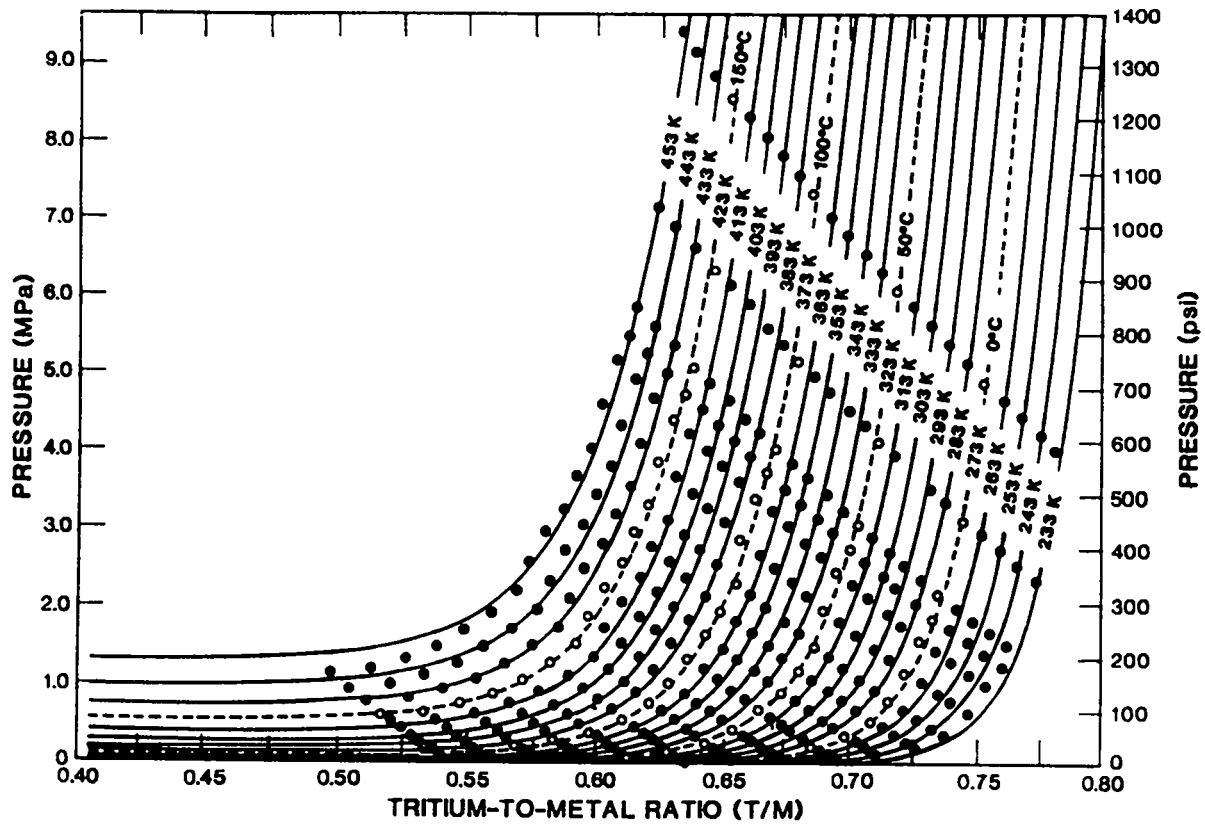


Fig. 5. Isotherms (absorbing) for the palladium-tritium system.

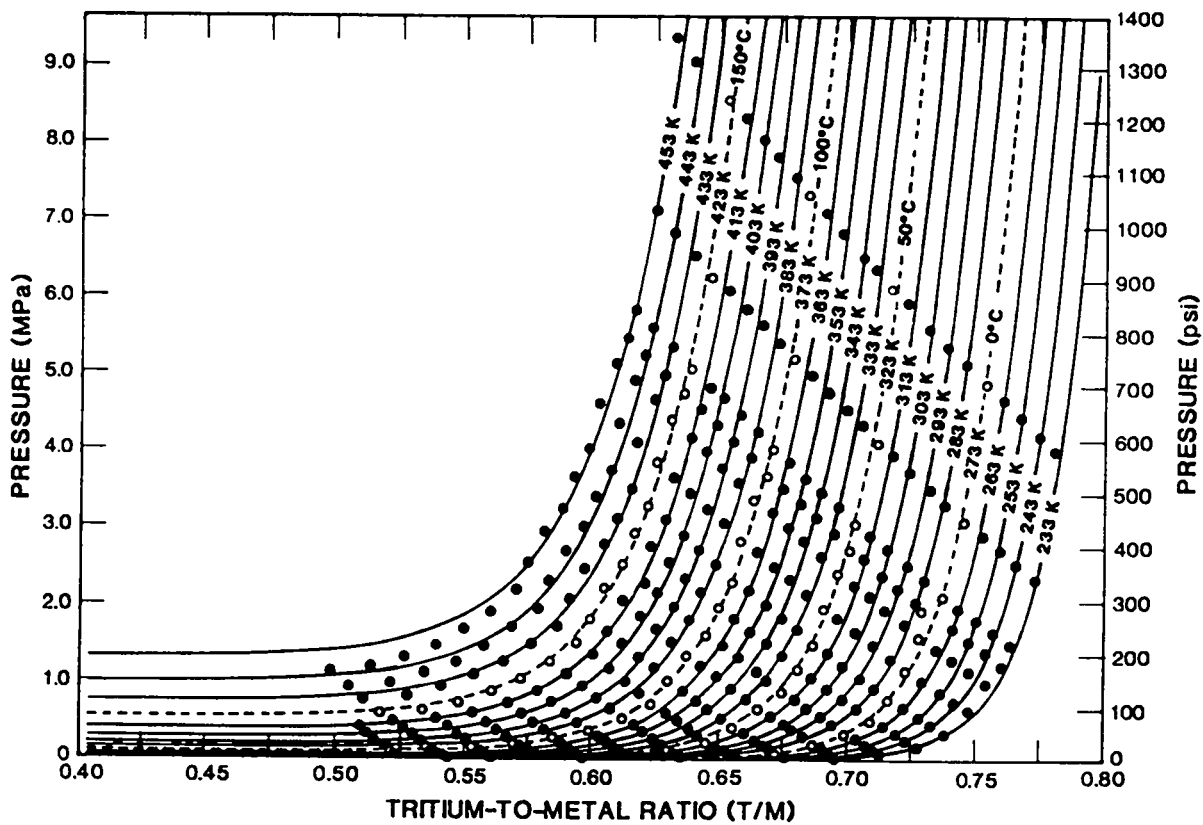


Fig. 6. Isotherms (desorbing) for the palladium-tritium system.

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