LA-13460-T
Thesis

Characterization of the β-Phase of the Palladium-Hydrogen Equation of State

Los Alamos
NATIONAL LABORATORY

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36.

This thesis was accepted by the Department of Mechanical Engineering, University of New Mexico, Albuquerque, New Mexico, in partial fulfillment of the requirements for the degree of Master of Science. The text and illustrations are the independent work of the author and only the front matter has been edited by the CIC-1 Writing and Editing Staff to conform with Department of Energy and Los Alamos National Laboratory publication policies.

An Affirmative Action/Equal Opportunity Employer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither The Regents of the University of California, the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by The Regents of the University of California, the United States Government, or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of The Regents of the University of California, the United States Government, or any agency thereof. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

LA-13460-T
Thesis

UC-901 and UC-910
Issued: July 1998

Characterization of the β-Phase of the Palladium-Hydrogen Equation of State

Kane J. Fisher

Los Alamos
NATIONAL LABORATORY
Los Alamos, New Mexico 87545

ACKNOWLEDGEMENTS

I would like to thank Dr. Dale G. Tuggle and Dr. Brad A. Meyer, for their instrumental assistance in my development as an engineer. I would also like to thank Los Alamos National Laboratory for sponsoring my research as part of its graduate research program.

I would like to thank Dr. Arsalan Razani for chairing my committee, and Dr. Yu-Lin Shen for serving on my committee. I would also like to thank Arden Ballantine for her patience as well as the University of New Mexico Mechanical Engineering Department.

TABLE OF CONTENTS

LIST OF FIGURES ix
LIST OF TABLES x
NOMENCLATURE xi

CHAPTER 1-OBJECTIVES 1
CHAPTER 2-INTRODUCTION
2.1 Background 3
2.2 P-C-T Investigations:Troost and Hautefeuille 3
2.3 Hoitsema 4
2.4 Gillespie and coworkers 4
2.5 Perminov, Orlov and Frumkin 8
2.6 Levine and Weale 9
2.7 Wicke and Nernst 10
CHAPTER 3-PALLADIUM HYDROGEN SYSTEM
3.1 Phase relationships 12
3.2 The α-Phase of the Palladium-Hydrogen System 13
3.3 The α+β Region, the Plateau of the P-C-T Curve 15
3.4 The β-Phase Region of the Palladium-Hydrogen System 16
3.5 High-Pressure β-phase Experiments 18
CHAPTER 4-EXPERIMENTAL SETUP
4.1 Design Parameters for the Experimental Apparatus 20
4.2 Preparation of the Palladium 20
4.3 Cleaning Manifold and Procedure 23
4.4 Design of High Pressure Manifold and Selection of Components 25
CHAPTER 5-EXPERIMENTAL PROCEDURE
5.1 Experimental Procedure 31
5.2 Pressure Loading of the Beds 32
5.3 Bed Weighing Procedure 33
CHAPTER 6-RESULTS AND DISCUSSION
6.1 Calculation of the Fugacity and Compressibility Factor 36
6.2 Calculation of the Atomic Ratio 37
6.3 Plots of Fugacity versus Atomic Ratio 40
6.4 Comparison of Curve Fit With Literature Data 42
6.5 Uncertainty Analysis 45
CHAPTER 7-CONCLUSIONS AND RECOMMENDATIONS
7.1 Conclusions and Recommendations 50
APPENDICIES 52
REFERENCES 77

LIST OF FIGURES

Figure 2.1. P-C-T Relationships of Hoitsema and Troost and Hautefeuille..... 5

Figure 2.2. Compilation of P-C-T Relationships..... 6

Figure 2.3. P-C-T Relationships..... 9

Figure 3.1. Phase Diagram..... 13

Figure 3.2. Isotherms of Hydrogen in the α-Phase..... 14

Figure 3.3. Desorption Isotherms of Pd Foil in the β-Phase..... 17

Figure 4.1. Photograph of Assembled Bed and Exploded Bed..... 26

Figure 4.2. Photograph of an Assembled Test Bed..... 27

Figure 4.3. Schematic of High-Pressure Manifold..... 28

Figure 4.4. Environmental Chamber Door with Beds Attached..... 29

Figure 4.5. Front View of Experimental Setup..... 30

Figure 5.1. Five Beds Utilized in the Experiment..... 31

Figure 5.2. Diagram Showing the Disconnection of Test Bed..... 33

Figure 5.3. Bed Placement on the Balance Pan..... 34

Figure 6.1. Diagram for the Calculation of the Atomic Ratio, H/Pd..... 37

Figure 6.2. Experimental Data of Fugacity versus Atomic Ratio, H/Pd..... 40

Figure 6.3. Fugacity versus Atomic Ratio at 20°C..... 41

Figure 6.4. Comparison of Low Temperature Curve Fit with Literature Data..... 43

Figure 6.5. Comparison of High Temperature Curve Fit with Literature Data..... 44

LIST OF TABLES

Table 3.1. Curve Fit Constants and Concentration Ratios.....17

Table 4.1. Measured Impurities in the Palladium Powder.....20

Table 4.2. Loading of the Palladium Beds.....22

Table 6.1. Compressibility Constants Used in Compressibility Calculation.....37

Table 6.2. Constants for the Palladium-Hydrogen Equation of State.....42

NOMENCLATURE

°C	degrees centigrade
α	hydride phase of hydrogen in palladium, characterized by low pressure
β	hydride phase of hydrogen in palladium, characterized by high pressure
$\alpha+\beta$	hydride phase of hydrogen in palladium referred as the plateau region
∂	partial derivative
μ	chemical potential
θ	concentration divided by the theoretical concentration
ϕ	fugacity coefficient, $=f/P$
Å	angstroms, unit of length
AA	atomic absorption
AE	Autoclave Engineering
atm	unit of pressure
bar	unit of pressure
D	deuterium
f or f	fugacity, chemical potential correction for the non-ideality of a gas
gm	gram
GDMS	glow discharge mass spectrometry
H, H_2	element hydrogen, atomic number 1, atomic mass 1.00794
H/Pd	atomic ratio of hydrogen within the palladium solid
ICP-ES	inductively coupled plasma emission spectrometer
ICP-MS	inductively coupled plasma mass spectrometry
in	inches

K	degrees Kelvin
K	thermocouple type, Chromel-Alumel, Omega engineering
MAWP	maximum allowable working pressure
mmHg	millimeters of mercury, unit of pressure, also Torr
MW	molecular weight
n	atomic ratio of hydrogen within the palladium solid
NIST	National Institute of Standards and Technology
P or p	pressure
P-C-T	Pressure-Composition-Isotherm
Pd	element palladium, atomic number 46, atomic mass 106.42
psi	unit of pressure, pounds force per square inch
psia	absolute unit of pressure, pounds force per square inch absolute
psig	unit of pressure, pounds force per square inch gage
r	atomic ratio of hydrogen within the palladium solid
R	universal gas constant
T	temperature
U	uncertainty
V, v	volume
Z	compressibility factor, compensates for a non-ideal gas

Characterization of the β-Phase Region of the Palladium-Hydrogen Equation of State

by

Kane J. Fisher

ABSTRACT

The β-phase of the P-C-T curves of the palladium-hydrogen system is encountered at high pressures of gaseous hydrogen and low temperatures of this system. The β-phase is characterized by an increase in the concentration of hydrogen in the palladium lattice with an increase in pressure of the free hydrogen gas surrounding the palladium.

The P-C-T curves in this study are determined by gravimetric measurements of the hydrided palladium sample to determine the amount of hydrogen within the palladium lattice. The amount of hydrogen is kept constant within the experimental system and the temperature is varied which changes the pressures. The objective of this experimental thesis is to accurately determine the P-C-T curves of palladium in the β-phase region to pressures of 20,000 psia and medium to low temperature region of -60°C to 100°C.

CHAPTER 1

Objectives

The objective of this investigation is to extend the range of palladium P-C-T curves in the β-phase region and to compare these experimental results with the published data. This will be done by accurately determining the P-C-T curves of palladium to 20,000 psia between -60°C to 120°C.

The P-C-T curves of palladium will be determined by gravimetric measurement, which should improve the accuracy in the high pressure, low temperature β-phase region. The method of taking gravimetric measurements has only been used on milligram samples of palladium (Buck, et al, 1972), (Friske, et al, 1973) and (Lewis, 1982). In this study 50.6 grams of palladium will be used.

The most frequently employed method for measuring P-C-T curves is equilibrium volumetric pressure measurements to determine the amount of hydrogen gas absorbed into the palladium lattice (Lewis, 1967). The errors that may occur when using the equilibrium volumetric pressure method to determine the quantity of gas in a system include systematic volume calibration errors, limitations of pressure, volume, and temperature measuring equipment.

Using gravimetric measurement the accuracy of the stoichiometric ratio, H/Pd, will be increased. In addition the fugacity of the hydrogen in this system will be fit to a function of atomic ratio, instead of pressure, of the form:

$$\ln(f_{H2}) = -A(T) + B(T)(H/Pd) \qquad (1\text{-}1)$$

where A and B are constants and H/Pd is the atomic ratio (stoichiometry) of hydrogen in palladium. A comparison of the results of Perminov, Orlov and Frumkin using this method will be shown.

The compressibility factor (Z) and fugacity are two parameters used to develop the hydrogen equation of state. Using an accurate determination of the compressibility factor may reduce errors in the β-phase of the P-C-T curve. An unpublished compressibility factor correlation developed by Meyer (1996) will be used in this investigation. This compressibility factor will be used to determine the fugacity, which is a chemical potential correction for the non-ideality of the hydrogen gas at these pressures.

An important goal of this investigation is to compare our data to that of Perminov, Orlov, and Frumkin in the range 0-1000 psia. Beyond 1000 psia the data collected in this study can be expected to deviate from that of Perminov, Orlov, and Frumkin because those authors used pressure instead of fugacity to generate their curves. In addition to the fugacity correction, improvement in material purity and availability of accurate, modern equipment should reduce the error of the high-pressure P-C-T curves.

CHAPTER 2

Introduction and Literature Survey

2.1 Background

The palladium-hydrogen system has been one of the most widely investigated metal-gas systems since the discovery of their interactions in 1866 by Thomas Graham (Graham, 1866). Graham noted that palladium allowed a large throughput of gas through the bulk of the material and also that palladium "occluded", adsorbed, a large amount of hydrogen when it was allowed to cool at room temperature. Graham then measured the amount of hydrogen that was adsorbed by the palladium lattice. Since then a large number of experimental investigations have been carried out concerning the high adsorption of hydrogen into palladium and the high permeation of hydrogen through palladium (Lewis, 1967), (Santandera, et al, 1986), and (Lässer, et al, 1983).

One of the primary concerns of investigators has been the isothermal pressure-composition-temperature (P-C-T) relationship that arises from the hydrogen adsorption into the palladium lattice. P-C-T relationships exhibit the solubility of hydrogen in palladium and the phase transformations that occur in the palladium-hydrogen system. A P-C-T curve is a plot of the pressure versus the atomic ratio of a gas within the lattice at selected temperatures, as shown in Figure 2.1, and Figure 2.2. In the palladium-hydrogen system the composition is plotted in terms of the atomic ratio, H/Pd.

2.2 Troost and Hautefeuille

The first investigators that plotted the P-C-T relationship were Troost and Hautefeuille in 1874, (Troost et al, 1874), shown in Figure 2.1. Troost and Hautefeuille

took measurements ranging from 20°C to 170°C. They realized that the atomic ratio increased with a constant pressure and roughly ended where the palladium to hydrogen ratio was 2:1. Thus, they concluded that the hydride formed a stoichiometric formula of Pd_2H. Several investigators (Lewis, 1967), (Santandera, et al, 1986), and (Gillespie, et al, 1926) later, refuted this stoichiometry.

2.3 Hoitsema

The studies and determination of P-C-T curves was then expanded by the work of Hoitsema (Hoitsema, 1895). Hoitsema published a more comprehensive compilation of P-C-T data in the temperature range of 10° to 250°C and pressures up to 6 atmospheres. A compilation of the P-C-T data from Troost and Hautefeuille, and Hoitsema is shown in Figure 2.1, from (Lewis, 1967).

Hoitsema extended the knowledge base of the palladium-hydrogen system by an expansion in the temperature and pressures of the palladium hydrogen system. Since Hoitsema's experiments, the palladium P-C-T curves have been expanded to 25,000 psia and a temperature range of -78°C to 500°C (Lewis, 1967), (Santandera, 1986).

2.4 Gillespie and coworkers

Gillespie and Hall expanded the knowledge of the P-C-T curves of palladium-hydrogen system (Gillespie et al, 1926). The isotherms that Gillespie and Hall manometrically measured from 0°C to 180°C used finely divided palladium black. The palladium was reduced from palladosammine chloride using sodium formate. Several heat treatments were also used to clean the palladium of gaseous impurities. Carbon

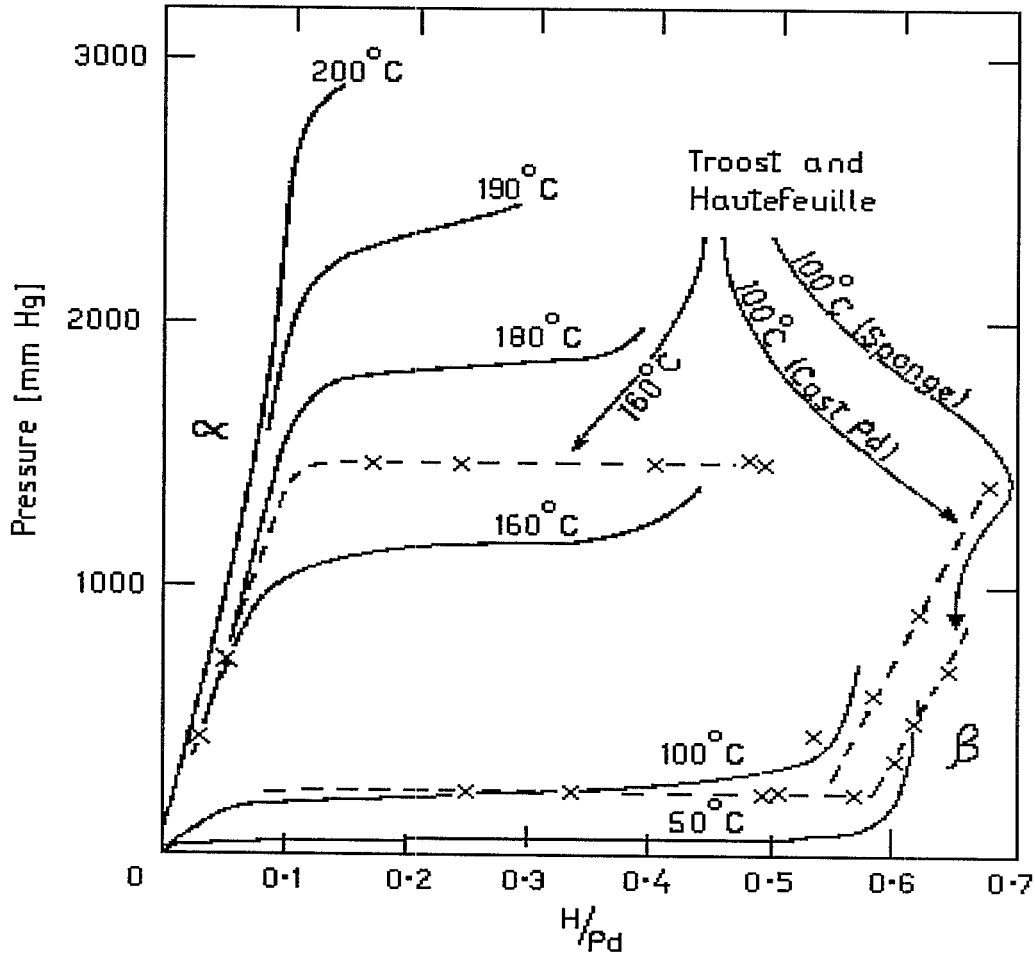

Figure 2.1. P-C-T relationships of Hoitsema, and Troost and Hautefeuille from (Lewis, 1967).

dioxide was then added to replace the hydrogen in the palladium. Large aliquots of hydrogen were adsorbed and desorbed from the palladium powder and hysteresis was observed. Gillespie and Hall then used a heat treatment of 200°C to achieve an equilibrium in the α+β region of the P-C-T curves at 0°C. This heat treatment liberated hydrogen that could not be drawn off of the palladium. Using this heat treatment alleviated the hysteresis effects that were observed and was thought to allow the system to achieve a true equilibrium. In subsequent investigations this heat treatment was not

considered to be a true equilibrium because in the absorption and desorption of hydrogen in palladium there is a noticeable hysteresis effect that occurs (Gillespie, et al, 1936), (Wicke and Nernst, 1964). The heat treatment of 360°C was used in the remainder of Gillespie and Hall's P-C-T measurements.

Later, Gillespie and Galstaun examined the P-C-T curves of palladium in the temperature range of 200 to 313°C and pressures up to 30 psia (Gillespie, et al, 1936). The use of very finely divided palladium black was used in the investigation. The palladium was prepared from palladosammine chloride and reduced by hydrochloric acid. Gillespie and Galstaun hypothesized the existence of the compounds Pd_8H, Pd_4H, Pd_3H, Pd_2H and determined that each had chemical individuality, Figure 2.2. The existence of

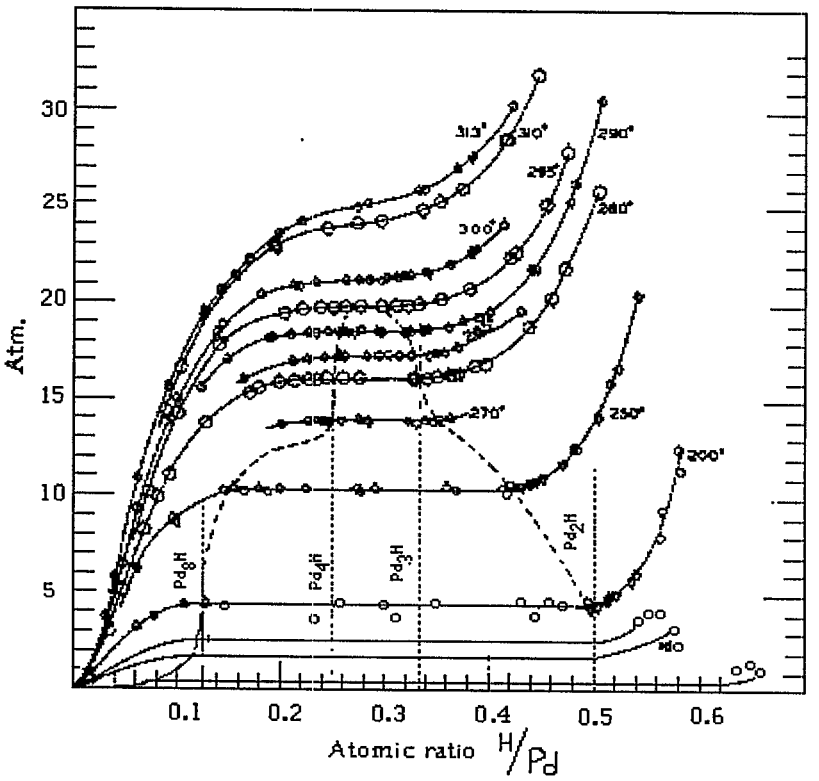

Figure 2.2. P-C-T diagram showing evidence for the existence of Pd_8H, Pd_4H, Pd_3H, Pd_2H, and the critical point determination, from (Gillespie, et al, 1936).

these compounds was determined from anomalies in the width of the $\alpha+\beta$ region at different temperatures, Figure 2.2. Each of these compounds is regarded as solid solutions that maintain their stoichiometrical compositions in a limited temperature range. Later the evidence of these compounds was refuted, (Gillespie, et al, 1939) conceded that there was no proof of the existence of these compounds. Wicke and Nernst later determined that envelope drawn through α_{max} and β_{min} is a smooth continuous curve. In the conclusion of Gillespie and Galstauns' investigation the possibility of the composition PdH is not supported by the P-C-T data (Gillespie, et al, 1936).

Gillespie and Galstaun empirically determined an equation to describe the pressure-temperature relationship in the $\alpha+\beta$ region of the P-C-T curve. Equation (2-1) accurately depicts the pressure-temperature absorption relationship that occurs in the $\alpha+\beta$ plateau region (Gillespie, et al, 1936). Equation (2-1) is:

$$\log P = 4.6018 - 1877.82/T \qquad (2\text{-}1)$$

where P is in atmospheres and T is in degrees Kelvin.

Gillespie and Galstaun determined the critical constants of palladium-hydride. The critical temperature, pressure, and atomic ratio are, 295.3°C, 19.87 atm, and 0.270 H/Pd, respectively. Gillespie and Galstaun characterized the α-phase and the $\alpha+\beta$ region of the palladium P-C-T curves.

Gillespie and Downs studied the adsorption of deuterium on palladium black in same pressures and temperatures as Gillespie and Galstaun (Gillespie et al, 1936), (Gillespie et al, 1939). Gillespie and Downs conceded that any further evidence did not support the analogous isothermal relationships and the compounds (Pd_8H, Pd_4H, Pd_3H, and Pd_2H) that were proposed in Gillespie and Galstaun. Gillespie and Downs

determined the critical constants of the palladium-deuterium system. The critical temperature, pressure and atomic ratio are 276°C, 35 atmospheres, and 0.25 of D/Pd (Gillespie et al, 1939). It was also noted by Gillespie and Downs that there is a significant effect of the preparation of the palladium in the determination of P-C-T curves. "Fresh" or "virgin" palladium produced repeatable isotherms, while an inactive sample was not reproducible.

Gillespie with Galstaun and Downs determined the starting point of the β-phase in the palladium-hydrogen and palladium-deuterium systems, termed β_{min} by Wicke and Nernst (Wicke and Nernst, 1964). The characterization and knowledge base of the β-phase region of the P-C-T curves of palladium with hydrogen and deuterium has been increased by several investigators, including Perminov, Orlov and Frumkin (Perminov et al, 1952).

2.5 Perminov, Orlov and Frumkin

Perminov, Orlov, and Frumkin investigated to high pressures (1700 Bar), low temperatures (195K), and noted that their results at low temperatures were probably inaccurate (Perminov, et al, 1952). The maximum atomic ratio reported by Perminov, Orlov, and Frumkin was 0.92 H/Pd. This atomic ratio was examined at the lowest temperature investigated, consequently the reliance of this measurement is questionable. Two types of palladium powder, and palladium foil were used in this investigation to determine if there is a logarithmic relationship in the high lattice filling region. Perminov, Orlov, and Frumkin utilized a volumetric determination of the atomic ratio, H/Pd.

2.6 Levine and Weale

Levine and Weale extended the P-C-T knowledge at pressures up to 1000 Bar, by experimenting at supercritical temperatures from 326°C to 477°C. They reported a concentration ratio of 0.691 H/Pd at their highest pressure and 326°C (Levine, et al, 1960). Levine and Weale compiled a summary of the P-C-T measurements and compared their results with (Gillespie, et al, 1926), (Gillespie, et al, 1936), and (Perminov, et al, 1952) as shown in Figure 2.3, reprinted from (Lewis, 1967). Where it is noted that Perminov, Orlov, and Frumkin determined the low temperature linear isotherms with palladium powder.

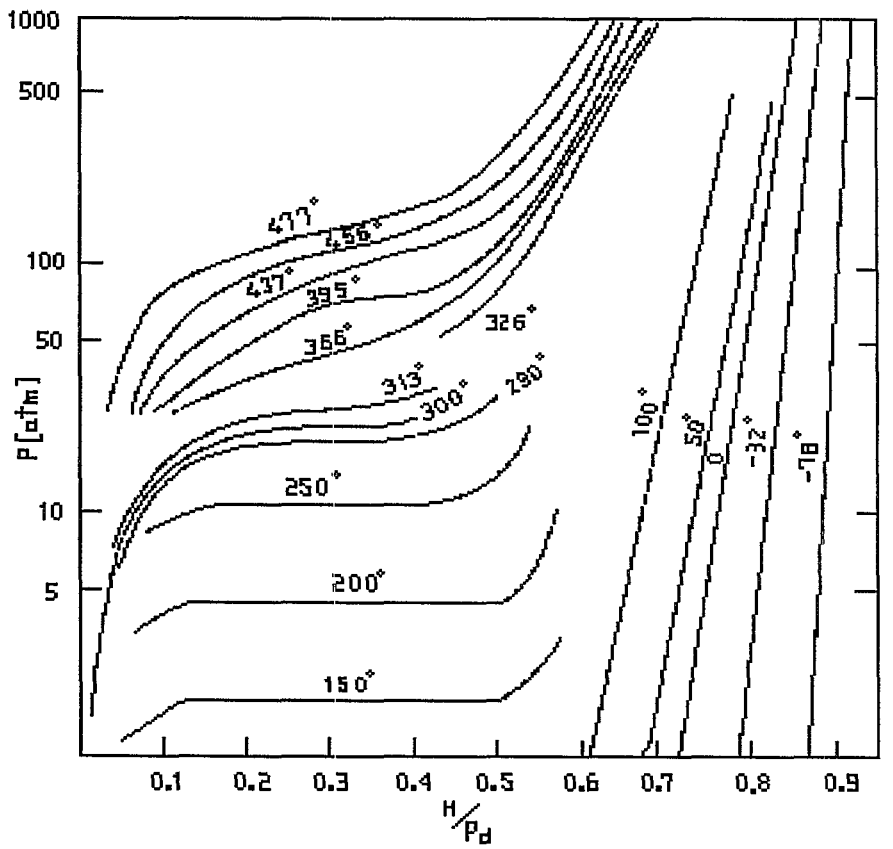

Figure 2.3. P-C-T relationships from Levine and Weale, Gillespie and Hall, Gillespie and Galstaun, Perminov et al, plot from (Lewis, 1967).

2.7 Wicke and Nernst

Wicke and Nernst examined P-C-T relationships in the α-phase, the α+β region, and the β-phase of the palladium-hydrogen and palladium-deuterium systems (Wicke and Nernst, 1964). Their examination included measurements on palladium foil, wire, sheet and powder. Volumetric measurements were employed in their method of determining the P-C-T relationships of hydrogen and deuterium in palladium. The highest hydrogen concentration ratio (H/Pd) reported by Wicke and Nernst in their investigation was observed at -78.5°C and 760 mmHg, this ratio is 0.838 ±0.003 H/Pd. Wicke and Nernst compared this value to the value put forth by Perminov, Orlov, and Frumkin, which is 0.870 H/Pd, measured at the same temperature and pressure. The temperature where this concentration ratio was measured was the lowest temperature taken by Wicke and Nernst and Perminov, Orlov and Frumkin.

Wicke and Nernst measured adsorption isotherms in the α-phase, α+β plateau region and the β-phase. Preparation of the palladium performs a significant role in the adsorption pressure, while desorption pressure is less affected by a pre-treatment of the palladium. Wicke and Nernst concluded desorption pressure represents more closely the true equilibrium pressure because no observable effects were seen due to the preparation of the palladium.

Wicke and Nernst determined a curve fit equation describing the temperature and composition (r) relationship for the hydrogen data in the α-phase region. This equation is:

$$\ln P(\text{atm}) = 12.9 + 2\ln\frac{r}{1-r} - \frac{r}{T}\left[\frac{2330}{r} + 4530 + \frac{2.017\times10^{6}}{T}\right] \qquad (2\text{-}2)$$

The constants in this equation were determined empirically from their desorption curves. In equations (2-2), (2-3), and (2-4) the atomic ratio is represented by r, T in Kelvin, and P_{H2} is the pressure in atmospheres. Wicke and Nernst also determined the relationship of the temperature dependence for the desorption pressure in the $\alpha+\beta$ region. This dependence is given by the equation (2-3), (Wicke and Nernst, 1964).

$$\ln P_{H2}\,(\text{atm}) = -4693/T + 10.97 \qquad (2\text{-}3)$$

Using a similar form of equation (2-2), Wicke and Nernst determined an equation for the desorption curves in the β-phase. This equation (2-4), (Wicke and Nernst, 1964):

$$\ln P_{H2}(atm) = 12.9 + 2\ln\frac{r}{1-r} - \frac{1}{T}[12070 - 10803r] \qquad (2\text{-}4)$$

T is the absolute temperature, r is the atomic ratio of H/Pd, and P_{H2} is the pressure in atmospheres. The constants in equations (2-2), (2-3) and (2-4) are given for hydrogen and differ for adsorption, desorption and deuterium (Wicke and Nernst, 1964). It must be noted that in equation (2-4) the natural logarithm term represents a limiting ratio of 1.0 for the atomic ratio.

CHAPTER 3

The Palladium-Hydrogen System

3.1 Phase relationships

The palladium hydrogen system has been greatly investigated since the discovery of an anomalous interaction of hydrogen in palladium by Graham (Graham, 1866). Since this discovery by Graham, a wealth of information has been compiled on the phase relationships, thermodynamics, kinetics, separation phenomena, magnetic properties, structure, and sorption of hydrogen in palladium and intermetallic compounds (Lewis, 1967), (Lewis, 1982), and (Santandera, et al, 1986).

The palladium face centered cubic (fcc) structure undergoes phase transitions when hydrided. These phase transitions are associated with different interactions of hydrogen in the palladium lattice.

The palladium-hydrogen system consists of two different phases, the α-phase and the β-phase. Both the α-phase and β-phase in the palladium-hydrogen system have the same face centered cubic crystal structure as pure palladium with different interatomic spacing, thus different lattice constants. Below the critical dissociation point at 295.3°C, 19.87 atm, and atomic ratio 0.270 H/Pd (Gillespie et al, 1936) and between the α-phase and the β-phase is a region where there is a transition of the α-phase and β-phase. This transition is called the $\alpha+\beta$ phase, also known as the plateau region. In the plateau, α and β phases of palladium co-exist, shown in Figure 3.1.

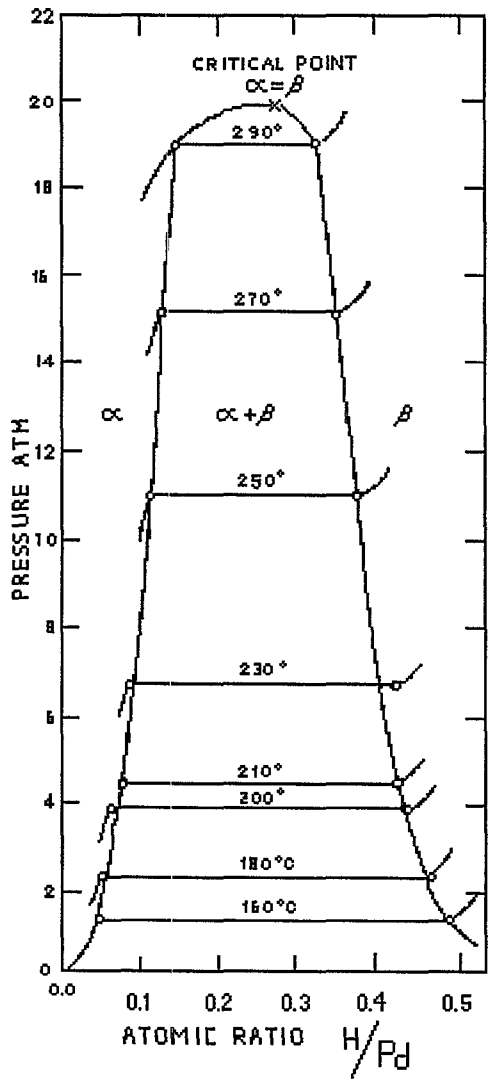

Figure 3.1 Phase diagram, showing the phase boundaries, the α-phase, the α+β region, the β-phase and the critical point, compiled by (Hansen, 1958).

3.2 The α-phase of the palladium-hydrogen system

The α-phase of the palladium P-C-T curve is characterized by a low concentration of hydrogen in palladium. The hydrogen within the palladium lattice is considered a homogeneous solid solution. The crystal lattice structure of the α-phase palladium very nearly matches the lattice of pure palladium (Santandera, 1986). In the α-phase the hydrogen occupies the interstitial octahedral sites of the palladium lattice. It has no effect

on the structure of this lattice. Pure palladium, and the α-phase of palladium have lattice constants of 3.8907Å and 3.902Å respectively (Santandera, 1986), (Lewis, 1967).

The α-phase is characterized by an increase in the ratio H/Pd with an increase in pressure. This increase continues until the point where the α+β region begins, called α_{max}. Wicke and Nernst empirically determined an equation to model the solubility in the α-phase using volumetric measurements. These α-phase isotherms are shown in Figure 3.2 (Wicke and Nernst, 1964).

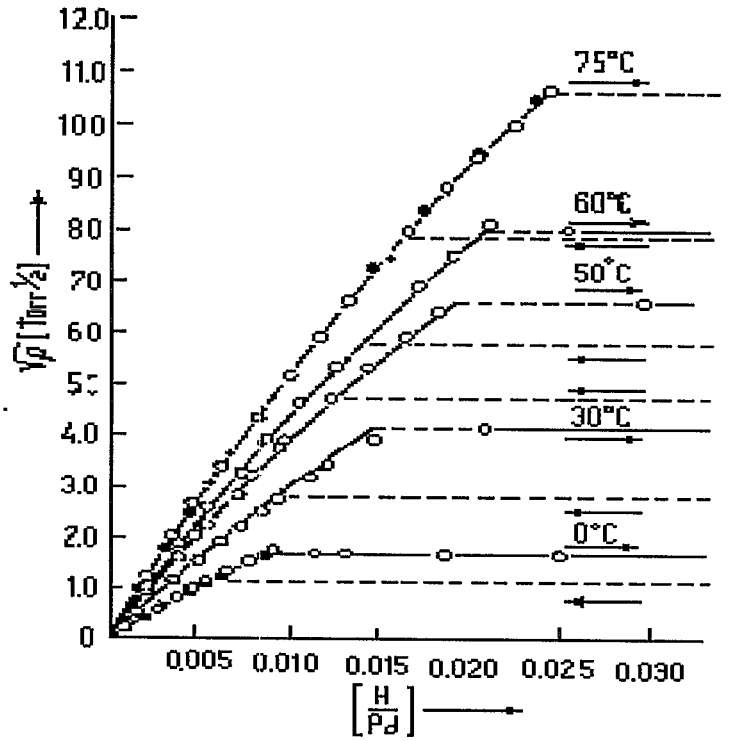

Figure 3.2 Isotherms of hydrogen in the α-phase, •, ∘ adsorption measurements; + desorption measurements, from (Wicke and Nernst, 1964).

Wicke and Nernst use a chemical potential approach to the solubility of hydrogen in palladium. The chemical potential of hydrogen in palladium can be set equal to equation (3-1), (Wicke and Brodowsky, 1978):

$$\mu_H = \mu_H^o + RT \cdot \ln \frac{r}{1-r} + \Delta\mu_H \tag{3-1}$$

Where μ_H^0 is the standard potential, $\Delta\mu_H$ is the deviation of the chemical potential from ideal behavior. This deviation has protonic and hydrogen electron contribution, shown in equation (3-2), (Wicke and Brodowsky, 1978):

$$\Delta\mu_H = \Delta\mu_{H^+} + \Delta\mu_e \tag{3-2}$$

In the solution equilibrium the chemical potential of the dissolved hydrogen atoms equals that of the hydrogen gas, which results in the equation (3-3), (Wicke and Brodowsky, 1978):

$$\mu_H = \frac{1}{2} \cdot \mu_{H2} = \frac{1}{2} \cdot \mu_{H2}^o + \frac{1}{2} RT \cdot \ln p_{H2} \tag{3-3}$$

With Sievert's constant being introduced, (Wicke and Brodowsky, 1978):

$$K = \exp[(\mu_H^0 - \frac{1}{2}\mu_{H2}^o) / RT] \tag{3-4}$$

Using equations (3-1) to (3-4) the equation (3-5) evolves, (Wicke and Brodowsky, 1978):

$$\ln \sqrt{P_{H2}} = \ln(K \cdot \frac{n}{1-n}) + \frac{1}{RT}(\Delta\mu_{H^+} + \Delta\mu_e) \tag{3-5}$$

This is the form of the equation used by Wicke and Nernst in their empirical determination of the α-phase desorption equilibrium.

3.3 The α+β region, the plateau of the P-C-T curve

In the α+β region of the P-C-T curve the α, and β phases co-exist and the palladium lattice expands and accepts more hydrogen at constant pressure. This region is called the plateau region of the P-C-T curve and exhibits a constant pressure between the limits of

the α-phase and the β-phase, shown in Figure 3.1 and Figure 3.3. Wicke and Nernst concluded that the α+β region is accurately characterized by a flat curve. The flatness of the α+β region was confirmed with palladium black (Wicke and Nernst, 1964). Wicke and Nernst determined the relationship of the temperature dependence in terms of the pressure in the α+β region. Wicke and Nernsts' relationship is shown in equation (2-3).

3.4 The β-phase region of the palladium-hydrogen system

The β-phase of the P-C-T curve is also characterized by an increase in the concentration with an increase in pressure. In the β-phase of the palladium P-C-T curve, the palladium lattice constant increases with more hydrogen pressure (Santandera, 1986). An increase in the lattice constant in the formation of the β-phase corresponds to a ≈10% volume expansion in bulk palladium. The first occurrence of the β-phase is in the α+β phase where the α-phase and the β-phase co-exist, shown in Figure 3.1. In this plateau region there are sections of the bulk palladium that are pure α-phase and sections of pure β-phase. The onset of the β-phase is called β_{min}, termed by Wicke and Nernst and shown in Figure 3.3.

Wicke and Nernst also empirically determined the constants in this equation to model the solubility in the β-phase using volumetric measurements. These determinations of the concentration ratio, H/Pd were on palladium black and on a palladium foil. It is noted by Wicke and Nernst that the values of A and B for palladium black lie within the range of scatter of the values on palladium foil.

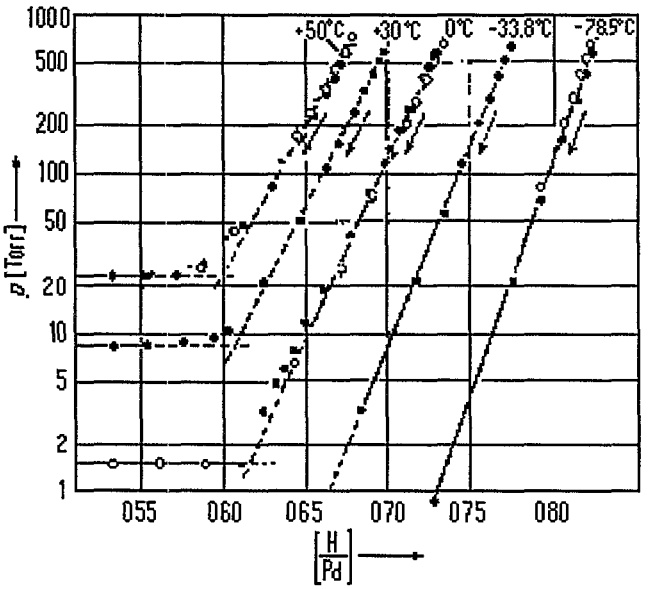

Figure 3.3 Desorption isotherms of Pd foil in the β-phase with the transition from the two-phase plateau region (Wicke and Nernst, 1964).

The concentration ratios, corresponding temperatures and curve fit constants of Wicke and Nernst and Perminov, Orlov and Frumkin at 760 torr are shown in the Table 3.1. The concentration ratios for Wicke and Nernst are for palladium black and a palladium foil.

Table 3.1 Curve Fit Constants and Concentration Ratios for (Wicke and Nernst, 1964).

°C	A Wicke Nernst	B Wicke Nernst	H/Pd at 760 torr on Pd black Wicke and Nernst	H/Pd at 760 torr on Pd foil Wicke and Nernst	H/Pd at 760 Torr on Pd black Perminov et al.
50	29.3	42.2	0.695	0.683	0.676
30	32.9	46.0	0.715	0.704	-
0	38.2	51.0	0.749	0.737	0.717
-78.5	55.6	66.4	0.838	0.826	0.870

In the β-phase of the palladium P-C-T curve, the inter-atomic spacing of the palladium lattice increases with increasing hydrogen pressure (Santandera et al, 1986). This increase in the lattice constant has been characterized by an equation of the form:

$$a(n) = a(\beta_{\min}) \cdot [1 + 0.044(n - \beta_{\min})] \qquad (3\text{-}6)$$

Equation (3-6) was determined at by x-ray analysis of hydrided palladium in the range of 0.8<H/Pd<0.98 at 77K by Schirber and Morosin, (Wicke and Brodowsky, 1978). An increase in the lattice constant in the formation of the β-phase corresponds to a ≈10% to 15% volume expansion in bulk palladium.

3.5 High-Pressure β-phase Experiments

Tkacz and Baranowski extended the pressure range to 15,000 Bar of gaseous hydrogen at temperatures of 25°C, 45°C, and 65°C (Tkacz, et al, 1976). Tkacz and Baranowski reported an experimental concentration ratio ranging from 0.85≤ H/Pd ≤ 1.0. In their investigation the concentration ratio did not exceed unity. Tkacz and Baranowski reported a high concentration ratio of 0.995 H/Pd at 12,200 Bar of gaseous hydrogen. A concentration of 1.0 (unity) corresponds to a condition where the number of hydrogen atoms in the palladium lattice equals the number of octahedral sites within this lattice.

According to Tkacz and Baranowski two opposite effects are produced at high-pressures of gaseous hydrogen. One of the effects at high hydrogen pressures is an increase in the thermodynamic activity of hydrogen. This high activity results in a higher solubility of hydrogen in the palladium. Another effect that Tkacz and Baranowski concluded is that an increase in the hydrogen pressure reduces the solubility in the palladium lattice due to the positive partial molar volume change in the bulk palladium.

With the use of high pressures of hydrogen gas over the palladium lattice the hydrogen gas deviates from an ideal gas. The chemical potential of a perfect gas, at a constant temperature, is a function of the logarithm of the pressure. From a thermodynamic standpoint the pressure P is replaced by the fugacity. The fugacity is a chemical potential correction for the non-ideality of the hydrogen gas at these pressures. The fugacity of a gas is defined by the following relationships where μ^0 is a function of T only. The quantity μ^0 is the chemical potential at the reference state pressure.

$$\mu=\mu^0 + RT\ln f \tag{3-7}$$

$$f/p \rightarrow 1 \text{ as } p \rightarrow 0 \tag{3-8}$$

At pressure P, and the temperature T, the equation gives the fugacity in terms of an integral that can be computed from experimental data:

$$\ln\left(\frac{f}{P'}\right) = \int_0^{P'} \frac{Z-1}{P} dP \tag{3-9}$$

Where the compressibility factor, Z is defined as:

$$Z \equiv \frac{Pv}{RT} \tag{3-10}$$

It is more convenient to write the fugacity in terms of the fugacity coefficient, Φ as

$$\ln \Phi = \int_0^{Ptot} (Z-1)\, d \ln P \tag{3-11}$$

where:

$$f \equiv \Phi P \tag{3-12}$$

CHAPTER 4

Experimental Setup

4.1 Design Parameters for the Experimental Apparatus

There are many design factors involved in the preparation of this high-pressure P-C-T experiment. The preparation of the palladium, the design of a high pressure manifold and high pressure containers for the palladium, the selection of the pressure and temperature equipment, and the use of cryogenic liquids and highly flammable gas are the main parameters involved in the design of the experimental apparatus.

4.2 Preparation of the Palladium

The palladium powder used is high purity and very well characterized. Engelhard manufactures the palladium powder. The quantities of the measured impurities are outlined in Table 4.1. The cleaning and preparation process outlined in section 4.3 will further purify the palladium from impurities that are adsorbed from the air in transit.

Table 4.1 Measured impurities in the palladium powder.

Impurities	parts per million	Impurities	parts per million
C	<45	B,Si,P,Br,Na,K	not detected
S	<1	Fe,Cr,Ni,Mo	not detected
N	<94	Pt,Rh,Ru,Os,Ir,Au,Ag	<100 total
O	<936	As,Cd,Sn,Pb,Bi,Hg,Tl,Zn,Cu	not detected
Cl	<96	all others	<10 total

The measured palladium purity is 99.87%. The palladium purity will increase to 99.99% after the cleaning process, which removes the surface impurities oxygen, nitrogen, carbon

and chlorine. This cleaning process is outlined in section 4.3. The elemental impurities As, Cd, Sn, Pb, Bi, Hg, Tl, Zn, Cu, Pt, Rh, Ru, Os, Ir, Au, Ni, Mo, B, were measured using an inductively coupled plasma-emission spectrometer (ICP-ES). The impurities Si, P, Fe, Cr, Ag were detected using inductively coupled plasma-mass spectrometry (ICP-MS). Sodium and Potassium were detected using atomic absorption (AA). All other impurities were analyzed by glow discharge mass spectrometry (GDMS).

The palladium powder is pressed into a pressure vessel with stainless steel filters on each end of the vessel to contain the powder. A small aliquot of powder is funneled into the pressure vessel and then pressed with a hydraulic press. This process of pressing small amounts of palladium powder is to insure the pressing forces are within the limits of the pressing hardware. The initial tap density of the palladium powder is 1.0gm/cc and 5.5gm/cc after the powder is pressed. The total weight of each of the palladium samples in this investigation is approximately 50.6gm. The amount of each aliquot of palladium is shown in Table 4.2 for palladium bed #5 loading. The amount of force required to compress the palladium as well as the pressing hardware spacer thickness is shown in Table 4.2. The palladium length is 3.75 inches the Pd diameter is 0.437 inches. The total volume occupied by the palladium is 9.217 cm^3.

A rough estimate of the palladium weight is known from the pressing of the powder into the pressure vessel. Initially the pressure vessel is weighed empty with the filters that will be used to cap the ends of the unit. A more accurate measurement of the amount of palladium in the vessel is then taken from the difference in the total weight of the palladium and vessel minus the empty weight of the vessel and filters.

Table 4.2 Loading of the Palladium Beds.

Load Number	Spacer Thickness (in)	Goal Amount Pd (gm)	Goal sum of Pd (gm)	Actual Pd in Loading (gm)	Compaction load (lb.)
1	0	6.759	6.759	6.753	3500
2	0.5	6.759	13.518	13.520	4500
3	1.0	6.759	20.277	20.279	4500
4	1.5	6.759	27.036	27.035	4800
5	2.0	6.759	33.795	33.794	5000
6	2.5	6.759	40.554	40.554	4500
7	3.0	6.759	47.313	47.351	4500
8	3.25	3.379	50.692	50.692	3000
9	3.375	filter			

After a palladium bed is assembled within the pressure vessel, the palladium must be leak checked and then cleaned of gaseous impurities. Each of the 5 palladium beds that will be used is acid etched on the pressure vessel with the bed number immediately before the leak check. Each assembled bed must pass a pressurized helium leak check with 10,000 psia of helium. Beds 1,2,3,4 and 7 passed the leak check with leak rates less than 10^{-7} standard cc/second.

The raw palladium powder used in this investigation has a 1.0 m^2/gm surface area. The palladium surface contains oxygen, nitrogen, carbon, and water impurities. The cleaning method used is a process of evacuating, hydriding and de-hydriding, and baking of the palladium powder. The test beds used were connected to a gas handling and cleaning station to clean the units of these gaseous impurities. To ensure that the gaseous

impurities were removed during the cleaning process a Leybold Inficon quadropole mass spectrometer was used to see if any more impurities in the gas phase.

4.3 Cleaning Manifold and Procedure

The manifold used in the palladium cleaning process uses a Balzers turbo molecular drag pump and a roughing pump to evacuate the system. Resistance heating tape is wrapped around the palladium beds. An Omega Engineering CN 2010 process controller controls power output to the heating tape. An Omega Engineering limit controller is used as a secondary backup in case the temperature limit is exceeded. A Leybold Inficon 100AMU quadropole mass spectrometer is used to analyze the gas stream. Nupro air operated, normally closed valves are used throughout the manifold. Two 100 psia Heise model 901B pressure transducers are used for the hydrogen loading. A Balzers PKR 060 full range gage is used to measure the vacuum.

The cleaning procedure for the palladium beds is used in this investigation is as follows:

The temperature of the beds will be maintained at 150°C ±10°C during the basic cleaning process. If the temperature of the unit goes outside of this set range, the cleaning process will be halted until the temperature can be stabilized by the operator. The operator will document abnormal conditions during the cleaning process.

1. Verify proper compressed air pressure (75 psig) for the Nupro valves, electrical power to the heaters, controllers, perform a vacuum system function test, and adjust the pressure of the hydrogen fill bottle to ≈50 psia.
2. Preset all high limit controllers for each cleaning station that will be used.

3. Preset temperature settings on each Omega controller to 150°C.

4. Connect beds to the manifold and leak check. Connect Omega type K thermocouples to the test bed.

5. Measure volume of each test bed if not known.

6. Start heating the test beds to the basic temperature of 150°C or a modified cleaning temperature.

7. Evacuate for 1 hour ±15 minutes.

8. Introduce 11.6 ± 0.4 psia hydrogen into the palladium beds.

9. Hold the 11.6 psia for 10 minutes.

10. Record the uptake of the hydrogen in psia and the temperature hydrogen in the fill bottle.

11. Evacuate the beds for 25 minutes.

12. Record the vacuum level after the 25 minutes of evacuation.

13. Repeat steps 8-12 for a total of 5 cycles. The uptake of the hydrogen should approach a constant level.

14. Record the vacuum level after 12 hours of evacuation.

15. After the final evacuation record the quadropole mass spectrometer trace for the peak heights of the measured gases.

16. Turn off heater and allow beds to cool to room temperature. Close the valves to the beds.

17. Record the vacuum level after cooling to room temperature.

It must be noted that the beds used in this experiment were cleaned with this procedure, and then further evacuated at 150°C for 210 hours to remove additional hydrogen from the palladium.

4.4 Design of High Pressure Manifold and Selection of Components

Limiting factors involved in the high-pressure component selection for this P-C-T investigation is the maximum allowable working pressure (MAWP) of the pressure equipment, temperature limits, and hydrogen compatibility. Other considerations are all metal construction to eliminate out gassing effects, minimization of the of the internal volume, and minimization of the total weight of the beds.

In the construction of the containment vessel and the high pressure manifold Autoclave Engineers (AE) 20,000 psia, 30,000 psia, and 60,000 psia MAWP components were used. The containment vessel for the palladium powder is an AE 3/4-inch OD, 0.437 inch ID, 20,000 psia MAWP pressure nipple. The overall length of the pressure nipple is 4.00 inches. The palladium is contained within this pressure nipple by two 75% dense, 0.440 inch diameter, 1/8 inch deep Mott stainless steel filters, thus the palladium occupies a right circular cylinder of 0.437 inch diameter by 3.750 inches in length. The assembly of the beds after pressing the powder was done by using the AE torque specifications. A photograph of an assembled bed and an exploded view of the parts of the bed are shown in Figure 4.1.

Figure 4.1 Photograph of Assembled Bed and Exploded View of the Bed.

One of the ends of the pressure nipple is capped, the other end used an AE 1/4 inch OD, 2.75 inch long 60,000 psia MAWP pressure nipple to an AE 30,000 psia straight through valve. A close up photograph of an assembled bed is shown in Figure 4.2.

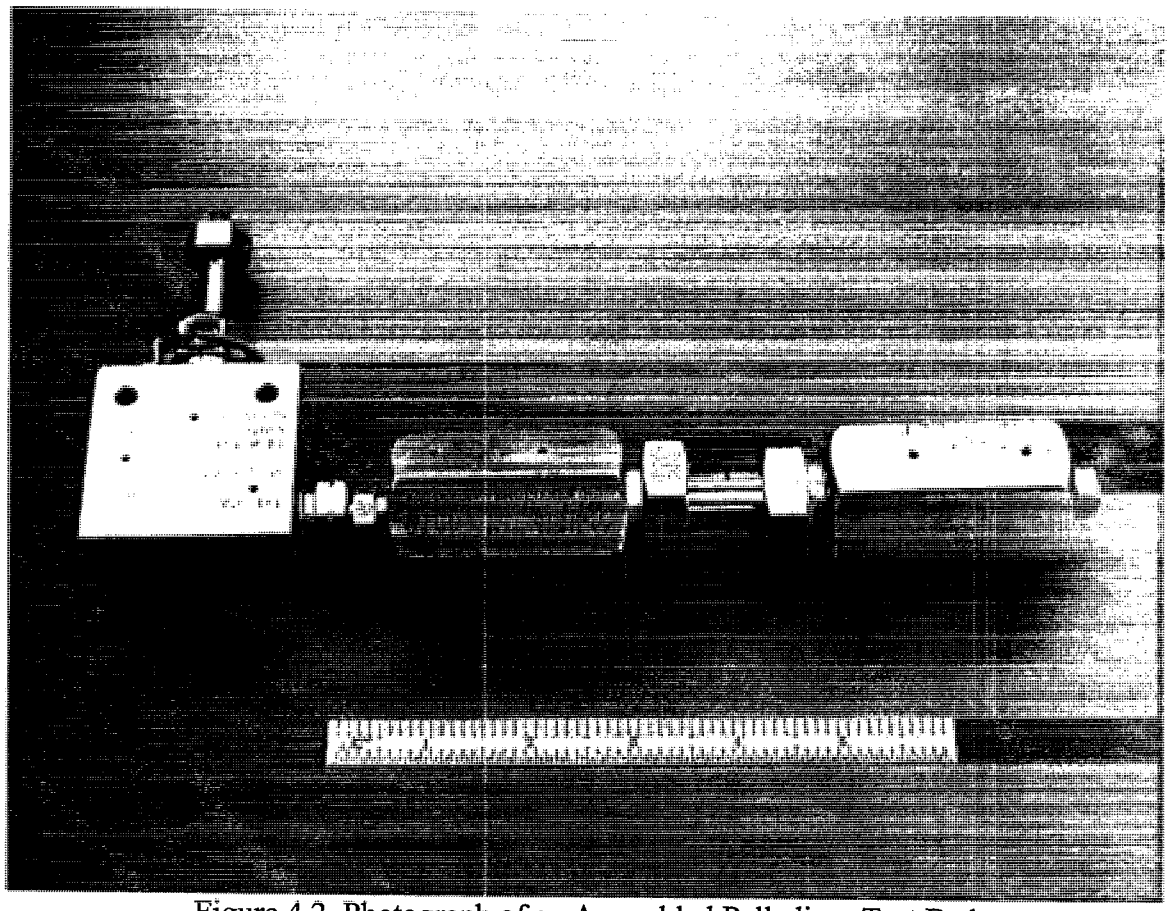

Figure 4.2 Photograph of an Assembled Palladium Test Bed

The rest of the manifold utilized AE 30,000 psia 3-way/2 on pressure valves, and AE 60,000 psia tees, nipples, glands, collars and plugs. A schematic of the high-pressure manifold is shown in Figure 4.3.

The chamber for the maintaining an accurate constant temperature was selected for its size, temperature range, and stated temperature control accuracy. A Despatch 936E environmental chamber with liquid nitrogen cooling is used, with a quoted temperature control of ±0.15 °C.

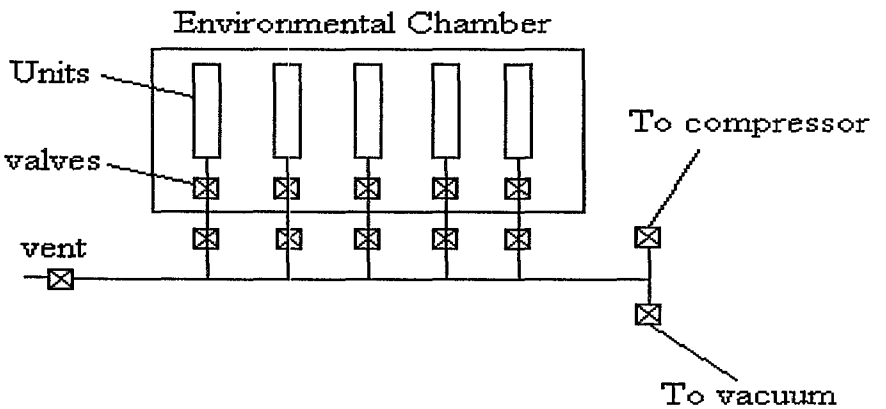

Figure 4.3 Schematic of High Pressure Manifold.

The temperature limits of the chamber are -184°C to 200°C. The physical size of the chamber allows 5 beds to be placed inside with AE ¼ inch 60,000 psia tubing being fed directly through the door. The environmental atmosphere within the chamber is dry nitrogen, which is necessary to alleviate condensation of water vapor on the test beds. The removable door to the chamber allows easy access to the beds, for disconnecting and reconnecting for the weighing of the beds, as shown in a photograph in Figure 4.4.

Thermocouples are selected for the temperature measurement because of their robustness and accuracy over the temperature range of the experiment. The thermocouples used are 0.020 inch diameter, 12 inch long, non-grounded Omega Engineering type K (Cromel-Alumel) thermocouples. The emf of the thermocouples is measured by a data acquisition system that averages 100 readings over a ½ second time interval. The thermocouples are placed in contact with the test beds in a hole that is meant for a helium leak probe. Each bed has two independent thermocouples that are monitoring the temperature. Hose clamps are put around the thermocouples to insure good thermal contact, as shown in Figure 4.4.

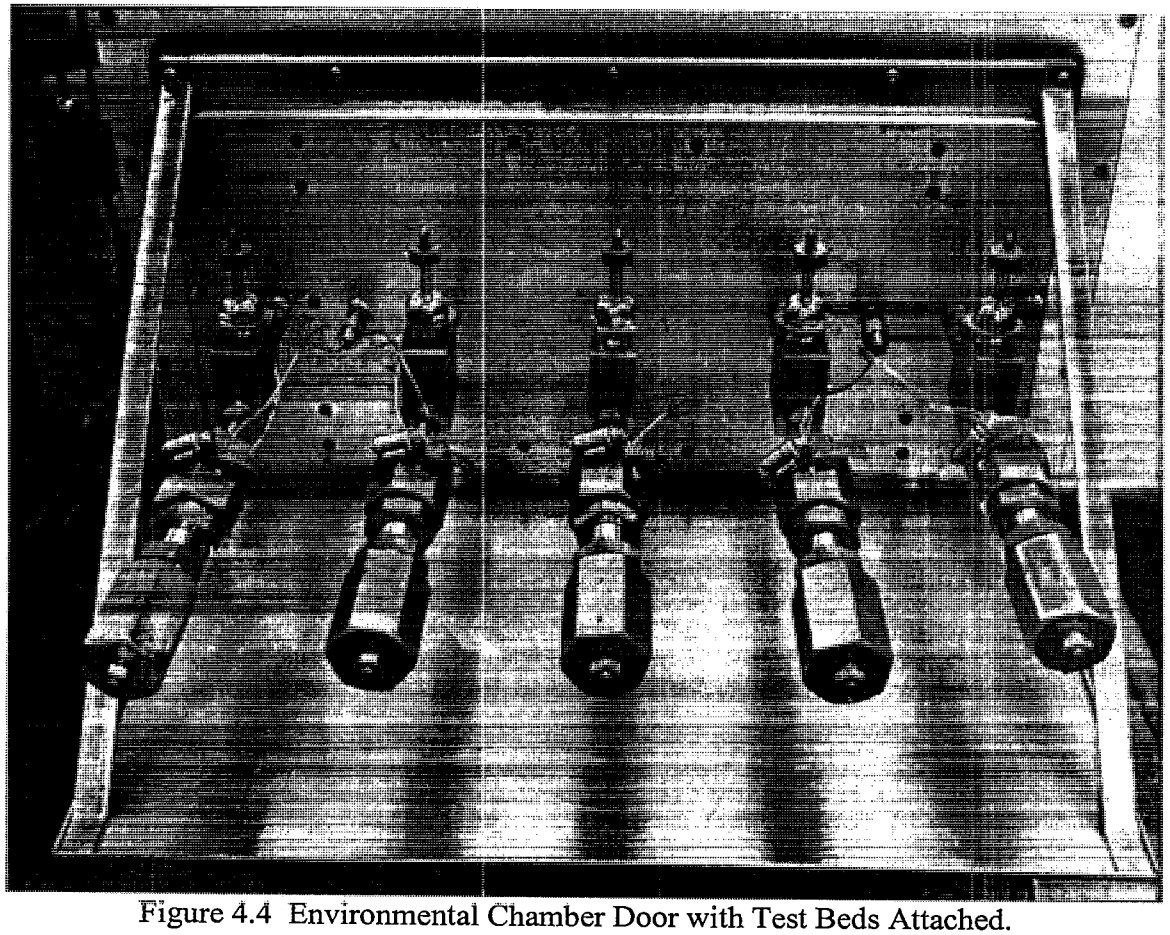

Figure 4.4 Environmental Chamber Door with Test Beds Attached.

The pressure transducers were selected for their accuracy, repeatability and pressure range. Heise model 901B and Precise Sensors model 6550 pressure transducers are used. The Heise transducers have a repeatability of 0.005% of the span and are calibrated in accordance with the National Institute of Standards and Technology, NIST. The full-scale pressure range of the Heise transducers used are 100, 1,000, 2,000, 5,000, and 20,000 psia. The pressure range of the Precise Sensors transducers used are 50, 1,000, and 10,000 psia. The calibration of the Precise Sensors is done utilizing the accurate Heise gages.

A complete front view of the high-pressure manifold, environmental chamber pressure transducers and digital readouts are shown in a photograph in Figure 4.5.

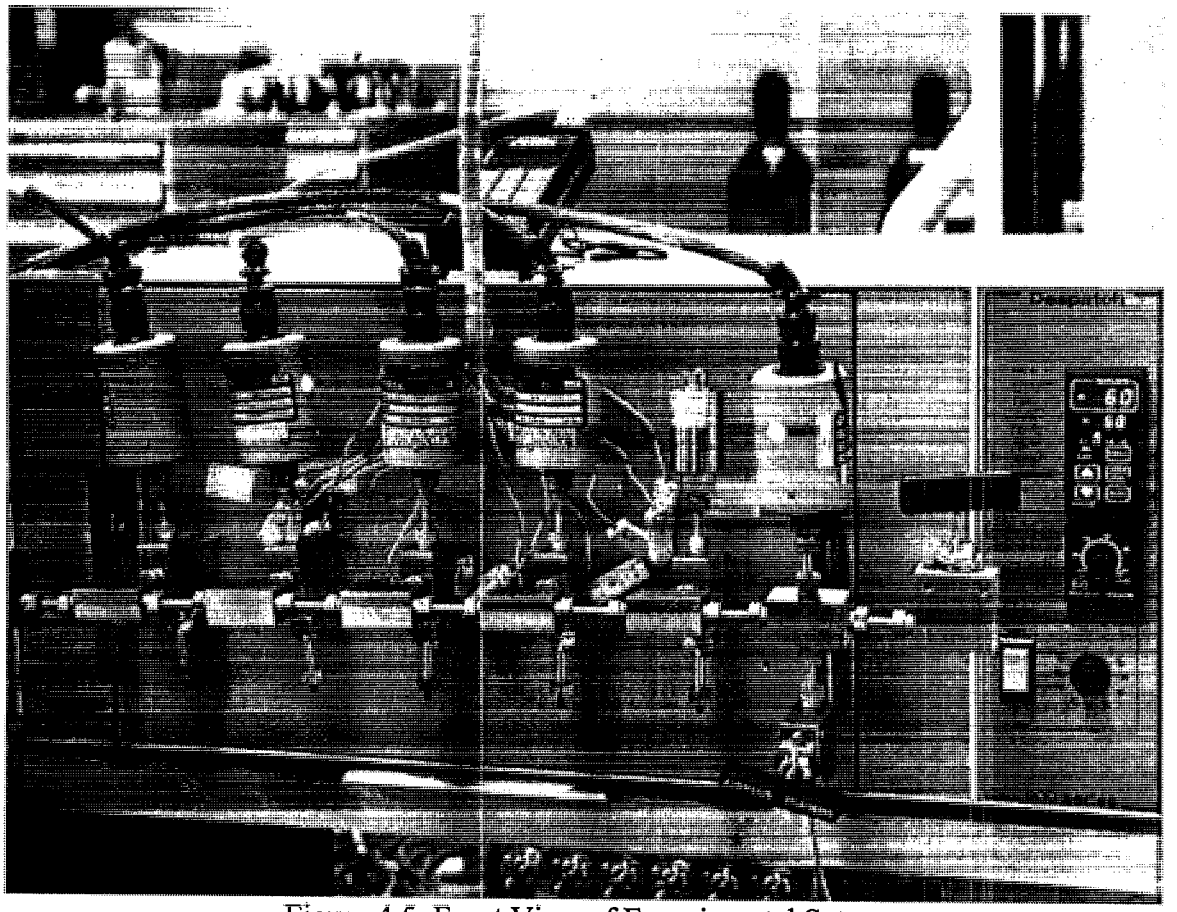

Figure 4.5 Front View of Experimental Setup.

The compressor used is a Newport Scientific 30,000 psi two stage compressor, catalog #4614021.

The mass balance used is a Mettler PM2000MC. The balance has a stated repeatability of 0.001gm and a maximum capacity of 2000.000gm. All standard weights used in the calibration and repeatability measurements are traceable to NIST.

CHAPTER 5

Experimental Procedure

5.1 Experimental Procedure

Five palladium test beds are employed in this experiment shown in Figure 5.1. Each of the test beds is loaded to a different pressure, for example, in the first data set, shown in Appendix A, the test beds were loaded at 20°C, to 667, 2502, 4022, 6340, and 10303 psia. The temperature of the environmental chamber was set to 20°C, and the test beds were allowed to equilibrate to this temperature.

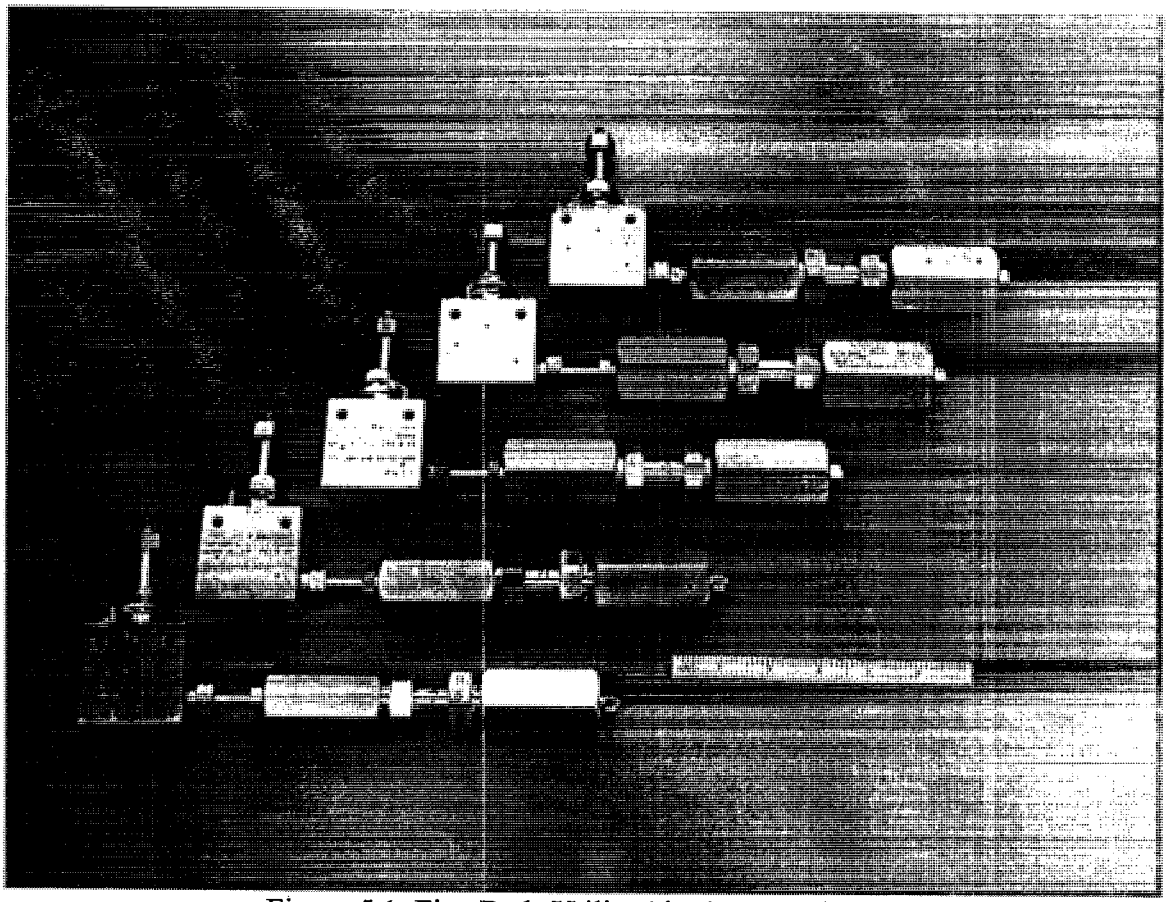

Figure 5.1 Five Beds Utilized in the Experiment.

Five different test beds are being utilized in this experiment, shown in Figure 5.1. The five beds will be achieve equilibrium at 20°C. Approximately 50 psia of hydrogen is

in the high-pressure manifold. The environmental chamber will be opened and the five beds will be opened with a half turn of the AE 30,000 psia valves. This is the beginning of the loading of the beds.

A calculation of the predicted pressures is done using the Fortran program Fill2, shown in the Appendix B, (Meyer, 1996). The inputs for the program are the moles of hydrogen, the amount of palladium in grams, the free volume of the un-hydrided unit, and the ambient temperature. The program can predict the pressure and the fugacity of the bed at different temperatures. When the maximum pressure at the highest temperature is needed a calculation of the initial loading pressure at 20°C is calculated.

5.2 Pressure Loading of the Beds

The initial loading of the each of the beds is at a different pressure. All of the beds are then controlled to an equilibrium baseline temperature of 20°C. The temperature and pressure are monitored every 15 minutes until equilibrium is reached. With this experimental setup the beds reach equilibrium in approximately 1 hour, the actual time for equilibration is shown in Appendix A. The baseline temperature, outside temperature of the outside valve and pressure are taken for each of the beds after equilibrium is reached. The temperature of the environmental chamber is then changed to another temperature and the process is repeated. In the first three P-C-T experiments the temperature of the baseline was 20°C. Then the beds were cycled through the temperatures 0°C, -20°C, -40°C, -60°C, 20°C, 40°C, 60°C, 80°C, 100°C, 120°C, 20°C and 20°C. Between the last two 20°C temperatures the chamber door is opened and the valve directly next to the palladium test beds is closed. When this valve is closed the

pressures within this now closed system change because of the movement of the valve seat slightly changes the internal volume. This volume change is on the order of ≈0.05 to 0.1 cm^3. At the 10,000 psia this change in volume increases the pressure by 35 psia. It is important to note that closing the valve will change the pressure in the palladium test bed.

5.3 Bed Weighing Procedure

When the test beds equilibrate at the last temperature the valves directly next to the beds are closed. When closed the last pressure and temperature data points are taken. Each of the beds is then individually disconnected from the high-pressure manifold, shown in Figure 5.2.

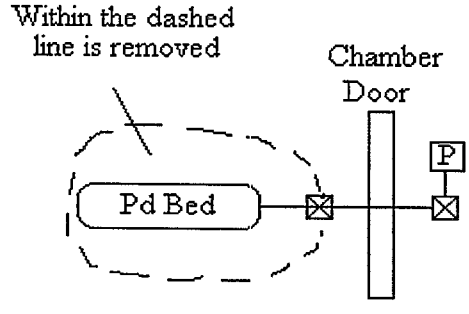

Figure 5.2. Diagram Showing Disconnection of Test Bed.

The beds are weighed to determine the amount of hydrogen within the bed. When handling a test beds, latex gloves are worn to minimize the possibility of adding contaminants to the beds. When measuring the weights one person is weighing the beds and another person is writing the weight down and verifying the correct weights are taken. The mass balance is first calibrated using a 2000.000gm weight. After the calibration the 2000gm standard weight is measured 3 times to insure that the balance is reading correctly. The standard weight must be repeatable to ±0.002 gm. The bed is then

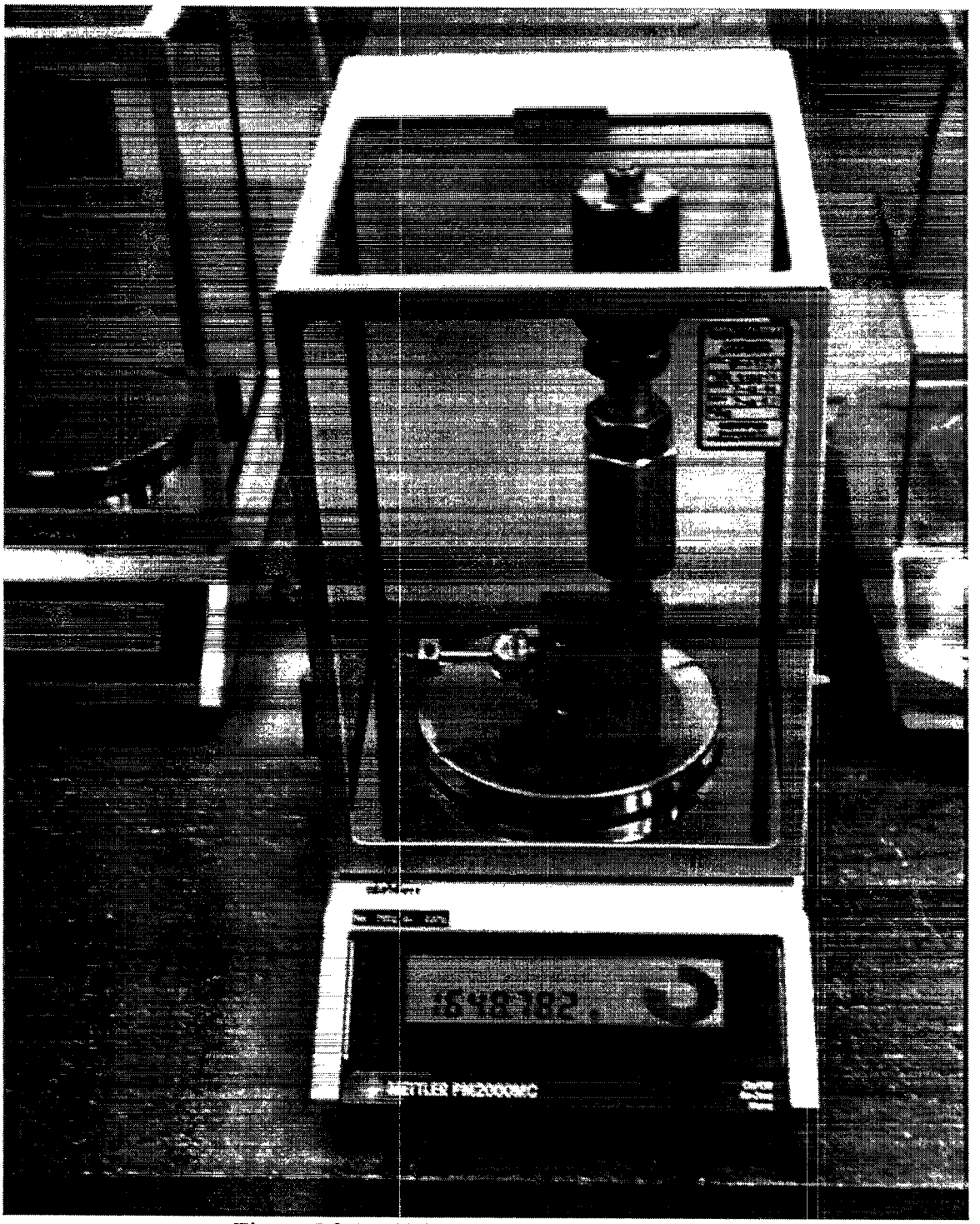

Figure 5.3 Bed Placement on the Balance Pan.

placed on the balance with special consideration to place the center of gravity of the bed in the center of the balance pan. The placement of a test bed is shown in a photograph in Figure 5.3.

The bed weight is then taken three times to insure that the test bed weight is within the 0.001 gm tolerance. After the three weights are taken the standard weight is then placed on the balance and weighed. The 2000gm standard weight traceable to NIST is weighed and must be within the ±0.002gm of the initial weight. Each bed is weighed using this procedure.

CHAPTER 6

Results and Discussion

6.1 Calculation of the Fugacity and Compressibility Factor

The fugacity-composition-temperature curves describe the equation of state for the palladium hydrogen system. The fugacity is calculated from the following integral equations:

$$\ln\left(\frac{f}{P'}\right) = \int_0^{P'} \frac{Z-1}{P}\,dP \tag{6-1}$$

where the compressibility factor, Z is defined by

$$Z \equiv \frac{Pv}{RT} \tag{6-2}$$

It is more convienient to write fugacity in terms of fugacity coefficient, Φ as:

$$\ln\ \Phi = \int_0^{Ptot} (Z - 1)d\ln P \tag{6-3}$$

where

$$f \equiv \Phi P \tag{6-4}$$

The fugacity coefficient with a conversion to atmospheres becomes:

$$\Phi = e^{((C0+C1T+C2T^2)(\frac{P}{T})+(C3+C4T+C5T^2)\frac{1}{2}(\frac{P}{T})^2+(C6+C7T+C8T^2)\frac{1}{3}(\frac{P}{T})^3+(C9+C1T+C11T^2)\frac{1}{4}(\frac{P}{T})^4)} \tag{6-5}$$

Where C0, C1, C2, C3, C4, C5, C6, C7, C8, C9, C10, C11 are compressibility constants for the compressibility factor Z, pressure P is in atmospheres. The compressibility factor Z is in the form of the equation:

$$Z = 1 + (C0 + C1*T + C3*T^2)(\frac{P}{T}) + (C4 + C5*T + C6*T^2)(\frac{P}{T})^2 + (C7 + C8*T + C9*T^2)(\frac{P}{T})^3 + (C10 + C11*T + C12*T^2)(\frac{P}{T})^4 \quad (6\text{-}6)$$

The compressibility constants used in equations (6-5) and (6-6) are in Table 6.1, from (Meyer, 1996).

Table 6.1 Compressibility Constants Used in Compressibility Factor Calculation

C1=0.022456	C2=8.3057e-4	C3=-1.0193e-6
C4=0.056181	C5=-1.9111e-4	C6=1.5657e-7
C7=-0.0036149	C8=-8.1655e-6	C9=3.0139e-8
C10=-1.5121e-4	C11=2.7545e-6	C12=-4.6721e-9

6.2 Calculation of the Atomic Ratio

The moles of hydrogen within the palladium lattice (palladium solid) are calculated. The weight of the hydrogen measured on the mass balance is the physical property used in the calculation to determine the atomic ratio, H/Pd. Figure 6-1 describes the control volumes for the conservation of mass in the calculation of the atomic ratio.

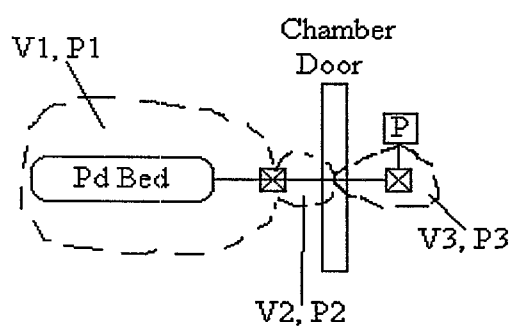

Figure 6.1 Diagram for the Calculation of the Atomic Ratio, H/Pd.

Equations (6-7) through (6-14) are used to determine how the actual weight measurements of the hydrogen are included in the calculation of the atomic ratio.

The moles of the hydrogen within the three dashed line volumes of Figure 6.1 are constant. Thus, equation (6-7) is true:

$$mol_1+mol_2+mol_3=constant \tag{6-7}$$

the moles of hydrogen in volume V2 are:

$$mol_2 = \frac{P_2V_2}{Z_2RT_2} \tag{6-8}$$

and the moles of hydrogen in volume V3 are:

$$mol_3 = \frac{P_3V_3}{Z_3RT_3} \tag{6-9}$$

In equation (6-7) "constant" is used for the total moles of hydrogen in the system, which remains constant throughout the experiment. Thus mol_1 is the moles of the hydrogen in the palladium solid plus the moles of the gaseous hydrogen in the volume 1 of the test bed. Equation (6-7), using (6-8) and (6-9) becomes equation (6-10), with mol_1 being split into two components. The two components of mol_1 are $mol_{H2\ solid}$ and the moles of the gaseous hydrogen, equation (6-7) becomes, at a specified temperature of 293.15K, equation (6-10):

$$constant = (mol_{H2\ solid} + \frac{P_1V_1}{Z_1R(293.15K)}) + \frac{P_2V_2}{Z_2R(293.15K)} + \frac{P_3V_3}{Z_3R(293.15K)} \tag{6-10}$$

$mol_{H2\ solid}$ is the moles of hydrogen in the palladium solid. P is the pressure for each respective volume V. The "constant" is determined at a specific temperature. R is the universal gas constant. The weight measured in grams at 293.15°K divided by the molecular weight of hydrogen is equation (6-11):

$$\frac{\text{weight measured at 293.15K}}{MW_{H2}} = (mol_{H2\,solid} + \frac{P_1V_1}{Z_1R(293.15K)}) \tag{6-11}$$

The constant in equation (6-10) using (6-11) becomes equation (6-12):

$$\text{constant} = \frac{\text{weight measured at 293.15K}}{MW_{H2}} + P(\frac{V_2}{Z_2R(293.15)} + \frac{V_3}{Z_3R(293.15)}) \tag{6-12}$$

The moles of the hydrogen in the solid the can be found with the measured weight of the hydrogen, and the pressure, volume, and temperature inputs using equations (6-11) and (6-12) combined to form (6-13):

$$mol_{H2\,solid} = \frac{\text{weight measured 293.13K}}{MW_{H2}} + P(\frac{V_2}{Z_2R(293.15K)} + \frac{V_3}{Z_3R(293.15K)}) - P(\frac{V_1}{Z_1RT_1} + \frac{V_2}{Z_2RT_2} + \frac{V_3}{Z_3RT_3}) \tag{6-13}$$

It must be noted that the V_1 is the volume of the dead space within the bed. As the palladium accepts hydrogen into the lattice, the palladium swells, thus reducing the volume of V_1. The reduction in the volume, V_1 is a direct function of the atomic ratio, H/Pd. Equation (6-14) is for the reduction in free volume due to the swelling of the palladium from (Wicke and Brodowsky, 1978).

$$\text{CorrectedVolume} = V_1 - \frac{(\text{Pd gm})(1.10777*(1+0.044*(H/Pd-0.607))^3 - 1}{12.02\frac{\text{gm Pd}}{cm^3}} \tag{6-14}$$

With equations (6-7) to (6-14) the atomic ratio can be calculated using the experimental weight measurement, the pressure, and temperature, and the known amount of palladium with equation (6-15):

$$\frac{H}{Pd} = \frac{2*\text{moles}\,H_2}{\text{moles Pd}} \tag{6-15}$$

The results of the experimentally measured atomic ratio are tabulated in the excel spreadsheet in Appendix A. The experimentally measured atomic ratio is in the plots of fugacity versus atomic ratio in Figures 6.2 and 6.3.

6.3 Plots of Fugacity Versus Atomic Ratio

The fugacity and the atomic ratio, H/Pd, can now be determined from the measured experimental data. The experimental data points for the temperatures -60°C, -40°C, -20°C, 0°C, 40°C, 60°C, 80°C, 100°C, and 120°C is plotted with the fugacity in psia versus the atomic ratio, H/Pd, in Figure 6.2. The curve fit to the data is also shown in Figure 6.2.

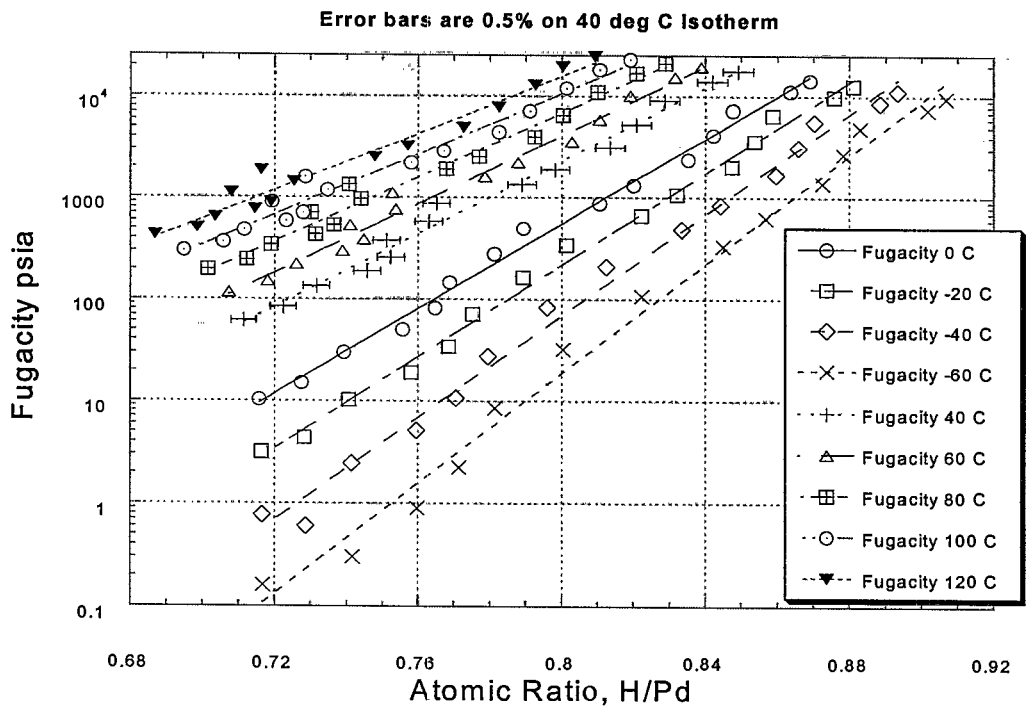

Figure 6.2 Experimental Data of Fugacity versus Atomic Ratio, H/Pd.

The experimental data points and the curve fit for the 20°C isotherm are shown in Figure 6.3. The error bars at 40°C and 20°C represent the 0.5% error on the atomic ratio axis.

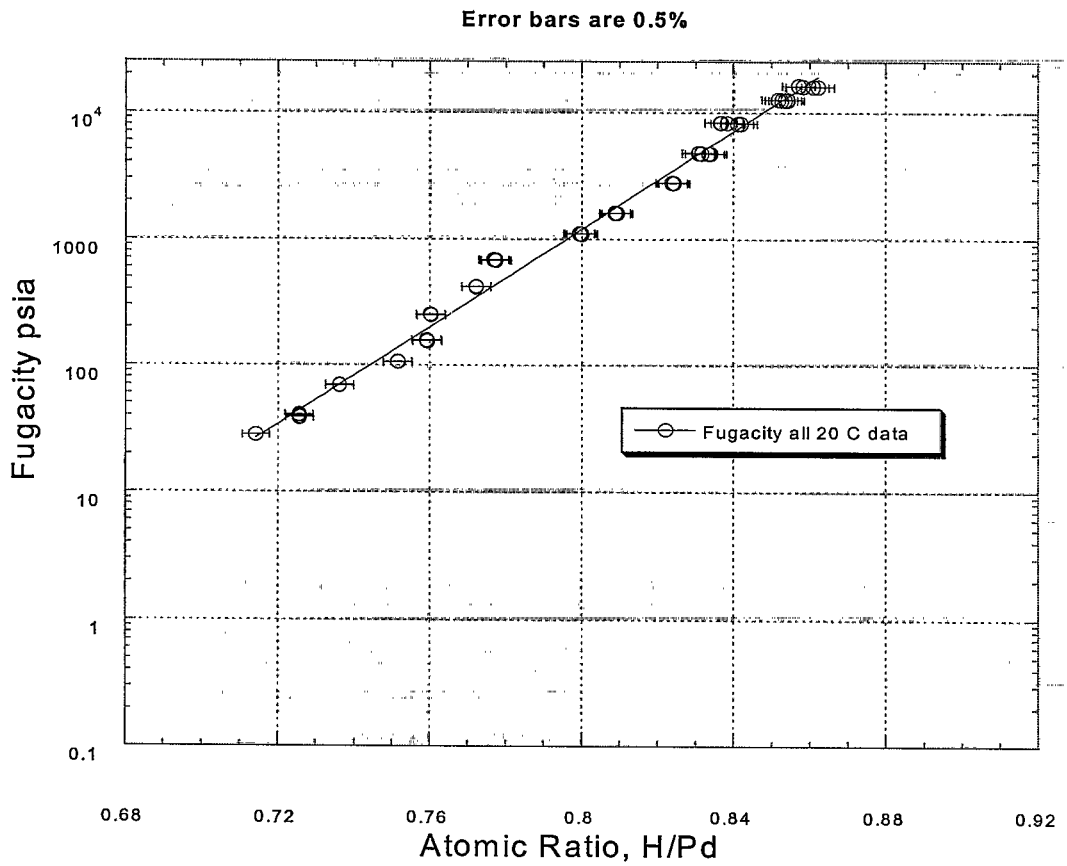

Figure 6.3 Experimental Data of Fugacity versus Atomic Ratio at 20°C.

Each of the isotherms in the experimental data shown in Figures 6.2 and 6.3 are curve fit to equation (6-16). The experimental constants, A and B, for the following curve fit are shown in Table 6.2.

$$\ln f\ (\text{psia}) = A(T) + B(T)(H/Pd) \qquad (6\text{-}16)$$

Table 6.2 Constants for the Palladium-Hydrogen Curve fit.

Temperature	A	B	Temperature	A	B
-60°C	-46.547	61.85	40°C	-25.461	41.516
-40°C	-41.743	57.472	60°C	-20.631	39.075
-20°C	-36.206	51.99	80°C	-20.494	36.669
0°C	-32.269	48.242	100°C	-18.297	34.465
20°C	-28.502	44.487	120°C	-16.276	32.422

6.4 Comparison of Curve Fit With the Literature Data

The data for each isotherm of the palladium-hydrogen equation of state has been curve fit to the equation (6-16).

Wicke and Nernst, and Perminov, Orlov, and Frumkin have all experimented in the β-phase region. Their low temperature data is shown in comparison with the experimental curve fits in Figure 6.4, the error bars represent 1% error in the atomic ratio. Perminov, Orlov, and Frumkins' experimental data was modified to express the pressure in terms of fugacity as shown in Appendix C.

Perminov, Orlov and Frumkins' modified data at 0°C is within the 1% error in atomic ratio to a fugacity of 1000 psia, as shown in Figure 6.4. At this point Perminov, Orlov and Frumkins' 0°C isotherm slopes up from this experimental curve fit. Perminov, Orlov and Frumkins' modified low-pressure data at -32°C begins between the -40°C and the -20°C curve fits. Perminov, Orlov and Frumkins' -32°C modified data then deviates from the curve fit of this study.

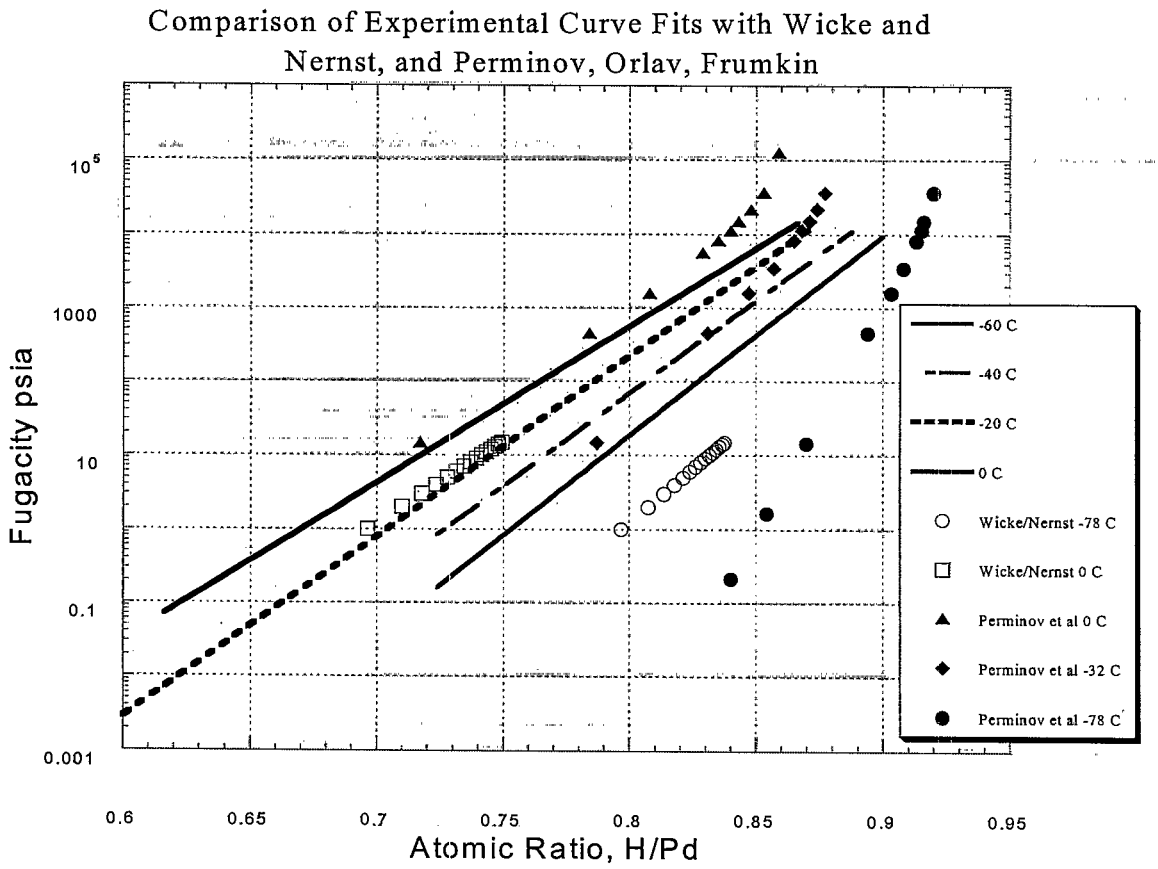

Figure 6.4 Comparison of Low Temperature Experimental Curve Fits (Perminov, et al, 1952) and (Wicke and Nernst, 1964) with literature data.

Wicke and Nernsts' -78°C and 0°C isotherms have the same general slope as the experimental isotherms in their vicinity. Wicke and Nernsts' 0°C isotherm is offset from the curve fit of this study by 2%. Wicke and Nernsts' 0°C isotherm is reads a higher atomic ratio than this study.

A comparison of Wicke and Nernst, and Perminov, Orlov and Frumkins' experimental data at -78°C is also shown in Figure 6.4. Perminov, Orlov and Frumkin noted that their data at this temperature was not very accurate.

A comparison of the higher temperature curve fits is shown in Figure 6.5. An error bar of 1% is shown on the experimental 40°C isotherm. All of Perminov, Orlov, and Frumkins' modified data at 50°C are within 1% of the experimental curve fit.

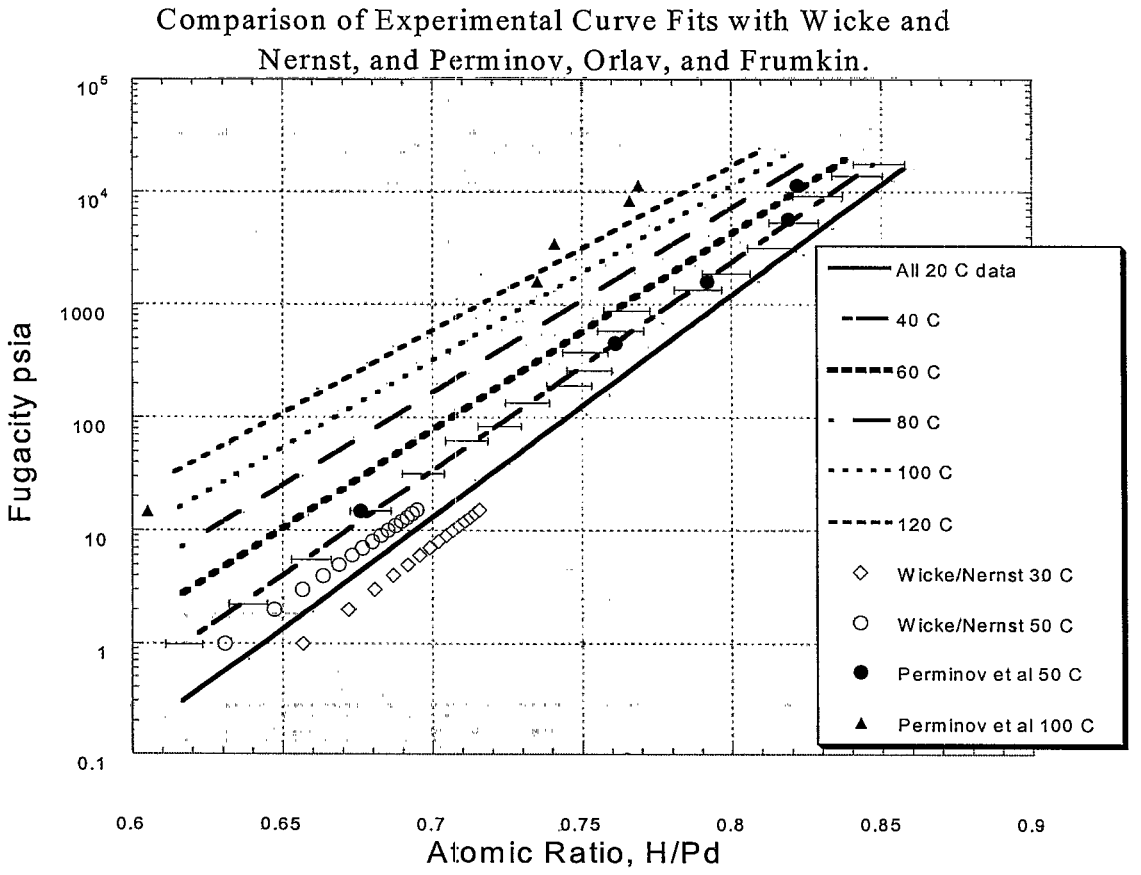

Figure 6.5 Comparison of High Temperature Experimental Curve Fits (Perminov et al, 1952) and (Wicke and Nernst, 1964) with literature data.

Perminov, Orlov, and Frumkins' 100°C modified data is within 1% of the experimental curve fit up to a fugacity of 1000 psia. At higher fugacities their 100°C isotherm has a lower atomic ratio than that shown by this study. Wicke and Nernsts' 30°C and 50°C data are offset and read a higher atomic ratio by 2% than the experimental curve fit. This 2% offset in Wicke and Nernsts' data was seen in the low temperature data as well.

6.5 Uncertainty Analysis

The general uncertainty analysis that is employed for the estimating the uncertainty in the fugacity and the atomic ratio is the Kline-McClintock method (Holman, 1989). This method uses the products of the sensitivities of the measured variable with respect to the independent variables and the uncertainties of the independent variables themselves. The form of the uncertainty for fugacity becomes equation (6-17),

$$U_f = \left[\left(\frac{\partial f}{\partial P} * U_P\right)^2 + \left(\frac{\partial f}{\partial T} * U_T\right)^2\right]^{\frac{1}{2}} \tag{6-17}$$

Equation (6-18) is the partial derivative of fugacity with respect to pressure.

$$\frac{\partial f}{\partial P} = \frac{\partial}{\partial P}\left[P\exp\left(\begin{array}{l}\left[C_0 + C_1T + C_2T^2\right]*\left(\frac{P}{T}\right) + \left[C_3 + C_4T + C_5T^2\right]*\frac{1}{2}\left(\frac{P}{T}\right)^2 \\ + \left[C_6 + C_7T + C_8T^2\right]*\frac{1}{3}\left(\frac{P}{T}\right)^3 + \left[C_9 + C_{10}T + C_{11}T^2\right]*\frac{1}{4}\left(\frac{P}{T}\right)^4\end{array}\right)\right] \tag{6-18}$$

Taking this partial derivative results in equation (6-19).

$$\begin{aligned}\frac{\partial f}{\partial P} = \exp&\left(\begin{array}{l}\left[C_0 + C_1T + C_2T^2\right]*\left(\frac{P}{T}\right) + \left[C_3 + C_4T + C_5T^2\right]*\frac{1}{2}\left(\frac{P}{T}\right)^2 \\ + \left[C_6 + C_7T + C_8T^2\right]*\frac{1}{3}\left(\frac{P}{T}\right)^3 + \left[C_9 + C_{10}T + C_{11}T^2\right]*\frac{1}{4}\left(\frac{P}{T}\right)^4\end{array}\right) \\ *&\left(1 + P\left[\begin{array}{l}\frac{\left[C_0 + C_1T + C_2T^2\right]}{T} + \frac{\left[C_3 + C_4T + C_5T^2\right]}{T^2}P + \\ \frac{\left[C_6 + C_7T + C_8T^2\right]}{T^3}P^2 + \frac{\left[C_9 + C_{10}T + C_{11}T^2\right]}{T^4}P^3\end{array}\right]\right)\end{aligned} \tag{6-19}$$

The equation for the partial derivative of fugacity with respect to temperature is:

$$\frac{\partial f}{\partial T} = P\left(\begin{array}{l} -\frac{C_0P}{T^2} + C_2P - \frac{C_3P^2}{T^3} - \frac{C_4P^2}{2(T^2)} - \frac{C_6P^3}{T^4} - \left(\frac{2}{3}\right)\frac{C_7P^3}{T^3} \\ -\frac{C_8P^3}{3(T^2)} - \frac{C_9P^4}{T^5} - \left(\frac{3}{4}\right)\frac{C_{10}P^4}{T^4} - \frac{C_{11}P^4}{2(T^3)} \end{array}\right) * \exp\left(\begin{array}{l} \left[C_0 + C_1T + C_2T^2\right] * \left(\frac{P}{T}\right) + \left[C_3 + C_4T + C_5T^2\right] * \frac{1}{2}\left(\frac{P}{T}\right)^2 \\ + \left[C_6 + C_7T + C_8T^2\right] * \frac{1}{3}\left(\frac{P}{T}\right)^3 + \left[C_9 + C_{10}T + C_{11}T^2\right] * \frac{1}{4}\left(\frac{P}{T}\right)^4 \end{array}\right) \tag{6-20}$$

With these two partial derivatives and the uncertainty in sensitivities of the pressure and temperature the uncertainty in the fugacity can be determined. This is shown in the equation (6-21).

$$U_f = \left[\left(\begin{array}{l} \left(\exp\left(\begin{array}{l} \left[C_0 + C_1T + C_2T^2\right] * \left(\frac{P}{T}\right) + \left[C_3 + C_4T + C_5T^2\right] * \frac{1}{2}\left(\frac{P}{T}\right)^2 + \\ \left[C_6 + C_7T + C_8T^2\right] * \frac{1}{3}\left(\frac{P}{T}\right)^3 + \left[C_9 + C_{10}T + C_{11}T^2\right] * \frac{1}{4}\left(\frac{P}{T}\right)^4 \end{array}\right) * \right. \\ \left.\left(1 + P\left[\begin{array}{l} \frac{\left[C_0 + C_1T + C_2T^2\right]}{T} + \frac{\left[C_3 + C_4T + C_5T^2\right]}{T^2}P + \\ \frac{\left[C_6 + C_7T + C_8T^2\right]}{T^3}P^2 + \frac{\left[C_9 + C_{10}T + C_{11}T^2\right]}{T^4}P^3 \end{array}\right]\right) * U_P \end{array}\right)^2 + \\ \left(\begin{array}{l} P\left(\begin{array}{l} -\frac{C_0P}{T^2} + C_2P - \frac{C_3P^2}{T^3} - \frac{C_4P^2}{2(T^2)} - \frac{C_6P^3}{T^4} - \left(\frac{2}{3}\right)\frac{C_7P^3}{T^3} \\ -\frac{C_8P^3}{3(T^2)} - \frac{C_9P^4}{T^5} - \left(\frac{3}{4}\right)\frac{C_{10}P^4}{T^4} - \frac{C_{11}P^4}{2(T^3)} \end{array}\right) * \\ \exp\left(\begin{array}{l} \left[C_0 + C_1T + C_2T^2\right] * \left(\frac{P}{T}\right) + \left[C_3 + C_4T + C_5T^2\right] * \frac{1}{2}\left(\frac{P}{T}\right)^2 + \\ \left[C_6 + C_7T + C_8T^2\right] * \frac{1}{3}\left(\frac{P}{T}\right)^3 + \left[C_9 + C_{10}T + C_{11}T^2\right] * \frac{1}{4}\left(\frac{P}{T}\right)^4 \end{array}\right) * U_T \end{array}\right)^2 \end{array}\right]^{\frac{1}{2}} \tag{6-21}$$

The general uncertainty analysis in the determination of the atomic ratio is calculated in terms of the uncertainty in the moles of hydrogen. Equation (6-22) is the general equation for the uncertainty in the moles of hydrogen.

$$U_{molH_2} = \left[\begin{array}{l} \left(\frac{\partial molH_2}{\partial weight} U_{weight}\right)^2 + \left(\frac{\partial molH_2}{\partial P} U_P\right)^2 + \left(\frac{\partial molH_2}{\partial V_1} U_{V1}\right)^2 + \left(\frac{\partial molH_2}{\partial V_2} U_{V2}\right)^2 \\ \left(\frac{\partial molH_2}{\partial V_3} U_{V3}\right)^2 + \left(\frac{\partial molH_2}{\partial T_{1,2}} U_{T1,2}\right)^2 + \left(\frac{\partial molH_2}{\partial T_3} U_{T3}\right)^2 \end{array} \right] \tag{6-22}$$

Equations for the partial deriatives involed in the determination of the uncertainty in the moles of hydrogen are shown in equations (6-23) thru (6-28)

$$\frac{\partial mol\,H_2}{\partial weight} = \frac{1}{MW_{H2}} \tag{6-23}$$

$$\frac{\partial mol\,H_2}{\partial P} = \left(\frac{V_2}{Z_2RT_2} + \frac{V_3}{Z_3RT_3}\right)_{20degC} - \left(\frac{V_1}{Z_1RT_1} + \frac{V_2}{Z_2RT_2} + \frac{V_3}{Z_3RT_3}\right) \tag{6-24}$$

$$\frac{\partial mol\,H_2}{\partial V_1} = -\frac{P}{ZRT_1} \tag{6-25}$$

$$\frac{\partial mol\,H_2}{\partial V_2} = \left(\frac{P}{Z_2RT_2}\right)_{20degC} - \frac{P}{Z_2RT_2} \tag{6-26}$$

$$\frac{\partial mol\,H_2}{\partial V_3} = \left(\frac{P}{Z_3RT_3}\right)_{20degC} - \frac{P}{Z_3RT_3} \tag{6-27}$$

$$\frac{\partial mol\,H_2}{\partial T_{1,2}} = \left(-\frac{PV_1}{Z_1RT_1^2} U_{T1,2}\right) \tag{6-28}$$

$$\frac{\partial mol\,H_2}{\partial T_3} = \left(\left(-\frac{PV_3}{Z_3 RT_3^2} \right)_{20\deg C} + \frac{PV_3}{Z_3 RT_3^2} \right) \tag{6-29}$$

The partial derivatives are inserted into the general uncertainty equation (6-22). The uncertainty in the moles of hydrogen can now be calculated using measured experimental quantities. With the collective equations (6-23) to (6-29) the uncertainty in the moles of hydrogen is stated in equation (6-30).

$$U_{mol\,H2} = \left[\begin{array}{l} \left(\frac{1}{MW_{H2}} U_{weight} \right)^2 + \left(\left(\left(\frac{V_2}{Z_2 RT_2} + \frac{V_3}{Z_3 RT_3} \right)_{20\deg C} - \left(\frac{V_1}{Z_1 RT_1} + \frac{V_2}{Z_2 RT_2} + \frac{V_3}{Z_3 RT_3} \right) \right) U_P \right)^2 \\ \left(\frac{P}{Z_1 RT_1} U_{V1} \right)^2 + \left(\left(\left(\frac{P}{Z_2 RT_2} \right)_{20\deg C} - \frac{P}{Z_2 RT_2} \right) U_{V2} \right)^2 + \\ \left(\left(\left(\frac{P}{Z_3 RT_3} \right)_{20\deg C} - \frac{P}{Z_3 RT_3} \right) U_{V3} \right)^2 \\ \left(-\frac{PV_1}{Z_1 RT_1^2} U_{T1,2} \right)^2 + \left(\left(\left(-\frac{PV_3}{Z_3 RT_3^2} \right)_{20\deg C} + \frac{PV_3}{Z_3 RT_3^2} \right) U_{T3} \right)^2 \end{array} \right]^{\frac{1}{2}} \tag{6-30}$$

The calculation for the uncertainty in the atomic ratio is derived from the definition of the atomic ratio, which is shown in equation (6-31).

$$\frac{\mathrm{H}}{\mathrm{Pd}} = \frac{2 \cdot \mathrm{mols\,H_2}}{\mathrm{mols\,Pd}} \tag{6-31}$$

The uncertainty in the atomic ratio of hydrogen to palladium can be calculated with respect to the independent variables, moles of hydrogen and moles of palladium. Utilizing the uncertainty in the moles of hydrogen found in equation (6-30) and knowing the uncertainty in the moles of palladium, the uncertainty of the atomic ratio can be

calculated. The calculation for the uncertainty in the atomic ratio is shown in equation (6-32).

$$U_{\frac{H}{Pd}} = \left(\left(\frac{2}{\text{mol Pd}} U_{\text{mol H2}} \right) + \left(-\frac{2 \cdot \text{mol H}_2}{(\text{mol Pd})} U_{\text{molPd}} \right)^2 \right)^{\frac{1}{2}} \tag{6-32}$$

The uncertainty in the atomic ratio is calculated for each of the individual atomic ratio data points, shown in Appendix A. A determination of the largest effect on the uncertainty in the atomic ratio was done by selectively zeroing the sensitivities of the each of the independent variables in the general uncertainty equation. The largest effect on the uncertainty of the atomic ratio is the uncertainty in the moles of hydrogen. This uncertainty is greatly affected by the sensitivity in the weight measurement. The uncertainty is larger for the palladium beds that have a low pressure and thus a lower mass of hydrogen. Conversely the uncertainty is smaller with high pressures and higher loads of hydrogen because of the higher weight of hydrogen. For instance the uncertainty at room temperature and 660 psia is 0.3% of the atomic ratio and at room temperature and 10,000 psia the uncertainty is 1.2% of the atomic ratio.

The sensitivity of the pressure transducers has the second largest effect on the uncertainty of our measurements. In this experiment many different ranges of the Heise pressure transducers are used. The sensitivity is quoted by the manufacturer to be better than ±0.005 of the span. The higher the range of the transducer the higher the uncertainty in the measurement. The pressure transducers were matched with each loading of the palladium bed to try to reduce unnecessary uncertainty in the measurements.

CHAPTER 7

Conclusions and Recommendations

7.1 Conclusions and Recommendations

This study demonstrates that taking a direct gravimetric weight measurement of a 50 gram hydrided palladium bed is a viable and accurate method of determining the equation of state for the palladium-hydrogen system. Curve fit data has been determined for the atomic ratio from -60°C to 120°C with a range in pressures of 0 to 20,000 psia.

The uncertainty of the measurement of the atomic ratio, H/Pd, is greatly influenced by the sensitivity, accuracy, and method of taking the weight measurement of the hydrided palladium bed. The largest contributor to the uncertainty is the sensitivity of the weight measurement. An increase in the accuracy and precision of the mass balance would further improve the results of a future experiment. The accuracy and precision of the pressure measurement is a secondary contributor to the uncertainty of the measurement. An improvement in the accuracy of the pressure transducers would improve the accuracy of the measurements. This improvement would not have as large an effect as an improvement in the weight measurement.

The accuracy in the determination of the equation of state of the palladium was improved upon in this investigation. The data was curve fit to a known equation used in the literature and 95% fugacity versus atomic ratio data points lie within 1% of the curve fit. The error in the data lie within the calculated uncertainty of the atomic ratio.

The experimental curve fit was compared to the literature. The experimental curve fit is within 1% of the atomic ratio of Perminov, Orlov, and Frumkins' data in the pressure region below 1,000 psia. Above this pressure Perminov, Orlov and Frumkins'

data slopes up and away from the experimental correlation. Wicke and Nernsts' data is also compared to this correlation and was found to have an atomic ratio that is 2% higher than this studies data. Factors that could cause this offset in the atomic ratio are impurities in the system, impurities in the palladium or hydrogen, or a systematic error in the volumetric method used by Wicke and Nernst.

An extension of this work could include the determination of the palladium-deuterium, palladium-tritium, metal-hydride equations of state. Other future work in this area could be to extend the pressure and temperature limits to determine if the experimental correlation could accurately predict the palladium-hydrogen equation of state in these ranges.

APPENDICIES

A. Raw Excel Data Sheets..... 53

B. Subroutine Fill2.....68

C. Conversion Data for Perminov, Orlov, and Frumkin, and Wicke and Nernst.... 76

Compressibility constants			
-60 deg C to 80 deg C(Meyer 1996)			
a1	0.022456	8.306E-04	-1.019E-06
a2	0.056181	-1.911E-04	1.566E-07
a3	-0.0036149	-8.166E-06	3.014E-08
a4	-0.00015121	2.755E-06	-4.672E-09

PCT Constants, Meyer 1995	
for equation lnf=a-(b-cn)/T-dT	
a=	-0.37970
b=	10653
c=	12035
d=	0.02737

Units were opened with one full turn

	V1 cc unhydrided	Pd gm	V2 cc in	V2 cc out	X-ducer no.	weight of unit (gm) before load	weight after load	weight H/Pd in grams
1	6.302	50.117	0.173	1.564	H 25743	1648.465	1648.855	0.3900
2	6.394	50.539	0.173	0.794	H 27163	1645.120	1645.758	0.6380
3	6.427	50.535	0.173	0.612	P 40454	1635.168	1635.636	0.4677
4	6.381	50.520	0.173	0.612	P 40456	1653.087	1653.596	0.5087
7	6.367	50.502	0.173	0.612	P 40457	1658.495	1659.056	0.5607

						Moles in the gas phase						hydrided	% Uncer
Date	time	unit	Pressure	Temp	Temp	moles bed	moles in	moles out	Fugacity	moles	H/Pd	free bed	tainty
			psia	bed °C	out °C	V1	V2	V3	psia	H2 solid		V1 cc	H/PD
2/28/98	7:45	1	666.9	21.4	22.3	0.0105	0.0003	0.0028	685.62	0.1829	0.777	5.74	0.29
		2	10303	21.4	22.3	0.1128	0.0034	0.0157	16160.86	0.2035	0.857	5.69	1.23
		3	2502	21.4	22.3	0.0364	0.0011	0.0039	2779.85	0.1956	0.824	5.72	0.45
		4	4022	21.4	22.3	0.0550	0.0017	0.0059	4771.87	0.1972	0.831	5.71	0.63
		7	6340	21.4	22.3	0.0794	0.0024	0.0085	8328.96	0.1985	0.837	5.70	0.88
2/28/98	8:16	1	664	21.2	22.2	0.0104	0.0003	0.0028	682.56	0.1830	0.777	5.74	0.29
		2	10292	21.2	22.4	0.1127	0.0034	0.0157	16139.69	0.2036	0.857	5.69	1.23
		3	2500	21.2	22.6	0.0364	0.0011	0.0039	2777.53	0.1956	0.824	5.72	0.45
		4	4020	21.2	22.8	0.0550	0.0017	0.0059	4769.49	0.1972	0.831	5.71	0.63
		7	6334	21.2	22.8	0.0794	0.0024	0.0085	8320.05	0.1986	0.837	5.70	0.88

Date	time	unit	Pressure psia	Temp bed °C	Temp out °C	moles bed V1	moles in V2	moles out V3	Fugacity psia	moles H2 solid	H/Pd	free bed V1 cc	% Uncertainty H/PD
2/28/98	9:37	1	488.5	0.4	20.5	0.0083	0.0003	0.0021	498.96	0.1859	0.789	5.73	0.28
		2	9335	0.4	21.5	0.1110	0.0034	0.0147	14372.75	0.2064	0.869	5.68	1.19
		3	2168	0.6	21.6	0.0342	0.0010	0.0034	2385.37	0.1983	0.835	5.71	0.43
		4	3571	0.9	21.8	0.0529	0.0016	0.0053	4187.17	0.1999	0.842	5.70	0.60
		7	5707	1	21.6	0.0775	0.0024	0.0079	7388.96	0.2012	0.848	5.69	0.85
2/28/98	10:35	1	336.4	-19.6	20.8	0.0062	0.0002	0.0015	341.55	0.1887	0.801	5.73	0.27
		2	8417	-19.8	21.1	0.1092	0.0033	0.0137	12698.79	0.2092	0.881	5.68	1.15
		3	1854	-19.6	21.3	0.0318	0.0010	0.0030	2019.29	0.2012	0.847	5.70	0.40
		4	3144	-19.4	21.8	0.0508	0.0015	0.0048	3641.45	0.2027	0.854	5.69	0.57
		7	5104	-19.2	21.7	0.0756	0.0023	0.0072	6507.24	0.2038	0.859	5.69	0.81
2/28/98	11:45	1	209.7	-39.6	20.7	0.0042	0.0001	0.0009	211.78	0.1913	0.812	5.72	0.26
		2	7540	-39.6	20.8	0.1074	0.0033	0.0126	11130.61	0.2122	0.893	5.67	1.11
		3	1568	-39.4	21.1	0.0294	0.0009	0.0025	1690.83	0.2041	0.86	5.70	0.37
		4	2744	-39.1	21.5	0.0485	0.0015	0.0042	3138.08	0.2055	0.866	5.69	0.54
		7	4532	-38.9	21.6	0.0736	0.0022	0.0065	5684.79	0.2065	0.87	5.68	0.78
2/28/98	12:22	1	106.8	-60.3	20.3	0.0024	0.0001	0.0005	107.36	0.1937	0.822	5.72	0.26
		2	6656	-60.1	20.8	0.1054	0.0032	0.0115	9587.46	0.2153	0.907	5.67	1.07
		3	1296	-59.7	21.2	0.0269	0.0008	0.0021	1383.27	0.2072	0.872	5.69	0.35
		4	2361	-59.2	21.6	0.0462	0.0014	0.0037	2664.82	0.2085	0.878	5.68	0.51
		7	3965	-59.1	21.5	0.0714	0.0022	0.0058	4885.88	0.2095	0.883	5.68	0.74

Date	time	unit	Pressure psia	Temp bed °C	Temp out °C	moles bed V1	moles in V2	moles out V3	Fugacity psia	moles H2 solid	H/Pd	free bed V1 cc	% Uncertainty H/PD
2/28/98	13:35	1	661.4	21.1	21.5	0.0104	0.0003	0.0028	679.82	0.1830	0.777	5.74	0.29
		2	10227	20.1	21.6	0.1126	0.0034	0.0156	16013.01	0.2038	0.858	5.69	1.23
		3	2486	20.9	21.8	0.0362	0.0011	0.0039	2760.52	0.1958	0.824	5.72	0.45
		4	4001	20.9	22.1	0.0549	0.0017	0.0059	4743.61	0.1974	0.832	5.71	0.63
		7	6295	21	22.2	0.0791	0.0024	0.0085	8255.70	0.1989	0.838	5.70	0.87
2/28/98	14:27	1	846.9	41	22.5	0.0124	0.0004	0.0036	875.94	0.1802	0.765	5.75	0.31
		2	11126	40.9	22.3	0.1138	0.0035	0.0165	17650.39	0.2017	0.849	5.70	1.26
		3	2826	41	22.7	0.0383	0.0012	0.0043	3166.68	0.1932	0.813	5.73	0.48
		4	4455	40.9	22.7	0.0568	0.0017	0.0064	5338.50	0.1949	0.821	5.72	0.66
		7	6905	40.9	22.8	0.0807	0.0024	0.0091	9165.17	0.1967	0.829	5.71	0.90
2/28/98	15:08	1	1051.9	61.3	22.6	0.0144	0.0004	0.0044	1094.90	0.1773	0.753	5.76	0.33
		2	12059	61.1	22.8	0.1153	0.0035	0.0174	19375.11	0.1992	0.839	5.71	1.29
		3	3181	61	23.1	0.0403	0.0012	0.0048	3595.19	0.1907	0.803	5.74	0.51
		4	4922	60.9	23.1	0.0586	0.0018	0.0069	5955.76	0.1924	0.811	5.73	0.69
		7	7531	60.8	23.2	0.0823	0.0025	0.0097	10104.64	0.1944	0.819	5.72	0.93
2/28/98	16:22	1	1270	81.5	23.2	0.0164	0.0005	0.0053	1330.10	0.1744	0.741	5.77	0.35
		2	12992	81.2	23.3	0.1168	0.0035	0.0182	21089.90	0.1969	0.829	5.72	1.33
		3	3553	81.2	23.7	0.0422	0.0013	0.0053	4047.94	0.1882	0.792	5.75	0.53
		4	5410	81.1	24	0.0605	0.0018	0.0075	6605.17	0.1900	0.8	5.74	0.72
		7	8170	80.9	23.8	0.0839	0.0025	0.0102	11064.34	0.1922	0.81	5.73	0.96

Date	time	unit	Pressure psia	Temp bed °C	Temp out °C	moles bed V1	moles in V2	moles out V3	Fugacity psia	moles H2 solid	H/Pd	free bed V1 cc	% Uncertainty H/PD
2/28/98	17:30	1	1504.2	101.7	23.5	0.0183	0.0005	0.0062	1584.91	0.1716	0.728	5.78	0.37
		2	13926	101.3	23.8	0.1183	0.0036	0.0190	22784.89	0.1946	0.819	5.73	1.36
		3	3934	101.2	24.1	0.0441	0.0013	0.0057	4514.55	0.1858	0.782	5.76	0.56
		4	5891	101.1	24.2	0.0621	0.0019	0.0080	7245.29	0.1878	0.791	5.75	0.75
		7	8808	100.8	25.4	0.0854	0.0026	0.0108	12019.06	0.1902	0.801	5.74	0.99
2/28/98	18:35	1	1754	122.1	24.4	0.0202	0.0006	0.0071	1858.82	0.1687	0.716	5.79	0.40
		2	14877	121.6	23.9	0.1198	0.0036	0.0198	24483.13	0.1922	0.809	5.74	1.40
		3	4330	121.5	24.1	0.0459	0.0014	0.0062	5001.21	0.1835	0.773	5.77	0.59
		4	6375	121.2	24.8	0.0636	0.0019	0.0085	7887.36	0.1857	0.782	5.77	0.77
		7	9450	120.8	24.8	0.0868	0.0026	0.0113	12970.86	0.1881	0.793	5.75	1.02
2/28/98	20:15	1	658	21	22.5	0.0104	0.0003	0.0028	676.23	0.1831	0.777	5.74	0.29
		2	10145	20.8	22.6	0.1118	0.0034	0.0155	15812.05	0.2048	0.862	5.69	1.21
		3	2492	21.1	23	0.0363	0.0011	0.0039	2767.76	0.1957	0.824	5.72	0.45
		4	3962	21.2	23.3	0.0544	0.0016	0.0058	4688.82	0.1980	0.834	5.71	0.62
		7	6220	21.2	23.4	0.0783	0.0024	0.0084	8129.11	0.1998	0.842	5.70	0.86
2/28/98	20:20	1	658.8	21	22.5	0.0104	0.0003	0.0028	677.08	0.1831	0.777	5.74	0.29
		2	10180	20.8	22.6	0.1120	0.0034	0.0156	15891.66	0.2044	0.861	5.69	1.22
		3	2499	21.1	23	0.0364	0.0011	0.0039	2776.37	0.1956	0.824	5.72	0.45
		4	3973	21.2	23.3	0.0545	0.0017	0.0058	4704.09	0.1978	0.833	5.71	0.62
		7	6242	21.2	23.4	0.0785	0.0024	0.0084	8165.83	0.1996	0.841	5.70	0.87

Compressibility constants			
-60 to 80 °C			
a1	0.022456	8.31E-04	-1.02E-06
a2	0.056181	-1.91E-04	1.57E-07
a3	-0.003615	-8.17E-06	3.01E-08
a4	-0.000151	2.75E-06	-4.67E-09

PCT Constants, Meyer 1995		
for the equation lnf=a-(b-cn)/T-dT		
a=	-0.3797	
b=	10653	
c=	12035	
d=	0.027373	

Units were opened with a half turn

	V1 cc unhydric	Pd gm	V2 cc in	V2 cc out	X-ducer no.	weight of unit (gm) before load	weight after load	weight measured in grams
1	6.302	50.1167	0.173	1.56	H 25743	1648.465	1648.834	0.3690
2	6.394	50.5392	0.173	0.79	H 27163	1645.12	1645.7297	0.6097
3	6.427	50.5348	0.173	0.61	P 40454	1635.168	1635.6013	0.4333
4	6.381	50.5204	0.173	0.61	P 40456	1653.087	1653.5027	0.4157
7	6.367	50.5015	0.173	0.61	P 40457	1658.495	1658.8777	0.3827

						Moles in the gas phase							% Uncer
Date	time	unit	Pressure	Temp	Temp	moles bed	moles in	moles out	Fugacity	moles	H/Pd	free bed	tainty
			psia	bed °C	out °C	V1	V2	V3	psia	H2 solid		V1 cc	H/PD
3/1/98	7:28	1	250.8	21.4	21.4	4.021E-03	1.209E-04	1.093E-03	253.42	0.17901	0.7601	5.754533	0.280635
		2	8673	21.3	21.4	1.002E-01	3.042E-03	1.395E-02	12644.66	0.20228	0.8517	5.695073	0.978963
		3	1509	21.4	21.4	2.287E-02	6.909E-04	2.445E-03	1607.21	0.19206	0.8088	5.726525	0.856459
		4	1061	21.5	21.4	1.639E-02	4.946E-04	1.751E-03	1108.92	0.18981	0.7995	5.73222	0.64719
		7	414	21.5	21.4	6.583E-03	1.982E-04	7.015E-04	421.16	0.18325	0.7722	5.746906	0.366162
3/1/98	8:30	1	144.5	0.6	21	2.501E-03	7.526E-05	6.331E-04	145.40	0.18104	0.7687	5.749169	0.275172
		2	7848	0.6	21.3	9.836E-02	2.992E-03	1.298E-02	11249.28	0.20509	0.8635	5.687702	0.942369
		3	1258	0.9	21.4	2.062E-02	6.238E-04	2.059E-03	1329.03	0.19476	0.8201	5.718115	0.7547
		4	849	1.1	21.6	1.417E-02	4.282E-04	1.412E-03	880.91	0.19244	0.8106	5.724041	0.554363
		7	276	1.2	21.8	4.732E-03	1.426E-04	4.697E-04	279.31	0.18539	0.7812	5.740336	0.31438

Date	time	unit	Pressure psia	Temp bed °C	Temp out °C	moles bed V1	moles in V2	moles out V3	Fugacity psia	moles H2 solid	H/Pd	free bed V1 cc	% Uncertainty H/PD
3/1/98	10:47	1	70.8	-19.6	21	1.326E-03	3.993E-05	3.112E-04	71.03	0.18257	0.7752	5.746293	0.272147
		2	7053	-19.7	21.2	9.650E-02	2.938E-03	1.200E-02	9922.73	0.20799	0.8758	5.681547	0.90561
		3	1021	-19.6	21.3	1.821E-02	5.517E-04	1.688E-03	1069.64	0.19762	0.8322	5.710837	0.651849
		4	651	-19.3	21.7	1.181E-02	3.573E-04	1.091E-03	670.50	0.19519	0.8222	5.717106	0.463485
		7	164.5	-19.1	22.1	3.057E-03	9.221E-05	2.810E-04	165.72	0.1873	0.7892	5.735521	0.281068
3/1/98	11:46	1	27.3	-39.6	21	5.563E-04	1.675E-05	1.202E-04	27.33	0.18356	0.7794	5.746059	0.270704
		2	6290	-39.7	21.2	9.457E-02	2.882E-03	1.100E-02	8673.38	0.21098	0.8883	5.676498	0.868865
		3	809	-39.5	21.2	1.577E-02	4.781E-04	1.350E-03	840.71	0.20047	0.8442	5.704826	0.554061
		4	479	-39.2	21.8	9.481E-03	2.872E-04	8.084E-04	489.96	0.19787	0.8335	5.711488	0.383452
		7	82.5	-39	22	1.669E-03	5.035E-05	1.414E-04	82.82	0.18887	0.7959	5.733061	0.265569
3/1/98	12:36	1	8.4	-59.9	20.7	1.877E-04	5.649E-06	3.705E-05	8.40	0.18402	0.7814	5.747271	0.270159
		2	5545	-59.8	21.1	9.250E-02	2.821E-03	9.963E-03	7481.12	0.21414	0.9017	5.672425	0.831086
		3	614	-59.6	21.2	1.318E-02	4.001E-04	1.033E-03	632.97	0.20345	0.8567	5.699833	0.458957
		4	326	-59.2	21.5	7.097E-03	2.151E-04	5.542E-04	331.27	0.20058	0.8449	5.707158	0.314788
		7	32	-59	21.7	7.093E-04	2.140E-05	5.503E-05	32.05	0.18995	0.8004	5.733064	0.261892
3/1/98	13:40	1	248.8	21.2	21.8	3.992E-03	1.200E-04	1.083E-03	251.37	0.17905	0.7603	5.754523	0.280511
		2	8647	21.1	21.7	9.999E-02	3.037E-03	1.391E-02	12594.65	0.20249	0.8526	5.69504	0.976125
		3	1499	20.9	21.9	2.276E-02	6.877E-04	2.426E-03	1596.00	0.19219	0.8093	5.726347	0.851534
		4	1052	20.8	22.1	1.629E-02	4.917E-04	1.733E-03	1099.17	0.18993	0.8	5.731942	0.642931
		7	413	21	22.2	6.578E-03	1.980E-04	6.980E-04	420.13	0.18326	0.7722	5.746624	0.36593

Date	time	unit	Pressure psia	Temp bed °C	Temp out °C	moles bed V1	moles in V2	moles out V3	Fugacity psia	moles H2 solid	H/Pd	free bed V1 cc	% Uncertainty H/PD
3/1/98	14:56	1	372	40.9	22.5	5.577E-03	1.675E-04	1.607E-03	377.53	0.1769	0.7511	5.761554	0.28812
		2	9439	40.8	22.6	1.016E-01	3.082E-03	1.476E-02	13942.94	0.19998	0.842	5.703092	1.009596
		3	1763	40.9	22.7	2.492E-02	7.517E-04	2.816E-03	1891.97	0.18958	0.7983	5.735529	0.95348
		4	1283	40.8	22.8	1.850E-02	5.575E-04	2.088E-03	1350.46	0.1873	0.7889	5.740918	0.740761
		7	569	40.8	23	8.457E-03	2.542E-04	9.530E-04	582.02	0.18107	0.763	5.754507	0.430381
3/1/98	15:55	1	519.1	60.9	23	7.291E-03	2.186E-04	2.225E-03	529.45	0.17451	0.741	5.770239	0.298699
		2	10254	60.8	23.1	1.032E-01	3.126E-03	1.561E-02	15335.27	0.19749	0.8315	5.712308	1.043646
		3	2037	60.7	23.3	2.695E-02	8.114E-04	3.211E-03	2202.37	0.1871	0.7878	5.745656	1.053637
		4	1522	60.6	23.5	2.054E-02	6.180E-04	2.448E-03	1613.21	0.18484	0.7786	5.750932	0.836435
		7	740.5	60.5	23.6	1.032E-02	3.096E-04	1.229E-03	761.69	0.17888	0.7537	5.763722	0.503119
3/1/98	17:12	1	688.5	81.4	23.3	9.081E-03	2.718E-04	2.927E-03	705.94	0.17197	0.7302	5.780644	0.312436
		2	11106	81.2	23.5	1.049E-01	3.171E-03	1.645E-02	16793.43	0.19491	0.8207	5.722773	1.079827
		3	2341	81.2	23.7	2.904E-02	8.725E-04	3.642E-03	2550.23	0.18452	0.777	5.757155	1.161056
		4	1789	81.1	24	2.264E-02	6.798E-04	2.842E-03	1909.74	0.18228	0.7678	5.762343	0.939499
		7	937	80.9	24.1	1.225E-02	3.671E-04	1.540E-03	969.52	0.17657	0.744	5.774505	0.586369
3/1/98	18:23	1	872.7	101.5	23.3	1.086E-02	3.244E-04	3.683E-03	899.53	0.16938	0.7192	5.792124	0.328871
		2	11934	101.1	23.7	1.065E-01	3.212E-03	1.724E-02	18196.83	0.19252	0.8106	5.734061	1.114305
		3	2643	101.1	24	3.092E-02	9.272E-04	4.059E-03	2898.39	0.18216	0.7671	5.769379	1.262293
		4	2055	100.8	24.2	2.454E-02	7.353E-04	3.228E-03	2207.65	0.17994	0.7579	5.774429	1.037242
		7	1139	100.5	24.4	1.407E-02	4.205E-04	1.855E-03	1185.06	0.17439	0.7348	5.78609	0.670086

Date	time	unit	Pressure psia	Temp bed °C	Temp out °C	moles bed V1	moles in V2	moles out V3	Fugacity psia	moles H2 solid	H/Pd	free bed V1 cc	% Uncertainty H/PD
3/1/98	19:49	1	1075.4	122.1	23.5	1.265E-02	3.770E-04	4.498E-03	1114.31	0.16673	0.7079	5.805223	0.348227
		2	12792	121.5	23.7	1.081E-01	3.253E-03	1.803E-02	19633.60	0.19007	0.8003	5.746755	1.150502
		3	2967	121.5	24.1	3.280E-02	9.814E-04	4.497E-03	3274.26	0.17978	0.7571	5.783017	1.367369
		4	2343	121.2	24.3	2.645E-02	7.906E-04	3.638E-03	2532.53	0.17757	0.7479	5.787955	1.139406
		7	1362	120.7	24.4	1.591E-02	4.746E-04	2.199E-03	1424.96	0.17215	0.7254	5.799117	0.760423
3/1/98	22:06	1	248.7	21	22	3.993E-03	1.201E-04	1.081E-03	251.27	0.17905	0.7603	5.754396	0.280511
		2	8603	20.9	22.2	9.968E-02	3.028E-03	1.384E-02	12508.42	0.20288	0.8542	5.695052	0.970841
		3	1507	21.05	22.4	2.287E-02	6.908E-04	2.434E-03	1605.03	0.19208	0.8088	5.726347	0.855919
		4	1064	21.15	22.7	1.645E-02	4.965E-04	1.748E-03	1112.23	0.18975	0.7993	5.731969	0.649443
		7	413.8	21.15	22.8	6.587E-03	1.983E-04	6.979E-04	420.96	0.18325	0.7722	5.74669	0.366188
3/1/98	22:22	1	248.6	20.9	22	3.993E-03	1.200E-04	1.081E-03	251.17	0.17906	0.7603	5.754336	0.280509
		2	8618	20.8	22.2	9.983E-02	3.032E-03	1.386E-02	12539.95	0.20271	0.8535	5.694967	0.97316
		3	1508	20.9	22.4	2.289E-02	6.916E-04	2.436E-03	1606.20	0.19205	0.8087	5.72625	0.85697
		4	1063	21	22.7	1.644E-02	4.963E-04	1.746E-03	1111.15	0.18976	0.7993	5.731895	0.649129
		7	413	21	22.8	6.578E-03	1.980E-04	6.966E-04	420.13	0.18326	0.7722	5.746624	0.365893

Compressibility constants -60 to 80 °C			
Const			
a1	0.022456	0.000831	-1.02E-06
a2	0.056181	-0.000191	1.57E-07
a3	-0.00361	-0.000008	3.01E-08
a4	-0.00015	0.000003	-4.67E-09

PCT Constants, Meyer 1995	
for the equation lnf=a-(b-cn)/T-dT	
a=	-0.3797
b=	10653
c=	12035
d=	0.027373

Units were opened with a half turn

	V1 cc unhydr	Pd gm	V2 cc in	V2 cc out	X-ducer no.	weight of unit (gm) before load	weight after load	weight measured in grams
1	6.302	50.1167	0.173	1.56355	H 25855	1648.465	1648.805	0.3400
2	6.394	50.5392	0.173	0.78414	P 60798	1645.12	1645.4687	0.3487
3	6.427	50.5348	0.173	0.78414	P 31381	1635.168	1635.5227	0.3547
4	6.381	50.5204	0.173	0.78414	P 31379	1653.087	1653.4501	0.3631
7	6.367	50.5015	0.173	0.78414	P 31380	1658.495	1658.8633	0.3683

Date	time	unit	Pressure psia	Temp bed °C	Temp out °C	Moles in the gas phase: moles bed V1	moles in V2	moles out V3	Fugacity psia	moles H2 solid	H/Pd	free bed V1 cc	%Uncertainty H/PD
3/2/98	10:45	1	27.81	20.87	22.3	4.534E-04	1.355E-05	0.000122	27.84	0.16820	0.714182	5.79	0.885000
		2	38.5	20.5	22.5	6.277E-04	1.878E-05	0.000085	38.56	0.17234	0.725665	5.78	0.863723
		3	68.5	20.67	23.3	1.113E-03	3.335E-05	0.000150	68.69	0.17483	0.736212	5.77	0.851444
		4	105.2	20.7	23.6	1.705E-03	5.114E-05	0.000230	105.66	0.17841	0.751486	5.77	0.834417
		7	154.9	20.72	24	2.502E-03	7.514E-05	0.000337	155.90	0.18019	0.759269	5.76	0.826250
3/2/98	11:58	1	10.3	0.41	22.5	1.806E-04	5.399E-06	0.000045	10.30	0.16856	0.715701	5.79	0.883119
		2	14.95	0.4	22.7	2.618E-04	7.835E-06	0.000033	14.96	0.17277	0.727469	5.78	0.861573
		3	29.9	0.65	23	5.220E-04	1.565E-05	0.000066	29.94	0.17553	0.739131	5.77	0.848060
		4	50.4	0.9	23.2	8.772E-04	2.633E-05	0.000110	50.51	0.17938	0.755578	5.76	0.829851
		7	81.3	1	23.4	1.411E-03	4.239E-05	0.000178	81.59	0.18147	0.764676	5.76	0.820313

Date	time	unit	Pressure	Temp	Temp	moles bed	moles in	moles out	Fugacity	moles	H/Pd	free bed	tainty
			psia	bed °C	out °C	V1	V2	V3	psia	H2 solid		V1 cc	H/PD
3/2/98	13:02	1	3.18	-19.77	22.5	6.021E-05	1.800E-06	0.000014	3.18	0.16871	0.71636	5.79	0.882307
		2	4.34	-19.9	22.8	8.216E-05	2.458E-06	0.000010	4.34	0.17298	0.728346	5.78	0.860535
		3	10.12	-19.6	23.1	1.909E-04	5.723E-06	0.000022	10.12	0.17591	0.740749	5.77	0.846205
		4	18.8	-19.3	23.3	3.537E-04	1.062E-05	0.000041	18.82	0.17999	0.758141	5.76	0.827038
		7	33.9	-19.1	23.5	6.360E-04	1.911E-05	0.000074	33.95	0.18237	0.768476	5.76	0.816234
3/2/98	16:01	1	0.77	-39.8	22.1	1.584E-05	4.734E-07	0.000003	0.77	0.16877	0.716599	5.79	0.882013
		2	0.6	-40	22.2	1.236E-05	3.692E-07	0.000001	0.60	0.17306	0.728684	5.79	0.860137
		3	2.47	-39.8	22.5	5.068E-05	1.518E-06	0.000005	2.47	0.17607	0.741428	5.77	0.845431
		4	5.14	-39.55	22.7	1.052E-04	3.156E-06	0.000011	5.14	0.18027	0.759345	5.77	0.825728
		7	10.63	-39.3	22.8	2.169E-04	6.518E-06	0.000023	10.64	0.18286	0.770509	5.76	0.814083
3/2/98	16:35	1	0.16	-59.36	21.3	3.594E-06	1.074E-07	0.000001	0.16	0.16878	0.716664	5.79	0.881933
		2											
		3	0.3	-59.4	22.2	6.732E-06	2.013E-07	0.000001	0.30	0.17612	0.741639	5.78	0.845192
		4	0.9	-58.9	22.5	2.011E-05	6.026E-07	0.000002	0.90	0.18037	0.759753	5.77	0.825286
		7	2.25	-58.9	22.7	5.018E-05	1.506E-06	0.000005	2.25	0.18305	0.77131	5.76	0.813241
3/2/98	18:37	1	27.82	20.92	22.2	4.535E-04	1.356E-05	0.000122	27.85	0.16820	0.714182	5.79	0.885000
		2	39.05	20.8	22.4	6.360E-04	1.903E-05	0.000086	39.11	0.17233	0.725624	5.78	0.863772
		3	69.2	20.88	22.8	1.124E-03	3.367E-05	0.000152	69.40	0.17482	0.736159	5.77	0.851506
		4	105.87	20.9	22.8	1.714E-03	5.143E-05	0.000232	106.33	0.17840	0.751435	5.77	0.834474
		7	155.65	20.9	22.7	2.513E-03	7.545E-05	0.000340	156.66	0.18018	0.75921	5.76	0.826315

Date	time	unit	Pressure	Temp	Temp	moles bed	moles in	moles out	Fugacity	moles	H/Pd	free bed	tainty
			psia	bed °C	out °C	V1	V2	V3	psia	H2 solid		V1 cc	H/PD
3/3/98	7:35	1	27.76	20.87	21.5	4.526E-04	1.353E-05	0.000122	27.79	0.16820	0.714186	5.79	0.884996
		2	39.04	20.8	21.6	6.358E-04	1.902E-05	0.000086	39.10	0.17233	0.725623	5.78	0.863772
		3	69.5	20.93	21.6	1.128E-03	3.381E-05	0.000153	69.70	0.17481	0.736134	5.77	0.851536
		4	106.33	20.92	21.8	1.722E-03	5.165E-05	0.000233	106.80	0.17839	0.751396	5.77	0.834518
		7	158.8	20.95	22	2.563E-03	7.696E-05	0.000348	159.85	0.18012	0.758961	5.76	0.826592
3/3/98	8:42	1	61.59	40.95	22.3	9.393E-04	2.806E-05	0.000270	61.74	0.16755	0.711431	5.79	0.888434
		2	83.3	40.9	22.3	1.268E-03	3.793E-05	0.000183	83.58	0.17158	0.722473	5.79	0.867572
		3	133.4	40.9	22.5	2.025E-03	6.062E-05	0.000292	134.11	0.17375	0.731661	5.78	0.856816
		4	188.7	40.87	22.6	2.855E-03	8.557E-05	0.000412	190.12	0.17704	0.745728	5.77	0.840997
		7	256.8	40.8	22.7	3.873E-03	1.162E-04	0.000558	259.43	0.17856	0.752388	5.77	0.834032
3/3/98	9:40	1	115.41	60.6	23.2	1.655E-03	4.939E-05	0.000503	115.92	0.16658	0.707313	5.80	0.893641
		2	148.5	60.4	23.3	2.126E-03	6.351E-05	0.000324	149.34	0.17056	0.71816	5.79	0.872868
		3	220.5	60.54	23.6	3.143E-03	9.401E-05	0.000479	222.36	0.17241	0.726022	5.78	0.863640
		4	293.85	60.48	23.7	4.175E-03	1.250E-04	0.000636	297.15	0.17546	0.739059	5.78	0.848848
		7	378.04	60.25	24	5.353E-03	1.604E-04	0.000815	383.52	0.17678	0.744884	5.78	0.842813
3/3/98	10:55	1	195.54	81.2	23.6	2.637E-03	7.861E-05	0.000848	196.93	0.16522	0.701553	5.80	0.901062
		2	243.1	80.9	23.8	3.273E-03	9.764E-05	0.000527	245.26	0.16918	0.71233	5.80	0.880203
		3	335.9	80.9	24	4.503E-03	1.345E-04	0.000725	340.02	0.17077	0.71909	5.79	0.872281
		4	426	80.74	24.1	5.690E-03	1.701E-04	0.000916	432.65	0.17362	0.731306	5.79	0.858290
		7	525.25	80.5	24.5	6.991E-03	2.091E-04	0.001123	535.39	0.17478	0.736477	5.78	0.853021

Date	time	unit	Pressure	Temp	Temp	moles bed	moles in	moles out	Fugacity	moles	H/Pd	free bed	tainty
			psia	bed °C	out °C	V1	V2	V3	psia	H2 solid		V1 cc	H/PD
3/3/98	12:34	1	296.5	101.3	24.3	3.778E-03	1.124E-04	0.001277	299.56	0.16362	0.694742	5.81	0.910046
		2	357.8	100.85	24.6	4.552E-03	1.356E-04	0.000770	362.27	0.16762	0.705764	5.81	0.888713
		3	470.5	100.84	24.8	5.957E-03	1.776E-04	0.001007	478.25	0.16899	0.711596	5.80	0.881944
		4	575.9	100.66	25	7.264E-03	2.167E-04	0.001227	587.54	0.17169	0.723172	5.80	0.868566
		7	687.5	101.27	25.1	8.620E-03	2.573E-04	0.001457	704.10	0.17277	0.728001	5.80	0.863718
3/3/98	14:15	1	420.27	121.8	25	5.069E-03	1.506E-04	0.001797	426.14	0.16177	0.686892	5.82	0.920685
		2	495.5	121.25	25.3	5.966E-03	1.773E-04	0.001058	503.69	0.16587	0.698421	5.82	0.898541
		3	626.4	121.2	25.7	7.505E-03	2.232E-04	0.001329	639.52	0.16707	0.703534	5.82	0.892720
		4	745.6	120.95	26	8.898E-03	2.649E-04	0.001572	764.24	0.16966	0.714631	5.81	0.879776
		7	868.25	120.4	26.1	1.033E-02	3.076E-04	0.001821	893.62	0.17065	0.719059	5.81	0.875456
3/3/98	16:30	1	27.95	20.95	23.2	4.556E-04	1.362E-05	0.000122	27.98	0.16820	0.714172	5.79	0.885013
		2	40.1	20.8	23.2	6.530E-04	1.954E-05	0.000088	40.17	0.17231	0.725541	5.78	0.863871
		3	69.7	20.96	23.5	1.131E-03	3.390E-05	0.000152	69.90	0.17481	0.736122	5.77	0.851549
		4	106.85	21	23.7	1.730E-03	5.188E-05	0.000233	107.32	0.17838	0.751363	5.77	0.834555
		7	155.95	21	23.9	2.517E-03	7.557E-05	0.000339	156.96	0.18017	0.759196	5.76	0.826331
3/3/98	16:48	1	27.95	20.98	23.2	4.555E-04	1.362E-05	0.000122	27.98	0.16820	0.714172	5.79	0.885012
		2	40.17	20.8	23.2	6.541E-04	1.957E-05	0.000088	40.24	0.17231	0.725536	5.78	0.863877
		3	69.7	20.94	23.5	1.131E-03	3.390E-05	0.000152	69.90	0.17481	0.736122	5.77	0.851549
		4	106.8	20.95	23.7	1.729E-03	5.187E-05	0.000233	107.27	0.17838	0.751366	5.77	0.834552
		7	156	20.97	23.9	2.518E-03	7.560E-05	0.000339	157.01	0.18017	0.759191	5.76	0.826337

Compressibility constants -60 to 80 °C			
Const			
a1	2.246E-02	8.306E-04	-1.019E-06
a2	5.618E-02	-1.911E-04	1.566E-07
a3	-3.615E-03	-8.166E-06	3.014E-08
a4	-1.512E-04	2.755E-06	-4.672E-09

PCT Constants, Meyer 1995		
for the equation lnf=a-(b-cn)/T-dT		
a=	-0.3797	
b=	10653	
c=	12035	
d=	0.027373	

Units were opened with a half turn

	V1 cc unhydride	Pd gm	V2 cc in	V2 cc out	X-ducer no.	weight of unit (gm) before load	weight after load	weight H/Pd in grams
1	6.302	50.1167	0.173	1.56	H 25855	1648.465	1648.797	0.3320
2	6.394	50.5392	0.173	4.96	H 27164	1645.12	1645.446	0.3260
3	6.427	50.5348	0.173	4.96	H 25854	1635.168	1635.484	0.3160
4	6.381	50.5204	0.173	4.96	H 25851	1653.087	1653.393	0.3057
7	6.367	50.5015	0.173	0.78	P 60828	1658.495	1658.79	0.2953

Date	time	unit	Pressure psia	Temp bed °C	Temp out °C	Moles in the gas phase: moles bed V1	moles in V2	moles out V3	Fugacity psia	moles H2 solid	H/Pd	free bed V1 cc	% Uncertainty H/PD
3/10/98	9:32	1	299.56	121.42	23.6	0.00363	0.00011	0.00129	302.54	0.15971	0.67814	5.83	0.93230
		2	178.73	120.9	24.3	0.00218	0.00006	0.00246	179.79	0.157084	0.66142	5.84	0.94771
		3	100.54	120.9	24.3	0.00123	0.00004	0.00139	100.87	0.154118	0.64898	5.85	0.96587
		4	56.4	120.62	24.1	0.00070	0.00002	0.00078	56.51	0.150152	0.63247	5.86	0.99135
		7	32.37	120.2	24	0.00040	0.00001	0.00007	32.40	0.145996	0.61519	5.87	1.01957
3/10/98	11:26	1	198.92	100.96	23.6	0.00255	0.00008	0.00086	200.30	0.161259	0.68472	5.82	0.92321
		2	113.86	100.6	24.2	0.00147	0.00004	0.00157	114.31	0.158709	0.66826	5.83	0.93795
		3	57.76	100.6	24.3	0.00075	0.00002	0.00080	57.88	0.155207	0.65357	5.84	0.95907
		4	29.55	100.43	24.2	0.00038	0.00001	0.00041	29.58	0.150844	0.63538	5.86	0.98680
		7	15.813	100.1	24.2	0.00021	0.00001	0.00003	15.82	0.146232	0.61618	5.87	1.01791

Date	time	unit	Pressure psia	Temp bed °C	Temp out °C	moles bed V1	moles in V2	moles out V3	Fugacity psia	moles H2 solid	H/Pd	free bed V1 cc	% Uncertainty H/PD
3/10/98	12:31	1	121.45	80.79	23.2	0.00165	0.00005	0.00053	121.99	0.162521	0.69008	5.81	0.91596
		2	65.92	80.52	23.8	0.00090	0.00003	0.00091	66.08	0.159952	0.67349	5.82	0.93063
		3	30.18	80.75	24	0.00041	0.00001	0.00042	30.21	0.155932	0.65662	5.84	0.95461
		4	14.21	80.67	23.8	0.00019	0.00001	0.00020	14.22	0.15125	0.63709	5.85	0.98415
		7	7.05	80.38	23.8	0.00010	0.00000	0.00002	7.05	0.146364	0.61674	5.86	1.01700
3/10/98	13:18	1	65.92	60.45	23.3	0.00095	0.00003	0.00029	66.09	0.163481	0.69415	5.81	0.91055
		2	33.35	60.25	23.6	0.00048	0.00001	0.00046	33.39	0.16083	0.67719	5.82	0.92554
		3	13.57	60.35	23.7	0.00020	0.00001	0.00019	13.58	0.156383	0.65852	5.83	0.95185
		4	5.87	60.25	23.6	0.00009	0.00000	0.00008	5.87	0.151478	0.63805	5.85	0.98267
		7	2.75	60.1	23.6	0.00004	0.00000	0.00001	2.75	0.146432	0.61702	5.86	1.01653
3/10/98	15:32	1	31.51	40.42	23.2	0.00048	0.00001	0.00014	31.55	0.164111	0.69683	5.80	0.90704
		2	14.9	40.3	23.6	0.00023	0.00001	0.00021	14.91	0.161346	0.67936	5.81	0.92257
		3	5.54	40.5	23.7	0.00009	0.00000	0.00008	5.54	0.156609	0.65947	5.83	0.95048
		4	2.23	40.5	23.6	0.00003	0.00000	0.00003	2.23	0.151581	0.63848	5.84	0.98200
		7	0.982	40.4	23.7	0.00002	0.00000	0.00000	0.98	0.146461	0.61715	5.86	1.01632
3/10/98	18:42	1	12.92	20.36	22.3	0.00021	0.00001	0.00006	12.93	0.164471	0.69836	5.80	0.90505
		2	5.68	20.2	22.5	0.00009	0.00000	0.00008	5.68	0.161613	0.68049	5.81	0.92105
		3	1.92	20.33	22.5	0.00003	0.00000	0.00003	1.92	0.156714	0.65992	5.83	0.94984
		4	0.72	20.35	22.6	0.00001	0.00000	0.00001	0.72	0.151625	0.63867	5.84	0.98171
		7	0.297	20.37	22.6	0.00000	0.00000	0.00000	0.30	0.146473	0.6172	5.85	1.01624

Compressibility constants -60 to 80 °C			
Const			
a1	2.246E-02	8.306E-04	-1.019E-06
a2	5.618E-02	-1.911E-04	1.566E-07
a3	-3.615E-03	-8.166E-06	3.014E-08
a4	-1.512E-04	2.755E-06	-4.672E-09

PCT Constants, Meyer 1995		
for the equation lnf=a-(b-cn)/T-dT		
a=	-0.3797	
b=	10653	
c=	12035	
d=	0.027373	

Units were opened with a half turn

	V1 cc unhydride	Pd gm	V2 cc in	V2 cc out	X-ducer no.	weight of unit (gm) before load	weight after load	weight H/Pd in grams
1	6.302	50.1167	0.173	1.56	H 25855	1648.465	1648.797	0.3320
2	6.394	50.5392	0.173	4.96	H 27164	1645.12	1645.446	0.3260
3	6.427	50.5348	0.173	4.96	H 25854	1635.168	1635.484	0.3160
4	6.381	50.5204	0.173	4.96	H 25851	1653.087	1653.393	0.3057
7	6.367	50.5015	0.173	0.78	P 60828	1658.495	1658.79	0.2953

						Moles in the gas phase							% Uncer
Date	time	unit	Pressure	Temp	Temp	moles bed	moles in	moles out	Fugacity	moles	H/Pd	free bed	tainty
			psia	bed °C	out °C	V1	V2	V3	psia	H2 solid		V1 cc	H/PD
3/10/98	9:32	1	299.56	121.42	23.6	0.00363	0.00011	0.00129	302.54	0.15971	0.67814	5.83	0.93230
		2	178.73	120.9	24.3	0.00218	0.00006	0.00246	179.79	0.157084	0.66142	5.84	0.94771
		3	100.54	120.9	24.3	0.00123	0.00004	0.00139	100.87	0.154118	0.64898	5.85	0.96587
		4	56.4	120.62	24.1	0.00070	0.00002	0.00078	56.51	0.150152	0.63247	5.86	0.99135
		7	32.37	120.2	24	0.00040	0.00001	0.00007	32.40	0.145996	0.61519	5.87	1.01957
3/10/98	11:26	1	198.92	100.96	23.6	0.00255	0.00008	0.00086	200.30	0.161259	0.68472	5.82	0.92321
		2	113.86	100.6	24.2	0.00147	0.00004	0.00157	114.31	0.158709	0.66826	5.83	0.93795
		3	57.76	100.6	24.3	0.00075	0.00002	0.00080	57.88	0.155207	0.65357	5.84	0.95907
		4	29.55	100.43	24.2	0.00038	0.00001	0.00041	29.58	0.150844	0.63538	5.86	0.98680
		7	15.813	100.1	24.2	0.00021	0.00001	0.00003	15.82	0.146232	0.61618	5.87	1.01791

Appendix B

```
      program fill2
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccc
c     !Date of modification. 11-28-96
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccc
c  This program is for gaseous replensihment & uses the following equation
s:
c     The separation factors need to be confirmed if a mixed gas is used!!
!
c     Relationships of two authors give significantly different results.
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccc
c     The accuracy of the PCT relationship in the beta region is ±0.5%
c         to 5,000 psia at 25¡C and 0 yrs. for pure gases.
c         lnf=a-(b-cn)/T+dT-2mew/RT (Meyer, 1995) beta region
c         lnf=c1+c2/T+c3(n-.3)-2mew/RT Plateau region (Ivar, Meyer Modifie
d)
c     z=1+ccP/T+dd(P/T)^2 (constants good to 1500 atm(22ksi))
c     Bed heating T=Tambient + DTexp(-k*age)
c     Separation factors:  The accuracy is not known and needs to be confi
rmed exp.
c     A flow program is used to determine the mass deficit from equilibriu
m.
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccc
      implicit none

      real*8  a(3),b(3),c(3),d(3),e(75),rr,r,k,sf(3,3),temp,tempa,
     1       phi,ptot,pold,mb(5),mbop(5),mbs(5),x(5),mpd,mt20b,mhe30b,
     2       moptot,vb,vrep,delp,zeff,vb0,mfn,nall,pall,yold,YY(3),
     3       tmp1,tmp2,tmp3,tmp4,tmp5,tmp6,tmp7,tmp8,tmp9,tmp10,tmp11,
     4       deld,delt,yoldd,yoldt,dtemp,aall,ball,calll,dall,aa,y(5),tot,
     5         cc(5),dd(5),ee(5),ff(5),gg(5),a1,a2,a3,a4,a5,del,zold
      integer igas,i,nep
      character*30 tmp
      character*1 good
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccc
c     data infomation
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccc
      data a / 5.83, 32.39, 28.49 /                    ! PCT constants
      data b /12640., 15313., 15349. /                 ! PCT constants
      data c /12832., 12832., 13832. /                 ! PCT constants
      data d /0.01853, -.03127, -.02363 /              ! PCT constants
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccc
c     data for compressibility factors for:
c         Form of the equation: z=1 + a1(P/T) + a2(P/T)^2 + a3(P/T)^3 +a4(
P/T)^4 [1]
c     where a, b, c & d are function of temperature f(T):
c     a1 = b(1) + b(2)*T + b(3)*T^2    [2]
c     a2 = b(4) + b(5)*T + b(6)*T^2    [2] etc.
c     H2, D2, T2, He-3, He-4, & N2 (note N2 has 5 pressure terms)
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccc
      data e/
     1         .022456,8.3057e-4,-1.0193e-6,            !Z constants a1 H2
     2         .056181,-1.9111e-4,1.5657e-7,                ! Z constants a2
 H2
     3         -.0036149,-8.1655e-6,3.0139e-8,              ! Z constants a3
 H2
     4         -1.5121e-4,2.7545e-6,-4.6721e-9,             ! Z constants a4
 H2
```

```
     5          0,0,0,                                          ! Z constants a4
 H2
     1          .0062142,8.9821e-4,-1.1201e-6,                ! Z constants a1 D2
     2           .058847,-2.1402e-4,2.0254e-7,                  ! Z constants a2
 D2
     3           -.0047847,1.3188e-6,1.2312e-8,                 ! Z constants a3
 D2
     4           -1.388e-5,1.6842e-6,-2.7094e-9,                ! Z constants a4
 D2
     5          0,0,0,                                          ! Z constants a4
 D2
     1          -2.109e-5,9.2529e-4,-1.1593e-6,               ! Z constants a1 T2
     2           .06076,-2.2813e-4,2.273e-7,                    ! Z constants a2
 T2
     3           -.0055349,6.8348e-6,2.7755e-9,                 ! Z constants a3
 T2
     4           7.1281e-5,1.0614e-6,-1.6328e-9,                ! Z constants a4
 T2
     5          0,0,0,                                          ! Z constants a4
 T2
     1          .15849,-2.6866e-5,-5.2201e-8,                 ! Z constants a1 He-
3
     2           .0018328,-4.0134e-5,5.8146e-8,                 ! Z constants a2
 He-3
     3           -5.2376e-4,5.0454e-6,-6.9967e-9,               ! Z constants a3
 He-3
     4           6.6813e-6,-2.3159e-8,-2.0797e-10,              ! Z constants a4
 He-3
     5          0,0,0,                                          ! Z constants a4
 He-3
     1          -1.7618,.0085229,-9.695e-6,                   ! Z constants a1 N2
     2           1.3616,-.0053109,6.0426e-6,                    ! Z constants a2
 N2
     3           -.35382,.0012511,-1.3966e-6,                   ! Z constants a3
 N2
     4           .037694,-1.0501e-4,1.1648e-7,                  ! Z constants a4
 N2
     5           -.00096532,-2.4486e-7,0./                      ! Z constants a5
 N2
      rr = 1.9872                                               ! gas constant c
al/gmole ¡K
      r = 82.057                                                ! cm^3 atm/gmole
 ¡K
      k = 0.056216
      zold=1.0                                                ! dk constant 1/year
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccc
c     read & confirm input file
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccc
      call read input(mb,vb,vrep,tempa,mpd,mfn,dtemp,y,tot)
      good(1:1) = 'N'
      write(6,*) 'Are these parameters correct [y or n]?'
          read(5,*) good
      if (good(1:1) .eq. 'n' .or. good(1:1) .eq. 'N') then
          write(6,*) 'Please edit the file delivery.inp and restart'
          goto 999
      endif
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccc
c     initialize
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccc
      call initialize(mb,mbop,mt20b,mhe30b,ptot,pall,tempa,vb0,vb,YY,y,
     1  aall,ball,calll,dall,a,b,c,d,cc,dd,ee,ff,gg,x,zeff,a1,a2,a3,a4,a5,
```

```
e)
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccc
c     open output file fill2.out1
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccc
      open(unit=2,file='fill2.out1',status='unknown')
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccc
c     write headers for output
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccc
      write(6,910)' stoic(all)   ptot(psia)  pTDH(psia)  mbs(H2)     mbop(
H2)    vb(cc)       '
      write(2,910)' stoic(all)   ptot(psia)  pTDH(psia)   mbs(t2)      mbo
p(t2)     vb(cc)       '
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccc
c     determine stoic given P & T
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccc
1     temp=tempa+dtemp                                  ! bed temp. with self he
ating
      sf(2,1) = exp(277.5/temp - 0.025)                 ! deuterium/protium sepa
ration factor
      sf(3,1) = exp(430.4/temp - 0.092)                 ! tritium/protium separa
tion factor
      sf(3,2) = exp(133.5/temp - 0.021)                 ! tritium/deuterium sepa
ration factor
      sf(1,2) = 1/sf(2,1)                            ! protium/deuterium separati
on factor
      sf(1,3) = 1/ sf(3,1)                           ! protium/tritium separation
 factor
      sf(2,3) = 1/ sf(3,2)                           ! deuterium/tritium separati
on factor
      phi = a1*(ptot/temp)+a2*(ptot/temp)**2/2+a3*(ptot/temp)**3/3+a4*(pto
t/temp)**4/4
      phi = phi + a5*(ptot/temp)**5/5
      phi = exp(phi)       ! fugacity coefficient
      write(6,*) 'phi=',phi
      tmp11=aall-ball/temp+dall*temp
      nall=mfn*(log(pall*phi)-tmp11)*temp/call1        ! total stoic
                 ! total moles tritium
       tmp2=exp(11.017-1000.*4.006/temp+0.12*(nall-.3)) !plateau pressure
atm
      if ((pall-tmp2) .lt. .001) then
       vb=vb0-(mpd*106.4/12.02)*nall*(.179*x(3)+.182*x(2)+.185*x(1))
       nall = 2*(mb(1) + mb(2) + mb(3) - tmp2*(vb+vrep)/(zeff*r*temp))/mpd
      endif
2     continue
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccc
cc    determine the pressure in the system
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccc
      mb(4) = mhe30b       ! total moles helium
       vb=vb0-(mpd*106.4/12.02)*nall*(.179*x(3)+.182*x(2)+.185*x(1))
      do 16 i = 1,3
          mbs(i) = x(i)*nall*mpd/2.0                        ! hydrogen solid
16    continue
      mbs(4)=0.
      do 18 i = 1,4
          mbop(i) = mb(i) - mbs(i)                          ! moles overpres
sure
18    continue
```

```
c       sum moles of gas
        moptot = 0.0
        do 20 igas = 1,5
            moptot = moptot + mbop(igas)                    ! moles total ga
s
20      continue
            a1 = 0
            a2 = 0.
            a3 = 0.
            a4 = 0.
            a5 = 0.
        if(moptot .le. 0) then
            ptot=tmp2
            pall=tmp2
            goto1
            endif
            nep = 1
        do 40 i = 1,5
            cc(i) = e(nep) + e(nep+1)*temp + e(nep+2)*temp**2       !
            dd(i) = e(nep+3) + e(nep+4)*temp + e(nep+5)*temp**2     !
            ee(i) = e(nep+6) + e(nep+7)*temp + e(nep+8)*temp**2     !
            ff(i) = e(nep+9) + e(nep+10)*temp + e(nep+11)*temp**2       !
            gg(i) = e(nep+12) + e(nep+13)*temp + e(nep+14)*temp**2      !
40          nep = 5*3*i +1
        do 30 i = 1,5
            y(i) = mbop(i)/moptot                       ! mole fraction
            a1 = a1 + cc(i)*y(i)
            a2 = a2 + dd(i)*y(i)
            a3 = a3 + ee(i)*y(i)
            a4 = a4 + ff(i)*y(i)
            a5 = a5 + gg(i)*y(i)
30      continue
101     zeff = 1 + a1*(ptot/temp)+a2*(ptot/temp)**2+a3*(ptot/temp)**3+a4*(pt
ot/temp)**4
        zeff = zeff + a5*(ptot/temp)**5
        ptot = zeff*(moptot*r*temp)/(vb+vrep)       ! atm
        del = abs((zeff-zold)/zold)
        zold = zeff
c       write(6,*) 'nall,zeff,ptot,pall=',nall,zeff,ptot,pall
        if(del .gt. .0001) goto 101
        aa = calll/temp
        pall = (mb(1) + mb(2) + mb(3) + (1/aa - nall)*mpd/2.0)/
     1   ((vb+vrep)/(zeff*r*temp) + mpd/(pall*2.0*aa))      !partial hydroge
n pressure
        if ((pall - tmp2) .lt. .002) pall = tmp2        !plateau pressure
        delp = abs(pall-pold)
        pold = pall
        phi = a1*(ptot/temp)+a2*(ptot/temp)**2/2+a3*(ptot/temp)**3/3+a4*(pto
t/temp)**4/4
        phi = phi + a5*(ptot/temp)**5/5
        phi = exp(phi)       ! fugacity coefficient
        nall=mfn*(log(pall*phi)-tmp11)*temp/calll
        if ((pall - tmp2) .lt. 0.002) then
            pall=tmp2
         nall = 2*(mb(1) + mb(2) + mb(3) - pall*(vb+vrep)/(zeff*r*temp))/mpd
     !two phase
            endif
        if (delp .gt. 0.0001) goto 2
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
cccc
c       mixture convergence on x(i)'s and YY(i)'s given p and stoic
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
cccc
c       Yi*pall*v/ZRT=Mb(i)-x(i)*n*mpd/2
c     iteratating the combined three eq. for protium, deuterium & tritium
```

```
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
cccc
c     solving for fraction of protium in gas phase
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
cccc
      yold = YY(1)
220   tmp1 = pall*(vb+vrep)*(1. - sf(2,3))/(zeff*r*temp)
      tmp2 = pall*(vb+vrep)*(sf(2,1)*yold + sf(2,3)*(1. - yold))/(zeff*r*t
emp) +
     1      nall*mpd/2. + mb(2)*(sf(2,3) - 1.)
      tmp3 = -mb(2)*(sf(2,3)*(1. - yold) + sf(2,1)*yold)
      tmp4 = pall*(vb+vrep)*(sf(2,1) - sf(2,3))*tmp2/(zeff*r*temp) +
     1      2.*tmp1*mb(2)*(sf(2,1) - sf(2,3))
      tmp4=tmp4/(tmp2**2. - 4.*tmp1*tmp3)
      tmp5 = ((pall*(vb+vrep)*sf(2,3)/(zeff*r*temp) + nall*mpd/2 + mb(2)*(
sf(2,3) - 1))
     1      *tmp2 + 2.*tmp1*mb(2)*sf(2,3) - 2.*tmp1*tmp3)/(tmp2**2. - 4.*tm
p1*tmp3)
      tmp6 = tmp4*sqrt(tmp2**2. - 4.*tmp1*tmp3)/(2.*tmp1) - (sf(2,1) - sf(
2,3))/
     1      (2.*(1 - sf(2,3)))
      tmp7 = tmp5*sqrt(tmp2**2. - 4.*tmp1*tmp3)/(2.*tmp1) - sf(2,3)/
     1      (2.*(1. - sf(2,3))) - (nall*mpd/2. + mb(2)*(sf(2,3) -1))/(2.*tm
p1)
      tmp8 = pall*(vb+vrep)*((1. - sf(1,3)) + (sf(1,2) - sf(1,3))*tmp6)/(z
eff*r*temp)
      tmp9 = pall*(vb+vrep)*(sf(1,3) + (sf(1,2) - sf(1,3))*tmp7)/(zeff*r*t
emp)
      tmp9 = tmp9 + nall*mpd/2 + mb(1)*(sf(1,3) - 1. - (sf(1,2) - sf(1,3))
*tmp6)
      tmp10 = -mb(1)*(sf(1,3) + (sf(1,2) - sf(1,3))*tmp7)
      YY(1) = (-tmp9 + sqrt(tmp9**2. - 4.*tmp8*tmp10))/(2.*tmp8)
      if(YY(1) .lt. 0.) YY(1)=0.
      if(YY(1) .gt. 1.) YY(1)=1.
      yold=(yold+yy(1))/2.
      if (abs(YY(1) - yold) .gt. 0.0002) goto 220
      yold = YY(1)
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
cccccc
c  tritium in gas phase
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
cccccc
      tmp1 = pall*(vb+vrep)*(1.0 - sf(3,2))/(zeff*r*temp)
      tmp2 = pall*(vb+vrep)*(sf(3,1)*YY(1)+sf(3,2)*(1 - YY(1)))/(zeff*r*te
mp) +
     1      nall*mpd/2 + mb(3)*(sf(3,2) - 1)
      tmp3 = -mb(3)*(sf(3,2)*(1 - YY(1)) + sf(3,1)*YY(1))
      YY(3) = (-tmp2 + sqrt(tmp2**2 - 4*tmp1*tmp3))/(2*tmp1)
      if(YY(3) .gt. 1.) YY(3)=1.
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccccccc
c  deuterium in gas phase
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccccccc
      tmp1 = pall*(vb+vrep)*(1.0 - sf(2,3))/(zeff*r*temp)
      tmp2 = pall*(vb+vrep)*(sf(2,1)*YY(1)+sf(2,3)*(1 - YY(1)))/(zeff*r*te
mp) +
     1      nall*mpd/2 + mb(2)*(sf(2,3) - 1)
      tmp3 = -mb(2)*(sf(2,3)*(1 - YY(1)) + sf(2,1)*YY(1))
      YY(2) = (-tmp2 + sqrt(tmp2**2 - 4*tmp1*tmp3))/(2*tmp1)
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccccccc
c  protium, deuterium & tritium in solid phase
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccccccc
```

```
      x(1) = YY(1)/(YY(1) + sf(1,2)*YY(2) + sf(1,3)*YY(3))
      x(2) = YY(2)/(YY(2) + sf(2,3)*YY(3) + sf(2,1)*YY(1))
      x(3) = YY(3)/(YY(3) + sf(3,1)*YY(1) + sf(3,2)*YY(2))
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
cccccccc
c  calculate new constants for PCT
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
cccccccc
      aall = 0.0
      ball = 0.0
      calll = 0.0
      dall = 0.0
      do 310 i = 1,3
          aall = x(i)*a(i) + aall
          ball = x(i)*b(i) + ball
          calll = x(i)*c(i) + calll
          dall = x(i)*d(i) + dall
310   continue
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
cccccccc
c  convergence check
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
cccccccc
      deld=abs(yoldd-YY(2))
      yoldd=YY(2)
      delt=abs(yoldt-YY(3))
      yoldt=YY(3)
      if(deld .gt. 0.00001) goto 1
      if(delt .gt. 0.00001) goto 1
      write(6,*) 'converged  on bed'

      write(6,900) nall,ptot*14.696,pall*14.696,mbs(1),mbop(1),vb,phi*ptot
*14.696
      write(2,900) nall,ptot*14.696,pall*14.696,mbs(3),mbop(3),vb,phi*ptot
*14.696
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
cccccccc
      close(unit=2)
900   format(10e12.5)
910   format(a80)
999   stop
      end
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
cccccccc
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
cccccccc
      subroutine read input(mb,vb,vrep,tempa,mpd,mfn,dtemp,y,tot)
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
cccccccc
      implicit none
      real*8 mb(1),vb,vrep,tempa,mpd,mfn,dtemp,y(1),tot
      character*30 tmp
      integer igas
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
cccccccc
ccc   hydrogen, igas = 1
ccc deuterium, igas = 2
ccc tritium, igas = 3
ccc helium 3, igas = 4
ccc others, igas = 5
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
cccccccc
c     read inputs from file fill2.inp
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
cccccccc
```

```
      open(unit=1,file='fill2.inp',status='old')
c     bed gas
      call skip
      call skip
      call skip
      tot = 0.
      do 110 igas = 1,5
          read(1,*) mb(igas),tmp
          write(6,*) mb(igas),tmp
          tot = mb(igas) + tot
110   continue
          do 100 igas = 1,5
          y(igas) = mb(igas)/tot
          write(6,*) y(igas)
100   continue

c     Volumes
      call skip
      call skip
      call skip
          read(1,*) vb,tmp                                    ! unhydrided
 bed
          write(6,*) vb,tmp
          read(1,*) vrep,tmp                                  ! replen
          write(6,*) vrep,tmp
c     System temperature
      call skip
      call skip
      call skip
          read(1,*) tempa,tmp                                 ! ambient te
mp.
          write(6,*) tempa,tmp
          read(1,*) dtemp,tmp                                 ! bed heatin
g rise
          write(6,*) dtemp,tmp
      call skip
          read(1,*) mpd,tmp                                   ! grams pall
adium
          write(6,*) mpd,tmp
          mpd=mpd/106.4                                       ! moles pall
adium
      call skip
          read(1,*) mfn,tmp                                   ! stoic muli
tiplier
          write(6,*) mfn,tmp                                  ! for hydrog
ens
      call skip
      close (unit = 1)
      return
      end
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccccc
      subroutine skip
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccccc
      character*30 tmp
      read(1,*) tmp
      write (6,*) tmp
      return
      end
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccccc
      subroutine initialize(mb,mbop,mt20b,mhe30b,ptot,pall,tempa,vb0,vb,YY
,y,
     1  aall,ball,calll,dall,a,b,c,d,cc,dd,ee,ff,gg,x,zeff,a1,a2,a3,a4,a5,
```

```
e)
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccccc
      implicit none
      real*8 mb(1),mbop(1),mt20b,mhe30b,ptot,pall,tempa,vb0,vb,YY(1),aall,
ball,
     1      calll,dall,a(1),b(1),c(1),d(1),cc(1),dd(1),x(1),zeff,a1,a2,a3,a
4,a5,e(1),
     2     ee(1),ff(1),gg(1),y(1)
      integer i,nep
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccccc
c     initial conditions
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
ccccc
      zeff=1.
      mt20b = mb(3)
      mhe30b = mb(4)
      ptot = 50.0                    ! atm total pressure
      pall=ptot
      mbop(5) = mb(5)
      tempa = tempa + 273.15
      vb0=vb
      aall=0.
      ball=0.
      calll=0.
      dall=0.
      do 10 i=1,3
          YY(i) = mb(i)/(mb(1)+mb(2)+mb(3))
          x(i) = YY(i)
          aall=x(i)*a(i) + aall
          ball=x(i)*b(i) + ball
          calll=x(i)*c(i) + calll
          dall=x(i)*d(i) + dall
10    continue
      nep = 1
      do 40 i = 1,5
          cc(i) = e(nep) + e(nep+1)*tempa + e(nep+2)*tempa**2      !
          dd(i) = e(nep+3) + e(nep+4)*tempa + e(nep+5)*tempa**2        !
          ee(i) = e(nep+6) + e(nep+7)*tempa + e(nep+8)*tempa**2        !
          ff(i) = e(nep+9) + e(nep+10)*tempa + e(nep+11)*tempa**2      !
          gg(i) = e(nep+12) + e(nep+13)*tempa + e(nep+14)*tempa**2
!
40        nep = 5*3*i +1
          a1 = 0.
          a2 = 0.
          a3 = 0.
          a4 = 0.
          a5 = 0.
      do 30 i = 1,5
          a1 = a1 + cc(i)*y(i)
          a2 = a2 + dd(i)*y(i)
          a3 = a3 + ee(i)*y(i)
          a4 = a4 + ff(i)*y(i)
          a5 = a5 + gg(i)*y(i)
30    continue
      return
      end
```

Data From Wicke and Nernst, and Perminov, Orlov and Frumkin												
Wicke	Constants A and B											
deg C	lnP=-A+B*(H/Pd)		H/Pd									
	A	B										
50	26.6124247	42.2	0.695									
30	30.2124247	46	0.715									
0	35.5124247	51	0.749			Perminov, Orlov and Frumkin						
-78.5	52.9124247	66.4	0.838			Pressure	Fugacity	H/Pd	H/Pd	H/Pd	H/Pd	H/Pd
Press	H/Pd (calc)	Wicke and Nernst				(atm)	(Meyer)	meas	meas	meas	meas	meas
(psia)	-78.5 deg C	0 C	30 C	50 C				-78.5 C	-32 C	0 C	50 C	100 C
1	0.79687387	0.69632	0.657	0.63		0.0146	0.21456	0.84				
2	0.80731283	0.70991	0.672	0.65		0.112	1.6461	0.854	0.787	0.717	0.676	0.605
3	0.81341923	0.71786	0.681	0.66		1	14.707	0.87	0.831	0.784	0.761	
4	0.81775179	0.7235	0.687	0.66		30	451	0.894	0.847	0.808	0.792	0.735
5	0.82111239	0.72788	0.692	0.67		100	1588.4	0.903	0.857			0.741
6	0.82385819	0.73145	0.696	0.67		200	3452.6	0.908		0.829	0.819	
7	0.82617974	0.73448	0.699	0.68		300	5654		0.865	0.835		0.766
8	0.82819076	0.7371	0.702	0.68		400	8260.1	0.913	0.868	0.84	0.822	0.769
9	0.8299646	0.7394	0.705	0.68		500	11346	0.915	0.871	0.843		
10	0.83155135	0.74147	0.707	0.69		600	14992	0.916	0.874	0.848		
11	0.83298675	0.74334	0.709	0.69		750	21714		0.877	0.853		
12	0.83429716	0.74505	0.711	0.69		1000	37127	0.92		0.859		
13	0.83550262	0.74662	0.713	0.69		1700	1.26E+05					
14	0.8366187	0.74807	0.714	0.69								
15	0.83765775	0.74942	0.716	0.69								

REFERENCES

Andreev, B.M., Magomedbekov, E.P. and Sicking, G.H. (1996) Interaction of Hydrogen Isotopes with transition Metals and Intermetallic Compounds. Berlin: Springer-Verlag.

Baranowski, B. (1972). Thermodynamics of Metal/Hydrogen Systems at High Pressures. Bericht der Bunsen-Gesellschaft 76(8), 714-724.

Buck, H. and Alefeld, G. (1972). Hydrogen in Palladium-Silver in the Neighbourhood of the Critical Point. Physical Status Solidii, 49(1), 317-327.

Frieske, H. and Wicke, E. (1973). Magnetic Susceptibility and Equilibrium Diagram of PdH_n. Berichte der Bunsen-Gesellschaft, 77(1), 48-52.

Gillespie, L.J. and Hall, F.P. (1926). The Palladium-Hydrogen Equilibrium and Palladium Hydride. Journal of the American Chemical Society,48, 1207.

Gillespie, L.J. and Galstaun, L.S. (1936). The Palladium-Hydrogen Equilibrium and New Palladium Hydrides. Journal of the American Chemical Society,58, 2565.

Gillespie, L.J. and Downs, W.R. (1939). The Palladium-Deuterium Equilibrium. Journal of the American Chemical Society,61, 2496.

Graham, T. (1866). On the Absorption and Dialytic Separation of Gases by Colloid Septa. Philosophical Transactions of the Royal Society of London,156, 399.

Hansen, M. (1958). Constitution of Binary Alloys. New York: McGraw-Hill. 790-793.

Hoitsema, C. (1895). Zhurnal of Physical Chemistry, 17, 1.

Holman, J. (1989). Experimental Methods for Engineers. New York: McGraw-Hill, Inc.

Levine, P.L. and Weale, K.E. (1960). The Palladium + Hydrogen Equilibrium at High Pressures and Temperatures. Transactions of the Faraday Society,56, 357-362.

Lacher, J.R. (1937). A Theoretical Formula for the Solubility of Hydrogen in Palladium. Royal Society of London, Proceedings, A161, 525.

Lässer, R. and Klatt, K.H. (1983). Solubility of Hydrogen Isotopes in Palladium. Physical Review B, 28(2), 748-758.

Lewis, F.A. (1967). The Palladium Hydrogen System. New York: Academic Press.

Lewis, F.A., (1982). A Survey of Hydride Formation and the Effects of Hydrogen Contained in the Metal Lattice. Platinum Metals Review, 26, 20.

Meyer, B. (1996). Fortran Program for the Determination of the Filling of Palladium Units. Fill2

Perminov, P.S., Orlov, A.A, Frumkin, A.N. (1952). The Effect of Pressure on the Solubility of Molecular Water in a β-Phase Palladium-Hydrogen System. Doklady Akademii nauk SSSR, 84(4), 749.

Santandera, R.P. and Behrens, R.G. (1986). A Review of the Thermodynamics and Phase Relationships in the Palladium-Hydrogen, Palladium-Deuterium and Palladium-Tritium Systems. High Temperature Materials and Processes, 7(2,3), 149-169.

Tkacz, M. and Baranowski, B. (1976). Solubility of Hydrogen in Palladium Hydride at High Pressure of Gaseous Hydrogen. Roczniki Chemii, 50, 2159-2166.

Troost, L. and Hautefeuille, P. (1874). Annuls of Chimestri Physical, 5, 273.

Wicke, E. and Nernst, G.H. (1964). Zustandsdiagramm und thermodynamisches Verhalten der Systeme Pd/H2 und Pd/D2 bei normalenTemperaturen; H/D-Trenneffekte. Berichte der Bunsengesellschaft, 68, 224-235.

Wicke, E. and Brodowsky, H. (1978). Topics in Applied Physics: Hydrogen in Metals II, 29, 74-155. New York: Springer-Verlag.

This report has been reproduced directly from the
best available copy.

It is available to DOE and DOE contractors from
the Office of Scientific and Technical Information,
P.O. Box 62,
Oak Ridge, TN 37831.
Prices are available from
(615) 576-8401.

It is available to the public from the
National Technical Information Service,
US Department of Commerce,
5285 Port Royal Rd.,
Springfield, VA 22616.

Los Alamos
NATIONAL LABORATORY
Los Alamos, New Mexico 87545