

INFORMATION TO USERS

This was produced from a copy of a document sent to us for microfilming. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help you understand markings or notations which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure you of complete continuity.
2. When an image on the film is obliterated with a round black mark it is an indication that the film inspector noticed either blurred copy because of movement during exposure, or duplicate copy. Unless we meant to delete copyrighted materials that should not have been filmed, you will find a good image of the page in the adjacent frame. If copyrighted materials were deleted you will find a target note listing the pages in the adjacent frame.
3. When a map, drawing or chart, etc., is part of the material being photographed the photographer has followed a definite method in "sectioning" the material. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.
4. For any illustrations that cannot be reproduced satisfactorily by xerography, photographic prints can be purchased at additional cost and tipped into your xerographic copy. Requests can be made to our Dissertations Customer Services Department.
5. Some pages in any document may have indistinct print. In all cases we have filmed the best available copy.

University
Microfilms
International

300 N. ZEEB RD., ANN ARBOR, MI 48106

8221212

Nelson, Stephen Otto

ACTIVITY OF HYDROGEN IN METAL-HYDROGEN SYSTEMS:
STRONTIUM, THORIUM-NITROGEN AND VANADIUM ALLOYS

Iowa State University

PH.D. 1982

University
Microfilms
International

300 N. Zeeb Road, Ann Arbor, MI 48106

PLEASE NOTE:

In all cases this material has been filmed in the best possible way from the available copy.
Problems encountered with this document have been identified here with a check mark ✓.

1. Glossy photographs or pages _____
2. Colored illustrations, paper or print _____
3. Photographs with dark background _____
4. Illustrations are poor copy _____
5. Pages with black marks, not original copy _____
6. Print shows through as there is text on both sides of page _____
7. Indistinct, broken or small print on several pages ✓
8. Print exceeds margin requirements _____
9. Tightly bound copy with print lost in spine _____
10. Computer printout pages with indistinct print _____
11. Page(s) _____ lacking when material received, and not available from school or author.
12. Page(s) _____ seem to be missing in numbering only as text follows.
13. Two pages numbered _____. Text follows.
14. Curling and wrinkled pages _____
15. Other _____

University
Microfilms
International

Activity of hydrogen in metal-hydrogen systems:
Strontium, thorium-nitrogen and vanadium alloys

by

Stephen Otto Nelson

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Department: Materials Science and Engineering
Major: Metallurgy

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1982

TABLE OF CONTENTS

	Page
GENERAL INTRODUCTION	1
SECTION I. EQUILIBRIUM HYDROGEN PRESSURES IN THE STRONTIUM-HYDROGEN SYSTEM	9
INTRODUCTION	10
EXPERIMENTAL	12
EXPERIMENTAL RESULTS	14
REFERENCES	22
SECTION II. EQUILIBRIUM HYDROGEN PRESSURES IN THE THORIUM-NITROGEN-HYDROGEN SYSTEM	23
INTRODUCTION	24
EXPERIMENTAL	25
RESULTS	27
REFERENCES	34
SECTION III. ISOPIESTIC SOLUBILITY OF HYDROGEN IN VANADIUM ALLOYS AT LOW TEMPERATURES	35
INTRODUCTION	36
EXPERIMENTAL	39
RESULTS	44
DISCUSSION	64
SUMMARY	66
REFERENCES	67
GENERAL SUMMARY	69
REFERENCES	73
ACKNOWLEDGMENTS	74

GENERAL INTRODUCTION

The increased study of metal-hydrogen systems in recent years has been motivated, in part, by the varied and interesting effects of dissolved hydrogen. These areas cover both applied and basic research. The applied research includes the deleterious embrittlement of many metals by very small amounts of hydrogen in solution and the use of metal-hydrogen systems as an alternative for fossil fuels. The basic research involves the extremely high mobility of hydrogen in metals and the thermodynamics and atomistics of the dissolution of hydrogen in metal systems. The volume of literature published concerning the applied research areas is too extensive to compile. There is an excellent recent review (1) covering hydrogen embrittlement of many metals and alloys. Reviews concerning hydrogen storage materials can be found in Hoffman et al. (2) and Garg and McClaine (3). For a better understanding of the above topics, fundamental knowledge of the energetics of the metal-hydrogen interaction needs to be developed. This can be accomplished, in part, by classical thermodynamic measurements.

Application of the basic principles of thermodynamics helps in interpreting the experimental results that have been obtained. When hydrogen dissolves in the solid-solution regime of the metal or alloy, the reaction is



and the corresponding equilibrium constant of

$$K = \frac{a_{[H]}}{P_{H_2}^{1/2}} \quad . \quad (2)$$

The standard state free energy change, ΔG° , is related to the equilibrium constant by

$$\Delta G^\circ = -RT \ln K \quad . \quad (3)$$

Diatomic hydrogen gas can be considered an ideal gas since low pressures and moderate temperatures are employed. The differential partial molar Gibbs free energy, expressed in cal/mol, is given by

$$d\bar{G} = -\bar{S}dT + \bar{V}dP \quad . \quad (4)$$

If one considers the reaction of Eq. (1), an isothermal reversible addition of hydrogen at one atmosphere to a condensed phase, Eq. (4) becomes

$$\bar{G}_{[H]}(X_H, P, T) - \frac{1}{2} G_{H_2}^\circ = \frac{1}{2} \int_1^{P_{H_2}} \bar{V}_{H_2} dP_{H_2} - \int_1^{P_T} \bar{V}_H dP_T \quad (5)$$

where X_H is the atomic fraction of hydrogen dissolved in the alloy and \bar{V}_{H_2} and \bar{V}_H are the partial molar volumes of hydrogen gas and of hydrogen dissolved in the condensed phase, respectively. Typically, the value of \bar{V}_H in metals is a few cm^3/mol so that this term is negligible. Since the hydrogen gas is considered ideal, Eq. (5) reduces to

$$\bar{G}_{[H]}(X_H, P, T) = \frac{1}{2} G_{H_2}^\circ + \frac{1}{2} RT \ln P_{H_2}(X_H, T) \quad . \quad (6)$$

If hydrogen gas dissolves in solution ideally, it will obey Sieverts' law, the analog to Henry's law for a dimer species. Sieverts' law states that the atomic fraction of hydrogen dissolved in solution is proportional to the square root of the equilibrium hydrogen pressure. This is expressed as

$$X_H = K_S(T) P_{H_2}^{1/2} \quad (7)$$

where $K_S(T) = K_0 e^{-\overline{\Delta H^\circ}/RT}$ and $\overline{\Delta H^\circ}$ is the relative partial molar enthalpy of solution at infinite dilution for Eq. (1). Thus, by plotting the logarithm of the Sieverts' law constant versus reciprocal temperature, the enthalpy of the solution reaction of hydrogen gas dissolving in the metal solid solution may be obtained. From the definition of activity, $\bar{G}_i - G_i^\circ = RT \ln a_i$ where $a_i = \gamma X_i$ and γ is the activity coefficient which can be temperature and composition dependent, it follows from Eq. (6) that

$$a_{H_2/2} = P_{H_2}^{1/2} = \gamma X_H \quad (8)$$

since the standard state of hydrogen is diatomic hydrogen gas at one atmosphere and the temperature of interest. When Sieverts' law is obeyed, the activity coefficient is only temperature dependent and

$$\gamma_H = K_S^{-1}(T) \quad (9)$$

Thus, Eq. (6) becomes

$$\bar{G}_{[H]} = \frac{1}{2} G_{H_2}^\circ - RT \ln K_S + RT \ln X_H \quad (10)$$

The partial molar enthalpy of solution of hydrogen in the metal at a given composition can be obtained from a plot of the logarithm of the equilibrium hydrogen pressure versus reciprocal temperature. This result is obtained by dividing each term in Eq. (6) by T and differentiating at constant composition with respect to $1/T$, thus,

$$\frac{R}{2} \frac{\partial \ln P}{\partial 1/T} = \bar{H}_{[H]} - \frac{1}{2} H_{H_2}^\circ = \frac{\partial \bar{G}_{[H]}/T}{\partial 1/T} - \frac{\partial \frac{1}{2} G_{H_2}^\circ/T}{\partial 1/T} \quad (11)$$

As the hydrogen content increases in metals which dissolve hydrogen exothermically, a concentration will be reached at which the formation of a hydride phase will begin. In a plot of the equilibrium pressure of hydrogen versus hydrogen content in a binary system, this will be represented by a horizontal line or plateau. Data on two reactions may then be obtained. The first is the temperature dependence of the concentration point where the plateau begins. This concentration is referred to as the terminal solid-solubility of hydrogen and is the boundary of the metal-hydrogen solid solution. This solution reaction is represented by



At equilibrium the standard state free energy change is

$$\Delta G^\circ = -RT \ln K = -RT \ln \frac{a_{[H]}^{Sat.}}{a_{MH_2}} \approx -2RT \ln X_{H(Sat.)} \quad (13)$$

since for a dilute solution $X_{H(Sat.)} \ll 1$. Thus, by plotting the

logarithm of the terminal hydrogen solubility versus reciprocal temperature, one may obtain the enthalpy of solution of the metal hydride in the saturated metal solid solution.

The second reaction is the formation of the nearly stoichiometric hydride phase and occurs in a two-phase region of metal hydride and metal solid solution. This reaction is represented by



At equilibrium, the standard state free energy change is

$$\Delta G^\circ = -RT \ln K = -RT \ln \frac{a_{MH_2}}{P_{H_2} \cdot a_M} \approx RT \ln P_{H_2} \quad . \quad (15)$$

Thus, by plotting the logarithm of the plateau pressure versus reciprocal temperature, one may obtain the enthalpy of formation of the metal hydride from the saturated metal phase. As can be seen from the preceding reactions, the important thermodynamic parameter for metal-gas reactions is the equilibrium pressure of the gas or, alternatively, the activity of the gas.

The measurement of the activity of hydrogen can be classified into two areas: direct and indirect measurements of the equilibrium vapor pressure. One indirect pressure measurement can be accomplished by the use of electrochemical cells to measure equilibrium voltages and by means of the Nernst equation convert to equilibrium pressures. Another indirect method is by means of an isopiestic technique. In this case the activity of hydrogen is known as a function of temperature and

hydrogen content in a particular metal, A. One makes intimate contact between metal A and another metal or alloy, B, such that hydrogen may flow freely between them. At equilibrium, the chemical potential of hydrogen will be equal in each metal and from Eqs. (6) and (8), it follows that the activity of hydrogen will be equal in each metal. The hydrogen content in each metal is measured and from the measured hydrogen content in specimen A, the equilibrium vapor pressure of the two specimens can be ascertained. Thus, hydrogen pressure-composition isotherms for metal B can be measured even at temperatures at which equilibrium with the gas phase could not be established.

Sections I and II of this thesis are reports of the direct measurements of the equilibrium vapor pressure of hydrogen in a binary and ternary system, respectively. Section I contains the first reported hydrogen pressure-composition isotherms for the Sr-H system. Section II contains the pressure-composition isotherms of the Th-N-H system at the metal-rich composition range.

Section III contains the pressure-composition isotherms, at near ambient temperatures, in various vanadium-based alloys. The results were obtained by the isopiestic technique. This research was initiated to investigate the trapping of hydrogen by substitutional solutes in Group VB metals.

The trapping of hydrogen by interstitial (4,5,6) and substitutional solutes (7,8,9,10,11) in Group VB metals has been reported by a number of investigators. It is believed an attractive interaction exists between hydrogen and the solute of interest. The magnitude of this

interaction in the Group VB metals is reported to be approximately 0.1 eV/atom to 0.2 eV/atom. In other systems such as Fe-H (12) and Ti-H in Fe (13), stronger interactions of 0.5 eV/atom and 0.3 eV/atom, respectively, have been reported. The data reported on Group VB alloys with substitutional solutes have been mainly hydrogen equilibrium vapor pressures above 300°C where the effect of the attractive interaction is reduced due to the greater thermal energy at high temperature. The hydrogen terminal solid solubility has been measured at ambient temperatures but not the hydrogen pressure-composition isotherms due to the extremely low hydrogen equilibrium pressures at these temperatures.

There are no models available to predict the equilibrium hydrogen pressure as a function of hydrogen content, temperature and solute content in alloy systems which are suspected of hydrogen trapping. Qualitatively, if the deep trap model is valid, a plot of the hydrogen activity versus hydrogen content should exhibit a small slope till the traps, interstitial or substitutional atoms, are saturated with hydrogen. At this point, the slope will change and have a much larger value.

An alternative means of expressing the effects of one solute on the thermodynamic properties of another solute is the interaction parameter or coefficient devised by Wagner (14). The interaction parameter is a means to quantify the effects of dilute solutes on the activity coefficient of the solute of interest, in this case hydrogen. The interaction coefficients are first-order terms in a Taylor series expansion, at a given temperature, of the logarithm of the activity coefficient of hydrogen. All but first-order terms are neglected. Thus, one obtains

$$\ln \gamma_H = \ln \gamma_H^c + X_H \cdot \epsilon_H^H + X_M \cdot \epsilon_H^M + \dots \quad (16)$$

where

$$\epsilon_H^H = \left. \frac{\partial \ln \gamma_H}{\partial X_H} \right|_{X_M, X_H \rightarrow 0} \quad \text{and} \quad \epsilon_H^M = \left. \frac{\partial \ln \gamma_H}{\partial X_M} \right|_{X_M, X_H \rightarrow 0} \quad (17)$$

If hydrogen in solution exhibits Sieverts' law, one can substitute the Sieverts' constant for the activity coefficient of hydrogen. Since the Sieverts' constant is independent of hydrogen concentration, ϵ_H^H is equal to zero. However, the ϵ_H^M term may be nonzero if additions of a substitutional solute change the value of the Sieverts' constant for the alloy.

SECTION I. EQUILIBRIUM HYDROGEN PRESSURES IN THE STRONTIUM-
HYDROGEN SYSTEM

INTRODUCTION

Investigation of the literature showed very little information on the thermodynamics of the strontium-hydrogen system. The enthalpy of formation of strontium dihydride had been determined mainly by calorimetric techniques. Guntz and Benoit (1), who measured the enthalpies of solution of strontium metal and of strontium dihydride in dilute hydrochloric acid, reported a value of -42.2 kcal/mol SrH_2 for the enthalpy of formation of strontium dihydride. Ehrlich, Peik and Koch (2) performed a similar experiment and reported a value of -43.0 kcal/mol SrH_2 . Hydrogen pressures reported by Ephraim and Michel (3) over several strontium metal-dihydride two-phase compositions were apparently not equilibrium pressures and the strontium metal that was used was of unknown purity. Banus and Bragdon (4), who measured the dissociation hydrogen pressures for the condensed-phase composition of 92.3 mol percent SrH_2 , reported a value of -47.0 kcal/mol H_2 for the enthalpy of formation of strontium dihydride. However, the stainless steel container used in this study probably caused high equilibrium pressures by alloying with the strontium metal.

The need for fundamental thermodynamic data for metal-hydrogen systems in extending our understanding of the interaction of hydrogen in metals, the availability of pure strontium, and the fact that there are no reported pressure-composition isotherms for the strontium-hydrogen system prompted this investigation. Peterson and Colburn (5) have established the phase diagram for strontium and strontium dihydride. Thus, it is possible to interpret the pressure-composition isotherms

with less ambiguity. The high equilibrium vapor pressures of the alkaline-earth metals and their high reactivities require sealed and chemically inert crucibles to contain the metal and hydride phases. Previous pressure-composition isotherm measurements of the alkaline-earths (4,6) have relied on iron crucibles which have the disadvantage of slow hydrogen permeations. Thus, long periods of time had to be allowed for hydrogen pressure equilibrium to be attained through the crucible. Tantalum was used as a container for the strontium specimens for this study. Tantalum acted as a semipermeable membrane that allowed the hydrogen to pass through reversibly and rapidly but prevented the strontium metal from escaping and was resistant to attack by strontium or strontium hydride.

EXPERIMENTAL

The strontium metal was obtained from King Laboratories, Syracuse, New York and purified by triple distillation at 300°C under 6 mm of helium pressure. The resulting purity would be equal to that reported by Fitzgibbon, Huber and Holley (7). The strontium metal was always handled in an argon-filled dry box to prevent reaction with water vapor and oxygen. The tantalum capsules were 12.7 mm in diameter and had a 0.25 mm wall thickness. The tantalum capsule was chemically cleaned and weighed. The strontium metal, ~6 g, was sealed in the tantalum capsule by arc welding in an argon-filled dry box. The sealed capsule was out-gassed for 3 days at 900°C under a residual pressure of 5×10^{-4} Torr to remove the hydrogen in the strontium metal and in the capsule.

Hydrogen pressures in the conventional Sieverts'-type apparatus were measured using a mercury manometer which could be read to ± 0.3 mm. The capsule was contained in a silica furnace tube that was inserted into an Inconel block positioned in the center of an electric furnace. The temperature was measured by a Chromel-Alumel thermocouple located above the sample between the silica tube and the Inconel block. This temperature was compared with the temperature in the tantalum capsule and they were found to never differ by more than 1.5°C. The temperature was controlled $\pm 2^\circ\text{C}$ during a run and was constant to one degree over a 5 cm length of the Inconel block. Since the amount of gas in the silica furnace tube at constant pressure decreased with increasing furnace temperature, the effective volume of the apparatus was determined at a number of furnace temperatures. Very pure hydrogen gas was obtained

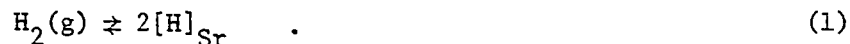
by the thermal decomposition of uranium hydride. The hydrogen pressure was taken to be the equilibrium pressure when it had been constant within ± 0.5 mm for at least 6 hours. Typically, the hydrogen pressure became constant within 1.5 hours after a change in either composition or temperature.

The amount of hydrogen in the tantalum capsule and specimen was determined by the difference between the total amount of hydrogen gas that had been added to the system and the amount of hydrogen remaining in the gas phase. The amount of hydrogen dissolved in the tantalum capsule, at a given pressure and temperature, was calculated from the high-temperature solubility of hydrogen in tantalum reported by Franzen, Kahn and Peterson (8). The distribution of hydrogen in the condensed phases was highly in favor of the strontium specimen and there were 1.6 times as many moles of strontium as of tantalum. The amount of hydrogen in the tantalum metal was always less than 1 percent of the total hydrogen in the condensed phases.

EXPERIMENTAL RESULTS

Hydrogen is very soluble in both liquid and solid strontium in the temperature range from 700–900°C. The solubility follows Sieverts' law in both the liquid and the solid state up to a hydrogen to metal ratio of 0.35, as shown in Fig. 1 which is a plot of $P_{H_2}^{1/2}$ versus the H/Sr atom ratio. The question of whether Sieverts' law is best expressed as a proportionality between the square root of the hydrogen pressure and the atomic fraction or the hydrogen to metal ratio is usually moot because at low concentrations these two concentration expressions are so nearly equal. However, the hydrogen atoms are going into interstitial positions and not replacing the metal atoms and so it seems reasonable to expect direct proportionality of concentration-related properties with the concentration expressed as interstitial to metal atom ratio. In the case of hydrogen in strontium, the concentration range extends to higher concentrations where there is a difference between the two expressions. However, our data fit either concentration function about equally well and the decision to use hydrogen to metal atom ratio was based on the opinion that this is a more logical and convenient way of expressing the concentration in interstitial alloy systems.

The dissolution of hydrogen gas in strontium metal corresponds to the reaction:



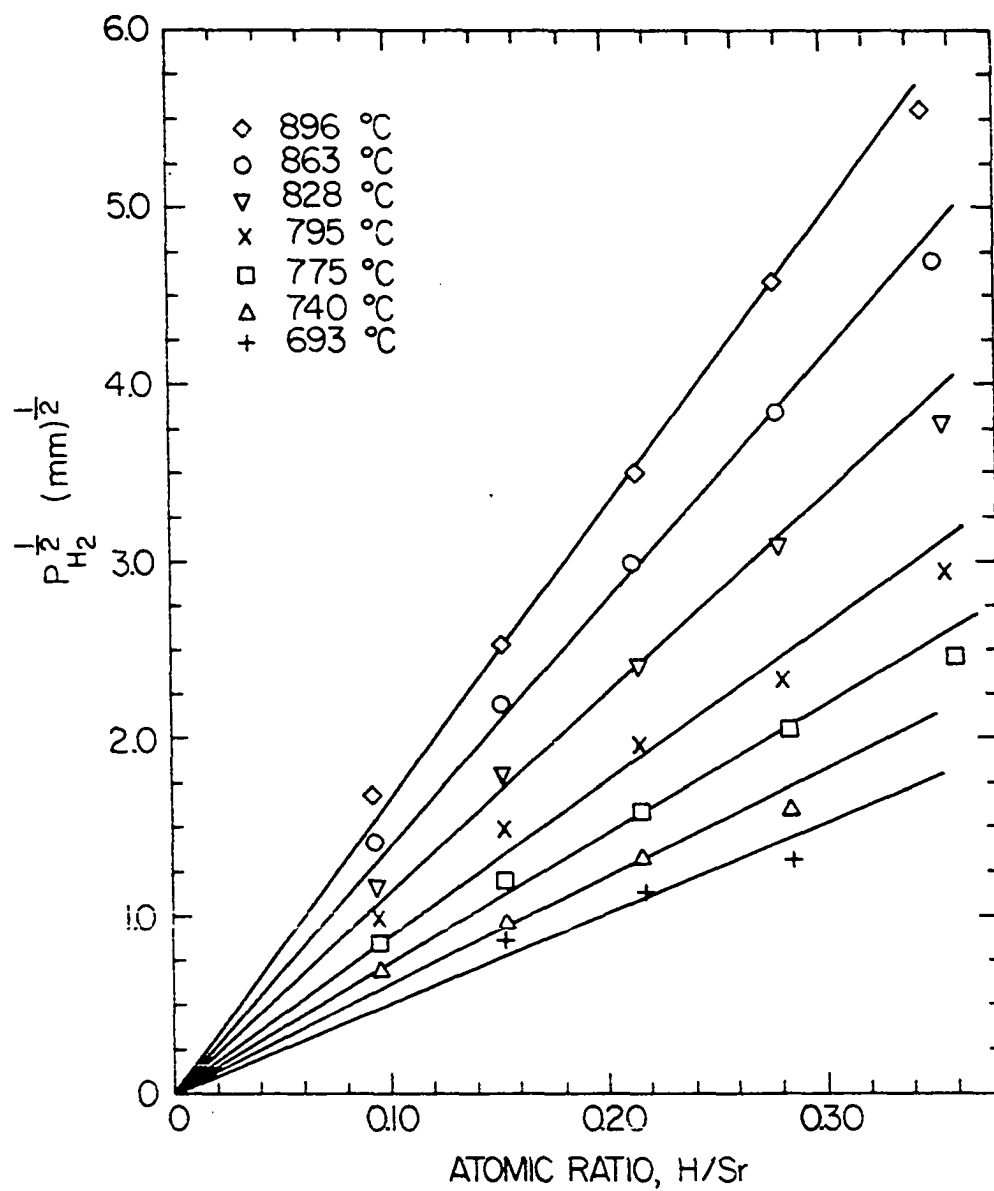


Figure 1. $P_{H_2}^{1/2}$ vs. H/Sr ratio in β -Sr metal

The enthalpy for the above reaction was obtained from the slope of a plot of the logarithm of the Sieverts' law constant versus reciprocal temperature. Data were combined from both the liquid and solid state ranges thus ignoring the heat of fusion of strontium metal. This was done because the data for either range alone covered a very small temperature interval and the heat of fusion was about equal to the uncertainty in the heat of solution. The enthalpy of solution of hydrogen gas in strontium metal was determined to be -28.6 ± 2.4 kcal/mol H_2 .

The measured equilibrium hydrogen pressures are shown as a function of composition in Fig. 2 in a log-log plot. In accordance with the Sieverts' law behavior, the pressure-composition isotherms in the region below the saturation of the strontium metal with SrH_2 are drawn with a slope of two. The data in Fig. 2 include both the absorption and desorption measurements as no hysteresis effects were observed in the strontium-hydrogen system. The solubility limit of SrH_2 dissolved in the strontium metal at each temperature was taken as the intersection of the two-phase, plateau pressure line and the Sieverts' law behavior line.

From the slope of the logarithm of the solubility of SrH_2 in strontium metal against reciprocal temperature, shown in Fig. 3, one may obtain the enthalpy of solution for the reaction:



The data from the present investigation and the results reported by

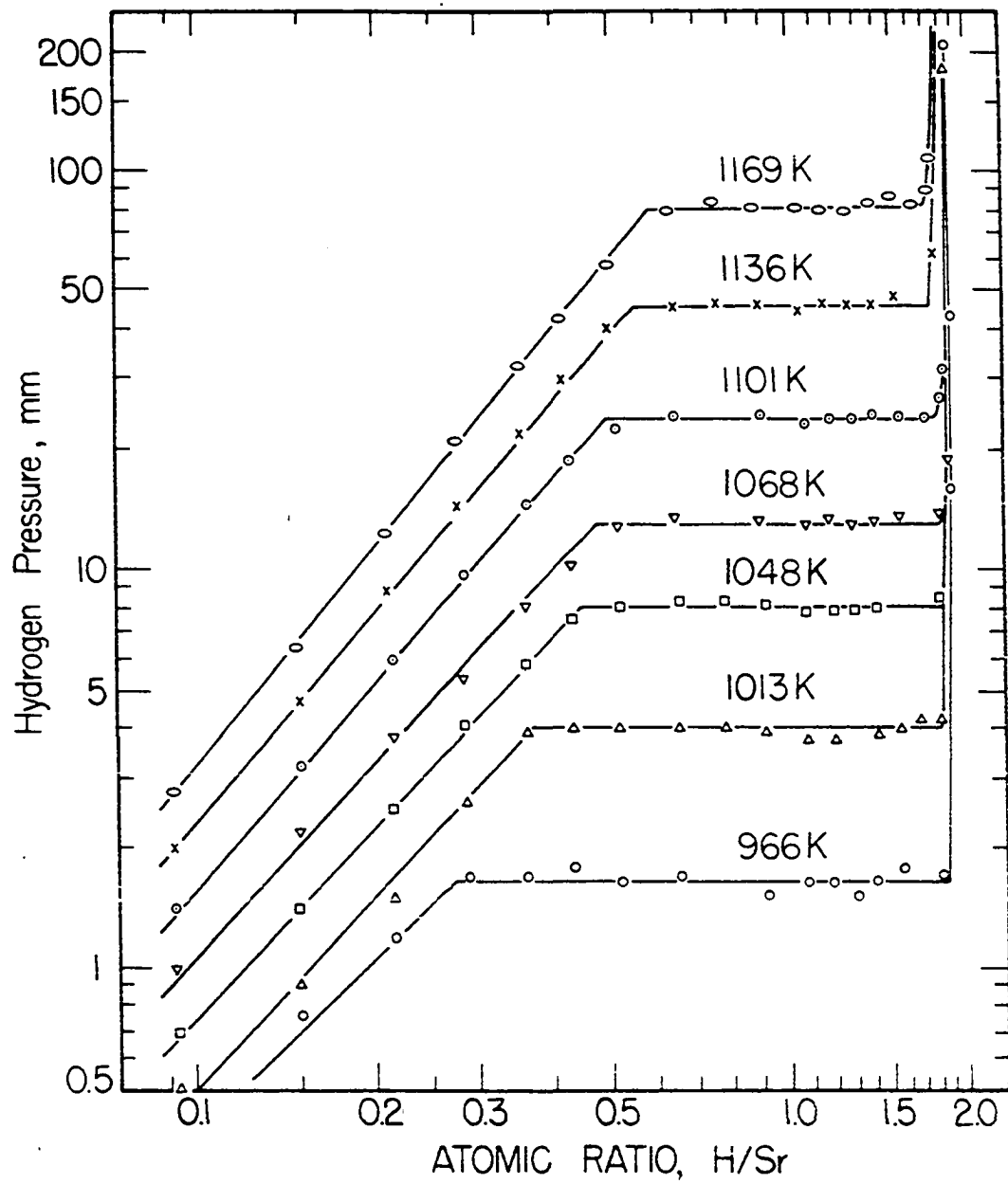


Figure 2. $\log P_{H_2}$ vs. $\log H/Sr$ ratio

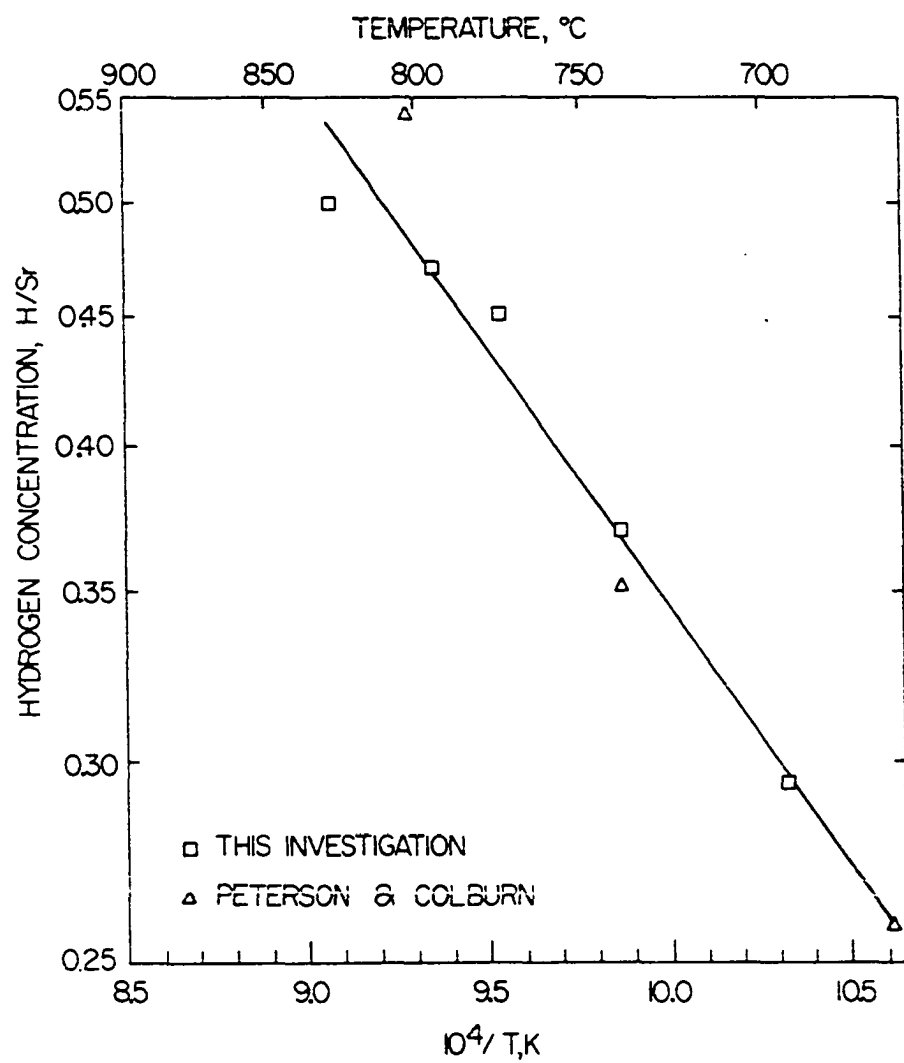


Figure 3. Log solubility of SrH_2 in β -Sr metal vs. reciprocal temperature

Peterson and Colburn (5) are shown in Fig. 3 where the solid line represents a least-squares treatment of the data from the present investigation. The enthalpy of solution of α -SrH₂ in β -Sr metal was found to be $+13.0 \pm 1.0$ kcal/mol SrH₂ in excellent agreement with $+15.9 \pm 2.0$ kcal/mol SrH₂ reported by Peterson and Colburn (5).

The plateau regime in Fig. 2 when the hydrogen pressure is constant over a range of H/Sr values corresponds to the reaction:



A plot of the logarithm of the equilibrium hydrogen pressure versus reciprocal temperature at a hydrogen to metal ratio of 1.4 is shown in Fig. 4. Pressure measurements were made at additional temperatures at this composition to give greater certainty in the enthalpies. The enthalpies of formation of α -SrH₂ and β -SrH₂, obtained from the slopes of Fig. 4, were -43.6 ± 0.7 kcal/mol H₂ and -45.2 ± 2.0 kcal/mol H₂, respectively. The plateau pressures for the formation of α -SrH₂ and β -SrH₂ are given by the expressions; $\log P(\text{mm}) = 10.0 - 9570/T$ and $\log P(\text{mm}) = 10.4 - 9980/T$, respectively. The large uncertainty in the enthalpy of formation of β -SrH₂ was due to the very narrow temperature range over which this reaction could be studied. The agreement of the enthalpy of formation of α -SrH₂ with the calorimetric results of -42.2 kcal by Guntz and Benoit (1) and -43.0 kcal by Ehrlich et al. (2) is quite good considering that these are obtained from different experimental techniques and reactions. The self-consistency of the thermodynamic data for the strontium-hydrogen system can be checked

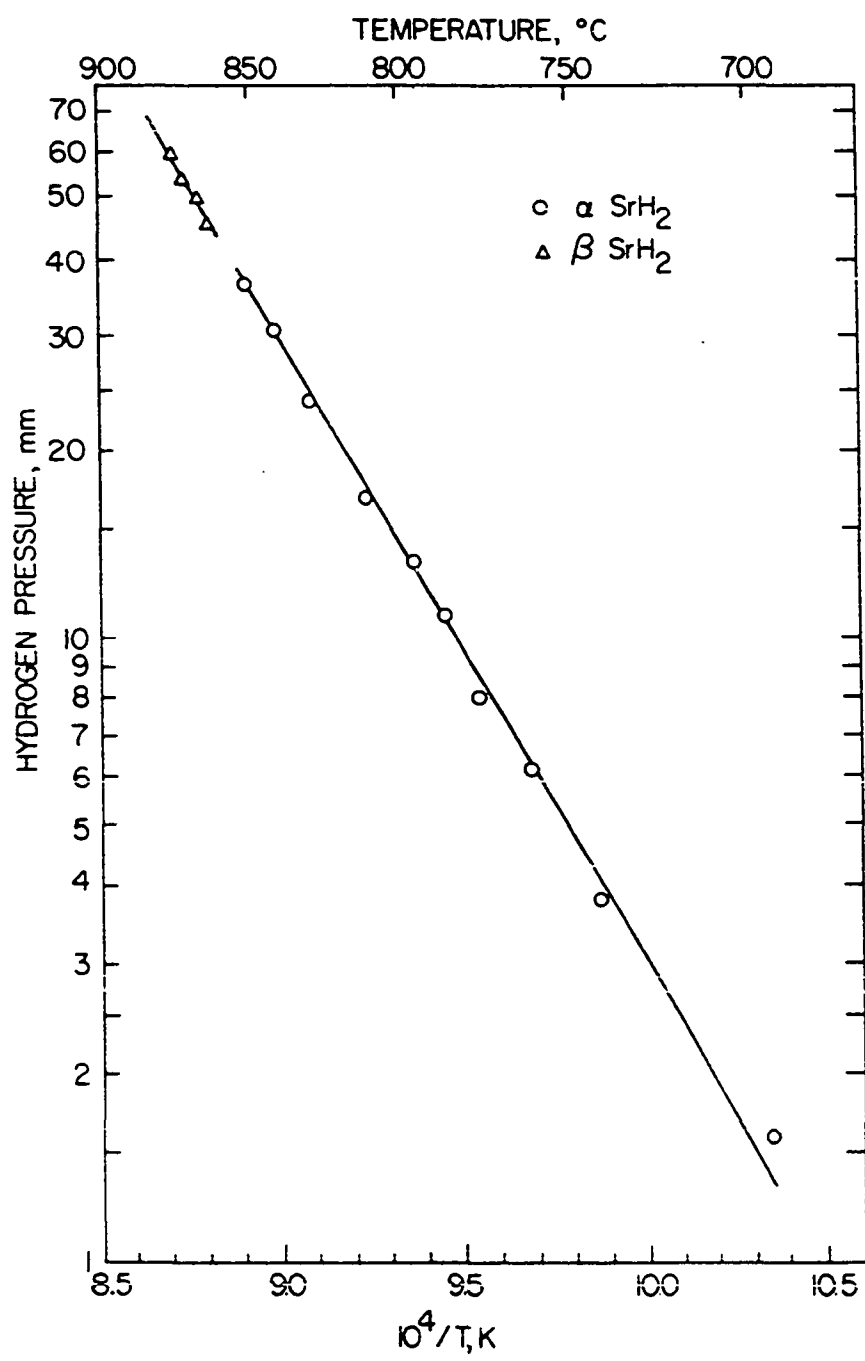


Figure 4. $\log P_{H_2}$ vs. reciprocal temperature in the plateau pressure regime²

by comparing the heat of reaction of H_2 to form SrH_2 with the sum of the heat of solution of H_2 in Sr metal and the heat of precipitation of SrH_2 from Sr metal. The heat of reaction of H_2 to form SrH_2 was -43.6 ± 0.7 kcal and the sum of the heat of hydrogen solution and of SrH_2 precipitation was -46.6 ± 3.4 kcal. This is not perfect agreement but is quite good when the uncertainty in the various values is included.

The composition range of strontium hydride appears to be quite narrow as shown in Fig. 2. The lower composition limit of the hydride decreases only slightly with increasing temperature. The hydrogen pressure rises very rapidly with composition in the hydride phase range. The lower composition limits of the hydride shown in Fig. 2 are from 1.80 to 1.90. These compositions are not very accurate because at this point in the determination of a pressure-composition isotherm there have been small additions of hydrogen and each increment increases the uncertainty in the composition. Also, the long times at high temperatures allow some hydrogen to permeate through the silica walls of the furnace tube and escape. A special run was made to establish this lower composition limit. The hydrogen was added in a few larger increments and the time at high temperature was kept very short. This run gave a value of 1.97 ± 0.02 for the lower hydride composition limit at $800^\circ C$. This agrees quite well with the value of 1.96 obtained by analysis of the hydride in equilibrium with strontium metal (5).

REFERENCES

1. A. Guntz and F. Benoit, *Ann. Chim. (Paris)* 20, 5 (1923).
2. P. Ehrlich, K. Peik and E. Koch, *Z. Anorg. Allg. Chem.* 324, 113 (1963).
3. F. Ephraim and E. Michel, *Helv. Chim. Acta* 4, 900 (1921).
4. M. D. Banus and R. W. Bragdon, Report No. CF-52-2-212 (Metal Hydrides Inc., Beverly, MA, 1952).
5. D. T. Peterson and R. P. Colburn, *J. Phys. Chem.* 70, 468 (1966).
6. R. W. Curtis and P. Chiotti, *J. Phys. Chem.* 67, 1820 (1963).
7. G. C. Fitzgibbon, E. J. Huber, Jr. and C. E. Holley, Jr., *J. Chem. Thermodyn.* 5, 577 (1973).
8. H. F. Franzen, A. S. Kahn and D. T. Peterson, *J. Less-Common Metals* 55, 143 (1977).

SECTION II. EQUILIBRIUM HYDROGEN PRESSURES IN THE THORIUM-
NITROGEN-HYDROGEN SYSTEM

INTRODUCTION

Peterson and Rexer (1) investigated the thorium-carbon-hydrogen system by means of pressure-composition isotherms and reported two ternary compounds between thorium monocarbide and thorium dihydride. Blunck and Juza (2) have reported a thorium-nitrogen-hydrogen ternary compound, $\text{ThHN}_{1.23}$, synthesized by reaction of thorium with ammonia under high pressures and moderate temperatures. They characterized the structure as face-centered cubic, $a_0 = 5.61 \text{ \AA}$, and reported no thermodynamic data. The present investigation was conducted to see whether the thorium-nitrogen-hydrogen system forms compounds similar to the thorium-carbon-hydrogen system, and to provide fundamental thermodynamic data.

EXPERIMENTAL

The thorium specimens were prepared from magnesium-reduced thorium with a purity equal to that reported by Peterson, Krupp and Schmidt (3). The thorium metal was arc melted with prepurified nitrogen gas to obtain the desired nitrogen content. The specimens, cut from arc-melted buttons, were slabs ~1.5 cm long and weighed ~2 g. The nitrogen content of each specimen was determined by the Kjeldahl method. Each specimen was also examined metallographically to confirm uniformity of the two-phase microstructure of thorium metal and thorium nitride. Very pure hydrogen gas was obtained by the thermal decomposition of uranium hydride.

The apparatus was a conventional Sieverts'-type apparatus with a mercury manometer which could be read to ± 0.3 mm. The specimens were contained in a fused silica tube with 3 mm thick walls which was inserted into an Inconel block positioned in the center of an electric furnace. The 3 mm thick walls in the furnace tube were needed to reduce the loss of hydrogen by permeation. With 1 mm thick walls, the pressure change by permeation through the walls resulted in serious hydrogen losses and difficulty in using a pressure change criterion for the attainment of equilibrium. There was still a small loss of hydrogen with the thicker walls as a consequence of the long times needed for equilibrium but it was not significant except after very long times at the higher temperatures. The temperature was measured by a Chromel-Alumel thermocouple located above the sample between the silica tube and the Inconel block. This temperature was compared with the temperature at the specimen and found to differ by no more than 1.5°C . The temperature was controlled

to $\pm 2^{\circ}\text{C}$ during a run and was constant to 1.0°C over a 5 cm length of the Inconel block. Since the amount of gas in the silica furnace tube at constant pressure decreased with increasing furnace temperature, the effective volume of the apparatus was determined at a number of furnace temperatures. The hydrogen pressure was taken to be the equilibrium pressure when it had been constant within ± 0.5 mm for 2 days. Typical equilibration times were on the order of 14 to 20 days, apparently because the attainment of equilibrium required diffusion of nitrogen as well as hydrogen. The amount of hydrogen dissolved in the condensed phases was determined by the difference between the total amount of hydrogen gas that had been added to the system and the amount of hydrogen remaining in the gas phase.

RESULTS

The pressure-composition isotherms showed that only one compound of thorium, nitrogen and hydrogen was formed which was more stable than Th_4H_{15} . Hydrogen first went into solid solution in the thorium metal with a very small amount into the thorium nitride phase till the formation of thorium dihydride occurred at a fixed pressure at each temperature. This is shown in Fig. 1 which is a plot of the square root of the equilibrium hydrogen pressure versus hydrogen to thorium ratio for a specimen with a nitrogen to thorium ratio of 0.484. There are two solid phases in the specimen at the beginning of the experiment and a third phase is forming in the constant pressure plateau region. This complicates the calculation of the hydrogen concentration in each phase. The start of the plateau in Fig. 1 marks the solubility limit of ThH_2 in thorium. The hydrogen concentration in the thorium phase at 800°C , calculated on the assumptions that ThN was exactly stoichiometric and dissolved no hydrogen, gave a solubility limit of 0.29 H/Th which agrees very well with the values reported by Peterson and Westlake (4) in pure thorium. The upper composition end of the plateau corresponds to the lower limiting composition of ThH_2 in equilibrium with thorium metal. The calculated composition at 800°C was 2.2 H/Th which is appreciably higher than the value reported by Peterson and Rexer (5). This increase in the amount of hydrogen in the hydride phase may have been caused by ThN dissolving in the hydride phase and increasing the amount of hydride phase.

After the formation of thorium dihydride was complete, the hydrogen pressure increased until the ternary compound began to form. This is

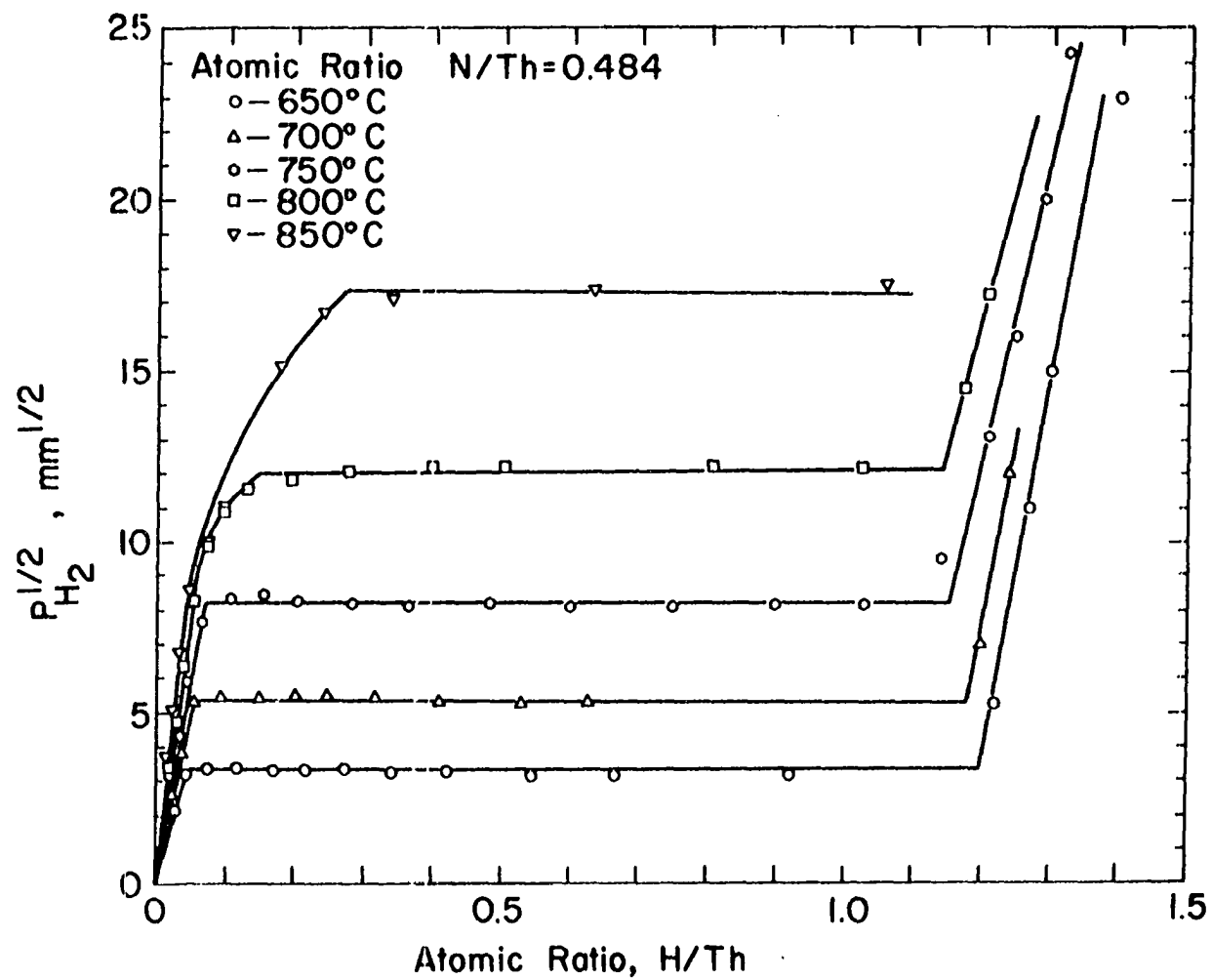


Figure 1. $P_{H_2}^{1/2}$ vs. atomic ratio, H/Th, for a specimen with a N/Th ratio of 0.484

shown in Fig. 2 which is a plot of the square root of the equilibrium hydrogen pressure versus hydrogen to thorium ratio for a specimen with a nitrogen to thorium ratio of 0.692. It can be seen from Fig. 2 that the thorium-nitrogen-hydrogen compound forms at a constant hydrogen pressure at the lower temperatures but at higher temperatures, the plateau pressure was not constant. Such sloping plateaus often are associated with a change in composition of the phase. After the thorium nitride phase disappeared, the hydrogen content of the ternary compound increased as the hydrogen pressure increased. This compound is not of fixed composition but apparently varies from $\text{ThNH}_{1.8}$ to $\text{ThNH}_{2.2}$.

The dissolution of hydrogen into thorium metal corresponds to the reaction

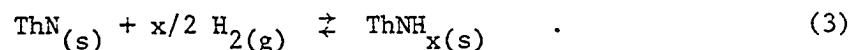


The enthalpy for this reaction was obtained from the slope of a plot of the logarithm of the Sieverts' constant versus reciprocal temperature which was obtained from data in Fig. 1. The value obtained from a linear least-squares treatment was $-20.9 \pm 0.9 \text{ kcal (mol H}_2\text{)}^{-1}$ which agrees very well with the value of $-21.7 \text{ kcal (mol H}_2\text{)}^{-1}$ reported by Mallett and Campell (6).

The plateau regime in Fig. 1 corresponds to the reaction



and that in Fig. 2 corresponds to



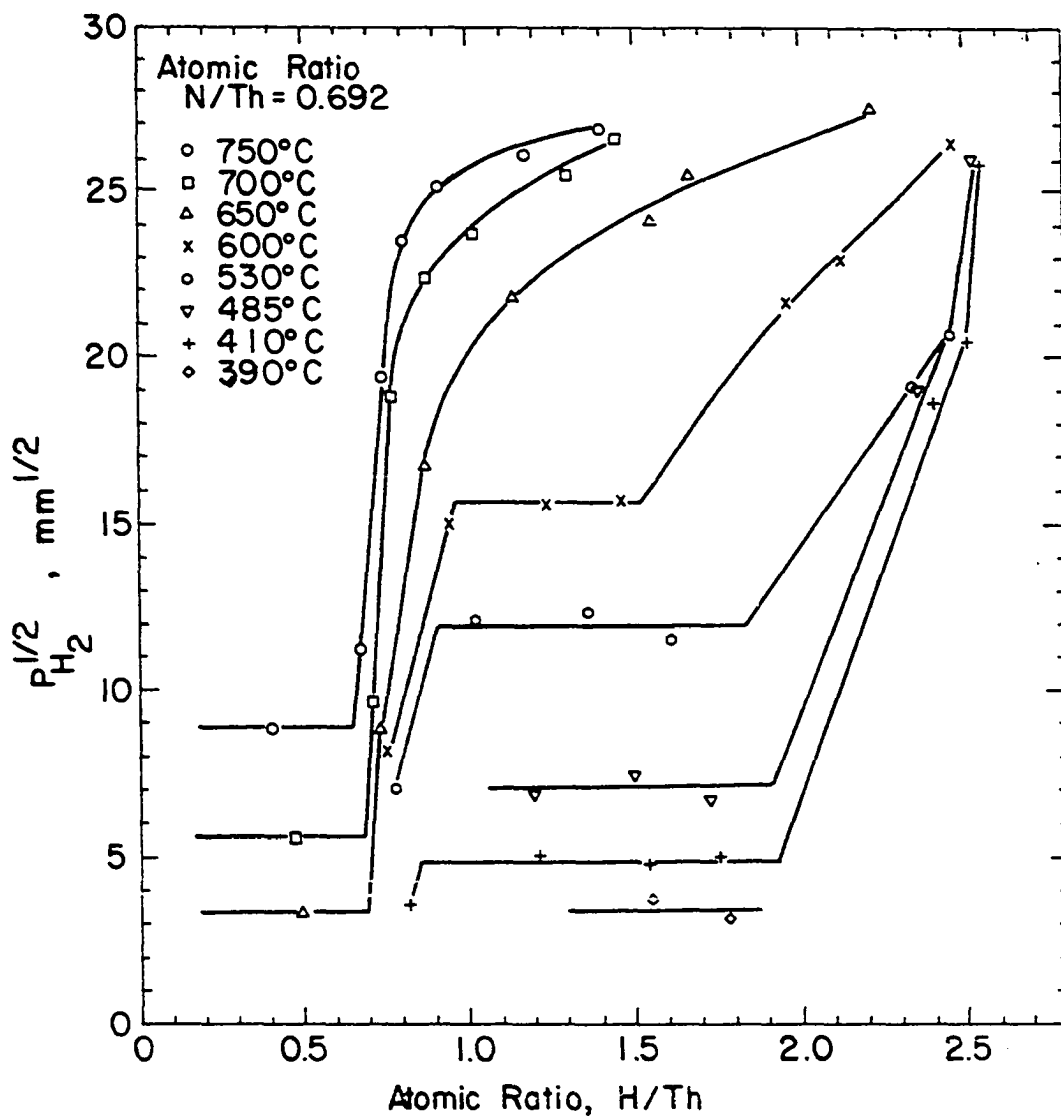


Figure 2. $P_{H_2}^{1/2}$ vs. atomic ratio, H/Th, for a specimen with a N/Th ratio of 0.692

Plots of the logarithm of the equilibrium hydrogen pressure versus reciprocal temperature are shown in Fig. 3. Included in Fig. 3 are the data reported by Peterson and Rexer (5) for thorium dihydride and Nottorf (7) for Th_4H_{15} . The plateau pressures for thorium dihydride in this investigation are slightly lower than those reported by Peterson and Rexer (5) which is probably due to the reduced activity of thorium dihydride due to dissolved nitrogen. A linear least-squares treatment yielded enthalpies of formation of $-34.1 \pm 0.1 \text{ kcal (mol H}_2\text{)}^{-1}$ and $-16.3 \pm 1.5 \text{ kcal (mol H}_2\text{)}^{-1}$ for ThH_2 and ThNH_x , respectively. The plateau pressure for the formation of ThNH_x in the range 390-600°C is given by the expression $\log P \text{ (mm)} = 6.50 - 3570/T$. The agreement of the enthalpy of formation for thorium dihydride with the values reported by Mallett and Campell (6), $-34.3 \text{ kcal (mol H}_2\text{)}^{-1}$, and Peterson and Rexer (5), $-35.0 \text{ kcal (mol H}_2\text{)}^{-1}$, is quite good.

Powder X-ray diffraction was performed using a 11.46 cm Debye-Scherrer camera with Ni filtered Cu K_α radiation. The specimens examined were the final product from the experiment in Fig. 2 and also a sample with a nitrogen to thorium ratio of 0.484 and a hydrogen to thorium ratio of ~ 2.2 . From the former specimen, the pattern of the ternary compound, ThNH_x , was indexed on the basis of a face-centered cubic unit cell with $a_0 = 5.596 \pm 0.008 \text{ \AA}$. The accuracy of the X-ray data is limited due to line broadening. The latter specimen confirmed the three-phase region of thorium dihydride, thorium nitride and thorium nitride hydride. The results obtained on the crystal structure and lattice parameter of the thorium-nitrogen-hydrogen compound agrees well

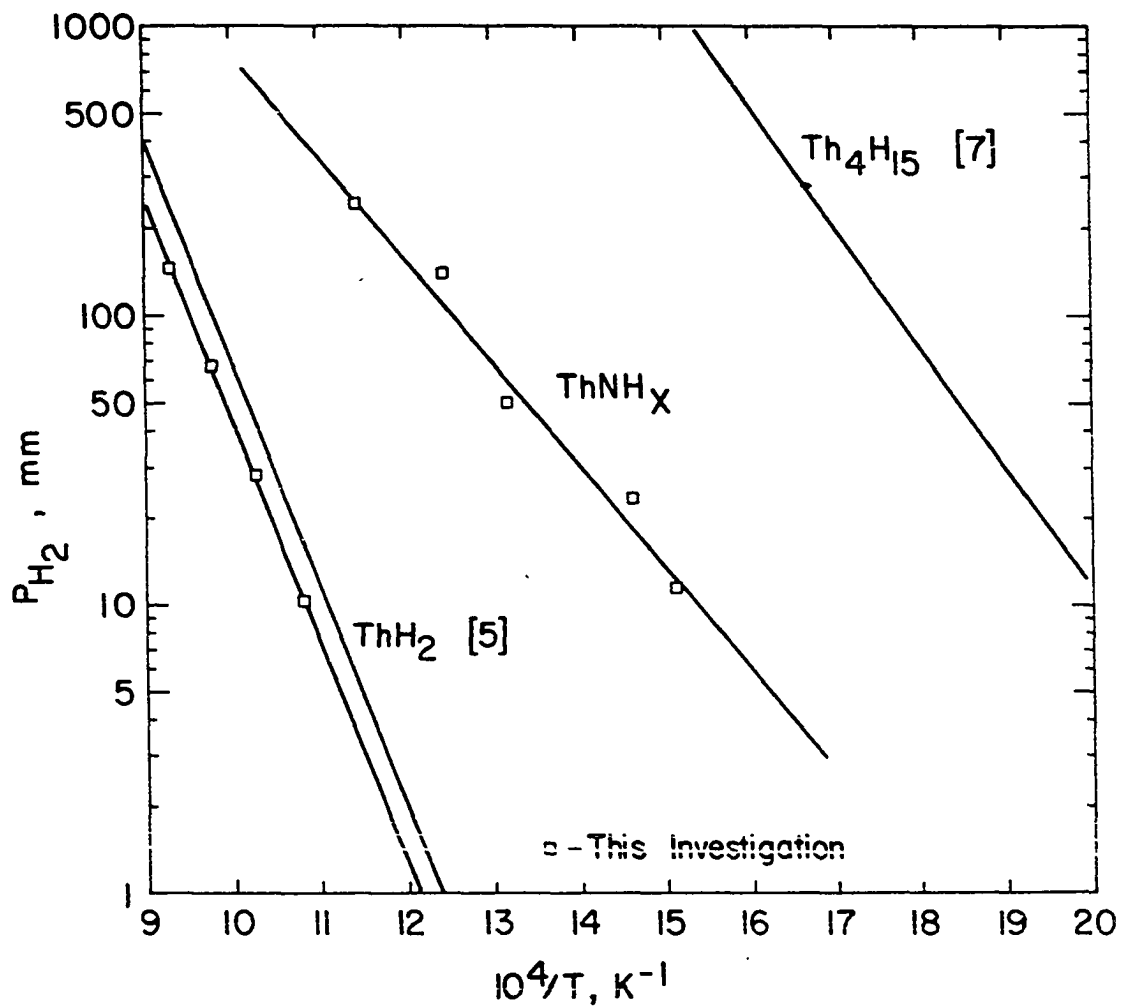


Figure 3. $\log P_{H_2}$ vs. reciprocal temperature in the plateau pressure regime of ThH_2 , $ThNH_x$ and Th_4H_{15}

with that of Blunck and Juza (2). They reported a face-centered cubic lattice with $a_0 = 5.61 \text{ \AA}$. The composition they reported for the ternary compound, $\text{ThHN}_{1.23}$, may not be exact. The methods of analysis were not mentioned other than that the hydrogen content was measured by acidic decomposition.

This thorium ternary nitride hydride differs in several ways from the thorium carbohydride ThC-ThH_2 . The crystal structure is based on a face-centered cubic arrangement rather than the hexagonal close-packed arrangement typical of the carbohydrides. In addition, the molar volume of ThC-ThH_2 was nearly the sum of the volumes of the appropriate quantities of ThC and ThH_2 . Thorium nitride hydride has a unit cell which is larger than ThH_2 and much larger than ThN . The hydrogen to metal atom ratios are also higher than one would expect based on the binary hydride. Lastly, the enthalpy of formation of this compound and its thermal stability are less than that of the binary hydride whereas in the carbohydride both of these were greater. The bonding in this thorium nitride hydride seems to be different from that in thorium carbohydride. Further studies would be interesting if this compound were not so slow to form and difficult to handle due to its extreme reactivity with water vapor.

REFERENCES

1. D. T. Peterson and J. Rexer, J. Inorg. Nucl. Chem. 24, 519 (1962).
2. H. Blunck and R. Juza, Z. Anorg. Allg. Chem. 410, 9 (1974).
3. D. T. Peterson, W. E. Krupp and F. A. Schmidt, J. Less-Common Metals 7, 288 (1964).
4. D. T. Peterson and D. G. Westlake, Trans. TMS-AIME 215, 444 (1959).
5. D. T. Peterson and J. Rexer, J. Less-Common Metals 4, 92 (1962).
6. M. W. Mallett and I. E. Campell, J. Am. Chem. Soc. 73, 4850 (1951).
7. R. W. Nottorf, Ph.D. thesis, Iowa State College, 1945 (unpublished).

SECTION III. ISOPIESTIC SOLUBILITY OF HYDROGEN IN VANADIUM
ALLOYS AT LOW TEMPERATURES

INTRODUCTION

Hydrogen behavior in the Group VB metals, V, Nb and Ta, has been the subject of many investigations. In part, this is because of the high solubility of hydrogen in these metals and the rapid rate of diffusion. Substitutional alloys of these metals have been suspected of showing hydrogen trapping. The hydrogen pressure-composition isotherm studies on such alloys that have been reported (1-8) have, with one exception, been above 500 K where the effects of hydrogen trapping are reduced due to the increased thermal energy. Measurements of the hydrogen equilibrium pressure have been made above 500 K because of the low equilibrium pressure at lower temperatures and the inability to establish equilibrium with the gas phase through a surface barrier. Hydrogen has been reported to be trapped by dislocations in iron (9) and by interstitial (10-12) or by substitutional solutes (13,14) in Group VB metals to explain the results of diffusion, resistivity, internal friction or NMR measurements. However, no hydrogen pressure-composition isotherms below 500 K have been reported in metal-hydrogen systems suspected of hydrogen trapping. Pressure-composition isotherms at lower temperatures should exhibit the effects of hydrogen trapping directly and provide information on whether any thermodynamic corrections are needed for transport phenomenon. Qualitatively, if a deep trap model is valid, the hydrogen activity should be low at low hydrogen concentrations until the traps, interstitial or substitutional atoms, are saturated with hydrogen. At this point, the activity of hydrogen should increase much more rapidly with concentration. This investigation was initiated to study the equilibria

and thermodynamics of hydrogen dissolution in alloy systems suspected of hydrogen trapping. The isopiestic, equal hydrogen pressure, solubility of hydrogen was measured from 223 to 473 K in vanadium-niobium, vanadium-chromium and vanadium-titanium alloys over a wide range of hydrogen concentrations.

The technique used a cluster specimen consisting of short rods of several of the alloys plus a rod of pure vanadium all welded together at one end. This cluster specimen was charged with a fixed amount of hydrogen in a Sieverts' apparatus and then held at the chosen temperature until the hydrogen had distributed so as to have an equal activity in all the alloy rods. The composite specimen was sectioned to provide several samples from each rod that were analyzed for hydrogen. Boes and Züchner (15) and Griffiths et al. (16) have reported that hydrogen in pure vanadium follows Sieverts' law from 293 to 463 K up to hydrogen to metal atom ratios of 0.03 giving the Sieverts' law constant as a function of temperature. At equilibrium, the activity of hydrogen was equal in each alloy rod and, from the hydrogen content measured within the Sieverts' law range in pure vanadium, the hydrogen equilibrium vapor pressure of the alloys was ascertained. Thus, hydrogen pressure-composition isotherms for these alloys can be measured even at temperatures at which equilibrium with the gas phase could not be established.

These vanadium alloys are good candidates for this study of alloy effects on solubility as they are either continuous solid solutions or have a wide range of solid solubility in the temperature and concentration ranges of interest. Thus, one is not restricted to small solute

concentrations as is the case of trapping by interstitial atoms in solid solution. Also, the selection of alloying elements from three adjacent columns of the periodic chart provided a variation in the electron to atom ratio. Titanium is a metal with a large affinity for hydrogen, chromium has a very low affinity and niobium is intermediate between these two. A concurrent investigation by Peterson and Herro (17) has shown that the diffusivity of hydrogen is moderately high in these alloys around ambient temperatures. The terminal solubilities of hydrogen for these alloys are also high (13,18,19). Thus, experiments based on an isopiestic technique could be performed in reasonable times and over a wide range of hydrogen concentrations.

EXPERIMENTAL

Short rods of each metal or alloy, 20 x 1.5 x 1.5 mm, were electro-polished and weighed. The metal and alloy rods were welded together at one end into cluster in an argon-filled drybox with each cluster containing a rod of the reference pure vanadium. A known number of moles of hydrogen gas was introduced to each cluster in a conventional Sieverts'-type apparatus at 1075 K. Very pure hydrogen gas for charging was obtained by the thermal decomposition of uranium hydride. After furnace cooling, each cluster was placed in silicone oil baths at 297, 373 and 473 \pm 1 K or into a chilled alcohol bath at 223 \pm 3 K until equilibrium was attained. Equilibrium was verified by the absence of hydrogen concentration gradients in each rod. The clusters were cleaned, the welded end removed, each metal rod was divided into four samples and the hydrogen content determined by hot vacuum extraction. The final hydrogen content of each metal specimen was the average of at least three analyses. The Sieverts' constants reported by Boes and Züchner (15) and Griffiths et al. (16) were treated by a linear least-squares treatment and yield the expression

$$\log K_S (\text{Pa}^{1/2}) = 5.766 - 1734/T \quad . \quad (1)$$

The value of the Sieverts' constant at a given temperature obtained from Eq. (1) was multiplied by the hydrogen concentration measured in the reference pure vanadium to obtain the activity of hydrogen for a given cluster specimen.

The vanadium alloys were prepared by arc melting on a copper hearth under argon. Weight losses in arc melting were negligible so that alloy

compositions were determined from the initial weights and were confirmed by chemical analyses. Thus, compositions of 10, 25, 50, 75 and 90 atomic percent niobium, 1, 5, 10, 20, and 30 atomic percent titanium and 10, 20 and 30 atomic percent chromium were prepared. All the above alloys are single phase, bcc alloys at room temperature. Metallographic and X-ray analyses confirmed that each alloy was a bcc single phase and had the lattice parameters listed in Table 1 which were, in each case, a linear function of solute concentration. The values for pure vanadium and niobium agree well with the values for similar purity vanadium and niobium reported by Carlson et al. (20) and Pfeiffer and Peisl (21), respectively. The alloy buttons were rolled to 1.5 mm thick sheet from which the specimens were cut. The specimens of each alloy were given an appropriate recrystallization anneal at pressures less than 10^{-4} Pa. Carbon, nitrogen and oxygen concentrations in the annealed specimens are listed in Table 2. Analyses of three specimens after charging with hydrogen showed that gas-phase charging did not alter the interstitial solute concentration significantly. Carbon was by combustion analysis; nitrogen and oxygen by vacuum fusion analysis. The amounts of other impurities were measured by a spark source mass spectrograph. The pure vanadium had a total substitutional impurity concentration of 0.03 atomic percent and the other pure metals used in alloying had total substitutional impurity concentrations ranging from 0.04 to 0.06 atomic percent.

The mass balance of hydrogen was confirmed by comparing the known number of moles of hydrogen added to a given cluster and the total moles

Table 1. Lattice parameters of
vanadium alloys at 297 K

Alloy (atomic percent)	$a_0 \pm 0.005$ (Å)
0 Nb	3.029
10 Nb	3.065
25 Nb	3.106
50 Nb	3.177
75 Nb	3.242
90 Nb	3.278
100 Nb	3.301
10 Cr	3.012
20 Cr	2.997
30 Cr	2.981
1 Ti	3.030
5 Ti	3.040
10 Ti	3.055
20 Ti	3.080
30 Ti	3.103

Table 2. Carbon, nitrogen, and oxygen concentrations
in annealed vanadium alloys

Alloy	<u>Concentrations, atomic percent</u>		Oxygen
	Carbon	Nitrogen	
0 Nb	0.004	<0.001	0.016
25 Nb	0.053	0.013	0.036
50 Nb	0.035	0.021	0.042
75 Nb	0.030	0.038	0.062
100 Nb	0.025	0.001	0.008
10 Cr	0.027	<0.001	0.023
20 Cr	0.013	<0.001	0.016
5 Ti	0.013	0.001	0.032
10 Ti	0.017	0.002	0.038
20 Ti	0.019	0.004	0.044
30 Ti	0.011	0.007	0.024

of hydrogen measured by hot vacuum extraction. The latter was obtained by summing the moles of hydrogen in each alloy in a cluster, taken as the average hydrogen to metal atom ratio times the initial number of moles of that alloy. These two values did not differ by more than 5 percent, which was within the combined experimental uncertainties of gas-phase charging and hot vacuum extraction, in ten separate cluster specimens. To determine whether the metal specimens gained or lost hydrogen when exposed to hot silicone oil, vanadium metal was charged with hydrogen and exposed to 473 K silicone oil for 7 days with no change in the hydrogen concentration.

RESULTS

Hydrogen pressure-composition measurements in the vanadium-hydrogen and niobium-hydrogen systems were made from 700 to 1120 K by a conventional Sieverts'-type apparatus in order to verify the literature data and extend the temperature range studied. The plots of $P_{H_2}^{1/2}$ versus H/M showed that hydrogen followed Sieverts' law in the pure vanadium and niobium systems up to hydrogen to metal atom ratios of 0.05 and 0.04, respectively. The Sieverts' constants which were obtained from the above study are shown in Fig. 1 versus reciprocal temperature with the values that have been reported by Boes and Züchner (15) and Griffiths et al. (16) for pure vanadium and by Pryde and Titcomb (22) and Boes and Züchner (15) for pure niobium. The agreement shown for vanadium in Fig. 1 between the present investigation and the other two investigators is extremely good. The significance of this is augmented by the fact that two experimental techniques were employed. Direct hydrogen pressure measurements were used in the present work and Griffiths et al. (16), while an electrochemical technique was used by Boes and Züchner (15). Thus, the accuracy of the hydrogen equilibrium pressures in the vanadium system, to which all the data in the present isopiestic study are referred, is quite good. The pressure-composition data reported by Veleckis and Edwards (23) and by Kleppa, Dantzer and Melnichak (24) showed deviations from Sieverts' law above 10 atomic percent hydrogen but the data below 5 atomic percent at low temperatures were too scanty and scattered to establish the behavior below that concentration with certainty. The variation that was observed in $\overline{\Delta H}_H$ with concentration

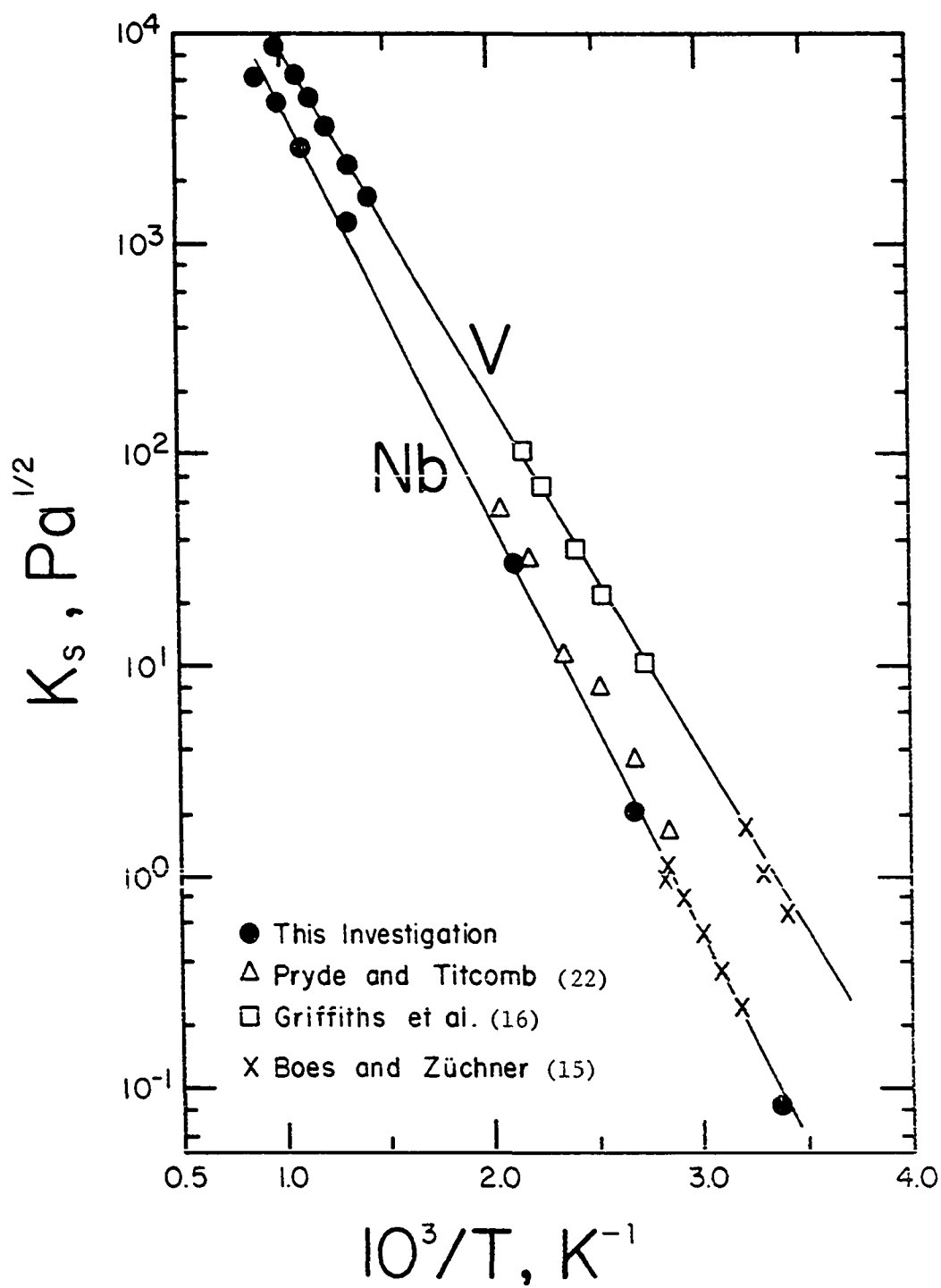


Figure 1. $\log K_s$ versus reciprocal temperature for pure vanadium and niobium

would predict a departure from Sieverts' law even at their higher temperatures unless there were a compensating change in $\overline{\Delta S}_H$ with concentration. The consensus is that Sieverts' law is followed in the vanadium-hydrogen system at concentrations below 0.05 H/V ratio and the concentration range in our reference vanadium sample was always less than 0.03 H/V. Our niobium results shown in Fig. 1 were obtained by direct hydrogen pressure measurements above 600 K and by the isopiestic technique below 600 K. These two techniques showed very good agreement between themselves. The data reported by Boes and Züchner (15) for pure niobium also agreed very well with the present investigation; Pryde and Titcomb (22) reported larger values of the Sieverts' constant at a given temperature but the temperature dependence was the same. The larger values of the Sieverts' constants could have been due to a different impurity concentration in the niobium metal used by Pryde and Titcomb (22) but this cannot be checked because they did not report the purity of their niobium specimens.

Sieverts' law is followed in the vanadium-niobium alloys studied up to surprisingly high hydrogen to metal atom ratios of 0.20 in some of the alloys. This Sieverts' law behavior and also the effects of additions of niobium to vanadium on the isopiestic solubility of hydrogen are shown in plots of $P_{H_2}^{1/2}$ versus H/M for the vanadium-niobium alloys in Figs. 2-4. The pressure-composition relationship for hydrogen in pure vanadium obtained from Eq. (1) is shown in each figure for comparison. Pure niobium and the high niobium alloys showed departures from a linear behavior at higher hydrogen concentrations but followed Sieverts'

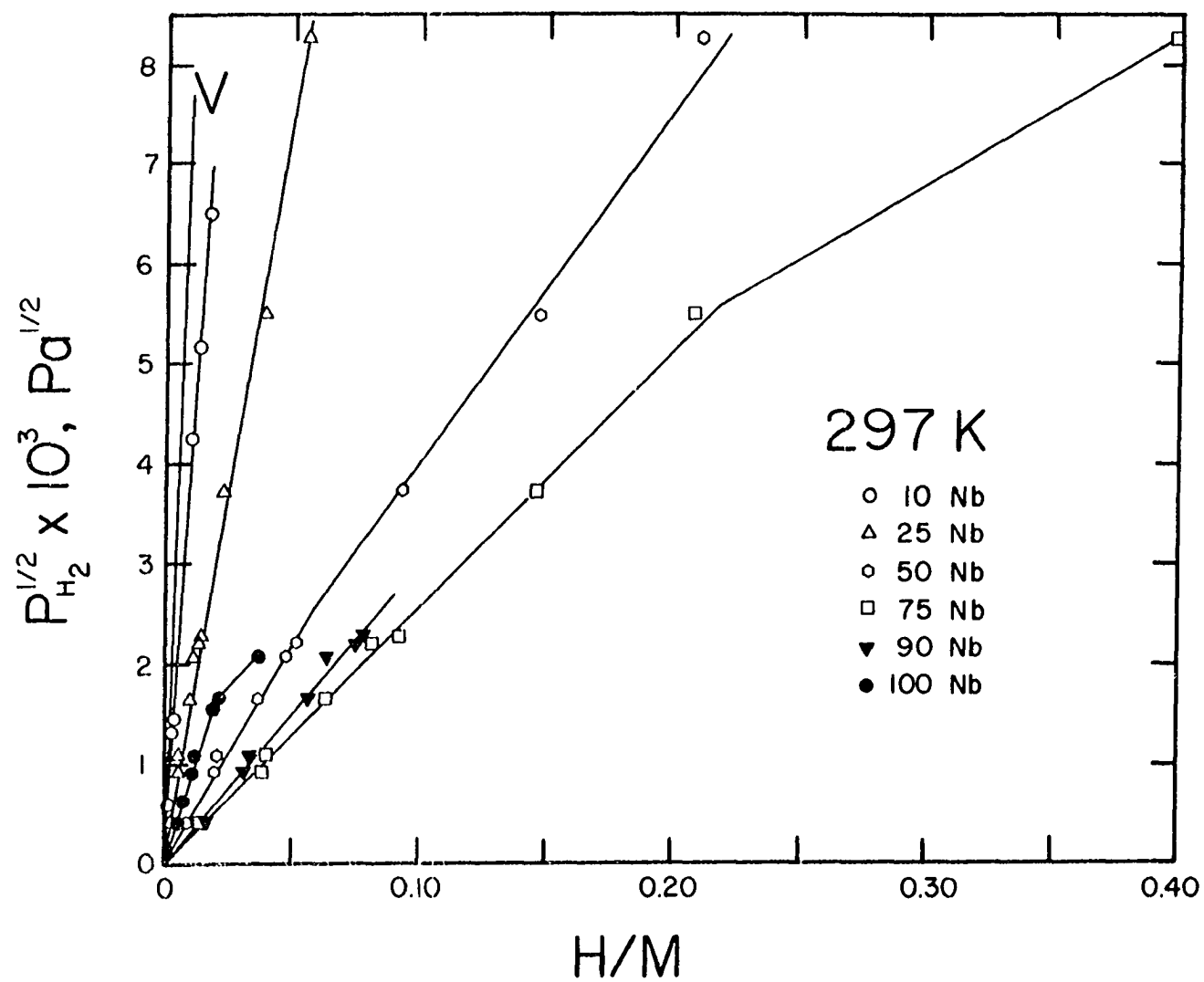


Figure 2. $P_{H_2}^{1/2}$ versus atom ratio, H/M , in vanadium-niobium alloys at 297 K

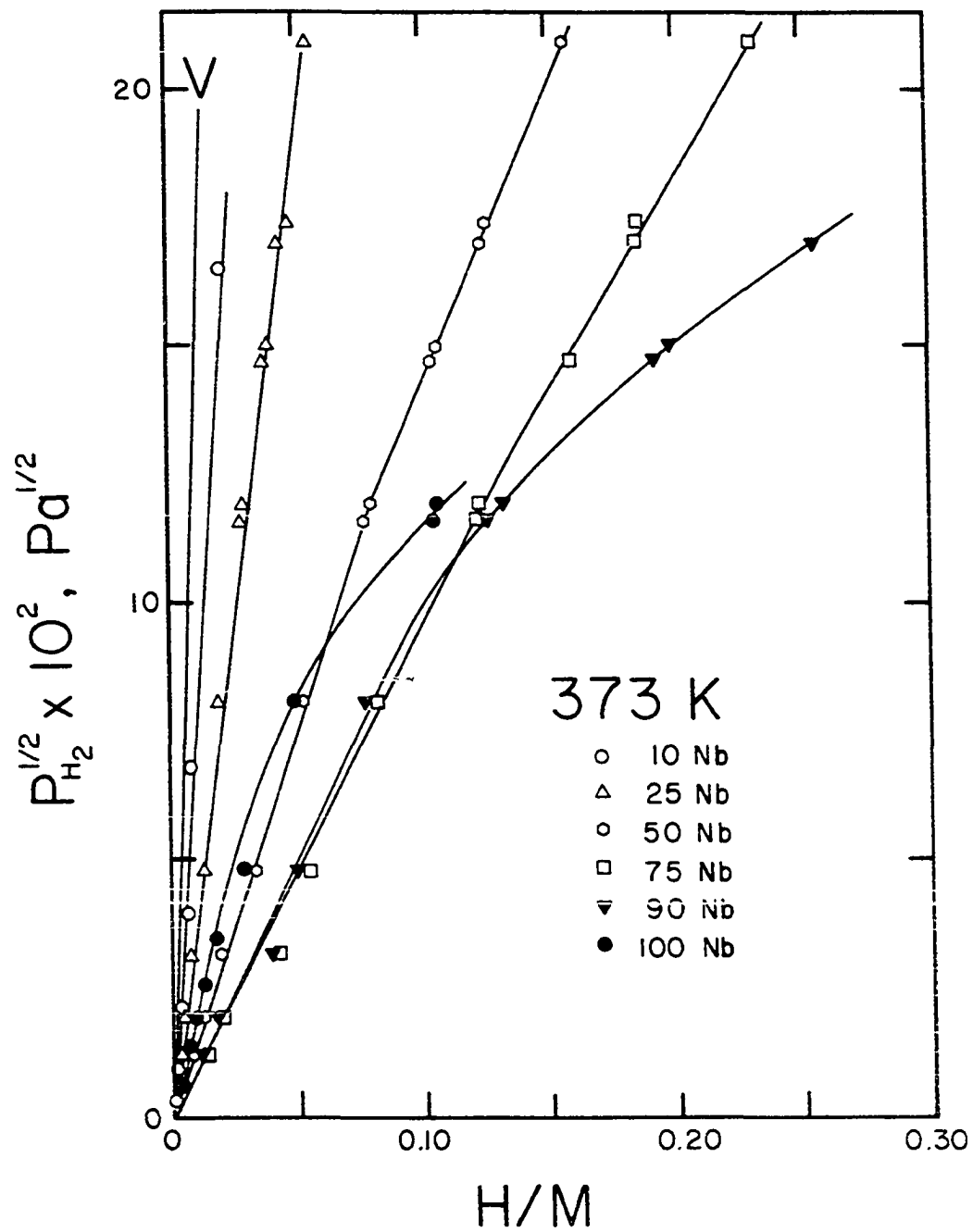


Figure 3. $P_{H_2}^{1/2}$ versus atom ratio, H/M , in vanadium-niobium alloys at 373 K

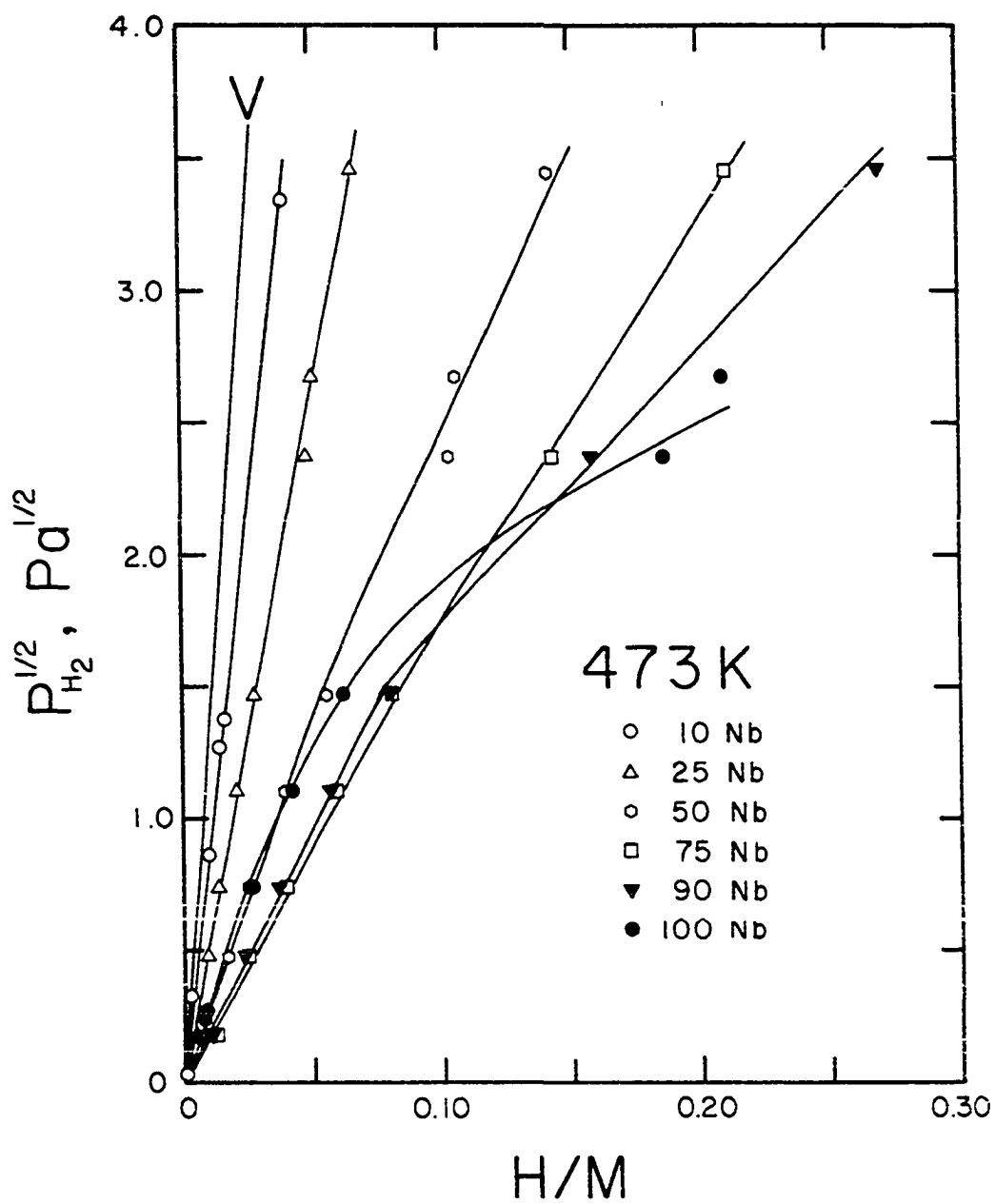


Figure 4. $P_{H_2}^{1/2}$ versus atom ratio, H/M , in vanadium-niobium alloys at 473 K

law at lower concentrations. The plots shown in Figs. 2-4 are all within the terminal solid-solution range of hydrogen which was much larger in these alloys than in the pure metals. All the specimens equilibrated at 297 K were examined by optical metallography to detect hydride phase precipitation. In any instance, when hydride phase was observed, the concentrations were very much higher than expected and were not used. From a linear least-squares treatment of the data in Figs. 2-4 within the Sieverts' law range, the Sieverts' constants were obtained and are listed in Table 3 and plotted versus reciprocal temperature in Fig. 9. The values for pure vanadium obtained from Eq. (1) and for pure niobium are shown for comparison. The standard deviations of the Sieverts' constants shown in Fig. 9 were approximately the size of the plotted points. The enthalpies of solution for hydrogen in these alloys for the reaction



were obtained from the slopes and the standard entropies of solution for hydrogen from the intercepts of Fig. 9 by a linear least-squares treatment and are listed in Table 4. The standard entropy of solution was referred to a standard state of hydrogen at one atmosphere pressure and a hydrogen concentration of 1.0 H/M. The uncertainty of each enthalpy of solution listed in Table 4 is either the standard deviation from the linear least-squares fit or 1.5 kJ/mol H, whichever is the greater. The latter value is an estimated precision based on the total experimental uncertainties and Eq. (1). The uncertainty of each standard entropy of

Table 3. Sieverts' constants for hydrogen in vanadium alloys

Alloy (atomic percent)	$K_s, \text{Pa}^{1/2}$			
	223K	297 K	373 K	473 K
0 Nb ^a	9.77×10^{-3}	0.846	13.1	126
10 Nb	---	0.394	7.41	84.8
25 Nb	---	0.145	3.65	50.7
50 Nb	---	0.0421	1.47	26.9
75 Nb	---	0.0261	0.959	18.4
90 Nb	---	0.0301	1.02	18.5
100 Nb	---	0.0817	2.00	31.7
10 Cr	---	2.62	34.4	299
20 Cr	---	9.07	107	754
30 Cr	---	41.2	409	2230
1 Ti	0.0126	0.604	10.5	105
5 Ti	1.51×10^{-3}	0.113	3.12	48.1
10 Ti	2.55×10^{-4}	2.55×10^{-2}	1.01	19.9
20 Ti	3.31×10^{-5}	3.99×10^{-3}	0.158	4.79
30 Ti	7.88×10^{-6}	1.46×10^{-3}	0.0598	2.16

^aData obtained from Eq. (1).

Table 4. Enthalpies and standard entropies of solution of hydrogen in vanadium alloys

Alloy (atomic percent)	$\overline{\Delta H_H}$ (kJ/mol H)	$\overline{\Delta S_H}$ (J/K-mol H)
0 Nb ^a	-33.2 ± 1.5	-62.5 ± 3.8
0 Nb ^b	-32.2 ± 1.5	-59.7 ± 3.8
10 Nb	-35.7 ± 1.5	-64.4 ± 3.8
25 Nb	-38.9 ± 1.5	-67.0 ± 3.8
50 Nb	-42.9 ± 1.5	-70.2 ± 3.8
75 Nb	-43.5 ± 1.5	-68.4 ± 3.8
90 Nb	-42.7 ± 1.5	-66.4 ± 3.8
100 Nb ^c	-39.4 ± 1.5	-64.3 ± 3.8
100 Nb ^d	-38.1 ± 1.5	-60.3 ± 3.8
10 Cr	-31.4 ± 1.5	-65.9 ± 3.8
20 Cr	-29.4 ± 1.5	-69.4 ± 3.8
30 Cr	-26.6 ± 1.5	-72.8 ± 3.8
1 Ti	-31.7 ± 1.5	-56.7 ± 3.8
5 Ti	-36.4 ± 1.5	-59.5 ± 3.8
10 Ti	-39.6 ± 1.9	-58.6 ± 5.6
20 Ti	-41.4 ± 2.3	-49.5 ± 6.7
30 Ti	-43.5 ± 2.1	-47.5 ± 6.3

^aData obtained from Eq. (1).

^bCombined data of Eq. (1) and high temperature study of this investigation.

^cData obtained from the isopiestic study.

^dCombined data from the isopiestic and high temperature studies of this investigation.

solution listed in Table 4 represents an estimated precision based on the experimental uncertainty in the slope. The increased isopiestic solubility of hydrogen in the vanadium-niobium alloys appears to be due to an increase in the enthalpy, which reaches a maximum at 75 atomic percent niobium, modified by an increase in the entropy term that has the effect of reducing the solubility. The enthalpy of solution of hydrogen in niobium is greater than in vanadium but there is no clear explanation for the still higher values in the alloys. The changes in the enthalpy of the solution reaction are not large and the values have a larger uncertainty but they do change smoothly and continuously with alloy composition.

The alloying of chromium with vanadium strongly decreased the isopiestic solubility of hydrogen as shown by the pressure-composition data shown in Figs. 5 and 6. These figures also have data for titanium alloys and have different $P^{1/2}$ scales on each side so that all of the experimental data could be presented without an excessive number of figures. However, the result is that the figures are quite full of data and require careful reading. The data for the 30 atomic percent chromium alloy were left out except at 473 K because the values were so low that they could not be plotted on the chosen concentration scale. The solubility of hydrogen in the 20 atomic percent chromium alloy is only about 10 percent of the value at the same pressure in vanadium. The concentrations were nicely proportional to $P_{H_2}^{1/2}$ although low concentrations were difficult to determine without some loss in precision and accuracy. The lower solubility was the result of smaller enthalpies of

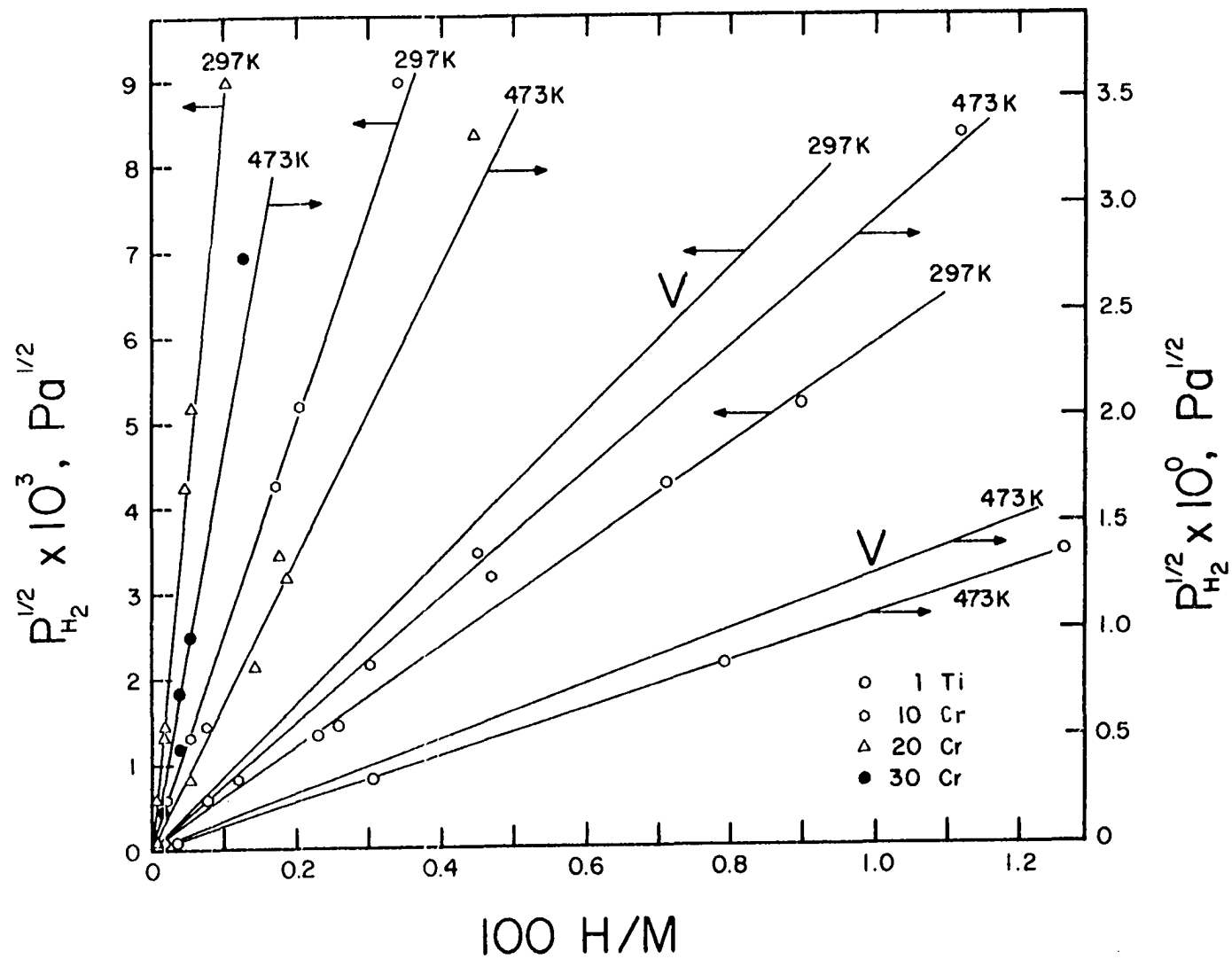


Figure 5. $P_{H_2}^{1/2}$ versus atom ratio, H/M , in vanadium alloys containing Cr and Ti at 297 K and 473 K

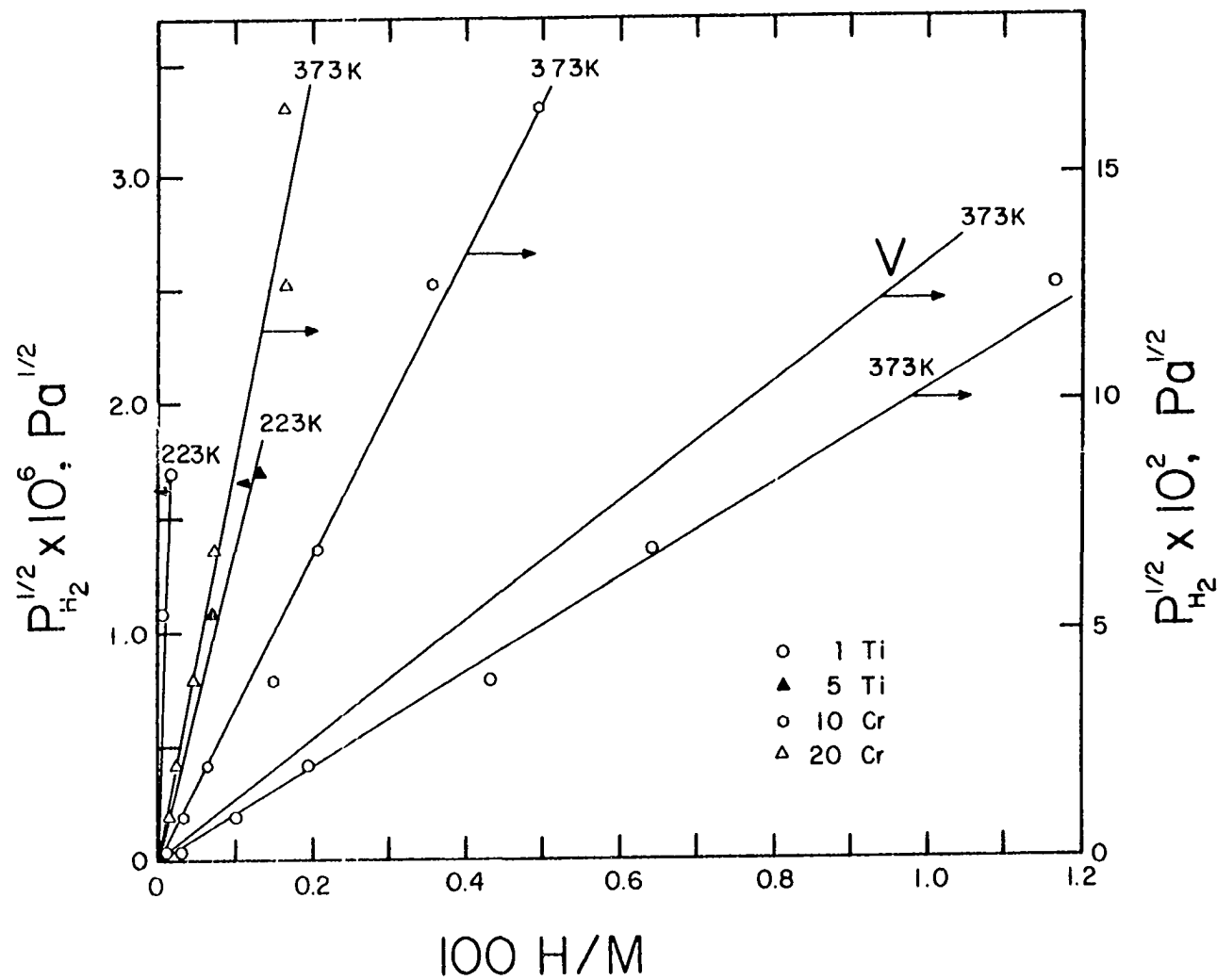


Figure 6. $P_{H_2}^{1/2}$ versus atom ratio, H/M , in vanadium alloys containing Cr and Ti at 223 K and 373 K

solution and increased entropies which both worked together to produce larger Sieverts' constants. The Sieverts' constants are plotted against reciprocal temperature in Fig. 9 and wide separation of the lines for pure vanadium and the three chromium alloys is obvious. The change in $\overline{\Delta H}_H$ at 30 atomic percent chromium was only 6.6 kJ/mol H but this is large enough to produce quite large composition changes. The present values of the enthalpies of solution of hydrogen for the vanadium-chromium alloys listed in Table 4 are in good agreement with the values reported by Lynch, Reilly and Millot (2) which were measured in the range 473 to 723 K and up to 20 atomic percent chromium.

The large increase in the isopiestic hydrogen solubility with increasing titanium concentration, at a given temperature and pressure, appears to arise from two simultaneous effects. These are the decrease in the value of the entropy of solution of hydrogen and the increase in the enthalpy of solution of hydrogen, with the effects being larger at higher titanium concentrations. The concentration of hydrogen in a 30 atomic percent titanium alloy at room temperature was more than 400 times as high as in pure vanadium at the same pressure. In addition to the increased isopiestic solubility, there was a large increase in the terminal solid solubility and the 30 atomic percent titanium alloy did not show precipitation of a hydride phase at room temperature even at 0.6 H/M concentrations. The hydrogen pressure-composition data for the titanium alloys are shown in Figs. 5-8. The extent of the Sieverts' law concentration range was also increased in the titanium alloys and in many of the alloys extended as far as 0.4 or 0.5 H/M. The two highest

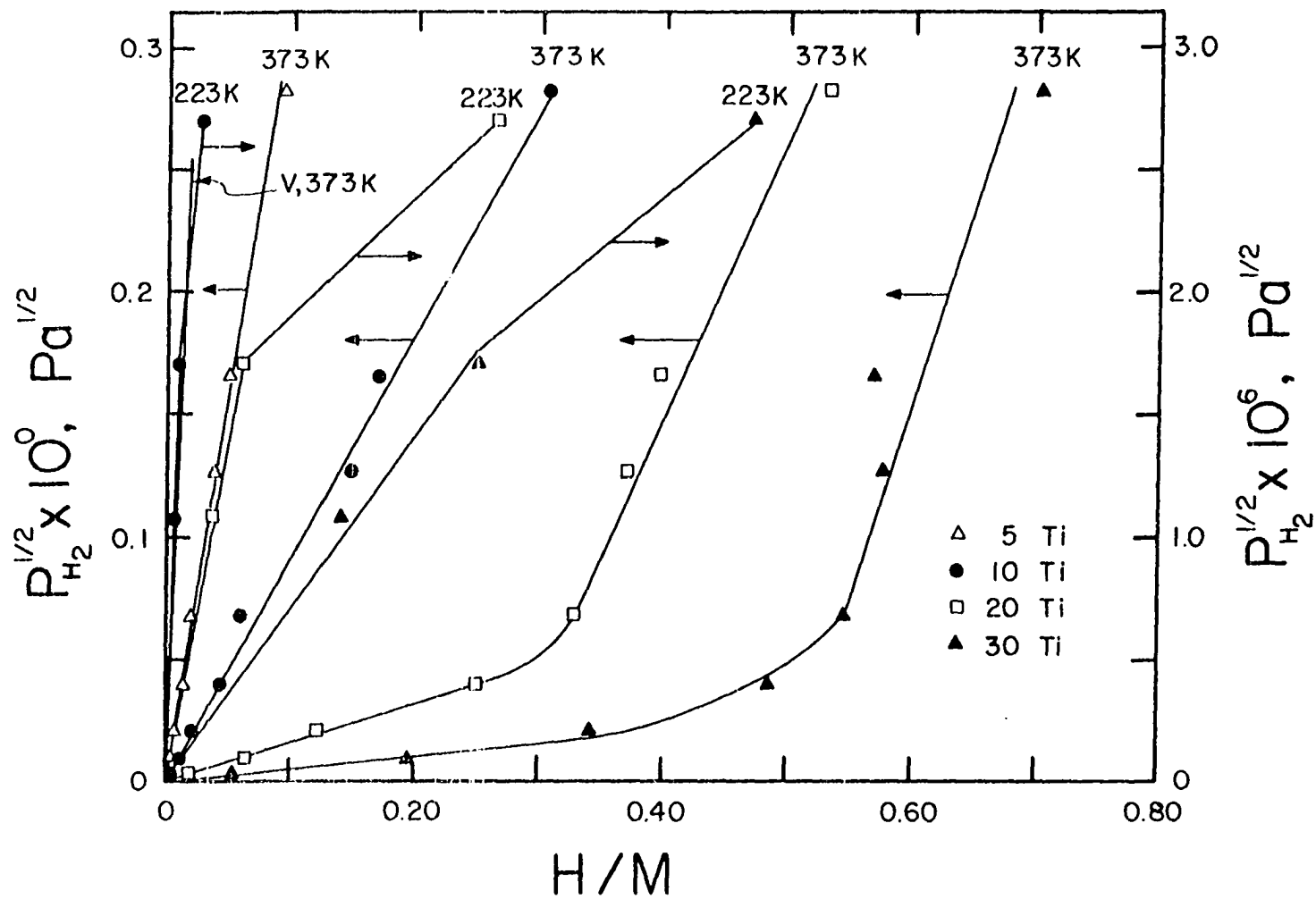


Figure 7. $P_{H_2}^{1/2}$ versus atom ratio, H/M , in vanadium-titanium alloys at 223 K and 373 K

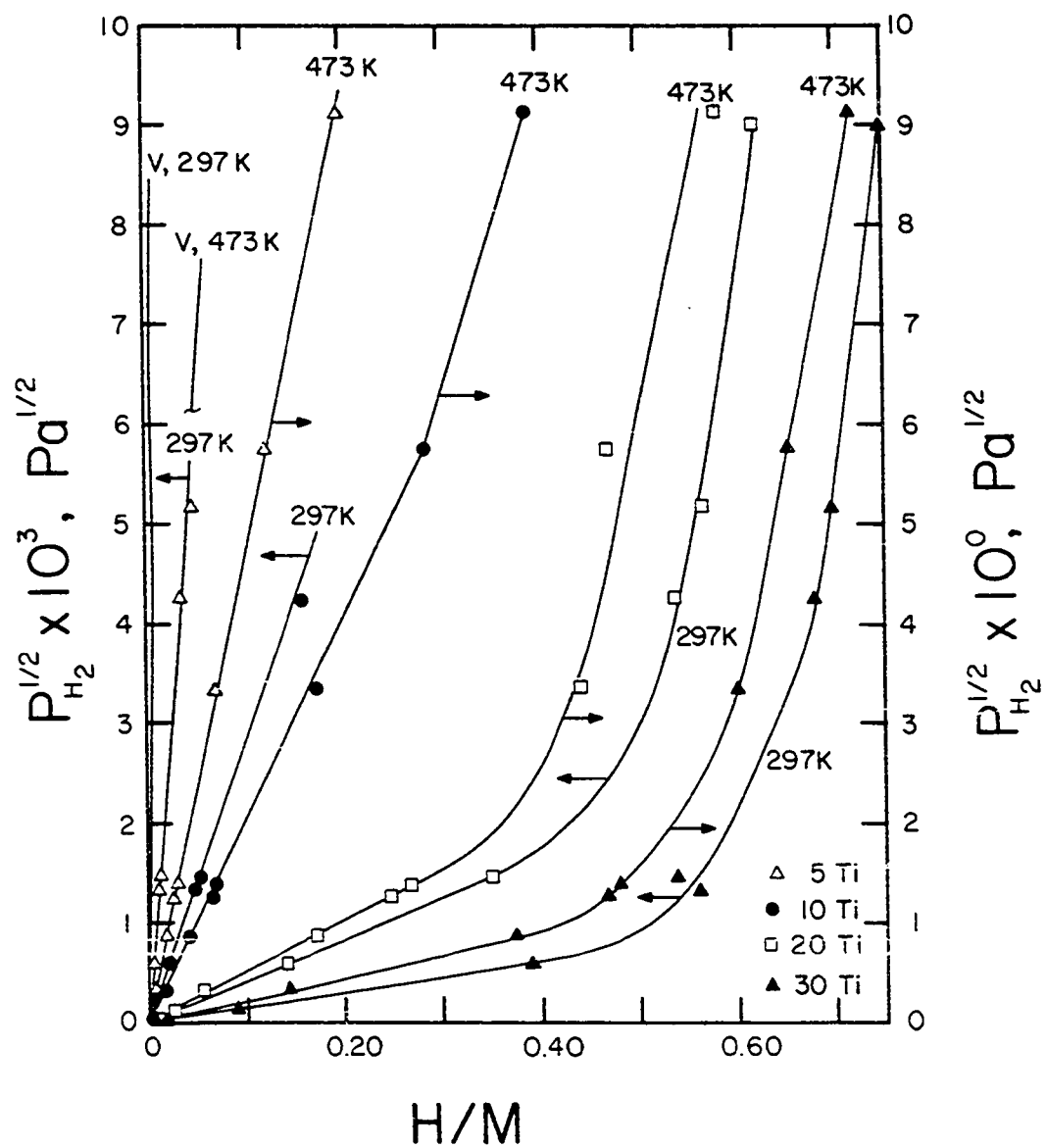


Figure 8. $P_{H_2}^{1/2}$ versus atom ratio, H/M , in vanadium-titanium alloys at 297 K and 473 K

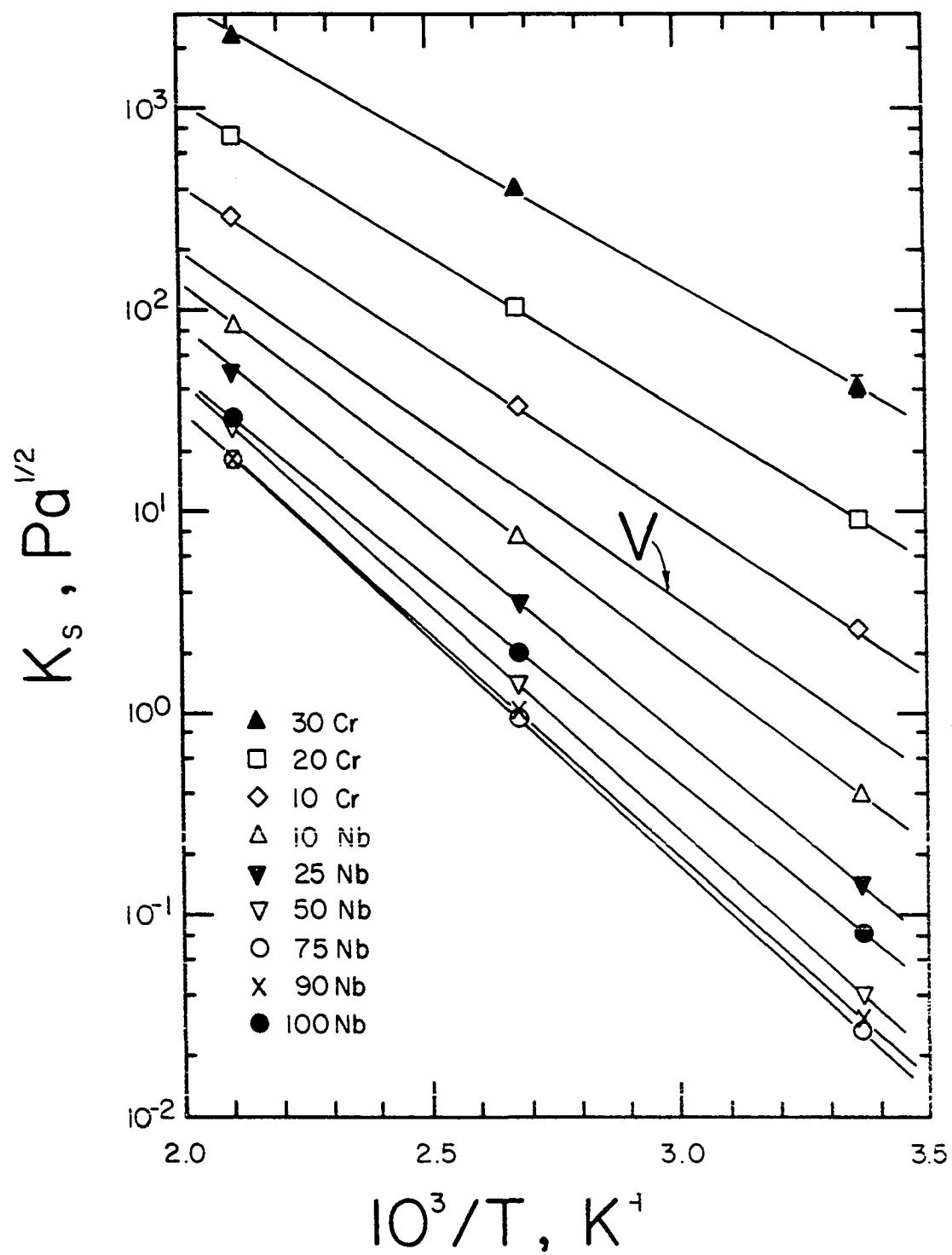


Figure 9. $\log K_s$ versus reciprocal temperature for vanadium alloys containing chromium and niobium

titanium alloys showed positive upward deviation of $P_{H_2}^{1/2}$ above 0.4 H/M. The shape of these curves is the shape that would be expected if hydrogen were being trapped and held very tenaciously until the traps were filled. However, at 30 atomic percent titanium, the concept of isolated traps is rather strained because the titanium atoms are really quite close together and each tetrahedral site probably has at least one titanium neighbor. The upward deviation could also be due to hydrogen-hydrogen repulsion as the hydrogen atoms are crowded too close together. The titanium alloys were studied at 223 K which significantly extended the temperature range. These measurements were slow because of the slower diffusion of hydrogen and also less precise because the allowable concentration of hydrogen in the pure vanadium was low. The specimen at 223 K with the highest hydrogen concentration showed deviation from Sieverts' law in the negative direction which was tentatively ascribed to precipitation of a small amount of hydride phase. The Sieverts' constants from the low concentration, linear ranges are tabulated in Table 3 and are shown as function of reciprocal temperature in Fig. 10. Error bars are shown in Fig. 10 whenever the standard deviation of the least-squares analysis was larger than the size of the plotted points. The enthalpy and entropy values for the solution reaction deduced from the data are given in Table 4 and show the increased heat of solution and decreased entropy that produce the large increase in the solubility of hydrogen.

An alternative means of analyzing the present isopiestic results is the phenomenological model of interaction parameters or coefficients

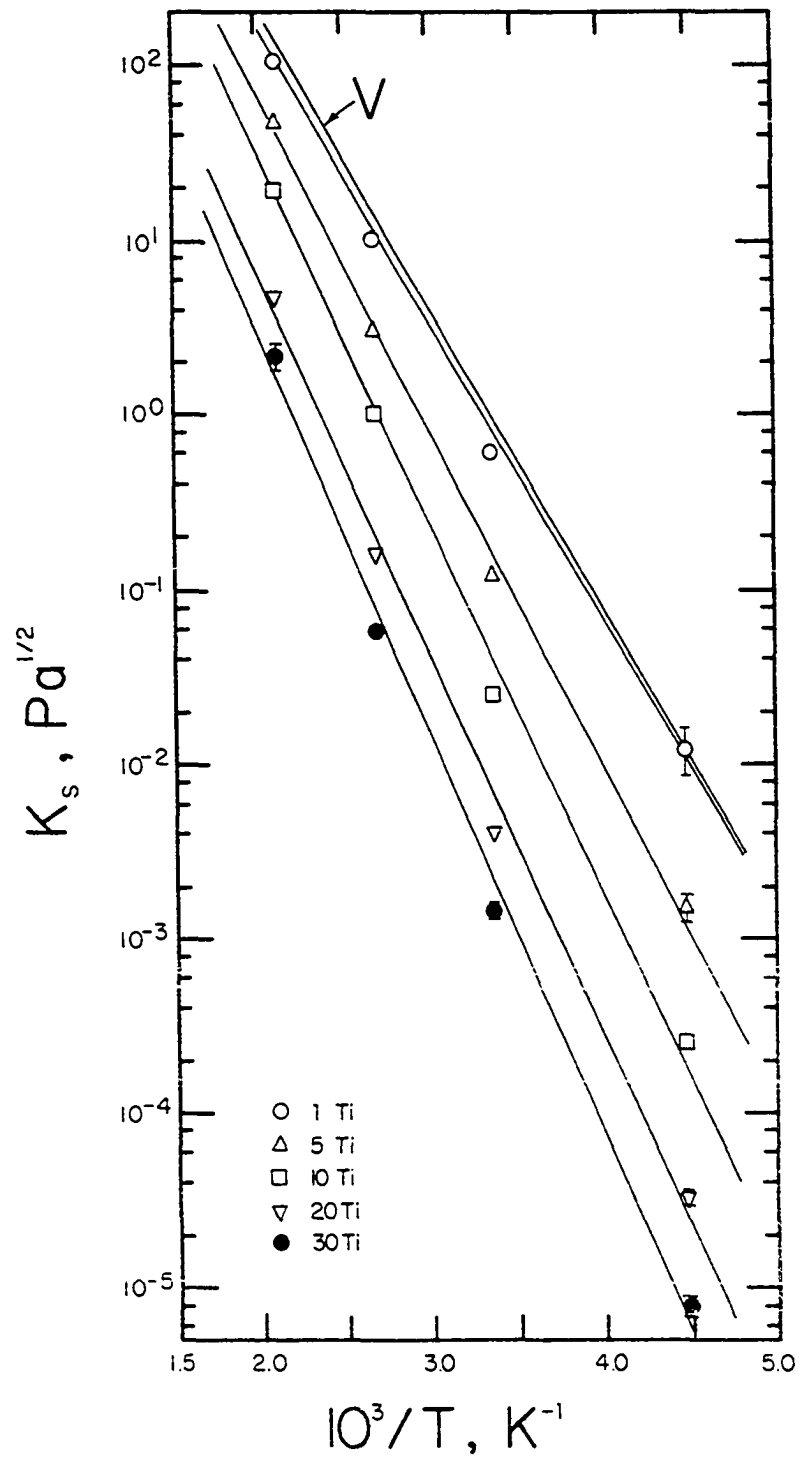


Figure 10. $\log K_s$ versus reciprocal temperature for vanadium-titanium alloys

devised by Wagner (25). The interaction coefficients are a means to quantify the effects of solutes on the activity coefficient of the solute of interest, in this case hydrogen. Thus, for a given vanadium-metal system containing hydrogen, the interaction coefficient between hydrogen and the metal solute, M, in solution is

$$\epsilon_H^M = \left. \frac{\partial \ln \gamma_H}{\partial X_M} \right|_{X_M, X_H \rightarrow 0} \quad (3)$$

where γ_H is the activity coefficient of hydrogen for the alloy with metal solute concentration, X_M , and X_H is the hydrogen concentration. The activity coefficient of hydrogen can be replaced by the Sieverts' constant when within the Sieverts' law range. Values of ϵ_H^M were obtained for each alloy system, at a given temperature, from the slope of plots of $\ln K_S$ versus X_M in the linear range at lower concentration and are listed in Table 5. The plots were linear to 25 atomic percent niobium, 20 atomic percent chromium and 10 atomic percent titanium.

Table 5. Hydrogen-solute interaction coefficients for vanadium alloys

Alloy System	ϵ_H^M , (atomic percent) ⁻¹			
	223 K	297 K	373 K	473 K
V-Nb	---	-0.0721	-0.0524	-0.0367
V-Cr	---	+0.114	+0.0967	+0.0875
V-Ti	-0.365	-0.358	-0.267	-0.185

DISCUSSION

One of the most striking features of the results obtained in the present investigation is the wide range of concentrations over which Sieverts' law behavior by hydrogen is found in the vanadium alloys studied. When hydrogen follows Sieverts' law, there is a constant metal matrix-hydrogen interaction and no hydrogen-hydrogen interactions. A constant interaction over a wide range of hydrogen concentration is a bulk or "global" phenomenon and would not be associated with a local phenomenon such as trapping of hydrogen. If the increases in hydrogen solubility found in the vanadium-niobium and vanadium-titanium systems were due to localized deep trapping by the metal solute atoms, there would be one value for the interaction for the hydrogen going into solution in the trap sites and a different interaction for hydrogen dissolved after the traps were filled. No such change in K_S or in the $\overline{\Delta H}_H$ or $\overline{\Delta S}_H$ of solution with hydrogen was found at concentrations that could be reasonably associated with the metal solute concentration. A consequence of hydrogen following Sieverts' law over a wide range of hydrogen concentrations is that no thermodynamic corrections are needed for hydrogen transport phenomenon such as diffusion and thermotransport within this range. This follows from the fact that the activity coefficient of hydrogen is independent of hydrogen concentration within this range.

In the alloy systems studied, the enthalpy of solution of hydrogen, at a given alloy concentration, becomes progressively smaller as one proceeds from titanium to niobium and to chromium. As mentioned earlier, this seems reasonable if one considers the relative affinity of hydrogen

for titanium, niobium and chromium. Although the electron to atom ratio increases as one progresses from titanium to niobium and to chromium, it would appear that electrons are more readily available for bonding in titanium, less so in niobium and hardly at all in chromium. This is also reflected by the stoichiometry of the stable hydrides formed by these metals: TiH_2 , NbH_1 and CrH_0 . An atomistic model for the effects of electronic interactions on the value of the enthalpy of solution, however, cannot be formulated quantitatively at this time. The decrease in the value of the entropy of solution with increasing titanium concentration and the increase in value with niobium and chromium concentration are due to the changes in the value of the entropy of hydrogen in solution. It is not possible at this point to partition the value of the entropy of hydrogen in solution and explain these trends for these alloy systems. In part, this is because this entropy is a small value which is the difference of two much larger values, the entropy of solution of hydrogen, $\overline{\Delta S}_\text{H}$, and the entropy of the gas phase, $\frac{1}{2} S_{\text{H}_2}^0$. Also, several effects contribute to the total value of the entropy in solution. These are lattice vibration, electronic interaction, configurational and lattice dilation effects. Many of the fundamental measurements of the individual terms that contribute to this entropy have not been made at present.

SUMMARY

The hydrogen pressure relationship to composition for vanadium alloys containing either niobium, chromium or titanium were measured in the solid-solution range from 223 to 473 K. Hydrogen followed Sieverts' law over a wide range of hydrogen concentrations in all the vanadium alloys studied. The values of the enthalpy and entropy of solution of hydrogen for each alloy system vary smoothly and continuously and show moderate changes in value relative to pure vanadium. The isopiestic solubility of hydrogen is dramatically enhanced by the additions of titanium, moderately increased by the additions of niobium and significantly decreased by the additions of chromium. The Sieverts' law behavior over wide hydrogen concentration ranges shows that hydrogen is not locally trapped by substitutional solutes in these vanadium alloys. The data indicate that a bulk interaction phenomenon occurs and not a local phenomenon such as hydrogen trapping. The results can be analyzed by means of classical thermodynamics or by the phenomenological model of interaction parameters devised by Wagner (25) but an atomistic or electronic interpretation is not possible at this time.

REFERENCES

1. M. A. Pick and D. O. Welch, Z. für Phys. Chem. 114, 37 (1979).
2. J. F. Lynch, J. J. Reilly and F. Millot, J. Phys. Chem. Solids 39, 883 (1978).
3. R. Burch and N. B. Francis, J. Less-Common Metals 49, 371 (1976).
4. A. Inoue, M. Katsura and T. Sano, J. Less-Common Metals 55, 9 (1977).
5. D. G. Westlake and J. F. Miller, J. Less-Common Metals 65, 139 (1979).
6. J. F. Lynch, J. Phys. Chem. Solids 42, 411 (1981).
7. T. Eguchi and S. Morozumi, J. Jpn. Inst. Met. 38, 1025 (1974).
8. H. Katsuta and Rex B. McLellan, J. Phys. Chem. Solids 40, 845 (1979).
9. A. J. Kumnick and H. H. Johnson, Acta Met. 28, 33 (1980).
10. C. Baker and H. K. Birnbaum, Acta Met. 21, 865 (1973).
11. H. Y. Chang and C. A. Wert, Acta Met. 21, 1233 (1973).
12. G. Pfeiffer and H. Wipf, J. Phys. F 6, 167 (1976).
13. S. Tanaka and H. Kimura, Trans. Jpn. Inst. Met. 20, 647 (1979).
14. T. Matsumoto, Y. Sasaki and M. Hihara, J. Phys. Chem. Solids 36, 215 (1975).
15. N. Boes and H. Züchner, Ber. der Bunsen Gesellschaft 80, 22 (1976).
16. R. Griffiths, J. A. Pryde and A. Righini-Brand, Trans. Faraday Soc. 68, 2344 (1972).
17. D. T. Peterson and H. M. Herro, Department of Materials Science and Engineering, Iowa State University and Ames Laboratory-USDOE, Ames, Iowa (unpublished data, 1981).
18. J. F. Miller and D. G. Westlake, Trans. Jpn. Inst. Met. 21, 153 (1980).
19. T. Schober and H. Wenzl, in Topics in Applied Physics, Hydrogen in Metals II, edited by G. Alefeld and J. Völkl (Springer-Verlag, Berlin, 1978), Vol. 29, pp. 11-71.

20. O. N. Carlson, F. A. Schmidt and D. G. Alexander, *Met. Trans.* 3, 1249 (1972).
21. H. Pfeiffer and H. Peisl, *Phys. Letters* 60A, 363 (1977).
22. J. A. Pryde and C. G. Titcomb, *J. Phys. C* 5, 1293 (1972).
23. E. Veleckis and R. K. Edwards, *J. Phys. Chem.* 73, 683 (1969).
24. O. J. Kleppa, P. Dantzer and M. E. Melnichak, *J. Chem. Phys.* 61, 4048 (1974).
25. C. Wagner, Thermodynamics of Alloys (Addison-Wesley, Cambridge, MA, 1952), pp. 51-53.

GENERAL SUMMARY

The equilibria and thermodynamics of hydrogen dissolution were studied in the Sr-H, Th-N-H, V-Nb-H, V-Cr-H and V-Ti-H systems by means of hydrogen pressure-composition isotherms. The hydrogen equilibrium pressures were measured directly for the strontium metal and thorium-nitrogen alloys and indirectly for the vanadium alloys by an isopiestic technique. Hydrogen followed Sieverts' law over a wide range of hydrogen concentrations in strontium metal and in the vanadium alloys and over a narrow range in the thorium-nitrogen alloy. In all cases, the reaction of hydrogen with the metal phase was exothermic. Several enthalpy of reaction values for hydrogen were the first to be reported. These are the enthalpy of solution for hydrogen in strontium metal, -14.3 ± 1.2 kcal/mol H, the enthalpy of formation of ThNH_x , -16.3 ± 1.5 kcal/mol H_2 , and the enthalpies of solution for hydrogen in the vanadium alloys containing niobium and titanium which have values ranging from -8.0 to -10.5 ± 0.3 kcal/mol H.

The most interesting result of the present research is that the model of substitutional solutes as local deep traps for hydrogen in Group VB metals is incorrect within the range 223 to 473 K. The results obtained show that a constant metal matrix-hydrogen interaction, as shown by Sieverts' law behavior, occurs over a wide hydrogen concentration range rather than a local interaction such as trapping of hydrogen. This conclusion is also verified from the results of a concurrent study by Peterson and Herro (15) on the diffusivity of hydrogen in these vanadium alloys in the same temperature range. Their results, at a

given temperature and alloy concentration, show no discontinuities in the value of the diffusivity for hydrogen at very dilute hydrogen concentrations and a small and smooth decrease in the value of the diffusivity for hydrogen with increasing hydrogen concentration. The argument used in the diffusivity study with respect to traps, substitutional solutes, and the hydrogen concentration dependence of the diffusivity is similar to that of the present isopiestic study and the hydrogen concentration dependence of the hydrogen pressure-composition isotherms. In plots of the diffusivity of hydrogen versus hydrogen concentration, at a given temperature and alloy concentration, the diffusivity should have a small value until the traps are saturated. At this point, the value of the diffusivity for hydrogen will change and have a much larger value.

The present investigation of these vanadium alloys has shown some possible areas of fruitful and interesting research. One such fruitful area is to study the structure and thermodynamic properties of the hydride phases of these vanadium alloys, if any can be found. The comment, if any, is included because Miller and Westlake (16) have reported that a vanadium alloy specimen containing 50 atomic percent niobium and charged with 30 atomic percent hydrogen did not show hydride precipitation even when slowly cooled to 77 K. The study of the hydride phases should prove useful since, at a given temperature, the extent of the two-phase region of hydride and saturated metal solid solution is determined by the thermodynamics of the metal solid-solution phase and of the hydride phase. A very interesting and, possibly, a very fruitful area

to investigate with these alloys is quenching very large hydrogen concentrations in solution to temperatures below 77 K where it might be possible to perform experiments at low temperatures and very large hydrogen concentrations. At present, few measurements of metals and alloys containing hydrogen in solution at these low temperatures have been made because precipitation of the hydride phase upon cooling leaves very little hydrogen in solution. Also, the presence of hydrogen in the hydride phase interferes with some measurements of properties of hydrogen in solution. Measurements that would be quite interesting are heat capacity as a function of hydrogen content and neutron diffraction studies to determine the location of the hydrogen atoms. From the specific heat capacity measurements at various hydrogen concentrations and temperatures, one may obtain the electronic specific heat coefficient, γ , and the Debye temperature, θ_D , as a function of hydrogen concentration. From these values, one may obtain the hydrogen concentration dependence of the density of states at the Fermi level and of the elastic properties of the alloy, respectively. Good candidates for study would be the vanadium alloys containing 50 atomic percent niobium or 20 atomic percent and 30 atomic percent titanium. The titanium alloys are promising since they have very high hydrogen solubilities at 297 K. Neutron diffraction studies could be made to determine the local mode vibrations of hydrogen in the alloys and possible diffusion paths. These measurements would be useful since good atomistic models for the mechanisms of diffusion and for the enthalpy of diffusion are sadly lacking. Finally, there is the more general problem of understanding the fundamental

behavior of interstitial solutes in metals and alloys. Atomistic interpretations for the enthalpies of solution and of transport processes are also poorly developed.

REFERENCES

1. I. M. Bernstein and Anthony W. Thompson, in Hydrogen Effects in Metals, edited by I. M. Bernstein and Anthony W. Thompson (AIME, New York, 1981).
2. K. C. Hoffman, J. J. Reilly, F. J. Salzano, C. H. Waide, R. H. Wiswall and W. E. Winsche, International J. Hydrogen Energy 1, 133 (1976).
3. S. C. Garg and A. W. McClaine, Report No. TN 1395 [AD-A014174] (Civil Engineering Laboratory, Port Hueneme, CA, 1975).
4. H. Y. Chang and C. A. Wert, Acta Met. 21, 1233 (1973).
5. G. Pfeiffer and H. Wipf, J. Phys. F 6, 167 (1976).
6. D. G. Westlake and S. T. Ockers, Met. Trans. 6A, 399 (1975).
7. T. Matsumoto, Y. Sasaki and M. Hihara, J. Phys. Chem. Solids 36, 215 (1975).
8. R. Burch and N. B. Francis, J. Less-Common Metals 49, 371 (1976).
9. A. Inoue, M. Katsara and T. Sano, J. Less-Common Metals 55, 9 (1977).
10. J. F. Lynch, J. J. Reilly and F. Millot, J. Phys. Chem. Solids 39, 883 (1978).
11. S. Tanaka and H. Kimura, Trans. Jpn. Inst. Met. 20, 647 (1979).
12. A. J. Kumnick and H. H. Johnson, Acta Met. 28, 33 (1980).
13. G. M. Pressouyre and I. M. Bernstein, Met. Trans. 9A, 1571 (1978).
14. C. Wagner, Thermodynamics of Alloys (Addison-Wesley, Cambridge, MA, 1952), pp. 51-53.
15. D. T. Peterson and H. M. Herro, Department of Materials Science and Engineering, Iowa State University and Ames Laboratory-USDOE, Ames Iowa (unpublished data, 1981).
16. J. F. Miller and D. G. Westlake, Trans. Jpn. Inst. Met. 21, 153 (1980).

ACKNOWLEDGMENTS

I wish to express my thanks to Prof. David T. Peterson for the privilege of working under him. Professor Peterson's strong desire to teach his students the abilities of questioning, reasoning, practicality, self-sufficiency and precision when expressing oneself is greatly appreciated. Many thanks go to Messrs. Ardis Johnson and Harlan Baker for their technical knowledge and teaching. Without their assistance, I may have been still a grad student emeritus. Thanks to Les Reed and Charles Owen for their help in preparation of the alloys. Finally, I wish to thank my wife, Elizabeth, for her lasting patience while I finish.