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*Measurement of Isotope Separation Factors
in the Palladium-Hydrogen System
Using a Thermistor Technique*

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in the Palladium-Hydrogen System
Using a Thermistor Technique*

Thomas Manuel Ortiz

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Thermistor Technique

by

Thomas Manuel Ortiz

ABSTRACT

The range of available data on separation factors in the palladium-hydrogen/deuterium system has been extended. A matched pair of glass-coated bead thermistors was used to measure gas phase compositions. The compositions of the input gas—assumed also to be the solid phase composition—were measured independently by mass spectrometry as being within 0.5 mole% of the values used to calibrate the thermistors. This assumption is based on the fact that > 99% of the input gas is absorbed into the solid. Separation factors were measured for $175 \text{ K} \leq T \leq 389 \text{ K}$ and for $0.195 \leq x_H \leq 0.785$. Separation factor is correlated with temperature and composition by

$$\alpha = \exp \left[-0.3 + B(x_H) \left(\frac{1000}{T} \right)^{0.75} \right]$$

$$B(x_H) = 0.50916 - 0.0037952x_H - 0.15589x_H^2.$$

CHAPTER 1

Introduction

1.1 Background

Palladium-hydrogen systems have been studied for many years; a great deal of information has been accumulated on their electronic structure, thermodynamic and kinetic characteristics of hydrogen sorption, separation phenomena and magnetic properties [1]. Palladium has a relatively large isotope effect (separation factor) [2] for which relatively few data exist in the literature. Palladium and its alloys have been studied for use in the storage, pumping, compression, separation and purification of hydrogen isotopes [3]. The first reported study of the palladium-hydrogen system was published in 1866; the ability of palladium to absorb hydrogen was discovered when researchers heated a small piece of foil *in vacuo* [4]. The palladium-deuterium system has been investigated since 1935 [5]. Three extensive modern reviews have also been published (1967, 1982, and 1986) [7]-[9]. In 1986, [8] separation factors were measured for H-T and D-T systems in the range of 10^{-9} to 10^{-7} mole percent tritium.

The palladium used in these studies has taken many forms, including powders, sponge, films, pellets, chips, strips, foils, sheets, wires, rods and bars [9]. Lewis mentions that alloys of palladium with various metals, including silver, nickel, vanadium, cerium, rhodium, manganese, copper, iron, lead, platinum and gold have also been studied. In addition, alloys of palladium with boron and silicon have also been formed and studied. It is believed [9] that hydrogen in palladium behaves either as a metallic

allotrope of palladium or as an alloying element acting as a proton and contributing electrons to the metallic electron gas.

1.2 Purpose and Scope

This study will extend the range of reported separation factors and confirm the results already in the literature. There is limited data available from which to develop a correlation between separation factor, temperature and solid phase composition. Thus, a comprehensive investigation of separation factors over a wider range of temperatures and compositions would add to the understanding of this system.

This study will also investigate the feasibility of thermistors as composition sensors for the purpose of measuring separation factor. Most separation factor measurements have been done using some form of gas chromatography to separate the isotopes; mass spectrometry has recently been a popular method to analyze the gas phase. This method is well-regarded but can be quite expensive. A thermistor thermal conductivity sensor which could match or improve upon the accuracy of a mass spectrometer at a lower cost would be useful.

1.3 Related Experimental Methods in the Literature

Gas chromatography involves the separation of distinct chemical compounds from a gas mixture which is passed through a column containing a solvent liquid (for gas/liquid chromatography—gas/solid chromatography is also possible). Messer [10] presents a general overview of the theory. The solvent liquid is chosen such that the various components of the sample gas mixture are soluble in it to varying degrees, based

on the nature of the sample and liquid, the component partial pressures and the system temperature. As the partial pressures of the sample components above the liquid phase drop, the dissolved components reenter the gas phase. Thus separated, the components traverse the column at different speeds and exit, or are eluted from, the column sequentially. However, in this case the separation medium is solid palladium powder. The hydrogen isotopes are adsorbed onto the palladium surface and then absorbed into the bulk of the solid in such a way that the gas phase composition is different than the solid phase composition. This phenomenon will be discussed in detail in Chapter 2.

The eluted gases (isotopes) may be analyzed by a variety of methods, but mass spectrometry has been popular among the more recent investigators. Mass spectrometry involves the ionization of a gas sample and electrical or magnetic acceleration of those ions in such a way as to "select" one mass at a time for introduction into a signal detector. Message also discusses mass spectrometry. Mass spectrometers may be divided into three basic components: the ionizer, the mass analyzer and the signal detector. Two principal methods of ionization are used, two basic types of mass analyzer are employed and Message discusses three types of signal detector.

Ionization of the gas sample requires that a small volume of the sample be diverted from the main gas stream to the mass spectrometer. This not only disturbs the system but raises the question of whether the small sample is representative of the total equilibrium gas. The two methods of ionization are electron impact (EI) and chemical ionization (CI). In either case a heated filament releases thermally emitted electrons. In EI, these electrons strike the sample gas directly causing ionization and, if the electrons are of high enough energy, fragmentation of the sample molecules into several smaller

ions. In CI, on the other hand, a reagent gas is introduced into the ion volume along with the sample gas; the reagent gas is bombarded by the electrons and ionized. Then, the reagent plasma reacts with the sample to form ionized chemical compounds. Because the sample is not colliding with energetic particles, CI generally causes less fragmentation than EI. Of course, one has the reagent gas to consider and, therefore, if contamination of the sample must be avoided, CI may not be a feasible technique.

After the sample has been ionized, a mass analyzer selectively filters ions of different mass to form a mass spectrum sensitive to the amount of each mass present. The two types of mass analyzer are magnetic sector and quadrupole. Magnetic sector mass analyzers use the force induced by a magnetic field to accelerate ions along a curved path and through an exit aperture. The radius of that path, all other things being equal, is a function of the ion's mass. Of course, by scanning over a range of magnetic field or ion voltage values different masses can be presented to the exit aperture in turn. Quadrupole mass analyzers operate on the basis of a complicated electric field theory which is dependent on the geometry of the poles, the ion entrance conditions and the voltage used to energize the assembly. Quadrupole refers to the fact that four identical metal poles are arranged symmetrically in a pattern designed to generate a particular electric field between them. Ions entering the quadrupole assembly are accelerated in the two directions perpendicular to the assembly axis in a sinusoidal fashion. The ion trajectories reflect the fact that the two sets of opposing poles are given equal and opposite dc voltages as well as ac voltages of equal magnitude 180° out of phase. The number of cycles an ion experiences while in the assembly is a function of its mass, and

there is an optimum number of cycles for mass transmission through the quadrupole.

Other mass ions strike the poles before exiting, losing their charge.

Signal detectors take the flow of ions leaving the mass analyzer and amplify the signal to a level detectable by the data processing hardware. The three types described by Message all involve the ions striking an emitting surface, changing the signal from positive ions to a proportionally higher number of electrons. Box-and-grid electron multipliers have a fine mesh that is held at a high negative potential. Ions pass through the grid and hit a beryllium-copper surface which emits several electrons for each ion. Venetian blind multipliers have a number of curved surfaces (like the slats in Venetian blinds). Ions hit the first surface, also of beryllium-copper, causing emission of electrons. The emitted electrons travel to the next slat, causing still more electrons to be emitted. The process continues until the final number of electrons exits the blind and is presented to the data processor. Finally, continuous dynode multipliers consist of a glass trumpet coated with tin oxide on the inner surface; a potential gradient is developed down the trumpet. Ions strike the tin oxide which emits electrons; the electrons are accelerated by the potential gradient to the small end of the trumpet and then to the data processor.

1.4 PCT Relationships

Palladium and hydrogen form a thermodynamic system which consists of three distinct regions. At very low stoichiometric (H/Pd) ratios, hydrogen and palladium co-exist as a solid solution; this solution is commonly referred to as the α phase. At ratios which equal approximately 0.1 at moderate temperatures, further hydrogen absorption begins to result in hydriding of the palladium solvent. This two phase (α - β) region

persists up to ratios of approximately 0.6, also at moderate temperatures [8]. The pressure of this two phase region is constant; it is for this reason that the two phase region is referred to as the plateau. The hydrided palladium phase (no dissolved hydrogen, only combined hydrogen) is known as the β region and exists at higher stoichiometries. The stoichiometry depends on temperature and pressure and the three variables pressure, composition and temperature (PCT) form the palladium-hydrogen (or deuterium or tritium) phase diagram. Figure 1-1 is a reproduction of PCT data compiled from the literature [7].

Figure 1-1 Palladium-hydrogen PCT data. Reprinted from [7]

The main features of the phase diagram are the three regions (α , plateau and β) and the critical point. The critical temperature for the palladium-hydrogen system is reported as 564 K; the critical temperature with deuterium is 543 K [8]. This study is concerned only with the β region of this phase diagram and all separation factor measurements will be made in the β region. In order to ensure that measurements are taken in the β region, one must take care to stay above the plateau pressure of the system at the given operating temperature.

CHAPTER 2

Thermodynamic Isotope Effect and Separation Factor

2.1 Connection with Phase Equilibrium

Andreev, et al. [1] describe the thermodynamic isotope effect in detail. The formation of the hydride (β) phase is the result of diatomic hydrogen dissociating on the palladium surface and diffusing through the crystal lattice. The dissociated atoms may occupy either octahedral or tetrahedral interstitial positions. Octahedral interstices are recognized by six surrounding lattice atoms; connecting these lattice atoms around the interstice would form an octahedron. Similarly, tetrahedral interstices are surrounded by four atoms, which when connected would form a tetrahedron. The illustrations of Figure 2-1 are from the on-line syllabus for Chemistry 302 at the University of Michigan [11].

Figure 2-1 Octahedral (left) and tetrahedral (right) sites. Downloaded from [11]

Palladium is a face-centered-cubic (fcc) metal which contains octahedral and tetrahedral interstices. Referring to Figure 2-1, octahedral interstices are located at the center of a fcc unit cell and at the centers of the cube edges and tetrahedral interstices are located between the cube faces and the cube center.

The connection between interstice type and thermodynamic isotope effect is described [1] in terms of potential wells and zero-point energies for the various hydrogen atoms and molecules. Considering the various species to be harmonic oscillators, the changes in zero-point energies (the total energy at absolute zero temperature) for both the gaseous substitution of H_2 with D_2 and the solid phase substitution of H with D have been calculated from inelastic neutron scattering data [1]. If an atom of deuterium were to replace an atom of protium in the solid (Pd) phase, the change in zero-point energy of the system would be -27 meV. Conversely, if a molecule of deuterium were to replace a molecule of protium in the gas phase, the change in zero-point energy of the system would be -35 meV. So, the gas-phase replacement of protium with deuterium leads to a lower overall energy state for the system than does solid-phase replacement of protium with deuterium. Therefore, the gas phase will prefer to be deuterium-rich and the solid-phase will prefer to be protium-rich in order to minimize the total system energy. Figure 2-2, adapted from Andreev, et al. [1], illustrates the energy wells for protium and deuterium in the gas phase, in a TiMn alloy and in Pd.

Figure 2-2 Potential wells for two metal hydride systems

The substitution just described—enrichment of the heavy isotope in the gas phase—is referred to as the “negative thermodynamic isotope effect [1].” In other metal systems, the “positive thermodynamic isotope effect” occurs. That is, the light isotope is enriched in the gas phase. Note that in the case these other systems, the dissolved hydrogen occupies tetrahedral rather than octahedral interstitial sites. In Figure 2-2, the TiMn alloy (center) exhibits the positive isotope effect; the replacement of protium with deuterium in the solid phase leads to a lower energy state than the replacement of protium with deuterium in the gas phase (left). Again, this is in contrast with the Pd solid phase (right). Of course, the gas phase energy difference is identical for any metal or alloy system.

Separation factor is a quantitative measure of the thermodynamic isotope effect described above [1]. It is a ratio of the relative abundances of the isotopes between the solid and gas phases. Separation factor is defined as: heavy/light (gas)/ heavy/light (solid). Or,

$$\alpha \equiv \frac{\left(\frac{y}{1-y} \right)}{\left(\frac{x}{1-x} \right)} \quad (2-1)$$

where x is the mole fraction of the heavy isotope in the solid and y is the mole fraction of the heavy isotope in the gas. In this case, $y = y_D$ and $x = x_D$.

2.2 Review of Literature

Figure 2-3 and Table 2-1 represent the data available in the literature on separation factors in the palladium hydrogen/deuterium system at the time of this publication.

Figure 2-3 Separation factor data for H-D systems in the literature

Table 2-1 Summary of results from the literature

Author	Temp. Range	H ₂ in Solid Phase	No. of Data Points
Andreev	228 K – 293 K	2%, 98%	5
Glueckauf	298 K	1% – 99%	11
Botter	233 K – 333 K	30%, 100%	8
Thomas	352 K – 355 K	50%	2
Fukada	233 K – 385 K	Not Available	11
Wicke	195 K – 323 K	50%	5

The most complete survey of separation factor results for the palladium-hydrogen system has been compiled by Fukada, Fuchinoue and Nishikawa [2]. These investigators have presented their own as well as several other authors' results for separation factors of H and D in Pd at 111 kPa total pressure. Total pressures up to 1200 kPa were investigated, and these authors found that separation factor decreases slightly with increasing total pressure.

For "moderate" values of solid-phase deuterium content, the separation factor (α) was correlated with temperature [2] by

$$\alpha_{H_2-HD} = \exp\left(\frac{228}{T} - 0.121\right). \quad (2-2)$$

These authors' separation experiments were performed using a chromatographic column packed with a spongy type of Pd particles screened from 48 to 80 mesh (0.174-0.295 mm diameter). The Pd powder purity was stated at greater than 99.9%; the purity of the hydrogen used was 99.99999%. The surface area of the packed powder was 4.5 m²/g; the amount was 15.26 g; the bed height was 20.5 cm.

Andreev, et al. [12,13] presented data for the temperature dependence of all hydrogen isotope separation factors at two solid-phase compositions—2% and 98% D₂. Andreev reports a temperature dependence of separation factor of

$$\log_{10} \alpha = \frac{a}{T} + b \quad (2-3)$$

with a and b tabulated for all binary isotope mixture combinations. These values are reproduced as Table 2-2.

Table 2-2 Constants for temperature correlation published by Andreev [12]

Isotopic Mixture	a	a	b	b
	$x_H=1$	$x_H=0$	$x_H=1$	$x_H=0$
H-T	123.4	186.9	0.013	-0.040
H-D	87.8	120.5	0.010	-0.011
D-T	49.4	58.0	0.001	-0.009

The dependence of α on the reciprocal of temperature can be rationalized by considering that the equilibrium constant and separation factor may be related [1] by

$$\alpha = \frac{K}{K_\infty} \quad (2-4)$$

where $K_\infty = 0.5$ for the H-D exchange reaction. The equilibrium constant is related to the standard free energy of reaction, ΔG^0 , by

$$\Delta G^0 = -RT \ln K \quad (2-5)$$

which yields

$$\ln \alpha = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad (2-6)$$

where ΔS and ΔH are the entropy and enthalpy of reaction, respectively. This model is valid for the α phase because it can be derived from classical thermodynamics. Chemical potential is defined to be [14]

$$\mu = \mu^0 + RT \ln p \quad (2-7)$$

for an ideal gas, where μ is the chemical potential and μ^0 is function of temperature only.

For a reaction involving a mixture of ideal gases, chemical equilibrium is established when [14]

$$\sum_i \nu_i \mu_i = 0, \quad (2-8)$$

where ν_i are the stoichiometric coefficients. Then,

$$-RT \sum_i \ln p_i^{\nu_i} = \sum_i \nu_i \mu_i^0 = \Delta G^0. \quad (2-9)$$

Invoking the definition of the equilibrium constant

$$K = \prod_i p_i^{\nu_i} \quad (2-10)$$

the reader is now referred back to Equation 2-7.

To take the steps necessary to validate the form of Equation 2-6, it is necessary to develop the relationship between gaseous reaction equilibrium and the equilibrium between the gas and solid phases of the palladium-hydrogen system. Thermodynamics demand that the chemical potential of each species be equal in all phases. For an ideal solution of hydrogen in palladium (corresponding to the α region of the phase diagram, Figure 1-1), the hydrogen isotopes are present as the same distinct chemical species in both the gas and solid phases. Raoult's law applied to the isotopes as solutes in a palladium solvent equates the partial pressure of each isotope in the gas overpressure to its mole fraction in the solid phase by [14]

$$p_i = p_i^* x_i \quad (2-11)$$

where p_i^* is the vapor pressure of pure i . Assuming further that a law of the form [14]

$$p_i = K_i x_i^n \quad n = 2 \quad (2-12)$$

is valid, and writing the expression as

$$K_i = \frac{p_i^{1/2}}{x_i} = \frac{(y_i p)^{1/2}}{x_i}, \quad (2-13)$$

separation factor by definition (Equation 2-1) is equal to K_D/K_H , where the K_i are independent of composition [14]; this has the form of Equation 2-6. The foregoing assumptions are valid for systems containing low quantities of dissolved isotopes in the palladium solvent; this situation corresponds to the α phase region.

The chemical potentials of individual species must always be equal in each phase present. However, in the β and two-phase regions of the Pd-H phase diagram, hydrogen exists not as a pure element but as a compound and as both element and compound, respectively. Therefore, the ideal solution analysis presented above is not strictly valid and the dependence of separation factor on temperature in the β region may well have a form different than that of Equations 2-3 and 2-9.

The equilibrium constant, K_{HD} , is for the isotope exchange reaction

$$K_{HD} = \frac{[HD]^2}{[H_2][D_2]}. \quad (2-14)$$

Table 2-3 is a reproduction of Andreev's tabulation of equilibrium constants.

Table 2-3 Equilibrium constants for hydrogen isotope exchange reactions [12]

T (K)	K_{HT}	K_{HD}	K_{DT}
233	2.19	3.04	3.74
279	2.43	3.19	3.79
313	2.66	3.30	3.84

There are actually two possible reactions that may take place between the gas and solid phases assuming each gas molecule can exchange only one atom with the solid per interaction with the surface:

and

The model of Equations 2-18 and 2-19 is called a "single site exchange" [15] process and is considered by Melius and Foltz to be an accurate reflection of the reaction between palladium, hydrogen and deuterium.

The gas analysis for Andreev's experiments was performed using a "spectral method on a DS-1 diffraction instrument." Isotopic separation was performed using "6 g of pelletized palladium black [with a] specific surface [area of] 2 m²/g [12]." Equilibrium was attained by circulating the gas phase repeatedly through the solid with a pump. Total pressures ranged between 600-700 mm Hg. At equilibrium (0°C) the stoichiometry of the solid phase was 0.55 H/Pd.

The initial gas was circulated for approximately 2 hrs. in order to establish equilibrium. Small samples of gas were periodically removed for sampling during the equilibration process. After each equilibrium measurement, the hydrogen was desorbed from the palladium at 260 °C. Finally, the desorbed gas was analyzed using the same spectral method. The equilibrium and desorbed gas compositions are sufficient data to calculate separation factors.

Thomas and Smith [16], who also used a thermistor thermal conductivity detector, found a separation factor-temperature correlation of the form

$$\log_{10} \alpha = \frac{222}{T} - 0.51. \quad (2-17)$$

They used a 7 g Pd sample and an "equimolar mixture of hydrogen and deuterium" in the solid phase. These authors also include Glueckauf and Kitt's correlation, which is

$$\log_{10} \alpha = \frac{215}{T} - 0.47. \quad (2-18)$$

Glueckauf and Kitt [17] also reported a concentration dependence at 25°C. Separation factor was reported to be constant between deuterium mole fractions of 0.01 and 0.99.

Beyond a mole fraction of 0.99, they claim the separation factor falls off very rapidly.

Wicke and Nernst [18] subsequently found the correlation to be

$$\ln \alpha = \frac{245}{T} + 0.055. \quad (2-19)$$

Finally, Botter, et al. [19] reported

$$\log_{10} \alpha = \frac{119}{T} - 0.07 \quad (2-20)$$

for near 0% D₂ solid phase and

$$\log_{10} \alpha = \frac{82}{T} + 0.025 \quad (2-21)$$

for 70% D₂ solid phase compositions, respectively.

By contrast, the separation factors for H-T mixtures are larger, and for D-T mixtures are smaller than for H-D mixtures at the same temperature. Separation factor data for the tritium systems are shown in Figure 2-4 [13].

Figure 2-4 Separation factor-temperature correlations for H-T and D-T [13]

The amounts of tritium used in these experiments ranged between 10^{-9} and 10^{-7} mole percent.

CHAPTER 3

Heat Transfer From Glass-Coated Bead Thermistors

3.1 Thermistor Properties

Thermistor is a contraction of the words thermal and resistor; they are in essence thermally sensitive resistors. Thermistors may be classed into two basic types, negative temperature coefficient (NTC) and positive temperature coefficient (PTC) [20]. The temperature coefficient refers to the change in resistance of the thermistor with temperature; NTC thermistors decrease in resistance with temperature; PTC thermistors increase in resistance with temperature.

Thermistors are manufactured from metal-oxides (NTC) or ceramics (PTC) and are normally fashioned into beads, bars, cylinders or thick films [20]. For bead-type thermistors, the material is sintered onto a fine metal wire, and may be coated with glass, potted into a metal housing or not coated at all. This study utilizes glass-coated bead NTC thermistors because of their ability to operate in what is known as self-heating mode.

Self heating refers to the Joule heating which takes place when these sensors are exposed to an excitation signal. This heating causes a corresponding rise in the temperature of the thermistor. Where thermistors are employed for temperature measurement (their usual application), self-heating is undesirable because the true temperature of the object being measured is obscured. For this study, self-heating allows a power balance to be made between the thermistor bead, the surrounding gas and a

Wheatstone bridge circuit used to measure gas composition. The circuit used in this study will be described in detail below.

The power dissipated by a thermistor is

$$\frac{dH}{dt} = \frac{dH_L}{dt} + \frac{dH_S}{dt} \quad (3-1)$$

where L is power lost and S refers to the energy absorbed by the thermistor body and stored in the thermistor's heat capacity [20]. In this case, there is no energy storage and the heat transfer is assumed to be at steady state during all measurements. The total power dissipated must equal the power supplied by the electric circuit:

$$\frac{dH}{dt} = P = Ei = i^2 R, \quad (3-2)$$

while the rate of heat lost is commonly defined in terms of the temperature rise due to self-heating:

$$\frac{dH_L}{dt} = hA(T_s - T_a) + \sqrt{hPkA_c}(T_s - T_a) \coth \left[\sqrt{\frac{hP}{kA_c}} L \right] \quad (3-3)$$

where T_s is the temperature of the thermistor surface, T_a is the temperature of the surrounding gas, P is the perimeter of the wire and L and A_c are the length and cross-sectional area of the wire, respectively. This corresponds to convection from the bead plus conduction from a fin of uniform cross-section (the wire) having a prescribed temperature (the gas temperature) at the tip. Then, at steady state, the total power supplied is equal to the heat dissipated by the thermistor to the surrounding gas:

$$i^2 R = hA(T_s - T_a) + \sqrt{hPkA_c}(T_s - T_a) \coth \left[\sqrt{\frac{hP}{kA_c}} L \right]. \quad (3-4)$$

3.2 Modes of Heat Transfer

For the present problem, the thermistors are considered to be spheres submerged in a large stagnant body of fluid. The beads are actually spheroidal in shape, but are given an effective diameter equal to the square root of the sum of the squares of the major and minor spheroid axes. The problem is one of free convection; the Nu correlation for free convection around a submerged sphere is [21]

$$Nu_D = 2 + 0.59(Gr Pr)^{\frac{1}{4}} = 2 + 0.59 \left(\frac{D^3 \rho^2 g \beta \Delta T}{\mu^2} \right)^{\frac{1}{4}} \left(\frac{\hat{C}_p \mu}{k} \right)^{\frac{1}{4}}. \quad (3-5)$$

Because the fluid in this study is nearly motionless, one can expect that the Nusselt number will be very nearly 2.0. This situation corresponds to a state of almost pure conduction from the bead to the gas [21].

In addition, there will be conduction from the thermistor bead along its lead wire. The thermistors used here are E-I Matched Beads from Fenwal Electronics (Model No. 115-802EDJ-801); one is shown in this figure adapted from the Fenwal catalog.

Figure 3-1 E-I matched bead thermistor from Fenwal Electronics

Conduction will take place along the 0.001 in. diameter lead wire which connects the bead to the 0.030 in. diameter structural members. The temperature of these structural members is equal to the temperature of the surrounding gas at steady state. Radiation from the bead to its surroundings was also considered and found to be negligible.

3.3 Thermistor Resistance-Temperature Characteristics

Both NTC and PTC thermistors exhibit a highly nonlinear relationship between resistance and temperature. The NTC thermistors used in this study are typically modeled in one of two ways [20]. The first, less accurate method is to approximate the R-T curve by a simple exponential of the form

$$R = R_0 \exp \left[B \left(\frac{1}{T} - \frac{1}{T_0} \right) \right], \quad (3-6)$$

where R_0 is the resistance at T_0 and B is a constant which fits the curve well in the temperature range of interest. The temperature of the gas mixture is equal to T_0 and the temperature rise of the thermistors is small due to the very low power supplied by the circuit. The second, more accurate R-T correlation used to model thermistor behavior is the Steinhart-Hart equation [20], which has been included for completeness only.

$$\frac{1}{T} = A + B \ln R + C \ln^3 R. \quad (3-7)$$

The exponential relation of Equation 3-6 yielded results which were $\pm 0.02^\circ\text{C}$ offset from the data of Figure 3-2, which shows the resistance-temperature correlations for the thermistors used here.

Figure 3-2 Resistance-temperature curves for matched bead thermistors

CHAPTER 4

Thermistor Thermal Conductivity Sensor

4.1 Thermal Conductivity of Hydrogen Isotope Mixtures

The thermophysical properties of the three hydrogen isotopes are well known [23]. The theoretical relationships among these isotopes are also fairly well understood, with the ratio of isotope conductivities being equal to the square root of the ratio of their molecular weights [24]. Calculations of mixture properties may be performed by many methods, all essentially empirical [25]. This study employs the Wassiljewa equation

$$k_{mix} = \frac{\sum_{i=1}^n y_i k_i}{\sum_{j=1}^n y_j A_{ij}} \quad (4-1)$$

with

$$A_{ij} = \frac{\left(1 + \left(\frac{\mu_i MW_j}{\mu_j MW_i} \right)^{0.5} \left(\frac{MW_i}{MW_j} \right)^{0.25} \right)^2}{\sqrt{8} \left(1 + \frac{MW_i}{MW_j} \right)^{0.5}} \quad (4-2)$$

Linear mixing rules of the form

$$z_{mix} = \sum_{i=1}^n y_i z_i \quad (4-3)$$

were used to model all of the other properties of the gas mixtures (e.g. ρ , C_p , etc.). A graph of the thermal conductivities of all three hydrogen isotopes is included as Appendix B.

4.2 Wheatstone Bridge Circuit

A thermal conductivity detector was used here to measure the composition of isotope mixtures. A Wheatstone bridge circuit is employed after the manner of previous diffusion experiments [27]. The circuit used in this study is detailed below.

Figure 4-1 Wheatstone thermistor bridge circuit

The thermistors were labeled R-R (red) and R-B (black) in order to differentiate between them. The values of the fixed resistors were chosen to reflect the recommendations of Kieselbach's study of the signal-to-noise ratio of similar sensors [28]. The variable resistance box (R5) was always placed in series with R-B. Balance was measured as a voltage with the digital multimeter (DMM) placed as shown.

Kieselbach [28] observed the following sources of noise in a thermistor of this type: flow variation, shock or vibration, gas temperature variation, bridge current variations and electrical noise generated within the thermistor.

Shock and vibration sensitivity result from turbulence in the flow path of the measured gas stream. Variations in ambient temperature or bridge current will generate noise if their periods are short compared to the time constants of the thermistors. Another method for increasing the signal-to-noise ratio for these sensors is to use relatively high fixed resistors in the other arms of the bridge. Sensitivity is reportedly maximized by using an excitation signal of 8V. Kieselbach recommended fixed resistances between 5000 and 10,000 Ω when using the Fenwal thermistors chosen for this study; 5000 Ω was chosen to correspond to the value used in a previous thermistor thermal conductivity detector [27].

A parameter study was done to validate some of these recommendations. An excitation voltage of 12V was used here because the balance resistance, and therefore, the resolution of the bridge, was maximized. Figure 4-2 illustrates the calculated resistance of the bridge given pure H_2 as a reference gas and pure D_2 as a test gas; experimental data used to benchmark the code is also displayed. A copy of the code is included as Appendix D.

Figure 4-2 Bridge circuit balance resistance vs. excitation voltage

The actual temperature rise of the thermistors due to self-heating can be 80 °C at 50 V excitation. Figure 4-3 illustrates the calculated temperature rise of both thermistors (R-R and R-B) as a function of excitation voltage. Figure 4-4 shows the power dissipated by the thermistors, also as a function of excitation voltage. For both Figures 4-3 and 4-4 the reference (R-R) was pure hydrogen and the test (R-B) was pure deuterium. All of these calculations were at 25 °C.

Figure 4-3 Thermistor temperature rise vs. excitation voltage

Figure 4-4 Thermistor power dissipation vs. excitation voltage

Since deuterium has a lower thermal conductivity than hydrogen, the thermistor R-B will not be able to transfer heat as effectively to the gas surrounding it. Therefore, it will experience a larger temperature rise, as indicated in Figure 4-3. Consequently, the thermistor R-B will dissipate less power, as is evident in Figure 4-4.

Large pulses of power supplied to this type of thermistor over a very short time can alter their resistance-temperature characteristics or even destroy them. Since no two thermistors are ever exactly balanced, power will be diverted toward the hotter sensor as its resistance decreases. The fixed resistors in the bridge serve to limit the current that may be supplied to each thermistor.

4.3 Measurement of Gas Thermal Conductivity

The output signal from the bridge circuit described above depends upon the operational mode chosen: balanced (null) or unbalanced. Yabsley and Dunlop [27] specifically compared these two modes for a bridge containing two thermistors and two fixed resistors. These authors favored the latter mode because they were able to develop a mathematical model for it in which the difference in resistance between the two thermistors R_1 and R_2 is directly proportional to the thermal conductivity difference between two ends of a diffusion cell. This difference, $R_1 - R_2$, is approximately equal to R_5 , the resistance supplied by the variable resistance box. In this study, R_5 is obtained by assuming a balanced bridge and solving for it in terms of the other resistances.

The conductivities of the gases seen by each of the thermistors will, in general, be different. The thermistor immersed in the mixture containing the most deuterium will draw a larger current than the other thermistor, owing to the smaller conductivity of the

surrounding gas and the corresponding increased temperature; recall that a larger temperature rise corresponds to a smaller resistance for this type of thermistor. The discrepancy in current supplied to the thermistors results in bridge imbalance. Since the thermistors are chosen to be as closely matched in resistance as possible (see Figure 3-2) this imbalance is due almost entirely to the difference in thermal conductivity between the gases seen by the thermistors.

It is possible that the thermistors' resistances may have been altered due to gas being dissolved in the glass coating supplied by Fenwal Electronics. This Pyrex type borosilicate glass coating is applied to these thermistors in order to protect them from adverse chemical environments [22], but acts as a solvent for hydrogen isotopes. Also, the resistance of a given thermistor with no excitation voltage applied varies repeatably; the resistance with hydrogen is approximately 15 Ω larger than with deuterium at a given temperature. This resistance difference appears to be a linear function over mixtures of the two isotopes, although more data are required to determine the functional form accurately. More research into these effects is needed. For this investigation, the problems were alleviated by calibration of the test gas before each set of temperature measurements.

CHAPTER 5

Experimental Apparatus and Procedure

5.1 Design of Gas Handling System

All tubing, valves and fittings are made of stainless steel in order to prevent hydrogen embrittlement and are rated for high pressure service by Autoclave Engineers' Group. The volume in the tubing, valves, etc. is minimized by using high pressure equipment. For this study, the majority (>99%) of the gas was absorbed by the palladium and remained in the solid phase; this simplifies calculation of the separation factor since the composition of the solid phase will be nearly equal to the input gas composition.

The palladium bed is mounted inside a Despatch Model 936E environmental chamber for which Despatch claims temperature control to ± 0.15 °C using liquid nitrogen and electrical heaters. The high-pressure tubing connected to the valves on the palladium bed is fed directly through the door of the chamber and connected to the circulating pump, gas fill line and thermistor block as shown in Figure 5-1. The thermistor block is a stainless steel manifold with four high-pressure ports for gas flow and two ports which house the thermistors as shown in Figure 5-2. No flow is shown for the reference side because once reference gas had been added, it was not disturbed. The same reference gas was used to collect all of the data for this study; leak checks were performed beforehand by evacuating the entire apparatus and observing that the vacuum held in the absence of pumping.

Figure 5-1 Schematic of experimental setup

Figure 5-2 Thermistor block

Figure 5-3 is a photograph of the actual apparatus. It is accurate except for the pump shown, which is a Newport Superpressure 10,000 psi compressor. Notice the bridge circuit, digital multimeter and power supply on the left side of the bench.

Figure 5-3 Photo of experimental setup

5.2 Installation of Thermistors into Gas Handling System

The stainless steel thermistor block was designed to be large enough so that its thermal response time is very long. This block also contains four high-pressure ports, two which communicate with each thermistor port and allow the flow of gas over the beads. The gas on one side of the block is analyzed for determination of separation

factors; the other side contains the reference gas composition. The entire block is immersed in a Julabo HD-33 constant temperature bath at 25.00 ± 0.01 °C.

To ensure that the gas analyzed is an accurate sample of the post-reaction equilibrium gas, the total amount of reagent gas is circulated around the system using a Senior Flexonics MB 601 metal bellows pump. The reference gas remains stagnant inside the block at atmospheric pressure. Equilibrium is established by noting that the resistance required to balance the bridge circuit has ceased to change. Note that during balance measurements the pump and palladium bed are isolated from the rest of the manifold to eliminate flow and, hence, forced convection heat transfer from the bead. The time required to measure one gas composition accurately is approximately eighteen minutes—three stages of two minutes of circulation followed by two minutes of resistance equilibration.

5.3 Experimental Procedure

These experiments required a substantial amount of preparation and testing. The first task was to construct and prepare the palladium beds, carefully weighing them at each stage. Concurrently, the Wheatstone bridge was constructed; the circuit went through a series of tests and validations before actual data were taken. The pump had to be shown to circulate the gas properly and the environmental chamber had to be fitted to house the bed and system plumbing. After all of these subsystems were operational, the entire system was assembled and the data collected.

5.3.1 Construction and Preparation of Palladium Beds

The palladium for these experiments was housed inside a four-inch section of Autoclave $\frac{3}{4}$ in. high-pressure tubing which has been coned and threaded at each end for assembly with corresponding valves and fittings. This experiment used powdered palladium which was pressed into the tube in six stages to limit the forces on the pressing hardware. The tube was weighed before and after filling; the resulting powder weight was 50.55 g. The powder had a specific surface area of $1.0 \text{ m}^2/\text{g}$.

After filling, the tube was assembled into the configuration shown in Figure 5-4. After assembly, the volume of the assembly was measured to be 6.91 cm^3 .

Figure 5-4 Photo of palladium-bed test assembly

The final step in preparing the palladium bed was to remove the water and oxide layer from the bed surface. This was done by alternately absorbing hydrogen into the bed and then evacuating it until the hydrogen uptake was relatively constant. After removing

the impurities from the bed, it can adsorb more hydrogen and the risk of unknown gases contaminating the thermal conductivity measurement is reduced. The chemical reaction between isotopes takes place on the palladium surface and if contaminants, such as carbon monoxide, are present they bond strongly to the surface and prevent hydrogen isotopes from interacting to exchange atoms with the bulk solid [15]. The assembly was weighed before and after this process to ascertain the weight of contaminants removed from the bed. This entire process was carried out with the bed held at 150 °C.

A pair of Dale 5000 Ω (nom.) resistors were selected as the fixed arms of the Wheatstone bridge circuit. These resistors were matched to 0.1 Ω in order to reduce the amount of imbalance in the test and reference sides of the bridge. The FORTRAN program in Appendix D which incorporated the R-T curves and heat transfer equations presented in Chapter 3 was used to obtain an estimate of the resistance required to balance the bridge. These calculated balance resistances were not accurate enough to predict balance resistances for gas compositions differing by less than one mole percent. This amount of resolution is necessary to determine separation factors for mixtures containing low amounts of hydrogen. One problem associated with the computer model is the fact that the thermistor beads are not really spherical.

Instead of relying on the equations, a calibration curve was generated using the six known gas compositions used during these experiments. Mixtures containing nominal values of 20%, 40%, 60% and 80% H₂ were ordered from Scott Specialty Gases; pure hydrogen and deuterium were also available. Independent analysis by mass spectrometry calculated the mixtures to each be within 1.0% of the listed compositions if only total H and total D are considered. That is, the amount of HD was not included in the analysis.

Such an analysis is valid because the thermal conductivity of HD approximately the average of the conductivities of the homomolecular species. Therefore, it would be impossible to determine with the thermistor technique whether the mixture was one of pure homomolecular species or one which contained the appropriate amount of HD to have an equal conductivity. The calibration was done by balancing the Wheatstone bridge with each of the Scott gases analyzed by mass spectrometry on one side and research grade H₂ from Air Products and Chemicals on the reference side. The calibration curve, generated at 25 °C, used to collect the data for this experiment is included as Figure 5-5.

Fig. 5-5 Calibration of bridge circuit to experimental gas mixtures

5.3.2 Validation of Bridge Circuit Operation

In order to test the bridge circuit's effectiveness, a series of experiments were conducted. The resistance-temperature data for each thermistor (see Figure 3-2) was collected by disconnecting them from the circuit at each temperature; values for the fixed resistors were also measured. Then, various values of excitation voltage were applied to the bridge. After it was shown that the circuit balanced (with air inside the block), pure hydrogen and pure deuterium were added to the block and the circuit rebalanced (see data in Figure 4-2). This initial study continued until repeatability was established.

5.3.3 Gas Circulation

Since >99% of the gas added to the system remains in the solid phase, circulation is necessary in order to obtain a representative sample of the equilibrium mixture. At the beginning of the reaction, hydrogen begins to separate out into the solid phase. Consequently, the input end of the bed becomes hydrogen rich and, therefore, the first gas leaving the bed is too high in deuterium to accurately reflect the separation factor at that temperature. Only by allowing the gas to react in a closed loop for several minutes can equilibrium be attained in a reasonable amount of time. The MB 601 pump has a design pressure rating of 40 psig. In order to avoid damaging the bellows, the experiment was run from hot to cold for each input gas composition, adding gas to the desired pressure of approximately 25 psia at each stage. That is, the bed was set to a nominal temperature of 110 °C in the morning, a data point was taken, the temperature was lowered to the next value with the fill valve left open and the process repeated over the entire temperature cycle. So, all of the data corresponding to a given input gas

composition was obtained in a single day's run. After each day's temperature cycle, all gas was desorbed from the bed by heating it to 110 °C and evacuating overnight.

5.3.4 Measurement of Separation Factor

The first task in the morning was to check the vacuum pressure (Hastings vacuum gauge) and the pressure of the Heise 901B transducer to ensure that they were both reading zero. Such a reading indicated that the pressure was less than one micron of mercury. Then, with the bed isolated from the manifold containing the thermistors, the input gas for the day was added to the manifold. The balance resistance obtained from this gas was checked against the calibration curve; values which differed by more than 1 Ω were not accepted; gas was flushed as many times as necessary to ensure that no air was introduced into the test gas.

Once the composition of the input gas had been established, the bed was allowed to absorb this gas at 110 °C until its temperature stabilized. The reaction is exothermic and the surface temperature of the bed rose between 3 °C and 6 °C each time; the actual bed temperature can increase as much as 200 °C [29]. As soon as the bed appeared to have reached thermal equilibrium, the gas was circulated for an initial period of one or two minutes. Long circulation times were to be avoided because the gas coming from the oil bath was at a different temperature than the bed and would change its temperature slightly and, consequently, the separation factor. It was discovered that the best course of action was to isolate the manifold from the pump and bed to eliminate flow and to allow the thermistor bridge to balance for a couple of minutes. At this point, the gas was recirculated for one or two minutes. Again, the manifold was isolated and this time a

balance resistance was recorded to the nearest 0.1 Ω . The pressure on the test side was maintained as near as possible to 25 psia.

The circulation/isolation procedure was repeated two or three times for each composition/temperature—until the balance resistances were within 0.9 Ω of each other. Approximately three minutes were required to allow the bridge to stabilize enough to record a balance measurement. Because the thermistors (and fixed resistors) are never exactly balanced, there is always a tendency to move away from equilibrium. However, it was fairly easy to observe the approach to and departure from the equilibrium balance value; this balance value remained for a couple of minutes during which time the actual data point was recorded.

The entire data range of seven points over a temperature range of 200 °C required about 12 hours of continuous operation with a subsequent desorption cycle of 12 hours at 110 °C.

CHAPTER 6

Results and Discussion

6.1 Experimental Data

Separation factors were measured from 116 °C to -98°C for four compositions of input gas. Data were taken at seven temperatures for each solid-phase composition and are presented as Figure 6-1.

Fig. 6-1 Separation factor data vs. temperature at four solid-phase compositions

Tables 6-1 through 6-4 are a tabulation of these data and the error at each point expressed as a percentage of the measured value.

Table 6-1 Experimental data for 19.5% H₂ in solid phase

1000/T (K ⁻¹)	Separation Factor	Uncertainty (%)
2.589	1.995	4.362
2.589	2.013	4.376
2.589	2.032	4.391
2.861	2.237	4.560
2.862	2.291	4.605
2.862	2.299	4.612
3.288	2.549	4.827
3.285	2.587	4.861
3.286	2.627	4.896
3.704	2.866	5.110
3.703	2.878	5.120
3.703	2.902	5.142
4.224	3.221	5.437
4.222	3.266	5.478
4.220	3.296	5.507
4.889	3.823	6.011
4.886	3.864	6.050
4.884	3.949	6.132
5.502	4.323	6.500
5.496	4.323	6.500

Table 6-2 Experimental data for 39.7% H₂ in solid phase

1000/T (K ⁻¹)	Separation Factor	Uncertainty (%)
2.588	2.070	1.954
2.590	2.086	1.959
2.591	2.083	1.958
2.592	2.070	1.954
2.979	2.291	2.206
2.978	2.295	2.207
2.977	2.302	2.030
3.612	2.640	2.144
3.604	2.675	2.156
3.609	2.675	2.156
3.613	2.684	2.160
3.713	2.745	2.181
3.711	2.755	2.184
3.711	2.761	2.186
4.185	3.018	2.277
4.187	3.060	2.292
4.183	3.066	2.295
4.183	3.091	2.304
4.913	3.611	2.495
4.913	3.619	2.498
4.908	3.660	2.513

Table 6-3 Experimental data for 59.1% H₂ in solid phase

1000/T (K ⁻¹)	Separation Factor	Uncertainty (%)
2.569	1.905	1.269
2.568	1.914	1.269
2.569	1.916	1.270
2.898	2.061	1.284
2.898	2.075	1.285
2.897	2.080	1.286
3.402	2.339	1.315
3.401	2.351	1.317
3.400	2.351	1.317
3.752	2.540	1.341
3.750	2.556	1.343
3.752	2.563	1.343
4.242	2.840	1.382
4.242	2.852	1.383
4.244	2.855	1.384
4.962	3.365	1.460
4.962	3.379	1.462
4.964	3.393	1.464
5.563	3.785	1.527
5.566	3.812	1.531
5.566	3.852	1.538

Table 6-4 Experimental data for 78.5% H₂ in solid phase

1000/T (K ⁻¹)	Separation Factor	Uncertainty (%)
2.572	1.715	1.272
2.573	1.729	1.269
2.574	1.734	1.268
2.915	1.849	1.245
2.913	1.856	1.243
2.912	1.863	1.242
3.339	2.042	1.214
3.339	2.044	1.213
3.338	2.049	1.213
3.804	2.234	1.191
3.804	2.242	1.190
3.803	2.250	1.189
4.276	2.475	1.171
4.274	2.484	1.170
4.280	2.484	1.170
4.939	2.848	1.152
4.942	2.871	1.151
4.942	2.881	1.151
5.713	3.311	1.144
5.713	3.326	1.144
5.722	3.337	1.144

The data exhibit an exponential relationship, which confirms the work of previous investigators, as discussed in Chapter 2. The curve fit equations for each line on Figure 6-1 were used to develop a single correlation between separation factor, temperature and composition. Specifically, the slopes of these lines were plotted against solid-phase hydrogen content and fit to a second order polynomial. The intercept was held constant at the average of the four values. Figure 6-2 shows the curve-fitting procedure for the slopes. The points at 0% H₂ and 100% H₂ represent estimations of the slopes at those points using engineering judgment; the derivative of slope should increase as hydrogen content decreases, but should remain negative for all compositions.

Figure 6-2 Curve fit of temperature correlation slopes

The complete correlation combines the results of Figures 6-1 and 6-2:

$$\alpha = \exp \left[-0.3 + B(x_H) \left(\frac{1000}{T} \right)^{0.75} \right] \quad (6-1)$$

with

$$B(x_H) = 0.50916 - 0.0037952x_H - 0.15589x_H^2. \quad (6-2)$$

Figure 6-3 shows Equations 6-1 and 6-2 plotted for the four nominal solid phase compositions studied here as well as extrapolations to pure H₂ and pure D₂ and a comparison with data from the literature.

Figure 6-3 Comparison of empirical correlation with literature data

Andreev's 98% H₂ data falls below the line representing 80% H₂ and is on the side closer to 100% H₂. Wicke's 50% H₂ data falls between the lines representing 40% and 60% H₂. Both of these comparisons are qualitatively correct, although neither data set appears to

be quantitatively comparable to the correlation of Equations 6-1 and 6-2 at the respective solid-phase compositions. The rest of the data shown on Figure 6-3 does not compare well to Equations 6-1 and 6-2.

6.2 Uncertainty Analysis

The uncertainty of the separation factor measurements illustrated in Fig. 6-1 was estimated using the Kline-McClintock [30] method. This method uses the products of the various sensitivities of the measurement variable with respect to the independent variables and the uncertainties of the independent variables themselves. The form of the uncertainty becomes, in this case,

$$u_{\alpha} = \left[\left(\frac{\partial \alpha}{\partial T} u_T \right)^2 + \left(\frac{\partial \alpha}{\partial R_5} u_{R_5} \right)^2 + \left(\frac{\partial \alpha}{\partial x_H} u_{x_H} \right)^2 \right]^{1/2} \quad (6-3)$$

with T being the temperature of reaction and α being described by the generalized correlation of Equations 6-1 and 6-2 as well as Equation 2-1. The partial derivative of α with respect to R_5 may be expressed as the product

$$\left(\frac{\partial \alpha}{\partial R_5} \right)_T = \left(\frac{\partial \alpha}{\partial y_H} \right)_T \left(\frac{\partial y_H}{\partial R_5} \right)_T \quad (6-4)$$

with

$$y_H(R_5) = \frac{92.175 - 0.25232R_5 - 6.9714 \times 10^{-5} R_5^2 - 1.6268 \times 10^{-9} R_5^3}{100} \quad (6-5)$$

from the calibration curve. The error bars plotted on Fig. 6-1 were obtained through the use of Equations 2-1, 6-3 and 6-4 as well as the correlation of Equations 6-1 and 6-2.

Temperature and bridge balance resistance are the only degrees of freedom in the

measurement of separation factor, but input gas (= solid phase) composition is also uncertain. The absolute uncertainty in R_s is estimated to be the amount of measurement uncertainty allowed at each temperature—1 Ω ; the absolute uncertainty in T is defined to be 0.2 K, the scatter in temperature at most points; the absolute uncertainty in x_H is defined to be 0.05—the largest difference between thermistor and mass spectrometer results. The R_s term dominates Equation 6-3. The error in each separation factor measurement is listed along with the raw data for the experiment in Appendix C.

6.3 Conclusions and Recommendations

This study confirms that the use of a thermistor thermal conductivity detector is a viable method for measuring separation factors based on the calculated error of these measurements and the detector's ability to completely determine a separation factor from gas composition data. Also, a correlation between separation factor, temperature and composition has been determined within the limits of these data ($0.195 \leq x_H \leq 0.785$ and $177 \text{ K} \leq T \leq 389 \text{ K}$).

The curve fits for 78.5% H_2 and 59.1% H_2 represent the data quite accurately, while the curves for 39.7% H_2 and 19.5% H_2 do not fit those data as well. Equation 6-1 assumes a common intercept for the lines shown on Figure 6-1; the choice of intercept was made to obtain the best fit of all the data as a group. However, more investigation of the theoretical basis of isotope separation is needed before a statement is made on the suitability of any one model.

Errors in measured gas composition are magnified when calculating separation factor for post-reaction mixtures containing large amounts of deuterium. This can be

seen from the definition of separation factor (see Equation 2-1). For deuterium-rich solid-phases, the denominator of Equation 2-1 will become small, such that even small errors in the measurement of y_D will correspond to large errors in separation factor. As the amount of deuterium in the solid is decreased, the denominator of Equation 2-1 will become larger, minimizing the impact of small errors in gas phase composition measurement. This theory is supported by the trends in calculated error. Referring to Tables 6-1 through 6-4, the errors range from approximately 1.1%-1.3% for 78.5% H_2 in the solid phase to 4.4%-6.5% for 19.5% H_2 in the solid phase. The errors decrease with increasing hydrogen content and also with decreasing temperature. This trend indicates caution should be exercised when extrapolating to deuterium-rich mixtures.

Nonetheless, the repeatability of the thermistor bridge as evidenced by the data of Figure 4-2 and of Tables 6-1 through 6-4 suggest that the thermistor technique is reliable under conditions of proper use. The gas seen by the thermistors must be pure and its temperature must be held as constant as possible. Control of gas temperature (as seen by the thermistors, not reaction temperature) is the most important experimental parameter and reflects directly on measurement accuracy. In this study, the thermistor bridge was used to measure both gas phase composition and solid phase composition, the latter indirectly through measurement of the input gas. Whatever methods are used to measure separation factor, both the gas phase and solid phase compositions must be known accurately.

Future work in this area could include an revisitation of the chemical thermodynamics of palladium-hydrogen separation factors in the beta and plateau regions. In addition, while the effect of pressure is thought to be small [2], more data

should be taken in order to produce a correlation over a wider range of pressures. The extension of separation factor data for the H-T and D-T systems would be another important addition to the literature.

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APPENDIX A: NOMENCLATURE

a	temperature correlation curve-fit parameter of Andreev [12]
A	Steinhart-Hart equation parameter; surface area of thermistor bead
A_c	cross-sectional area of thermistor lead wire
A_{ij}	Wassiljewa equation parameter
α	separation factor; solution phase of hydrogen in palladium
b	temperature correlation curve-fit parameter of Andreev [12]
β	hydride phase of hydrogen in palladium; coefficient of thermal expansion
B	thermistor R-T curve constant; Steinhart-Hart equation parameter
c_p	specific heat at constant pressure
C	Steinhart-Hart equation parameter
CI	chemical ionization ⁻
D	diameter; deuterium
EI	electron impact ionization
E_{ex}	bridge excitation voltage
g	acceleration due to gravity
ΔG	Gibbs free energy of reaction
Gr	Grashof number
h	heat transfer coefficient
H	hydrogen (or protium), heat supplied to thermistor
H_L	heat dissipated by thermistors
H_S	heat stored by thermistors

HD	hydrogen/deuterium heteromolecular isotope
ΔH	enthalpy of reaction
H/Pd	stoichiometry of palladium-hydrogen solution
i	current
k	thermal conductivity
K_{HD}	equilibrium constant for single exchange reaction
K_{∞}	reaction constant used by Andreev [1]
K_i	Henry's law proportionality coefficient [14]
L	length of thermistor lead wire
MW	molecular weight
μ	viscosity, chemical potential
v_i	stoichiometric coefficients
Nu	Nusselt number
p	total gas pressure
p_i	gas partial pressure
P	power supplied by bridge circuit, perimeter of thermistor lead wire cross-section
PCT	pressure-composition-temperature
Pd	palladium
Pr	Prandtl number
Q	heat dissipated by thermistors
ρ	density
R	resistance, universal gas constant
R-R	reference thermistor

R-B	test thermistor
R_5	balance resistance
ΔS	entropy of reaction
t	time
T	temperature; tritium
x_H	mole fraction of hydrogen in the solid phase
x_D	mole fraction of deuterium in the solid phase
y_H	mole fraction of hydrogen in the gas phase
y_D	mole fraction of deuterium in the gas phase

APPENDIX B: THERMAL CONDUCTIVITY OF HYDROGEN ISOTOPES

Conductivity Data from the Center for Information
and Numerical Data Analysis and Synthesis
(CINDAS) at Purdue University

APPENDIX C: RAW DATA

Thesis Data: 19.5% H2

				Cal. % h2	
Mixture 20% hydrogen		R5=	268	19.51473064	
		Rref=	6894.2		
		Rmix=	6802.1		
		volhot cc=	25		
		vol cold	15		
Date	time	pressure	temp	1000/T	circulation
		psia	°C		minutes
20-Feb	10:55	21.91	113.1	2.588996764	2+2
20-Feb	11:03	21.78	113.1	2.588996764	1
20-Feb	11:10	21.68	113.1	2.588996764	1
20-Feb	12:25	24.72	76.4	2.860821056	1
20-Feb	12:34	24.81	76.3	2.86163972	1
20-Feb	12:43	24.87	76.3	2.86163972	1
20-Feb	13:46	24.76	31	3.287851389	2+2
20-Feb	13:55	24.78	31.3	3.284611595	1
20-Feb	14:03	24.84	31.2	3.285690816	1
20-Feb	15:15	25.98	-3.2	3.704389702	2
20-Feb	15:25	26.03	-3.1	3.70301796	1
20-Feb	15:32	26.11	-3.1	3.70301796	1
20-Feb	16:40	26.78	-36.4	4.223864836	2+2+1
20-Feb	16:46	26.9	-36.3	4.222081486	1
20-Feb	16:55	26.98	-36.2	4.220299641	1
20-Feb	17:46	26.36	-68.6	4.888780249	2+2
20-Feb	17:55	26.63	-68.5	4.8863914	1
20-Feb	18:02	26.81	-68.4	4.884004884	1
20-Feb	18:56	28.81	-91.4	5.502063274	2+2+1
20-Feb	19:03	29.44	-91.2	5.496015389	1

Thesis Data: 19.5% H2

R5	% H2	free vol	free vol	Separation
ohms	gas	H2 mol	D2 mol	factor
297.7	10.83793293	0.000226852	0.001866281	1.994710292
298	10.74964845	0.000223669	0.001857045	2.013083703
298.3	10.66135116	0.000220814	0.001850347	2.031764139
301.3	9.777673702	0.000244528	0.002256357	2.23730215
302	9.571297941	0.000240279	0.002270133	2.290770708
302.1	9.541809994	0.000240118	0.002276365	2.298599398
305	8.68604019	0.000236619	0.00248751	2.548951083
305.4	8.567908997	0.000233447	0.002491218	2.587438084
305.8	8.449755019	0.000230832	0.002500986	2.627008949
308	7.799500833	0.000240435	0.002842266	2.866240463
308.1	7.769927446	0.000239927	0.002847967	2.878072607
308.3	7.710776399	0.000238832	0.002858552	2.902010919
310.7	7.00051942	0.00024264	0.003223391	3.22104222
311	6.911679605	0.000240566	0.003240002	3.26556066
311.2	6.852445939	0.000239145	0.003250777	3.295884595
314.2	5.963257094	0.000225115	0.003549917	3.82349216
314.4	5.903932244	0.00022508	0.003587299	3.864348354
314.8	5.785265444	0.00022197	0.003614852	3.948586876
316.4	5.310370244	0.000238552	0.004253639	4.323383652
316.4	5.310370244	0.000243572	0.00434316	4.323383652

Thesis Data: 39.7% H2

					Cal. % h2
Mixture 40% hydrogen		R5=	197		39.74994867
		Rref=	6890.7		
		Rmix=	6801.9		
		volhot cc=	25		
		vol cold	15		
Date	time	pressure	temp	1000/T	circulation
		psia	°C		minutes
17-Feb	10:35	23.52	113.3	2.587656877	2
17-Feb	10:42	23.36	112.9	2.590338039	2
17-Feb	10:51	22.81	112.8	2.591009198	2
17-Feb	12:36	22.5	112.7	2.591680705	1
17-Feb	14:02	24.16	62.5	2.979293907	2
17-Feb	14:14	24.75	62.7	2.977519726	2
17-Feb	14:23	24.53	62.8	2.976633428	2
17-Feb	15:42	25.35	3.7	3.612064295	2
17-Feb	15:50	25.53	4.3	3.604253019	2
17-Feb	16:00	25.86	3.9	3.609456777	2
17-Feb	16:07	25.86	3.6	3.613369467	1
17-Feb	17:22	26.83	-3.8	3.712641544	2+2+2+2
17-Feb	17:31	26.8	-3.7	3.711263685	2
17-Feb	17:40	26.62	-3.7	3.711263685	2
17-Feb	18:35	25.4	-34.2	4.184975936	2
17-Feb	18:43	25.71	-34.3	4.186728072	2
17-Feb	18:55	25.66	-34.1	4.183225267	2
17-Feb	19:07	25.66	-34.1	4.183225267	1
17-Feb	19:51	25.85	-69.6	4.912797838	2
17-Feb	20:00	27.41	-69.6	4.912797838	2
17-Feb	20:10	27.48	-69.4	4.90797546	1
17-Feb	21:12	28.67	-92.6	5.538631958	2
17-Feb	21:20	44.89	-91.9	5.517241379	1

Thesis Data: 39.7% H2

R5	% H2	free vol	free vol	Separation
ohms	gas	H2 mol	D2 mol	factor
252.2	24.17130591	0.000542957	0.001703331	2.069724844
252.7	24.02538266	0.00053632	0.001695986	2.086302885
252.6	24.05456872	0.000524405	0.001655566	2.082971026
252.2	24.17130591	0.000519864	0.001630886	2.069724844
258.4	22.36064824	0.000559815	0.001943756	2.29074455
258.5	22.33142316	0.000572533	0.001991266	2.294605854
258.7	22.27297107	0.000565858	0.001974701	2.302359119
266.5	19.99142538	0.000591632	0.002367796	2.640413375
267.2	19.78649774	0.000588907	0.0023874	2.674592977
267.2	19.78649774	0.000597071	0.002420497	2.674592977
267.4	19.72794201	0.000595718	0.002423948	2.684489847
268.6	19.37656177	0.000617754	0.002570396	2.745135264
268.8	19.31799083	0.00061505	0.00256877	2.755458661
268.9	19.28870456	0.000609993	0.002552443	2.760644013
273.5	17.94097614	0.000586122	0.002680823	3.017584421
274.2	17.73579442	0.000586656	0.002721095	3.060126734
274.3	17.70648082	0.000584217	0.002715237	3.066285097
274.7	17.58922168	0.000580348	0.002719106	3.091124835
282	15.44797975	0.000573872	0.003140994	3.611032924
282.1	15.41863206	0.000607348	0.003331703	3.619161897
282.6	15.27188764	0.000602684	0.003343679	3.660277074
287.1	13.95076385	0.000626682	0.003865415	4.069379406
286.3	14.18568393	0.000994925	0.006018661	3.991063312

Thesis Data: 59.1% H2

					Cal. % h2
Mixture 60% hydrogen		R5=	126.6		59.11061884
		Rref=	6890.7		
		Rmix=	6801.9		
		volhot cc=	25		
		vol cold	15		
Date	time	pressure	temp	1000/T	circulation
		psia	°C		minutes
19-Feb	10:03	20.31	116.1	2.569043031	1
19-Feb	10:12	20.23	116.3	2.567723713	1
19-Feb	10:20	20.28	116.1	2.569043031	1
19-Feb	11:26	24.3	71.9	2.898130706	2+2
19-Feb	11:36	24.45	71.9	2.898130706	1
19-Feb	11:43	24.61	72	2.897291033	1
19-Feb	12:51	25.33	20.8	3.401939105	2+2
19-Feb	13:00	25.54	20.9	3.40078218	1
19-Feb	13:09	25.65	21	3.399626041	1
19-Feb	14:08	25.42	-6.6	3.751641343	2+2
19-Feb	14:16	25.57	-6.5	3.75023439	2
19-Feb	14:27	25.51	-6.6	3.751641343	1
19-Feb	15:28	26.26	-37.4	4.241781548	2+2
19-Feb	15:38	26.67	-37.4	4.241781548	2
19-Feb	15:46	26.6	-37.5	4.243581583	1
19-Feb	16:40	25.79	-71.6	4.961548003	2+2
19-Feb	16:47	25.94	-71.6	4.961548003	1
19-Feb	16:56	25.94	-71.7	4.964010921	1
19-Feb	19:10	26.41	-93.4	5.563282337	2+2
19-Feb	19:21	26.59	-93.5	5.56637907	2
19-Feb	19:30	26.37	-93.5	5.56637907	1

Thesis Data: 59.1% H2

R5	% H2	free vol	free vol	Separation
ohms	gas	H2 mol	D2 mol	factor
186.5	43.14244957	0.00083346	0.001098419	1.905190088
186.9	43.02846667	0.000827745	0.00109597	1.91406643
187	42.99996747	0.00082948	0.001099545	1.916293139
193.2	41.23034904	0.001021354	0.001455836	2.060587535
193.8	41.05882184	0.001023384	0.001469098	2.075235067
194	41.00163556	0.00102847	0.001479894	2.080145719
203.8	38.19323098	0.001087266	0.001759485	2.33940067
204.2	38.07834827	0.00109275	0.00177699	2.35082012
204.2	38.07834827	0.001097222	0.001784263	2.35082012
210.5	36.26643915	0.001102919	0.001938236	2.540494364
211	36.1224392	0.001104752	0.001953602	2.556384781
211.2	36.06483126	0.001100671	0.001951252	2.562777364
219.3	33.72798614	0.001149613	0.00225887	2.840499555
219.6	33.64130052	0.001164561	0.002297139	2.851543871
219.7	33.61240322	0.00116084	0.002292767	2.855238237
232	30.05037778	0.001121573	0.002610735	3.365041352
232.3	29.96331767	0.001124828	0.002629188	3.379019007
232.6	29.87624933	0.001121955	0.002633385	3.393079458
240.3	27.63876541	0.001147421	0.00300407	3.784794435
240.8	27.49329861	0.00114963	0.003031862	3.812468526
241.5	27.2896104	0.001131672	0.003015224	3.851714642

Thesis Data: 78.5% H2

					Cal. % h2
Mixture 80% hydrogen		R5=	53.5		78.47608696
		Rref=	6890.7		
		Rmix=	6801.9		
		volhot cc=	25		
		vol cold	15		
Date	time	pressure	temp	1000/T	circulation
		psia	°C		minutes
18-Feb	10:16	20.45	115.6	2.572347267	2
18-Feb	10:25	20.31	115.5	2.573009134	2
18-Feb	10:34	20.28	115.4	2.573671342	2
18-Feb	11:46	25.45	69.9	2.915026964	2
18-Feb	11:55	25.58	70.1	2.913328478	2
18-Feb	12:05	25.73	70.2	2.912479977	2
18-Feb	13:11	25.66	26.3	3.339455669	2
18-Feb	13:19	25.8	26.3	3.339455669	1
18-Feb	13:28	25.92	26.4	3.338340845	1
18-Feb	14:46	27.32	-10.3	3.804451208	2+1
18-Feb	14:54	27.48	-10.3	3.804451208	1
18-Feb	15:04	27.59	-10.2	3.803004373	1
18-Feb	16:03	26.99	-39.3	4.276245456	2+1
18-Feb	16:16	27.17	-39.2	4.274417611	1
18-Feb	16:27	27.32	-39.5	4.279905842	1
18-Feb	17:29	26.13	-70.7	4.939491232	2+1
18-Feb	17:41	26.06	-70.8	4.941932296	1
18-Feb	17:51	26.01	-70.8	4.941932296	1
18-Feb	19:14	28.84	-98.1	5.712653528	1
18-Feb	19:22	28.71	-98.1	5.712653528	1
18-Feb	19:32	28.55	-98.4	5.722460658	1

Thesis Data: 78.5% H2

R5	% H2	free vol	free vol	Separation
ohms	gas	H2 mol	D2 mol	factor
96.8	68.01499879	0.001323978	0.000622619	1.714580135
97.5	67.82717059	0.001311471	0.000622077	1.729424735
97.7	67.7734845	0.001308686	0.000622285	1.733682821
103	66.34744999	0.001727248	0.00087609	1.849310576
103.3	66.26653951	0.001733357	0.000882378	1.856020265
103.6	66.18560869	0.001741093	0.000889529	1.862748051
111.3	64.1015129	0.001827278	0.001023322	2.041850672
111.4	64.07436081	0.001836469	0.001029684	2.044260948
111.6	64.0200501	0.001843063	0.001035821	2.049088215
119	62.00451304	0.002045141	0.001253233	2.234214287
119.3	61.92255712	0.002054399	0.001263292	2.241996879
119.6	61.84058237	0.002059381	0.001270764	2.249801895
127.9	59.56525443	0.002098197	0.001424322	2.475014938
128.2	59.48275163	0.002108653	0.001436329	2.483504802
128.2	59.48275163	0.002122143	0.001445518	2.483504802
140.3	56.14044055	0.00211625	0.001653314	2.848423496
141	55.94622635	0.002104017	0.001656767	2.870968508
141.3	55.86296367	0.002096855	0.001656714	2.880681919
153.7	52.40709568	0.002422664	0.002200115	3.311068965
154.1	52.29516137	0.002406592	0.002195349	3.325960097
154.4	52.21119247	0.002392369	0.002189731	3.337172779

Error in Thesis Data

1000/T 20%	R5 20%	Alpha 20%	% H2 Gas 20	Error 20%	% Error 20%
2.5889966	297.70001	1.9947103	10.837933	0.087004596	4.361766022
2.5889966	298	2.0130837	10.749648	0.088102201	4.376479772
2.5889966	298.29999	2.031764	10.661351	0.089224816	4.391495079
2.860821	301.29999	2.2373021	9.7776737	0.102026027	4.560225769
2.8616397	302	2.2907708	9.5712976	0.105492549	4.605111491
2.8616397	302.10001	2.2985995	9.54181	0.106004904	4.611717018
3.2878513	305	2.5489511	8.6860399	0.123036988	4.826965416
3.2846117	305.39999	2.5874381	8.5679092	0.12576777	4.86070642
3.2856908	305.79999	2.6270089	8.4497547	0.128607006	4.895567943
3.7043898	308	2.8662405	7.7995009	0.146456446	5.10970541
3.703018	308.10001	2.8780725	7.7699275	0.147369965	5.120439633
3.703018	308.29999	2.9020109	7.7107763	0.149226754	5.142184465
4.223865	310.70001	3.2210422	7.0005193	0.175113107	5.436535623
4.2220817	311	3.2655606	6.9116797	0.178894343	5.478212319
4.2202997	311.20001	3.2958846	6.8524461	0.181493917	5.506683012
4.8887801	314.20001	3.8234921	5.9632573	0.229819909	6.010733197
4.8863912	314.39999	3.8643484	5.9039321	0.233806761	6.050354084
4.8840051	314.79999	3.9485869	5.7852654	0.242138947	6.13229374
5.5020633	316.39999	4.3233838	5.3103704	0.2810283	6.500193204
5.4960155	316.39999	4.3233838	5.3103704	0.2810283	6.500193204

Error in Thesis Data

1000/T 40%	R5 40%	Alpha 40%	% H2 Gas 40	Error 40%	% Error 40%
2.587657	252.2	2.0697248	24.171307	0.04044648	1.954196054
2.590338	252.7	2.086303	24.025383	0.040880782	1.959484407
2.5910091	252.6	2.0829711	24.054569	0.040793328	1.958420282
2.5916808	252.2	2.0697248	24.171307	0.04044648	1.954196054
2.9792938	258.4	2.2907445	22.360649	0.046409288	2.025947801
2.9775198	258.5	2.294606	22.331423	0.0465168	2.027223848
2.9766333	258.7	2.3023591	22.27297	0.046733026	2.029788739
3.6120644	266.5	2.6404133	19.991425	0.056617189	2.144254797
3.6042531	267.2	2.674593	19.786497	0.05766666	2.156091024
3.6094568	267.2	2.674593	19.786497	0.05766666	2.156091024
3.6133695	267.4	2.68449	19.727942	0.05797227	2.159526404
3.7126415	268.6	2.7451353	19.376562	0.059862001	2.180657576
3.7112637	268.8	2.7554586	19.317991	0.060186601	2.184268028
3.7112637	268.9	2.760644	19.288704	0.060349967	2.186082916
4.1849761	273.5	3.0175843	17.940975	0.068714986	2.277152151
4.186728	274.2	3.0601268	17.735794	0.070151355	2.292432942
4.1832252	274.3	3.0662851	17.70648	0.070360497	2.294649534
4.1832252	274.7	3.0911248	17.589222	0.071207188	2.303601197
4.9127979	282	3.611033	15.44798	0.090085347	2.494725124
4.9127979	282.1	3.6191618	15.418633	0.090398155	2.497764961
4.9079757	282.6	3.6602771	15.271888	0.09198867	2.513161361
5.5386319	287.1	4.0693793	13.950764	0.108579117	2.66819848
5.5172415	286.3	3.9910634	14.185684	0.105295271	2.638276091

Error in Thesis Data

1000/T 60%	R5 60%	Alpha 60%	% H2 Gas 60	Error 60%	% Error 60%
2.5690429	186.5	1.9051901	43.142448	0.024169426	1.268609675
2.5677238	186.9	1.9140664	43.028465	0.024297401	1.269412644
2.5690429	187	1.9162931	42.999966	0.024329549	1.26961525
2.8981307	193.2	2.0605876	41.23035	0.026451288	1.283676963
2.8981307	193.8	2.0752351	41.058823	0.026670912	1.285199548
2.8972909	194	2.0801458	41.001637	0.026744717	1.285713594
3.4019392	203.8	2.3394008	38.19323	0.030766674	1.315151884
3.4007821	204.2	2.3508201	38.07835	0.030949508	1.31654091
3.399626	204.2	2.3508201	38.07835	0.030949508	1.31654091
3.7516413	210.5	2.5404944	36.266438	0.034056794	1.340557711
3.7502344	211	2.5563848	36.12244	0.034323159	1.342644474
3.7516413	211.2	2.5627773	36.064831	0.034430581	1.343487029
4.2417817	219.3	2.8404996	33.727985	0.039244222	1.38159575
4.2417817	219.6	2.8515439	33.6413	0.039441598	1.38316642
4.2435818	219.7	2.8552382	33.612404	0.039507722	1.38369269
4.9615479	232	3.3650413	30.050377	0.049124434	1.459846385
4.9615479	232.3	3.379019	29.963318	0.049401913	1.462019403
4.9640107	232.6	3.3930795	29.876249	0.049681784	1.464209249
5.5632825	240.3	3.7847943	27.638765	0.057780638	1.526652009
5.5663791	240.8	3.8124685	27.493299	0.05837491	1.531157822
5.5663791	241.5	3.8517146	27.28961	0.059222693	1.537567001

Error in Thesis Data

1000/T 80%	R5 80%	Alpha 80%	% H2 Gas 80	Error 80%	% Error 80%
2.5723472	96.8	1.7145802	68.014999	0.021813446	1.272232456
2.5730093	97.5	1.7294247	67.827171	0.02194454	1.268892455
2.5736713	97.7	1.7336829	67.773483	0.021982207	1.267948523
2.9150269	103	1.8493105	66.34745	0.023015893	1.244566172
2.9133284	103.3	1.8560202	66.266541	0.023076517	1.243333311
2.9124799	103.6	1.862748	66.185608	0.023137376	1.242109837
3.3394556	111.3	2.0418506	64.101509	0.024783482	1.213775495
3.3394556	111.4	2.044261	64.074364	0.024805976	1.213444641
3.3383408	111.6	2.0490882	64.02005	0.024851053	1.212785894
3.8044512	119	2.2342143	62.004513	0.026607137	1.190894595
3.8044512	119.3	2.2419968	61.922558	0.02668213	1.190105637
3.8030043	119.6	2.2498019	61.840584	0.026757434	1.189324
4.2762456	127.9	2.4750149	59.565254	0.028971111	1.170542883
4.2744174	128.2	2.4835048	59.48275	0.029056102	1.169963579
4.2799058	128.2	2.4835048	59.48275	0.029056102	1.169963579
4.9394913	140.3	2.8484235	56.140442	0.03281507	1.152043214
4.9419322	141	2.8709686	55.946228	0.033054084	1.151321693
4.9419322	141.3	2.880682	55.862965	0.033157306	1.151022775
5.7126536	153.7	3.311069	52.407097	0.037877958	1.143979711
5.7126536	154.1	3.3259602	52.295162	0.038046438	1.143923428
5.7224607	154.4	3.3371727	52.211193	0.038173527	1.143888269

APPENDIX D: CODE USED TO MODEL THERMISTOR BRIDGE

!Subroutine balance, written by Thomas M. Ortiz on November 14, 1997

!This program will determine the resistance required to balance a
!Wheatstone bridge containing two fixed resistors and two Fenwal
!Electronics model 115-802EDJ-801 matched bead thermistors. Required
!inputs are Eex (V) and the mole fractions of the heavy isotope in
!the reference (1) and test (2) vessels. Output is written to file 'output.txt'.

```
subroutine balance(Eex,ref,test)
implicit none
double precision R(5),R0(2),T(2),T0,deltaT(2),i(2),Eex,P(2),Q(2),pi,perim(2),Nub(2)
double precision Nuw(2),rho(2),beta(2),cte,mu(2),cp(2),kgas(2),kw(2),Pr(2)
double precision Grb(2),Grw(2),Ab(2),Aw(2),Lw(2),a1(2),a2(2),Db(2),Dw(2),ref,test
double precision tol,g,temp(2),Told(2),tmp1,tmp2,sens,m(2),kh2,kd2,mratio,A(2,2)
integer k,iter(2),max
```

!All physical quantities are entered in SI units; all temperatures are
!absolute (K).

```
pi=3.14159265359
g=9.79737      !m/s**2
```

!The following parameters will be changed to fit experimental conditions
!!
T0=298.15 —

```
tol=1E-5      !W
```

```
do k=1,2
      iter(k)=0
enddo
```

```
max=1E3
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
```

!The remaining parameters are material properties and should not change.
!Most properites are input as vectors to keep the program general enough
!to accomodate differences in properties between the thermistors.

```
cte=1/T0
```

```
R(3)=4978.1  !Ohms
R(4)=4977.9  !Ohms
beta(1)=-3587.4      !K
beta(2)=-3550.6      !K
```

```

R0(1)=(0.55676 + 1/(7.1298E-6 + 1/7241.2*exp(beta(1)*(1/T0-1/298.15))))+((1-
ref)*15.0)      !Ohms
!R(1) is the reference (red) side
R0(2)=(4.9584 + 1/(6.982E-6 + 1/7125.7*exp(beta(2)*(1/T0-1/298.15))))+((1-test)*15.0)
      !Ohms
!R(2) is the test (black) side
R(1)=R0(1)
R(2)=R0(2)

```

```

!Set power in/out to unbalanced level for each thermistor to trigger
!iteration loop.

```

```

temp(1)=1.0
temp(2)=1.0
T(1)=T0
T(2)=T0
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!

```

```

!Thermophysical properties of pure components taken from the McGraw-Hill/
!CINDAS Data Series on Material Properties.

```

```

m(1)=2.0159
m(2)=4.0282
mratio=m(1)/m(2)

```

```

rho(1)=(1-ref)*0.08991+ref*0.1796 !kg/m**3
rho(2)=(1-test)*0.08991+test*0.1796 !kg/m**3
mu(1)=(1-ref)*8.96E-6+ref*1.64E-5 !N*s/m**2
mu(2)=(1-test)*8.96E-6+test*1.64E-5      !N*s/m**2
cp(1)=(1-ref)*1.43E4+ref*7.24E3      !J/kg*K
cp(2)=(1-test)*1.43E4+test*7.24E3      !J/kg*K
kh2=0.13294*(T0/200.0)**0.76108      !W/m*K
kd2=0.10479*(T0/200.0)**0.67619      !W/m*K

```

```

A(1,1)=1.0
A(1,2)=(1+(8.96E-6/1.64E-5)**0.5*mratio**0.25)**2.0/(8*(1+mratio))**0.5
A(2,1)=(1+(1.64E-5/8.96E-6)**0.5*(1/mratio)**0.25)**2.0/(8*(1+1/mratio))**0.5
A(2,2)=1.0

```

```

!Wassiljewa equation mixing rule

```

```

kgas(1)=(1-ref)*kh2/((1-ref)*A(1,1)+ref*A(1,2))+ref*kd2/((1-ref)*A(2,1)+ref*A(2,2))
kgas(2)=(1-test)*kh2/((1-test)*A(1,1)+test*A(1,2))+test*kd2/((1-
test)*A(2,1)+test*A(2,2))

```

```

!Linear mixing rule

```

```

!kgas(1)=(1-ref)*kh2+ref*kd2
!kgas(2)=(1-test)*kh2+test*kd2

```

```

do k=1,2

```

```

    Db(k)=4.339E-4      !m
!Bead diameter is an effective diameter. Bead is treated as a sphere, but
!actually is a prolate spheroid with major axis = 0.020 in. and minor axis
!= 0.015 in.
    Dw(k)=2.54E-5      !m
    Lw(k)=9.525E-3     !m
    Ab(k)=pi*Db(k)**2  !m**2
    Aw(k)=pi*Dw(k)**2/4 !m**2
!Bead area is surface area and wire area is cross-sectional area
    perim(k)=pi*Dw(k) !m
    kw(k)=19.1        !W/m*K
    Pr(k)=cp(k)*mu(k)/kgas(k) !dimensionless
enddo

```

!Equations for heat balance are coupled. Program will iterate until the
!power supplied (P) is equal to the power dissipated (Q) for each thermistor.

```

do while(abs(temp(1)).gt.tol.or.abs(temp(2)).gt.tol)
    R(5)=R(3)/R(4)*(R(4)+R(1))-R(3)-R(2)
    do k=1,2
        deltaT(k)=T(k)-T0
        Told(k)=T(k)
        Grb(k)=Db(k)**3*rho(k)**2*cte*deltaT(k)*g/mu(k)**2
        Grw(k)=Dw(k)**3*rho(k)**2*cte*deltaT(k)*g/mu(k)**2
        Nub(k)=2 + 0.59*(Grb(k)*Pr(k))**0.25
        Nuw(k)=0.518*(Grw(k)*Pr(k))**0.25 + 1E-15
!The term 1E-15 is added solely to prevent a divide-by-zero error the
!first time this loop is executed (that is, when deltaT(k)=0)
        a1(k)=Nub(k)*Ab(k)/Db(k)
        a2(k)=2*Aw(k)*sqrt(Nuw(k)*perim(k)*kgas(k)**2/(Dw(k)*Aw(k)))
        a2(k)=a2(k)/tanh(sqrt(Nuw(k)*perim(k)/(Dw(k)*Aw(k)))*Lw(k))
    enddo

```

!a1 and a2 are constants that multiply deltaT and represent the free convective,
!conductive and conductive and radiative losses from the bead and wire, respectively.
!Note that the wire is being treated as a fin with prescribed tip temperature.

```

    R(1)=(0.55676 + 1/(7.1298E-6 + 1/R0(1)*exp(beta(1)*(1/T(1)-
1/T0))))+((1-ref)*15.0)
    R(2)=(4.9584 + 1/(6.982E-6 + 1/R0(2)*exp(beta(2)*(1/T(2)-1/T0))))+((1-
test)*15.0)
    i(1)=Eex/(R(4)+R(1))
    i(2)=Eex/(R(3)+R(2)+R(5))
    P(k)=R(k)*i(k)**2
    Q(k)=(a1(k)*kgas(k)+a2(k))*deltaT(k)+(5.6705E-8*Ab(k)*(T(k)**4-
T0**4))

```

```

        T(k)=P(k)/(a1(k)*kgas(k)+a2(k)+5.6705E-
8*Ab(k)*(T(k)+T0)*(T(k)**2+T0**2))+T0
        temp(k)=abs(T(k)-Told(k))
        T(k)=(T(k)+Told(k))/2
    enddo
enddo

10    format(f8.4,3x,f8.4,3x,f8.4,3x,f8.4,3x,f8.4,3x,f8.4,3x,f8.6,3x,f8.6)

if(test.eq.0) tmp1=R(5)
tmp2=R(5)-tmp1
sens=tmp2/Eex

if(test.gt.0.99)then
    write(8,10)Eex,test,R(5),sens,DeltaT(1),DeltaT(2),P(1),P(2)
else
    return
endif

return

end

```

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