Kinetics and mechanisms of hydrogen isotope exchange over solid storage media

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for the degree of Doctor of Philosophy

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Abstract

Society’s need for hydrogen and its isotopes is growing every year. Hydrogen isotopes find uses in a wide variety of industries. Ordinary hydrogen (or protium) is used in a number of industrial processes, including hydrogenation processes, ammonia production, methanol production and in metal production. It is also widely touted as a future energy vector offering a clean and sustainable means of storing and using energy. Deuterium and tritium, the other isotopes of hydrogen, on the other hand, finds less uses but is none the less important. These isotopic species are the main fuels proposed for future fusion devices. Currently there is a worldwide effort to understand and harness the power of nuclear fusion, in the form of the TOKAMAK reactor based International Thermonuclear Experimental Reactor (ITER) in Cadarache, France and the laser induced fusion reactor at the National Ignition Facility (NIF) in the USA, to name a couple among many experimental fusion reactors in operation. As the international effort to harness fusion power moves ever closer to fruition the need for an efficient hydrogen isotope separation system increases.

Hydrogen isotope separation systems using palladium (Pd) are currently being designed for both reactor designs with the aim of separating and purifying the reactor exhaust products which contain valuable unspent hydrogen isotopes. Hydrogen isotope exchange in Pd offers an efficient, ambient condition process that can produce pure isotopic species in a process far simpler and less costly than the current state of the art cryogenic distillation processes. The method is applicable whether separating hydrogen (protium), deuterium or tritium and any combination of these. If practical fusion devices are ever to be realised it is essential to produce an economical and efficient fuel cycle capable of separating and purifying hydrogen isotopes. Hydrogen isotope exchange in Pd is also of interest to the waste separation and purification industries, in particular those using hydrogen separation membranes which used Pd and Pd-alloy membranes. Understanding hydrogen isotope exchange, with particular regard to the formation of the intermediate (and often unwanted) hydrogen deuteride (HD), will aid significantly in future designs of hydrogen isotope separation systems.

Novel hydrogen isotope exchange experiments involving hydrogen and deuterium at a number of temperatures (208 K, 293 K and 373 K) and pressures (1.3 bar – 8 bar) not yet explored are presented in this thesis. The experiments were carried out on a unique
piece of laboratory apparatus provided to and further developed at the University of Bath. Alongside experimentation, a novel comprehensive multidimensional multi-physics model has been created to analyse the experimental data obtained using the new apparatus and elucidate the kinetics and mechanisms of the reactions occurring between hydrogen isotopic species and Pd during hydrogen isotope exchange based on Langmuir-Hinshelwood surface reaction mechanism. The surface reaction rates, kinetic rate constants and heat effects have been examined in detail, and in tandem, for the first time. The model was capable of reproducing all the experimental data with remarkable accuracy for both high (6 – 8 bar) and low pressure (1 – 1.5 bar) hydrogen isotope exchange reactions. Kinetic rate constants for each of the adsorption and desorption reactions considered in the model are presented and activation energies for each process have been calculated. The Langmuir-Hinshelwood surface reaction mechanism was found to be applicable to hydrogen isotope exchange reactions carried out above atmospheric pressure. Further surface reaction mechanisms (i.e. Eley-Rideal) were not investigated but could prove insightful when addressing aspects of the exchange profiles that the current kinetic model could not reproduce.

The temperature effects occurring during hydrogen isotope exchange reactions in both directions, PdD to PdH and PdH to PdD, have been investigated. The thermodynamically favourable PdD to PdH exchange was found to be exothermic, while the unfavourable PdH to PdD exchange was found to be endothermic, in accordance with the available literature. The magnitude of the temperature change in each exchange was found to be significantly affected by the incoming gas pressure and flowrate. During the high pressure exchanges the temperatures within the Pd bed were found to be +/- 100 K at 5 seconds into the exchanges, depending on the exchange direction. However, it was concluded that more model development is needed to include the derived activation energies alongside physical temperature detection within the Pd bed. Whilst the derived kinetic model was very capable of reproducing experiments, more investigation is needed to produce a comprehensive set of experimental data at a number of different temperatures in order for the model to be validated.

The findings presented herein will enable future designs of hydrogen isotope separation processes to be designed with a better understanding of the kinetics of the exchange process. This will enable processes to be tailored to produce high purity isotopes with minimal production of the undesirable intermediate isotopomer hydrogen deutride.
Preface

These words have been a long time coming. The journey to this point of thesis submission has taken 10 years of work, both in the learning imparted to me during my undergraduate years and the significant undertaking of this work. The decision to undertake this PhD was an easy one and part of a significant drive to improve my understanding of chemical engineering and the physical sciences. I was particularly drawn to this PhD project because of the potential to improve my skills and abilities to analyse complex real world problems. In my opinion the PhD topic and I were a good fit and I think I have achieved a great deal in these years. The journey has not always been an easy one, but great achievements do not come without hard work and some amount of stress.

These achievements are in no means only down to me. There are a number of people who I need to acknowledge and thank for their continued support and encouragement during this journey. First of all I must thank my academic supervisor, Dr Tim Mays, who encouraged me to follow the path into postgraduate studies and offered me such a great project. He supported me in every endeavour and has been a fantastic guide in my professional development. I will be indebted to him for the rest of my career and will look fondly upon the years I have spent as his student and, hopefully in his opinion, friend. The next person I want to acknowledge is Dr Tim Barnes from my industrial sponsors, AWE. His knowledge, practical ability and down to earth nature have provided me with great guidance during the project. I do not think it would have been possible to complete this work without his continued input, and for that reason I will be forever grateful. Having worked closely with Tim for a number of years I consider him a good friend and wish him all the future success he deserves. Another important contributor to my work was Mike Le Flufy from AWE. His extensive knowledge of the palladium-hydrogen system has been invaluable and I could always rely on Mike to assist me during times of (moderate) despair at some ‘interesting’ experimental data. I hope this thesis provides him with more insights into this fascinating topic! I must also thank Dr Dave Johnson for being my mentor in the early stages of this work. I hope his new career proves fruitful and he is happy.
I must also express my heartfelt appreciation to my friends, especially Iain, Nuno, Andy, Dom and Antonio. You guys made my (extensive!) time in Bath so much fun. Fond memories and laughter will live with me till my dying days.

My deepest thanks go to my family. Mum and Dad, you have supported me through thick and thin and I will forever be indebted to you! Mum, you’re the greatest and the best mother anyone could ask for. Dad, believe it or not, you have been my inspiration and it was you who made me want to be an engineer. Thank you for the years of discussions and support! I hope this thesis makes you both proud.

Finally, Fatima, my love, I can’t imagine where I would be without you. Thank you for these years and the love you have given me. No te puedes imaginar cuánto te amo. Tú eres mi vida!

I dedicate this thesis to the ones I love, my father Ralph, my mother Janet and my beautiful Fatima.

May 2015
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Dissemination

The author has written one complete manuscript during this work. The paper (described below) is to be submitted for publication. This journal publication constitutes the MATLAB modelling results presented in Chapter 5. A follow up publication is scheduled to present the main findings of the COMSOL Muliphysics kinetic model alongside unique hydrogen isotope exchange experimental data, which the author believes is the main outcome of this work.


Conference and workshop

The author has participated in the following conference, workshop and industrial oral presentations. These events have been used to present the majority of the work presented in this thesis. All the presentations have been led by the author with no additional contributors. The presentations are presented in chronological order.

1. 3rd UK-SHEC Researchers Workshop, Bath, September 2011
   *Hydrogen isotope exchange over solid storage media*
   S. Owens

   *Kinetics and mechanisms of hydrogen isotope exchange over solid storage media*
   S. Owens

3. COMSOL Multiphysics Workshop, Bath, May 2013
   *Kinetics of hydrogen isotope exchange over palladium packed beds*
   S. Owens
Poster presentations

The author has participated in the following poster presentations. The poster presentations are presented in chronological order and all were presented by the author of this work.

   *Kinetics and mechanisms of hydrogen isotope exchange*
   S. Owens

2. 8th International Hydrogen Conference – Hydrogen-Materials Interactions, Wyoming, USA, September 2012
   *Kinetics and mechanisms of hydrogen isotope exchange over solid storage media*
   S. Owens, T. J. Mays, T. Barnes

3. ChemEngDayUK 2014, University of Manchester, Manchester, April 2014
   *Kinetics and mechanisms of hydrogen isotope exchange over solid storage media*
   S. Owens

   *Kinetics of hydrogen isotope exchange over solid storage media*
   S. Owens; T. J. Mays; T. Barnes

The author has also been a contributor to the following oral and poster presentations. Again they are presented in chronological order.

   *Hydrogen Energy Research in the Department of Chemical Engineering, University of Bath, UK*
S. Owens, J. Sharpe, A. Noguera-Diaz, N. Bimbo, A. Rushworth, M. Smith, M. Berry, P. Hayes and T. J. Mays

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This thesis would have not been possible without the input, insight, knowledge and assistance of a number of people whose contribution I wish to acknowledge here.

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Secondly, I must acknowledge the input of Tim Barnes. Tim’s practical knowledge and ability were invaluable during this work. I honestly don’t think the experimental work would have been completed without his input! Tim also supported me in expanding the research project to pursue my desire to model the process with high fidelity which I appreciate greatly. Without our discussions of ideas over coffee I do not know where I would have been now! Tim was an inspirational mentor with a great attitude to practical, useful research. I am indebted to both Tim M and Tim B for their hard work and support during this project, and for (hopefully) teaching me how to do good research!

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I also need to extend a big thank you to Dr Edmund Dickinson from COMSOL UK for his assistance during the (lengthy!) modelling stages of this work. Without his input and thorough guidance the outcome of this work would have been a lot different. I truly believe that with Edmund’s guidance I have become a ‘modeller’!

I would also like thank Richard Murden from Hiden Isochema and Robert Stannard from Hiden Analytical. Without Richard’s input during the commissioning and initial
stages of this work the project would have never taken off. The quality of the Hiden Isochema IsoEx rig is in a large part down to Richard’s skill and ingenuity. Richard’s guidance helped me to understand the foibles of the rig; an extremely necessary process when using prototype apparatus! Thanks also to Robert Stannard who was a great help whilst I was using the Hiden Analytical mass spectrometer. Robert was very patient and always available when all hell was breaking loose in lab 1.04 with regards to the mass spec!
**Nomenclature**

**Acronyms**

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0D</td>
<td>Zero-dimensional</td>
</tr>
<tr>
<td>1D</td>
<td>One-dimensional</td>
</tr>
<tr>
<td>2D</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>AWE</td>
<td>Atomic Weapons Establishment</td>
</tr>
<tr>
<td>BOC</td>
<td>British Oxygen Company</td>
</tr>
<tr>
<td>CDC</td>
<td>Cleanroom Design and Construction</td>
</tr>
<tr>
<td>CFD</td>
<td>Computational Fluid Dynamics</td>
</tr>
<tr>
<td>CRE</td>
<td>Chemical Reaction Engineering</td>
</tr>
<tr>
<td>COMSOL</td>
<td>Comsol Multiphysics finite element analysis software</td>
</tr>
<tr>
<td>D-H</td>
<td>Deuteride to Hydride Exchange (Palladium Deuteride to Palladium Hydride)</td>
</tr>
<tr>
<td>EU</td>
<td>European Union</td>
</tr>
<tr>
<td>FEA</td>
<td>Finite Element Analysis</td>
</tr>
<tr>
<td>FEM</td>
<td>Finite Element Method</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast Fourier Transform</td>
</tr>
<tr>
<td>GB</td>
<td>Gigabyte</td>
</tr>
<tr>
<td>H-D</td>
<td>Hydride to Deuteride Exchange (Palladium Hydride to Palladium Deuteride)</td>
</tr>
<tr>
<td>HETP</td>
<td>Height Equivalent to a Theoretical Plate</td>
</tr>
<tr>
<td>IsoEx</td>
<td>Isotope Exchange Apparatus</td>
</tr>
<tr>
<td>ISS</td>
<td>Isotope Separation System</td>
</tr>
<tr>
<td>ITER</td>
<td>International Thermonuclear Experimental Reactor</td>
</tr>
<tr>
<td>JET</td>
<td>Joint European Torus</td>
</tr>
<tr>
<td>MATLAB</td>
<td>Matrix Laboratory software</td>
</tr>
<tr>
<td>MFC</td>
<td>Mass Flow Controller</td>
</tr>
<tr>
<td>MID</td>
<td>Multiple Ion Detection</td>
</tr>
<tr>
<td>MoD</td>
<td>Ministry of Defence</td>
</tr>
<tr>
<td>NIF</td>
<td>National Ignition Facility</td>
</tr>
<tr>
<td>NTP</td>
<td>Normal Temperature and Pressure</td>
</tr>
</tbody>
</table>
ODE  Ordinary Differential Equation
P&ID  Process and Instrumentation Diagram
PDE  Partial Differential Equation
PFD  Process Flow Diagram
PdD\textsubscript{y}  Palladium Deuteride
PdH\textsubscript{x}  Palladium Hydride
Pd-H(D)  Palladium Hydride (Deuteride) system
PGM  Platinum Group Metal
QMS  Quadruple Mass Spectrometer
RAM  Random Access Memory
RE  Reaction Engineering
RF  Radio Frequency
RGA  Residual Gas Analyser
SEM  Secondary Electron Multiplier
SDS  Storage and Delivery System
STP  Standard Temperature and Pressure
TEP  Tokamak Exhaust Processing
TOKAMAK  Toroidal Chamber with Magnetic Coils (translated from Russian acronym)
UK  United Kingdom
USA  United States of America
VGA  Video Graphics Array
WDS  Water Detritiation System

**Symbols**

\begin{align*}
A & \quad \text{m}^2 \quad \text{Cross-sectional area of packed powder Pd bed} \\
A_1 & \quad \text{s}^{-1} \quad \text{Pre-exponential factor} \\
a & \quad \text{m} \quad \text{Radius of particle} \\
a_i & \quad - \quad \text{Activity of species ‘i’} \\
a_v & \quad \text{m}^{-2} \quad \text{Specific surface area (Fukada et al)} \\
C & \quad - \quad \text{Sutherland’s constant}
\end{align*}
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Units</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_p)</td>
<td>J kg(^{-1}) K(^{-1})</td>
<td>Specific heat capacity of fluid at constant pressure</td>
</tr>
<tr>
<td>(C_{pg})</td>
<td>J mol(^{-1}) K(^{-1})</td>
<td>Molar fluid heat capacity at constant pressure</td>
</tr>
<tr>
<td>(C_{pPd})</td>
<td>J mol(^{-1}) K(^{-1})</td>
<td>Molar heat capacity of Pd</td>
</tr>
<tr>
<td>(C_{pPd,spec})</td>
<td>J kg(^{-1}) K(^{-1})</td>
<td>Specific heat capacity of Pd</td>
</tr>
<tr>
<td>(c_i)</td>
<td>mol m(^{-3})</td>
<td>Concentration of species ‘i’ in the gas phase</td>
</tr>
<tr>
<td>(c_{D_2})</td>
<td>mol m(^{-3})</td>
<td>Concentration of D(_2) in the gas phase</td>
</tr>
<tr>
<td>(c_{D_2})(_{\text{initial}})</td>
<td>mol m(^{-3})</td>
<td>Initial concentration of D(_2) in the gas phase</td>
</tr>
<tr>
<td>(c_{D_2})(_{\text{inlet}})</td>
<td>mol m(^{-3})</td>
<td>Inlet concentration of D(_2) in the gas phase</td>
</tr>
<tr>
<td>(c_{D})</td>
<td>mol m(^{-3})</td>
<td>Concentration of D atoms in the Pd bed</td>
</tr>
<tr>
<td>(c_{D_{\text{surface}}})</td>
<td>mol m(^{-2})</td>
<td>Concentration of D atoms on the Pd surface</td>
</tr>
<tr>
<td>(c_{H_2})</td>
<td>mol m(^{-3})</td>
<td>Concentration of H(_2) in the gas phase</td>
</tr>
<tr>
<td>(c_{H_2})(_{\text{initial}})</td>
<td>mol m(^{-3})</td>
<td>Initial concentration of H(_2) in the gas phase</td>
</tr>
<tr>
<td>(c_{H_2})(_{\text{inlet}})</td>
<td>mol m(^{-3})</td>
<td>Inlet concentration of H(_2) in the gas phase</td>
</tr>
<tr>
<td>(c_{HD})</td>
<td>mol m(^{-3})</td>
<td>Concentration of HD in the gas phase</td>
</tr>
<tr>
<td>(c_{HD})(_{\text{initial}})</td>
<td>mol m(^{-3})</td>
<td>Initial concentration of HD in the gas phase</td>
</tr>
<tr>
<td>(c_{HD})(_{\text{inlet}})</td>
<td>mol m(^{-3})</td>
<td>Inlet concentration of HD in the gas phase</td>
</tr>
<tr>
<td>(c_{H_s})</td>
<td>mol m(^{-3})</td>
<td>Concentration of H atoms in the Pd bed</td>
</tr>
<tr>
<td>(c_{H_{\text{surface}}})</td>
<td>mol m(^{-2})</td>
<td>Concentration of H atoms on the Pd surface</td>
</tr>
<tr>
<td>(c_i)</td>
<td>mol m(^{-3})</td>
<td>Concentration of species ‘i’ in the gas phase</td>
</tr>
<tr>
<td>(c_{i_s})</td>
<td>mol m(^{-2})</td>
<td>Concentration of species ‘i’ sorbed to the solid phase</td>
</tr>
<tr>
<td>(c_{V_s})</td>
<td>mol m(^{-3})</td>
<td>Concentration of vacant sites in the Pd bed</td>
</tr>
<tr>
<td>(c_{V_{\text{surface}}})</td>
<td>mol m(^{-2})</td>
<td>Concentration of vacant sites on the Pd surface</td>
</tr>
<tr>
<td>([D(b)])</td>
<td>mol m(^{-2})</td>
<td>Amount of D atoms on the Pd surface (Outka and Foltz)</td>
</tr>
<tr>
<td>([D(b)]_{\text{max}})</td>
<td>mol m(^{-2})</td>
<td>Max. D concentration on Pd surface (Outka and Foltz)</td>
</tr>
<tr>
<td>(D^{\ast})</td>
<td>m(^{-2}) s(^{-1})</td>
<td>Einstein diffusion coefficient</td>
</tr>
<tr>
<td>(D_D)</td>
<td>m(^{-2}) s(^{-1})</td>
<td>Diffusion coefficient for D atoms in Pd</td>
</tr>
<tr>
<td>(D_{Di})</td>
<td>m(^{-2}) s(^{-1})</td>
<td>Dispersion tensor</td>
</tr>
</tbody>
</table>
\begin{align*}
D_e & \text{ m}^{-2} \text{s}^{-1} \quad \text{Effective diffusivity of each gas species in porous Pd} \\
D_{Fi} & \text{ m}^{-2} \text{s}^{-1} \quad \text{Single phase diffusivity of species ‘i’} \\
D_H & \text{ m}^2 \text{s}^{-1} \quad \text{Diffusion coefficient for H atoms in Pd} \\
D_l & \text{ m}^2 \text{s}^{-1} \quad \text{Longitudinal dispersion coefficient (Fukada et al)} \\
D_s & \text{ m}^2 \text{s}^{-1} \quad \text{Diffusion coefficient in the solid phase} \\
dH_{D_2} & \text{ kJ mol}^{-1} \quad \text{Dissolution enthalpy of D}_2 \text{ absorption in Pd} \\
dH_{eq} & \text{ kJ mol}^{-1} \quad \text{Equilibrium coproportionation reaction enthalpy} \\
dH_{H_2} & \text{ kJ mol}^{-1} \quad \text{Dissolution enthalpy of H}_2 \text{ absorption in Pd} \\
dH_{HD} & \text{ kJ mol}^{-1} \quad \text{Dissolution enthalpy of HD absorption in Pd} \\
\Delta E & \text{ meV} \quad \text{Zero point energy change} \\
E_a & \text{ kJ mol}^{-1} \quad \text{Activation energy} \\
E_{desorb}(D_2) & \text{ kJ mol}^{-1} \quad \text{Desorption enthalpy of D}_2 \text{ from Pd} \\
E_{desorb}(H_2) & \text{ kJ mol}^{-1} \quad \text{Desorption enthalpy of H}_2 \text{ from Pd} \\
E_{desorb}(HD) & \text{ kJ mol}^{-1} \quad \text{Desorption enthalpy of HD from Pd} \\
F & \text{ N m}^{-3} \quad \text{Volume force vector} \\
H_L & \text{ m s}^{-1} \quad \text{Average linear velocity in the pores of the media} \\
I & - \quad \text{Identity matrix} \\
J_i & \text{ mol m}^{-2} \text{s}^{-1} \quad \text{Diffusive flux of component ‘i’} \\
K & \text{ m}^2 \quad \text{Permeability of Pd bed} \\
K_1 & - \quad \text{Correction factor identified by Larson et al} \\
K_2 & - \quad \text{Correction factor identified by Larson et al} \\
K_{app} & - \quad \text{Apparent equilibrium constant/concentration ratio} \\
K_D & \text{ m}^3 \text{ mol}^{-1} \quad \text{Capacity coefficient of deuterium (Fukada et al)} \\
K_{eq} & - \quad \text{Equilibrium constant for equilibration reaction} \\
k & \text{ m}^2 \text{ mol}^{-1} \quad \text{Isotope exchange rate coefficient} \\
k_{eq} & \text{ W m}^{-1} \text{ K}^{-1} \quad \text{Equivalent thermal conductivity} \\
k_f & \text{ m}^3 \text{ mol}^{-1} \text{s}^{-1} \quad \text{Forward rate constant for equilibration reaction} \\
k_G & \text{ W m}^{-1} \text{ K}^{-1} \quad \text{Thermal conductivity of the gas/fluid phase} \\
k_g & \text{ m s}^{-1} \quad \text{Gas phase mass transfer coefficient (Fukada et al)} \\
k_i & \text{ m}^5 \text{ mol}^{-2} \text{s}^{-1} \quad \text{Forward rate constant for reaction ‘i’ (COMSOL)}
\end{align*}
\( k_{-i} \) \( \text{m}^2 \text{mol}^{-1} \text{s}^{-1} \) Reverse rate constant for reaction ‘i’ (COMSOL)

\( k_p \) \( \text{W m}^{-1} \text{K}^{-1} \) Thermal conductivity of solid (COMSOL)

\( k_p \) \( \text{m s}^{-1} \) Mass transfer coefficient for pore diffusion

\( k_{pi} \) \( - \) Adsorption isotherm for species ‘i’ on the solid

\( k_r \) \( \text{m}^3 \text{mol}^{-1} \text{s}^{-1} \) Reverse rate constant for equilibration reaction

\( L \) \( \text{m} \) Length of Pd bed

\( M \) \( \text{kg} \) Average molecular mass of gas species

\( M_{D_2} \) \( \text{kg} \) Molecular mass of D\(_2\)

\( M_{H_2} \) \( \text{kg} \) Molecular mass of H\(_2\)

\( M_{HD} \) \( \text{kg} \) Molecular mass of HD

\( m_{exp} \) \( \text{kg} \) Experimental mass of Pd used

\( N_{D_2} \) \( \text{mol m}^{-2} \text{s}^{-1} \) Molar flux vector for D\(_2\)

\( N_{H_2} \) \( \text{mol m}^{-2} \text{s}^{-1} \) Molar flux vector for H\(_2\)

\( N_{HD} \) \( \text{mol m}^{-2} \text{s}^{-1} \) Molar flux vector for HD

\( N_{SD} \) \( \text{mol} \) Total mols of D atoms in Pd

\( N_{SH} \) \( \text{mol} \) Total mols of H atoms in Pd

\( N_{surf} \) \( \text{mol m}^{-2} \) Total surface density of H and D atoms

\( n \) \( - \) H/Pd atom ratio

\( n_{GD} \) \( \text{mol m}^{-3} \text{s}^{-1} \) Rate of change of D atom species in the gas phase

\( n_{GH} \) \( \text{mol m}^{-3} \text{s}^{-1} \) Rate of change of D atom species in the gas phase

\( n_{SD} \) \( \text{mol m}^{-3} \text{s}^{-1} \) Rate of change of D atom species in the solid

\( n_{SH} \) \( \text{mol m}^{-3} \text{s}^{-1} \) Rate of change of H atom species in the solid

\( \Delta P \) \( \text{Pa} \) Pressure drop over Pd bed

\( P_{in} \) \( \text{Pa} \) Inlet pressure into IsoEx system

\( P_{out} \) \( \text{Pa} \) Outlet pressure out of IsoEx system

\( p \) \( \text{Pa} \) Pressure

\( p_0 \) \( - \) Pre-exponential factor for exchange probability

\( p_c \) \( \text{bar} \) Critical pressure of Pd-H or Pd-D system

\( p_D \) \( - \) Probability that a D atom will penetrate fluid film

\( p_{exch} \) \( - \) Isotope exchange probability
\( p_H \) - Probability that a H atom will penetrate fluid film
\( p_{D_2} \) Pa Partial pressure of \( D_2 \) above Pd system
\( p_{H_2} \) Pa Partial pressure of \( H_2 \) above Pd system
\( p_{HD} \) Pa Partial pressure of HD above Pd system
\( p_T \) - Probability that a T atom will penetrate fluid film
\( Q \) W m\(^{-3}\) General heat sources or sinks
\( Q_{\text{heat}} \) W m\(^{-3}\) Heat generated by chemical reaction (source)
\( Q_{\text{loss}} \) W m\(^{-3}\) Heat loss to environment through reactor wall
\( Q_m \) kg m\(^{-3}\) s\(^{-1}\) Mass source term (COMSOL kinetic model)
\( q \) W m\(^{-2}\) Heat flux vector
\( R \) J K\(^{-1}\) mol\(^{-1}\) Universal gas constant
\( R_{D_2} \) mol m\(^{-3}\) s\(^{-1}\) Vol. reaction rate expression for molecular \( D_2 \)
\( R_{D_s} \) mol m\(^{-3}\) s\(^{-1}\) Vol. reaction rate expression for surface D atoms
\( R_{D_{\text{surface}}} \) mol m\(^{-2}\) s\(^{-1}\) Rate law expression for surface D atoms
\( R_{D_{2\text{surface}}} \) mol m\(^{-2}\) s\(^{-1}\) Surface reaction rate of \( D_2 \)
\( R_{\text{exch}} \) mol m\(^{-3}\) s\(^{-1}\) Isotope exchange rate (Foltz and Melius notation)
\( R_{H_2} \) mol m\(^{-3}\) s\(^{-1}\) Vol. reaction rate expression for molecular \( H_2 \)
\( R_{H_s} \) mol m\(^{-3}\) s\(^{-1}\) Vol. reaction rate expression for surface H atoms
\( R_{H_{\text{surface}}} \) mol m\(^{-2}\) s\(^{-1}\) Rate law expression for surface H atoms
\( R_{H_{2\text{surface}}} \) mol m\(^{-2}\) s\(^{-1}\) Surface reaction rate of \( H_2 \)
\( R_{HD} \) mol m\(^{-3}\) s\(^{-1}\) Vol. reaction rate expression for molecular HD
\( R_{HD_{\text{surface}}} \) mol m\(^{-2}\) s\(^{-1}\) Surface reaction rate of HD
\( R_i \) mol m\(^{-3}\) s\(^{-1}\) Volumetric reaction rate expression
\( R_{i_{\text{ads,surface}}} \) mol m\(^{-2}\) s\(^{-1}\) Adsorption reaction rate for reaction ‘i’
\( R_{i_{\text{des,surface}}} \) mol m\(^{-2}\) s\(^{-1}\) Desorption reaction rate for reaction ‘i’
\( R_{V_s} \) mol m\(^{-3}\) s\(^{-1}\) Vol. reaction rate expression for vacant sites
\( R_{V_{\text{surface}}} \) mol m\(^{-2}\) s\(^{-1}\) Rate law expression for surface vacant sites
\( r \) mol m\(^{-3}\) s\(^{-1}\) Overall reaction rate for equilibration reaction
\( S \) - Strain rate tensor
\( S_0 \) m\(^2\) m\(^{-3}\) Specific surface area
\[ S_t \quad \text{kg m}^{-3}\text{s}^{-1} \quad \text{Arbitrary source term} \]
\[ s \quad \text{s}^{-1} \quad \text{Laplace parameter (Fukada et al)} \]
\[ s_{d0} \quad \text{mol m}^{-2} \quad \text{Initial concentration of D atoms (MATLAB)} \]
\[ s_{H0} \quad \text{mol m}^{-2} \quad \text{Initial concentration of H atoms (MATLAB)} \]
\[ T \quad \text{K} \quad \text{Temperature} \]
\[ T_0 \quad \text{K} \quad \text{Reference temperature for Sutherland’s equation} \]
\[ T_{amb} \quad \text{K} \quad \text{Ambient (surroundings) temperature} \]
\[ T_c \quad \text{K} \quad \text{Critical temperature of Pd-H or Pd-D system} \]
\[ t \quad \text{s} \quad \text{Time} \]
\[ u \quad \text{m s}^{-1} \quad \text{Velocity field} \]
\[ u \quad \text{m s}^{-1} \quad \text{Velocity} \]
\[ v_f \quad \text{m s}^{-1} \quad \text{Flow velocity in x-direction (Foltz and Melius)} \]
\[ x \quad \text{m} \quad \text{Length} \]
\[ x_{Dg} \quad - \quad \text{Atomic mole fraction of D in the gas phase} \]
\[ x_{D_2} \quad - \quad \text{Molecular mole fraction of D}_2 \text{ in the gas phase} \]
\[ x_{HD} \quad - \quad \text{Molecular mole fraction of HD in the gas phase} \]
\[ x_{Hg} \quad - \quad \text{Atomic mole fraction of H in the gas phase} \]
\[ x_{H_2} \quad - \quad \text{Molecular mole fraction of H}_2 \text{ in the gas phase} \]
\[ V_{bed} \quad \text{m}^3 \quad \text{Volume of Pd bed} \]

**Greek symbols**

\[ \alpha \quad - \quad \text{Separation factor} \]
\[ \alpha^- \quad - \quad \text{Alpha phase palladium} \]
\[ \alpha_{highD} \quad - \quad \text{Separation factor when D is in majority in gas} \]
\[ \alpha_{highH} \quad - \quad \text{Separation factor when H is in majority in gas} \]
\[ \beta^- \quad - \quad \text{Beta phase palladium} \]
\[ \varepsilon_G \quad - \quad \text{Fluid volume fraction} \]
\[ \varepsilon_p \quad - \quad \text{Porosity of porous medium} \]
\[ \mu \quad \text{Pa s} \quad \text{Fluid viscosity} \]
\[ \mu_0 \quad \text{Pa s} \quad \text{Reference viscosity for Sutherland’s equation} \]
\( \mu_{D_2} \) Pa s Viscosity of \( D_2 \) gas
\( \mu_{H_2} \) Pa s Viscosity of \( H_2 \) gas
\( \mu_i \) Pa s Viscosity of gaseous specie ‘i’
\( \mu_{HD} \) Pa s Viscosity of HD gas
\( \mu_{mix} \) Pa s Viscosity of gas mixture
\( \rho_b \) kg m\(^{-3}\) Bulk fluid density
\( \rho_{D_2} \) kg m\(^{-3}\) Density of \( D_2 \) mixture
\( \rho_G \) kg m\(^{-3}\) Fluid density
\( \rho_{H_2} \) kg m\(^{-3}\) Density of \( H_2 \) mixture
\( \rho_{HD} \) kg m\(^{-3}\) Density of HD mixture
\( \rho_{mix} \) kg m\(^{-3}\) Density of gas mixture
\( \rho_p \) kg m\(^{-3}\) Density of solid phase material
\( \tau \) Pa Viscous stress tensor
\( \tau_L \) Pa Tortuosity of porous medium
\( \tau_{F,i} \) - Tortuosity factor for species ‘i’
\( \phi \) - Correction factor for Foltz and Melius model
\( \nabla \) - Del operator

**Physical constants and conversion factors**

\( eV \) J \( = 1.602 \times 10^{-19} \) electron-Volt
\( h \) J s \( = 6.626 \times 10^{-34} \) Planck constant
\( k_b \) J K\(^{-1}\) \( = 1.381 \times 10^{-23} \) Bolzmann constant
\( M_{H_2} \) g mol\(^{-1}\) \( = 2.016 \) Molar mass of hydrogen
\( N_A \) mol\(^{-1}\) \( = 6.022 \times 10^{23} \) Avogadro’s constant
\( R \) J mol\(^{-1}\) K\(^{-1}\) \( = 8.314 \) Universal gas constant
\( \pi \) - \( = 3.1415 \) pi
Declaration of authorship

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The work presented in this thesis, except where otherwise noted, was done by the author with supervision and guidance from his academic supervisor, Dr Timothy J Mays, Head of Department and Senior Lecturer of Chemical and Materials Engineering in the Department of Chemical Engineering at the University of Bath.

Most of the work reported in this thesis has been presented at conferences and workshops in the form of oral and poster presentations as described in the dissemination section. The equilibrium modelling work performed on MATLAB will be reported in forthcoming journal articles. The COMSOL modelling work will be submitted to journals in the future.
“It doesn’t matter how beautiful your theory is, it doesn’t matter how smart you are...if it doesn’t agree with experiment, it’s wrong”

Richard P. Feynman
Chapter One

Introduction
Chapter 1. Introduction

1.1 Scope and motivation

Hydrogen and its isotopes are vital in the energy future model for mankind. Hydrogen is a key energy vector of the future, capable of meeting humanity’s ever increasing hunger for energy. Hydrogen represents a clean, efficient, safe and renewable energy source which can reduce our dependence on fossil fuels. Deuterium and tritium (the naturally occurring isotopes of hydrogen) are the proposed fuels for future thermonuclear fusion reactors, and therefore have a vital role in development of fusion energy. Deuterium exists in all water and tritium exists in small quantities in the atmosphere due to interactions with cosmic rays. Research and development is currently underway across the world to establish fusion reactors as a practical energy source. The International Thermonuclear Experimental Reactor (ITER) is currently under construction in Cadarache, France, to prove the concept in a near commercial scale device. The theoretical physics behind these devices has, for all intents and purposes, been solved. The remaining challenge is the engineering to bring designs into fruition. The main obstacle, at present, is establishing a working fuel cycle to process and recycle the valuable un-spent fuels (deuterium and tritium) from reactor discharge.

A number of techniques have been proposed to achieve separation in the different areas of the fuel cycle. The main separation technique will be cryogenic distillation due to the ability to process varied feed stream compositions. The ancillary clean-up of tritium containing gas streams for discharge to atmosphere and separation of hydrogen isotopes from inert gases will be achieved by chromatographic and membrane techniques, respectively. Chromatographic separation studies have mostly involved palladium due to its remarkable ability to absorb large quantities of hydrogen isotopes at room temperature with rapid kinetics during hydride formation. Membrane separations also predominantly use palladium or its alloys because of their selectivity to hydrogen and its isotopes. Any separation of hydrogen isotopes using palladium hydride (and palladium membranes) will involve hydrogen isotope exchange on the surface of the metal. Hydrogen isotope exchange involves the exchange of one hydrogen isotope atom (for instance, deuterium (D)) held within the palladium face-centred cubic (fcc) lattice for another isotope of hydrogen (for instance, hydrogen (H)). The reaction takes place...
through a multi-step mechanism involving steps in the gas-, surface- and solid phases. This process is poorly understood, with definitive conclusions about the kinetics and mechanisms of the reaction still eluding many investigators.

In particular, the rate of exchange of hydrogen isotopes on palladium hydride surface has been particularly troublesome. A number of authors have investigated the process, but using very specific palladium-particle morphology and different reactor setups (i.e. Sievert’s type or flow apparatus’). To establish a model for the rate profile of exchange, a complete suite of information is needed, considering the effects of temperature, pressure, flowrate, particle morphology, and parameter space. As of yet, no investigator has achieved this. Some studies have focussed on the exchange process, such as Foltz and Melius, Outka and Foltz, Carstens and Encinias and Fukada et al [1-4]. However, all have limitations, and did not investigate a wide variety of experimental conditions. It is, therefore, quite difficult to make any generalisations about the exchange process.

It is proposed that in this research a thorough study of the kinetics and mechanisms of hydrogen isotope exchange over solid storage media will be performed. This will involve characterising the kinetics, and elucidating the reaction mechanisms and rate determining step, of hydrogen isotope exchange under a variety of different conditions within the solid storage medium. To enable analysis of the process a bespoke piece of equipment was designed by AWE, Aldermaston and installed in the Department of Chemical Engineering, University of Bath. The purpose of the project was to develop a numerical model, such that the gas composition exiting the flow device can be accurately simulated as a function of time. The novelty of the proposed experiments lies in the wish to understand the kinetics and mechanisms of hydrogen-uptake, exchange and liberation processes as opposed to simply measuring the hydrogen-storage capacity of palladium metal or other materials. This has been extensively studied since the 19th century [5-9]. After experimentation, a thorough numerical model was constructed considering the role of the gas and surface processes taking place during hydrogen isotope exchange in palladium (Pd). Developing a greater understanding of these processes will aid in the design of systems using hydrogen isotope exchange. This was of interest to AWE, but also to other UK companies with interests in gas separation and waste purification; not to mention future fusion devices.
1.2 Aims and objectives

The overall objective of this research is:

- To carry out hydrogen isotope exchange experiments at a number of temperatures and pressures with the aim of producing a model capable of accurately reproducing experimental data. The objective will be to develop a kinetic based numerical model of hydrogen isotope exchange, such that the gas composition exiting a flow device can be simulated as a function of time for both isotope exchange directions (PdD to PdH and PdH to PdD). This will be achieved by using a unique and bespoke piece of equipment to investigate the effects of different experimental variables on the exchange process.

Specific aims of this research:

1. To understand the timescales and rates of D₂ for H₂ (and H₂ for D₂) isotope exchange over solid palladium, and the formation of HD;
2. To understand the dependency of these time-resolved processes on:
   a. Rates of gaseous flow through the solid porous medium;
   b. Temperature of the system;
   c. Gas-pressure in the flowing system;
   d. Initial hydrogen/deuterium loading characteristics of the palladium.
3. To produce a numerical model based on a parameterised representation of the major chemical processes occurring during the exchange of one isotope for another.
4. To develop an understanding of the underlying kinetics and mechanisms of the hydrogen isotope exchange process and to trial at least one existing surface reaction mechanism, such as the Langmuir-Hinshelwood mechanism.
5. To investigate how such a model relates to what is already known and reported about the kinetics of the interactions of hydrogen (and deuterium) with solid palladium including:
   i. Adsorption and desorption processes;
   ii. Isotope effects.
1.3 Structure of thesis

This thesis is divided into seven chapters, including this Introduction (Chapter 1). Chapter 2 introduces the motivation and background for the work, in terms of the need for hydrogen isotopes. The chapter aims to cover the key aspects of the palladium-hydrogen system rather than an lengthy review of the topic. It does however give an extensive review of hydrogen isotope exchange in solid storage media since this is the main topic of this thesis. The background aims to review the majority of the published literature involving hydrogen isotope exchange to date. This is done using recent references and historic work from authoritative sources which give context to the work presented in the following pages. Chapter 3 presents the materials and methods used in the thesis, including an overview of the experimental flow apparatus, the new isotope exchange (IsoEx) rig, and the palladium powder used in the experiments. Chapter 4 is the main results section of the thesis. It presents the experimental data for hydrogen isotope exchanges carried out at a number of different temperatures and inlet gas pressures. Alongside this, additional analyses of the experimental data are presented to complement the experimental results and allow the reader to compare the findings to the existing understanding of the isotope exchange process in palladium. Chapter 5 is the main modelling chapter. It describes the models produced in the thesis to simulate the experimental data obtained on the IsoEx rig. Two models are presented. One was created using MATLAB based on an existing model in the literature, albeit with extensive modifications. The second is a full kinetic model of the hydrogen isotope exchange process created in COMSOL Multiphysics which provides insights into the process in two and three dimensions. In Chapter 6, the thermodynamics of the hydrogen isotope exchange process are presented in the form of heat profiles calculated from modelling the experimental data presented in Chapter 4. Chapter 7 presents the concluding remarks and suggests directions for further work.
Chapter Two

Background
Chapter 2. Background

2.1 Introduction

This chapter introduces the existing literature surrounding hydrogen isotope exchange in solid storage media. The need for hydrogen isotopes is discussed alongside the existing knowledge surrounding the palladium-hydrogen system, which forms the solid media used in this work. The section then progresses to the existing literature studies surrounding hydrogen isotope exchange in a number of materials, including palladium (Pd). Finally, the studies investigating the kinetics of hydrogen isotope exchange are discussed with the aim of introducing some concepts which are used in later chapters of this work. All references for the work presented in this chapter are presented in the Bibliography accompanying this thesis.

2.2 Hydrogen and Hydrogen Isotopes

Hydrogen is element number 1 in the periodic table and the lightest of all gases. It has the remarkable ability to form compounds with almost every element. However, at normal temperatures, and without the presence of a catalyst, the hydrogen molecule, \( \text{H}_2 \), is very stable, having an intermolecular bond strength of 436 kJ mol\(^{-1}\).

Three isotopes of hydrogen exist in nature: \(^1\text{H}\) (protium), \(^2\text{H}\) (deuterium) and \(^3\text{H}\) (tritium) which have the abundances 99.985%, 0.015% and trace amounts, respectively.

2.3 Protium

Hydrogen\(^1\) (protium), \( \text{H} \), is the lightest and most abundant element in the universe, accounting for 75% of the elemental mass by species. Its molar mass is 1.00797 g mol\(^{-1}\) (atomic number 1) and is the first element in the periodic table, having an electron configuration of 1s\(^1\). Hydrogen is composed of a single proton in the nucleus and an orbiting electron. Its natural state is in the form of a low density diatomic molecule, \( \text{H}_2 \).

\(^1\) Throughout the rest of this thesis, the term ‘hydrogen’ can refer protium, deuterium or tritium. Likewise, the term ‘hydride’ can refer to (palladium) hydride, deuteride or tritide. In discussing specific chemical systems (e.g. palladium deuteride) then specific nomenclature is employed.
which can be burnt with oxygen to produce water, $\text{H}_2\text{O}$, yielding 121 MJ kg$^{-1}$ heat energy (this is the lower standard specific enthalpy of oxidation of $\text{H}_2(\text{g})$ at 298 K, i.e. yielding $\text{H}_2\text{O}(\text{l})$; this is the highest specific energy density of any chemical fuel). Hydrogen gas was artificially produced by T. Von Hohenheim (also known as Paracelsus) in the years 1493-1541 via mixing metals with strong acids. It took until ca. 1766 for Henry Cavendish to first recognise that hydrogen gas was a discrete substance, identifying the gas from the metal-acid reaction as ‘flammable air’. It was this observation by Cavendish that stimulated Antoine Lavoiser, in 1783, to give hydrogen its name, which in Greek means ‘water-creator’, after investigating the products of hydrogen combustion.

At standard temperature and pressure, hydrogen is a colourless, odourless, tasteless, highly combustible gas. Hydrogen is present in low concentrations in Earth’s atmosphere, approximately 1 ppm [10]. However, it is the third most abundant element on the Earth’s surface due to its presence in water, hydrocarbons and many other chemical compounds.

### 2.3.1 Physical and Thermodynamic properties:

The hydrogen (protium) molecule, $\text{H}_2$, can exist in two forms, either ortho- or para-, depending on the nuclear spins of its constituent atoms. If both nuclear spins rotate in the same direction (parallel) then it is deemed ortho-hydrogen and if the nuclear spins are in opposite directions (anti-parallel) then the hydrogen molecule is referred to as para-hydrogen. Many physical and thermodynamic properties of $\text{H}_2$ depend on the nuclear spin orientation, but the chemical properties of both forms (which depend on electronic configuration) are the same. For example, properties that involve heat, such as enthalpy, entropy, and thermal conductivity can show significant differences between ortho- and para-hydrogen [10].

At room temperature, an equilibrium ratio of 3:1 ortho- to para-hydrogen is established. At very low temperatures however, the equilibrium ratio shifts to almost pure para-hydrogen [10]. This is apparent because para-protium is the lower energy form of protium. Figure 2-1 presents various physical and thermodynamic properties for normal (ortho-) and para-protium.
Deuterium is a stable isotope of hydrogen, existing in natural abundance in the oceans of Earth. Approximately one atom in every 6400 atoms of hydrogen is deuterium (~156 ppm). Unlike normal hydrogen, deuterium’s nucleus has one proton and one neutron, orbited by a single electron. At ordinary temperatures, deuterium (D\textsubscript{2}) exists in the form of gas. Deuterium was first discovered by Harold Urey in 1931, earning him the Nobel Prize three years later after James Cavendish’s discovery of the neutron in 1932 helped elucidate its structure.

**Physical and Thermodynamic Properties:**

Although the molar mass of deuterium (D) is twice that of H, chemically it behaves similarly. However, isotopic differences between hydrogen isotopes are greater than any other element. Deuterium’s melting point is -254 °C, compared with -259 °C for protium, and its normal boiling point is -249 °C compared with -253 °C for protium. Its macroscopic properties of colour, odor, taste, etc are the same as those for protium.
Compounds containing deuterium have slightly different properties, compared with those containing protium. Bonds involving deuterium (and tritium) are stronger than the corresponding bonds in protium. Some of these small changes can be enough to make significant changes in some reactions, particularly biological reactions. Deuterium can replace normal hydrogen in water molecules to form heavy water ($\text{D}_2\text{O}$), which is 10.6% denser than normal water.

### 2.5 Tritium

Tritium is a radioactive isotope of hydrogen. The nucleus is composed of one proton and two neutrons, giving tritium ($\text{T}$) a molar mass of about $3 \text{ g mol}^{-1}$. Naturally occurring tritium is almost non-existent, some trace amount may be found high in the atmosphere due to interactions with cosmic rays. Tritium was first prepared by Ernest Rutherford and co-workers in 1934 by bombardment of a deuterium containing acid with fast moving deuterons. Tritium decays into helium-3 by beta decay, and has a half-life of approximately 12.3 years. At standard temperature and pressure (STP) tritium is a gas. Tritium easily combines with oxygen to form tritiated water, which is a radiation hazard. Tritium’s ability to fuse with lighter hydrogen isotopes is being exploited in numerous experimental thermonuclear fusion reactors in operation around the world. Some physical properties of molecular tritium are displayed in the table below.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>melting point, at $21.6 \text{kPa}^4$, K</td>
<td>20.62</td>
</tr>
<tr>
<td>boiling point, K</td>
<td>25.04</td>
</tr>
<tr>
<td>critical temperature, K</td>
<td>40.44$^c$</td>
</tr>
<tr>
<td>critical pressure, MPa$^d$</td>
<td>1.850</td>
</tr>
<tr>
<td>critical volume, cm$^3$/mol</td>
<td>57.1$^c$</td>
</tr>
<tr>
<td>heat of sublimation, J/mol$^f$</td>
<td>1840</td>
</tr>
<tr>
<td>heat of vaporization, J/mol$^g$</td>
<td>1390</td>
</tr>
<tr>
<td>entropy of vaporization, J/(mol K)$^f$</td>
<td>54.0</td>
</tr>
<tr>
<td>molar density of liquid, mol/L</td>
<td></td>
</tr>
<tr>
<td>$20.62 \text{K}$</td>
<td>45.35</td>
</tr>
<tr>
<td>$25 \text{K}$</td>
<td>42.65</td>
</tr>
<tr>
<td>$29 \text{K}$</td>
<td>39.88</td>
</tr>
</tbody>
</table>

$^a$Values are from Ref. 11 unless otherwise indicated.
$^b$Value represents the triple point (162 mm Hg).
$^c$From Ref. 10.
$^d$To convert MPa to psi, multiply by 145.
$^e$Value is calculated.
$^f$To convert J to cal, divide by 4.184.

Figure 2-2 Physical properties of molecular tritium. Reprinted from [11]
Figure 2-3 shows a comparison of the three isotopes of hydrogen, and there isotopologues. Isotopologues of chemical species are molecules that have at least one atom with a different number of neutrons than the parent. The isotopologues, HD, HT and DT arise in hydrogen isotope separations involving catalytic surfaces, so this information is provided for reference and comparison.

<table>
<thead>
<tr>
<th></th>
<th>n-H₂</th>
<th>n-D₂</th>
<th>n-T₂</th>
<th>HD</th>
<th>HT</th>
<th>DT</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>M</strong>&lt;sub&gt;r&lt;/sub&gt;</td>
<td>2.016</td>
<td>4.029</td>
<td>6.034</td>
<td>3.022</td>
<td>4.025</td>
<td>5.022</td>
</tr>
<tr>
<td>Bond length, pm</td>
<td>74.6</td>
<td>74.2</td>
<td>74.1</td>
<td>431.6</td>
<td>439.2</td>
<td>435.1</td>
</tr>
<tr>
<td>Dissociation energy, kJ/mol</td>
<td>7.3</td>
<td>17.1</td>
<td>21.6</td>
<td>12.8</td>
<td>17.7</td>
<td>19.4</td>
</tr>
<tr>
<td>Triple point temperature, K</td>
<td>32.98</td>
<td>38.35</td>
<td>40.44</td>
<td>35.91</td>
<td>37.13</td>
<td>39.42</td>
</tr>
<tr>
<td>pressure, kPa</td>
<td>1.31</td>
<td>1.67</td>
<td>1.85</td>
<td>1.48</td>
<td>1.57</td>
<td>1.77</td>
</tr>
<tr>
<td>Critical point temperature, K</td>
<td>20.39</td>
<td>23.67</td>
<td>25.04</td>
<td>22.13</td>
<td>22.92</td>
<td>24.38</td>
</tr>
<tr>
<td>pressure, MPa</td>
<td>70.811</td>
<td>162.50</td>
<td>260.17</td>
<td>114.80</td>
<td>158.62</td>
<td>211.54</td>
</tr>
<tr>
<td>Normal boiling point, K (atmospheric pressure)</td>
<td>1.316</td>
<td>2.230</td>
<td>3.136</td>
<td>1.802</td>
<td>2.310</td>
<td>2.694</td>
</tr>
<tr>
<td>Density at normal boiling point</td>
<td>825</td>
<td>1175</td>
<td>1400</td>
<td>1000</td>
<td>1100</td>
<td>1290</td>
</tr>
<tr>
<td>Heat of vaporisation (25 K), J/mol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2-3 Atomic and molecular data of hydrogen isotopes and their isotopologues [11]

### 2.6 The Need for Hydrogen Isotopes

Concentrated hydrogen isotopes are used in a wide variety of applications. Hydrogen (protium) is seen by many as the future energy vector, offering a sustainable and clean means of storing energy from renewable sources. Molecular protium (H₂) is used heavily in the oil industry, for the hydrogenation of hydrocarbon streams, and also in many organic and inorganic chemical reactions. It is also finding increasing use in fuel cells for automotive and stationary uses. These require very high purity protium streams to prevent poisoning and subsequent deactivation of the anode catalytic metal (i.e. platinum).

Deuterium (D), the other naturally occurring isotope of hydrogen, exists in sea water and has been used in many applications since its discovery in 1931 by Harold Urey. Nuclear magnetic resonance (NMR) spectroscopy makes use deuterium solvents to allow accurate analysis of organic molecules spectra. Differences in the nuclear spin properties of deuterium mean that NMR spectra are highly differentiable from those obtained from protium (or protium containing molecules) and can be ignored by an instrument tuned for protium. In essence, the deuterium signal is ignored leaving only
the signal of the compound of interest. Neutron scattering techniques also make use of differences in physical properties of the isotopes. Deuterium and protium have significantly different incoherent neutron cross section. This property can be used to reduce scattering noise by substituting protium atoms for deuterium atoms in compounds of interest, increasing the accuracy of analysis. Neutron scattering techniques are popular for analysing biological molecules as well as metal hydride systems. A further use of deuterium and its compounds, which is important in chemistry, biochemistry and environmental sciences, is in tracing of molecules. It is used as a stable, non-radioactive tracer capable of bonding with molecules without significant changes to their structure and behaviour. It can, therefore, be used to study the mechanisms of various chemical and biological (including metabolic) reactions.

Heavy water (D\textsubscript{2}O) is an important neutron moderator in the nuclear industry. D\textsubscript{2}O is used in nuclear fission reactors to slow fast moving neutrons to generate heat for power generation. It is also one of the two primary fuels for a D-T thermonuclear fusion reaction. An unprecedented international effort is currently underway to develop a fusion device as a practical and commercial energy source. The International Thermonuclear Experimental Reactor (ITER), in Cadarache, France, is under construction after a long period of design and testing at smaller fusion facilities, such as the Joint European Torus (JET) at Culham, Oxford. This international effort has been driven by investigators and governments from the USA, China, India, Japan, South Korea, Russia and the European Union (EU).

The other fuel in fusion reactors is tritium, a radioactive isotope of hydrogen. Tritium fuses with deuterium at very high temperatures (ca. 150,000,000 °C) within a thermonuclear fusion reactor releasing a neutron and a large amount of energy. Its production, and separation from unspent fuel, is therefore crucial in achieving a practical fusion reactor. A brief overview of fuel cycle of a thermonuclear fusion reactor is given in the next section (see below). Another fusion technique currently under investigation is inertial confinement. Here, deuterium and tritium again form the fuels but in this case they are formed into pellets containing a mixture of the two isotopes. Tritium also finds uses in nuclear weapons, self-powered lighting assemblies and in analytical chemistry as a radiolabel in organic molecules. Tritium has a value of ~$30,000/g (2003) [12].
2.7 Thermonuclear Fusion and ITER

As outlined above, an international endeavour to build a net energy producing thermonuclear fusion reactor is underway in France. If successful, the reactor would produce more ~ 10x more energy than required to initiate nuclear fusion. The D-T nuclear fusion reaction can be represented by the following equation:

\[ _2^3D + _1^3T \rightarrow _2^4He + _0^1n + 17.6 \text{ MeV} \]  

[2-1]

where: deuterium (D) fuses with tritium (T) forming a helium (He) atom, a neutron (n) and 17.6 mega electron-volts (MeV) of energy which is absorbed by the plasma.

The typical magnetic confinement reactor is configured in a doughnut shaped torus, or TOKAMAK, vacuum vessel surrounded by a number of strong electro-magnets (see Figure 2-4). Gaseous deuterium and tritium are admitted into the vessel (typically in the order of 1/100g of gases in JET and approximately ½ g in ITER) whereby they undergo ohmic heating to raise the temperature, causing the gases to form plasma. Further heating is needed to reach 150,000,000 °C required for atoms to overcome the strong nuclear force and fuse together. This is supplied by neutral beam injectors, radio frequency (RF) or microwave heating. In the first case, neutral atoms (usually deuterium) are fired into the plasma where they collide with atoms imparting their kinetic energy to raise the temperature.

One of the main challenges of achieving practical nuclear fusion is establishing the fuel cycle for supply and recovery of hydrogen isotopes. The majority of the theoretical physics hurdles have been overcome, leaving the engineering associated with construction and operation of a fusion reactor as the remaining challenge. The main issues are: testing of compounds suitable for first wall materials and the hydrogen isotope fuel cycle. Simulating these in a laboratory is difficult, creating the need for a full-scale experimental reactor (ITER). The fuel cycle has been the subject of much study in a number of laboratories across the world, and has focussed on a number of key technologies.
The purpose of the fuel cycle is to recover un-spent hydrogen isotopes from the D-T fusion reactor. A diagram of the proposed fuel cycle for a thermonuclear reactor is shown in Figure 2-5. The key areas relating to hydrogen isotope separation are the Isotope Separation System (ISS), Tokamak Exhaust Processing (TEP), Atmosphere Detritiation Systems (ADS), Water Detrititation System (WDS) and the Storage and Delivery System (SDS). Isotope separation techniques are required in a number of units associated with fuel recovery and inert gas clean-up. Efficient methods of hydrogen isotope separation from inert gas streams and from streams of mixed isotopes are required for thermonuclear fusion reactors to reach commercial fruition. The most effective technology for use in the ISS is cryogenic distillation because of its ability to deal with varying feed compositions whilst maintaining high product purity. Separation of hydrogen isotopes from inert gases (such as He) is dealt with in the TEP typically.
using palladium-silver (Pd-Ag) alloy membranes. Here, trace amounts of tritium make their way into the inert gas stream for discharge to atmosphere and must be removed. Promising techniques for this are chromatographic separations using metal hydrides and hydrogen isotope exchange. Metal hydrides also form the basis for the intermediate storage of hydrogen isotopes in the SDS. Understanding these chromatographic and metal hydride processes is therefore crucial in developing the fuel cycle for a fusion device.

It is worth mentioning the other form of fusion research currently in development across the world, inertial confinement fusion (as outlined above). Here, high-energy lasers are used to heat the outer layer of a D-T pellet, causing it to explode outwards. This explosion causes a large reaction force travelling inwards towards the centre of the pellet. This force compresses and creates shockwaves within the pellet. If these shockwaves are sufficient in energy they can compress and heat the pellet to levels required for fusion of deuterium and tritium to occur. An example of a facility currently testing this form of fusion is the National Ignition Facility (NIF) in the USA. A different fuel cycle is required in this form of fusion. An efficient system of isotope separation is required to process un-spent fuel from the reaction chamber, similar to that of a magnetic confinement device. There is also the need to produce a significant number of pellets to be used in a functional laser-induced fusion reactor. There are a number of estimates for the number of pellets required per second, but the majority of investigators think of 10 pellets per second would be required. Therefore, a large number of D-T pellets (or microcapsules) would need to be produced every day to sustain a practical fusion reactor using lasers. This process would require hydrogen isotope separation and storage on a large scale. Hydrogen isotope exchange and chromatographic techniques using metal hydrides could be used for an efficient means of hydrogen isotope separation, and metal hydrides offer a promising means of storage. Both of these requirements are relevant to the research project undertaken in the PhD ‘Kinetics and Mechanisms of Hydrogen Isotope Exchange over Solid Storage Media’.
For the reasons discussed in the above two sections of this report, it is expected that there will be a substantial and growing market for efficient techniques for the production and separation of pure hydrogen isotopes.

### 2.8 The Need for Characterisation of Hydrogen Isotope Exchange

The phenomenon of exchange, which occurs when one isotope of hydrogen (e.g. protium) is passed through a storage bed containing a different isotope (e.g. deuterium) and replaces the stored gas, has not previously been characterised in detail. This process is of interest to areas such as gas separation and purification, particularly relating to hydrogen isotopes. A detailed understanding of the kinetics and mechanisms of the exchange process will enable future systems based on these technologies to be designed more efficiently and with improved performance. This project aims to provide information and knowledge that will help to optimise future system designs, reducing raw materials requirements, reducing weight and size impacts and furthermore, increase the understanding of system performance. Improving understanding and knowledge of the process mechanisms (and kinetics) associated with chemical separation of hydrogen isotopes by hydrogen isotope exchange has the potential to contribute to developments...
in waste separation and purification that will be of interest to other UK companies, as well as the international endeavours to develop fusion energy.

2.9 The Palladium-Hydrogen System

2.9.1 Introduction

Of the main methods used to separate hydrogen isotopes (including distillation and chromatography, see section 2.11) metallic membranes systems especially using palladium (Pd) are the most common. Pd, is a group 10 transition metal with atomic number 46 and molar mass 106.42 g mol\(^{-1}\). It is a rare and lustrous silvery-white (or black if powder) metal discovered by William Hyde Wollaston in 1803. Palladium falls into a group of elements called the platinum group metals (PGMs), which all have similar chemical properties; palladium having the lowest normal melting point (1828.05 K) and density (12.023 g cm\(^{-3}\)). The largest commercial use of palladium is in catalytic converters for vehicles. It also finds use in electrical contacts, jewellery, dentistry and aircraft spark-plugs. Industrially, palladium is the main catalyst in hydrogenation and dehydrogenation reactions, as well as in petroleum cracking, because of its ability to dissociate molecular hydrogen upon contact with the surface.

In 1866, Thomas Graham [5] investigated the palladium-hydrogen system and found that palladium had a remarkable ability to absorb large amounts of hydrogen. He referred to this absorbed hydrogen as ‘hydrogenium’ because of the dissolved hydrogen’s metallic-like character. Palladium can, in fact, absorb up to 900 times its own volume of hydrogen at standard temperature and pressure (STP). The palladium hydride formed is referred to as an interstitial hydride because hydrogen occupies the interstitial sites in the palladium lattice. Also, the ratio of hydrogen atoms to metal atoms does not remain constant, and can be changed with varying hydrogen pressure or system temperature. The following equations can be used to describe the formation of the hydride phase:

\[
\frac{2}{x} \text{Pd} + \text{H}_2 \rightleftharpoons \frac{2}{x} \text{PdH}_x + \text{heat}
\]  

[2-2]
Since Graham’s discovery, a number of other papers have been published on this metal-hydrogen system [6, 9, 15-17]. When referring to ‘hydrogen’ in the following sections, the principals discussed can apply to any of the three isotopes. The individual isotope names will be referred to when necessary. Protium will be used interchangeable to mean normal hydrogen. Since the early studies into the Pd-H system, there have been a numerous additional studies on the palladium-hydrogen-deuterium (Pd-H(D)), palladium-deuterium (Pd-D) and palladium-tritium (Pd-T) systems [8, 17-51].

Attempting to review the vast quantity of literature surrounding the palladium-hydrogen isotope systems would prove excessive and counterproductive to the aim of the Background section. For this reason only the most relevant papers are discussed in the following sections. The author points the reader towards the aforementioned papers (which include a number of detailed review articles) for more information.

The following sections review the palladium-hydrogen system; highlighting important aspects, such as, preparation of palladium hydride and the associated phase change, structure, hydrogen (and deuterium) diffusion, thermodynamics of the system, isotope effects, and finally the kinetics and the surface.

### 2.9.2 Characteristics of the Palladium-Hydrogen System

The absorption of hydrogen from the gaseous phase by palladium is characterised by the following steps [43]:

1. Movement of H$_2$ to the palladium surface
2. Adsorption of H$_2$ onto palladium surface
3. Dissociation of H$_2$ into elemental hydrogen
4. Loss of two electrons into the metal to form two H$^+$ ions
5. Conduction of the electrons through the bulk metal
6. Diffusion of the protons via interstitial hopping

Two phases can be formed in the palladium-hydrogen system. At low hydrogen concentration, a randomly dispersed solid solution of hydrogen in the palladium bulk is formed, called the $\alpha$-phase. Here, the atoms of hydrogen are located around the surface with no interactions with each other. Upon introduction of higher hydrogen concentration, palladium hydride is formed, the $\beta$-phase, characterised by the long range
ordering of the hydrogen atoms [43]. In the β-phase, the hydrogen atoms occupy a significant amount of the surface interacting with adjacent hydrogen atoms.

Elemental palladium has holes in its 4d conduction band, i.e. in the 4d electron sub-shell. The conduction band refers to the range of electron energies sufficient for an electron to move freely within the atomic lattice (escaping the valence band where electrons are bound to their atoms). 4 refers to the 4th electron shell, and ‘d’ refers to the d sub-shell which can hold a maximum of 10 electrons. Palladium has two ‘holes’ or spaces in its 4d sub-shell. Each absorbed hydrogen atom contributes some portion of its own electron to the palladium-hydride band structure. The maximum hydrogen-to-palladium atomic ratio easily obtainable is ~0.7. Flanagan [15, 52] postulated that at this atomic ratio, the ‘4d’ electron band has become filled, and any hydrogen absorbed in excess of this value contributes its electron to the ‘5s’ palladium electronic band.

2.9.3 The Palladium-Hydrogen Phase Diagram

Two hydrogen phases exist within the palladium lattice [8, 15]. Upon introduction of hydrogen into the lattice an isotropic expansion occurs, swelling the lattice. Most noticeable swelling is observed upon entry into the β-phase. The most characteristic feature of the palladium-hydrogen phase diagram is the formation of two solid phases below the critical point:

Palladium-protium system (Pd-H): \[ T_c = 563 \text{ K}; \ p_c = 19 \text{ bar}; \ r_c = 0.257 \]

* Palladium-deuterium system (Pd-D): \[ T_c = 556 \text{ K}; \ p_c = 39 \text{ bar}; \ r_c = 0.257 \]

*Obtained from [15]. \( r_c \) is the atomic fraction of isotope in Pd i.e. H/Pd

No critical data for the palladium-tritium system. Lasser [37] investigated the palladium-tritium system up to temperatures of 125 °C and pressures upto 2 bar; which was not sufficient enough to go in excess of the critical point.
The two hydrogen phases are phases in the Gibbs sense; where the phase rule predicts if two solid phases exist with one gaseous phase, there should be one degree of freedom. This is observed in the palladium-hydrogen system, for example, if the temperature is chosen, the pressure will be fixed. Figure 2-6 shows an isobaric phase diagram for the Pd-H(D) system. Here, the miscibility gap can be seen as the \((\alpha+\beta)\) region. This area represents a coexistence of both \(\alpha\)- and \(\beta\)-phases which do not mix.
The critical temperature \( (T_c) \) of the palladium-hydrogen system is defined as the temperature below which any \( P-C-T \) isotherm traverses a two-phase region (\( \alpha \)-phase + \( \beta \)-phase), see Figure 2-8 [43]. A characteristic of any isotherm below the critical temperature is hysteresis between the absorption leg and desorption leg. Isothermal pressure hysteresis occurs when the pressure of hydride formation, \( p_f \), is greater than that for decomposition, \( p_d \). Flanagan and co-workers [15] believe that this hysteresis occurs because of the abrupt lattice expansion accompanying hydriding and the contraction accompanying dehydriding. Above \( T_c \), the transition from \( \alpha \)-phase to \( \beta \)-phase is smooth, and it is generally accepted that the critical temperature and pressure marks the point where hysteresis stops [43]. In Figure 2-8, this can be taken as any point under the point of inflection on the 298 °C curve. Above \( T_c \), two solid hydride phases cannot exist together under equilibrium conditions for any hydrogen concentration. Below \( T_c \), the \( \alpha \)- and \( \beta \)-phases of the system can co-exist, represented by the horizontal, pressure invariant, portion of the isotherm (Figure 2-8).
2.9.4 Preparation of Palladium Hydrides

Preparation of palladium hydride is usually achieved by introducing the hydrogen into the metal via the gas phase. Upon contact with the metal surface the diatomic hydrogen molecule chemisorbs to the surface, and dissociates $[\text{H}_2 \rightarrow 2\text{H}]$ into two hydrogen atoms and begins to follow the steps identified in the above section. The absorption of hydrogen from the gas phase is dependent on the cleanliness (and morphology) of the palladium surface. It is therefore necessary, when preparing a palladium hydride, to ensure the surface is clean of impurities. Likely contaminants are oxygen, $\text{O}_2$, and carbon monoxide, $\text{CO}$. Since any oxygen on the surface will react with $\text{H}_2$ to form $\text{H}_2\text{O}$, no special precautions are needed for palladium to absorb hydrogen other than mechanical cleaning to remove grease and other contaminants from the surface. CO can be removed from the surface by heating the palladium sample.

Equilibrium between gaseous molecular hydrogen and hydrogen dissolved in the palladium should be rapidly established, provided the surface is clean and the diffusion paths in the solid are not too long [15]. Clewley [20] showed that equilibrium in bulk palladium powder can be achieved down to $\sim 167$ K. The thermodynamic criterion for equilibrium between the solid and gaseous hydrogen phases is the equality of the hydrogen atom chemical potentials $\mu_\text{H}$ in the co-existing two phases [15]. The following
equation describes the hydrogen atom chemical potential in the gas phase, with the standard designation referring to 1 bar:

\[
\mu_H(g) = \frac{1}{2}(\mu_{H_2}^0 + RT\ln p_{H_2}) \tag{2-3}
\]

Where: \(\mu_{H_2}^0\) is the standard chemical potential of gaseous molecular hydrogen, \(R\) is the molar gas constant, \(T\) is the temperature and \(p_{H_2}\) is the pressure of the molecular hydrogen in the gas phase. The chemical potential of hydrogen in an ideal solid solution may be written as:

\[
\mu_H = \mu_H^0 + RT\ln\left(\frac{n}{1-n}\right) \tag{2-4}
\]

where \(n\) is the atomic ratio (H/Pd) of hydrogen in the solid, and \(\mu_H^0\) is the standard chemical potential of H. Flanagan & Oates [15] noted that even at high temperatures, the equilibrium concentration of H atoms in the gas phase will be extremely small. At 1 bar H\(_2\) and 300 K (STP), \(p_H = 10^{-30}\) bar. The hydrogen potential in the gas phase is therefore small, preventing high concentrations of hydrogen in the metallic phase. The only direct method that permits the formation of high hydrogen contents in the metal phase is the use of high pressures or non-equilibrium methods. Hemmes [53] determined that at temperatures of \(T = 100\) K and pressures of \(> 30,000\) bar, it is possible to synthesize PdH\(_x\) with \(x > 0.999\). There are a number of other non-equilibrium methods to increase the H/Pd ratio to near stoichiometric levels, or even above. RF-discharge can be used to approach stoichiometric concentrations, while ion implantation at low temperatures has achieved hydrogen to palladium ratios in excess of 1. The hydrogen chemical potential within the solid palladium is governed by kinetic factors, rather than thermodynamic ones. The amount of hydrogen within the lattice will be determined by the rate of recombination reaction compared to the chemisorbed to absorbed transition rate (i.e. the two processes that effect hydrogen content in the metal).

### 2.9.5 Structure and Hydrogen Occupancy

Palladium is a face-centred cubic (fcc) structure. The atoms are arranged in the crystalline structure such that one atom is located at each corner of the cube and one at the centre of each face, see Figure 2-9 below. There are two types of sites available for
adsorption within the palladium crystal structure, tetrahedral and octahedral. Hydrogen occupies the octahedral sites and uses the tetrahedral sites to transition from one octahedral site to the next, via diffusion. Complete occupancy of the octahedral sites results in a stoichiometric hydride formation, PdH, although, as discussed in the above section, this requires high pressures or special implantation techniques. Tetrahedral occupancy has been evidenced in the literature [54], after special preparation of the sample palladium powder by loading in the supercritical region.

Figure 2-9: Face-centered cubic lattice structure of Palladium

The distance between the palladium atoms in the lattice, the so-called lattice parameter, is 0.3890 nm at 298 K. During hydrogen absorption the lattice undergoes an isotropic expansion while retaining its fcc structure. In low hydrogen loading, the α-phase, the lattice parameter of PdH$_\alpha$ is 0.3894 nm [15], representing a small expansion in the lattice associated with a small protium content, H/Pd ~ 0.015. This can be explained by the lack of long-range ordering of the hydrogen atoms in the α-phase. Hydrogen atoms are spread across the surface sites and have little interaction with each other. In the β-phase, which co-exists with the α-phase up to $\sim$PdH$_{0.6}$, there is long range ordering between the hydrogen atoms in the palladium lattice. These closely packed hydrogen atoms feel repulsion from their neighbours; causing the lattice structure to undergo a much larger isotropic expansion compared with that associated with the α-phase alone.
The lattice parameter for the β-phase is 0.4025 nm at STP [15], where H/Pd ~ 0.7. In transitioning from the α- to β-phase the lattice experiences a volume expansion of 10.4 % [15]. In both phases the hydrogen is disordered. It should also be noted that the lattice parameter also varies as a function of the H/D concentration.

Absorption of deuterium causes a smaller expansion in the lattice structure than that caused by hydrogen (protium). Flanagan [15] and Harris [55] accredit this difference to the lower zero-point energy of deuterium, Figure 2-11. Zero-point energy is the energy atoms retain even at absolute zero, it is the lowest energy state of a quantum mechanical system, its ground state. The protium isotope has a greater zero-point energy in the palladium lattice (than deuterium) and therefore has a larger root-mean-displacement. Protium atoms vibrate at a higher frequency than deuterium atoms, and such, they have a greater displacement. This greater displacement can be observed as the greater expansion of the palladium lattice in the presence of protium atoms. When the protium atom is covalently bonded in a molecule, the frequency of vibration is higher than when atomic H is dissolved in the Pd lattice. Upon dissolution in the lattice the vibrational motion of the H atoms slows and the amplitude of vibration becomes larger. However, when compared to the vibrations of the Pd atoms in the lattice, protium has a higher frequency.

![Figure 2-11: Relative zero point energies of H₂ and D₂ (left). Zero point energies of hydrogen isotopes in the gas phase, in intermetallic compound TiMn₁₅H₂₅ and PdH₀₆₅ (right). [15, 56]](image)

Rush et al [57] determined that the potential well created by a cage of Pd atoms is very similar for both hydrogen and deuterium. They also conclude that the potential well created by the Pd atom cage (in which the hydrogen and deuterium atoms reside) is strongly anharmonic; meaning the frequency and amplitude of vibration are in constant flux (i.e. changing).
2.9.6 Isotope Effects

Isotope effects of hydrogen isotopes are caused by differences in mass, and hence oscillating frequency within the palladium lattice. The relative mass differences between the hydrogen isotopes are the largest in the periodic table. Hydrogen isotope effects are therefore the most pronounced of any element. Different isotopes of hydrogen have quite different equilibrium pressures in the plateau region of the isotherms, see Figure 2-12. These differences occur because of the difference in solubility of the three different isotopes. Protium is considerably more soluble in the palladium lattice than the heavier isotopes (deuterium/tritium). This large isotope effect comes about because of the difference in zero-point energy levels of the gas phase molecules and the dissolved atoms for the three isotopes see Figure 2-11. It can be seen from this figure that deuterium, for example, prefers to be in the gas phase rather than the solid phase. The zero point energy change for substitution of H atoms for D atoms in the gas phase is larger ($\Delta E = 35$ meV) than the zero point energy change for substitution of H atoms for D atoms in the hydride phase ($\Delta E = 27$ meV). This means that it is more favourable to form HD in the gas phase than form palladium deuteride (PdD). This leads to an enrichment of deuterium in the gas phase. At higher deuterium concentrations in the gas phase an increase in the thermodynamic effect is observed. This is because the difference in zero point energy between the gaseous molecules HD and D$_2$ ($\Delta E = 43$ meV) is larger than the difference between H$_2$ and HD ($\Delta E = 35$ meV); so it becomes even more favourable (thermodynamically) for deuterium atoms to remain in the gas phase rather than move into the hydride phase (where the change in zero point energy is $\Delta E = 27$ meV) [56]. Lasser [37] considered that the system gains more energy by the absorption of a H$_2$ molecule, rather than a molecule of the heavier isotopes (D$_2$ and T$_2$). The zero point energy change between hydrogen in the gas phase and in the solid phase is larger than the difference in zero point energies of the gaseous and solid phases of deuterium. This gives rise to the differences in solubility of the three isotopes; the lighter isotopes being more soluble in the palladium lattice than the heavier isotopes. The difference in stability of each isotope in the palladium lattice can be visualized in the equilibrium plateau pressures shown in Figure 2-12.

These isotope effects give rise to the separation factor, $\alpha$. This defines the ratio of isotopic species in the gas and solid phases at equilibrium (i.e. the partitions of the
isotopes in the gas and solid phases when an H-D-Pd system reaches equilibrium). The isotopic separation factor for, e.g. H and D, is defined as:

\[
\alpha = \frac{\frac{x_{Dg}}{x_{Ds}}}{\frac{x_{Hg}}{x_{Hs}}} \tag{2-5}
\]

where \(x\) refers to the mole fraction of the given isotope in the gaseous (g) or solid (s) phases. This can be used to determine the amount of each isotope in each phase.

Wicke and Nernst [9] investigated the separation factor for \(\beta\)-phase palladium black powder over a temperature range of 50 °C to -78.5 °C, see Figure 2-12. They found a strong temperature dependence which could be represented by the following expression:

\[
\ln \alpha = \frac{245}{T} + 0.055 \tag{2-6}
\]

Note: [This expression was validated by prior confidential studies performed at AWE, Aldermaston. It will, therefore, be used to evaluate the separation factor in future experimental work]. This model allows prediction of the solid phase composition based on knowledge of the gas phase composition over the palladium compact.

Other authors [7, 16] have also investigated the temperature dependence of the separation factor, each finding similar results to Wicke and Nernst. Much less pressure dependence was observed by Wicke and Nernst and Trentin [9, 50]. Trentin [50] has reported that there is a small amount of dependence on the H-D composition of the gas phase, with higher separation factors achieved with a lower hydrogen content in the gas phase.
2.9.7 Diffusion

Hydrogen diffuses rapidly in palladium at 298 K. The diffusion constants of the palladium-hydrogen system have been determined by a variety of methods; permeation, hydrogen uptake, the Gorsky technique and quasi-elastic neutron scattering. The diffusion coefficients for hydrogen (H) and deuterium (D) ions in palladium at low concentrations can be calculated from the following equations, identified by Wicke and Brodowsky [58]:

\[
D_H = 2.5 \times 10^{-7} \exp \left( - \frac{21.8 \text{ kJ} \cdot \text{K}^{-1} \text{ mol}^{-1} H}{RT} \right) m^2 s^{-1} \tag{2-7}
\]

\[
D_D = 1.7 \times 10^{-7} \exp \left( - \frac{19.9 \text{ kJ} \cdot \text{K}^{-1} \text{ mol}^{-1} D}{RT} \right) m^2 s^{-1} \tag{2-8}
\]

The diffusion coefficient for hydrogen and deuterium are therefore, \(3.8 \times 10^{-11} \text{ m}^2 \text{s}^{-1}\) and \(5.5 \times 10^{-11} \text{ m}^2 \text{s}^{-1}\) at 298 K, respectively. At higher loadings (i.e. the β-phase), hydrogen
has a diffusion coefficient of \( \sim 6 \times 10^{-11} \text{ m}^2 \text{ s}^{-1} \), and deuterium \( \sim 1.6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \) [59]. The diffusion of H (and D) is seen to obey an Arrhenius type relation, and this is observed over a wide range of temperatures [59]. It is apparent that the diffusion constant for deuterium is greater than that of protium, which seems counter-intuitive considering the increased mass of deuterium. The reason for this difference is that hydrogen and deuterium have different activation energies, causing more rapid diffusion of D. Flanagan and Oates [15] discuss the findings of Bohmholdt & Wicke, and suggest that the transition state for diffusion is the tetrahedral interstitial position within the palladium lattice. Here, the vibrational frequency is much larger than the octahedral sites, which hydrogen isotopes occupy in palladium hydride. The lower zero-point energy of deuterium is enough to favour diffusion of the heavier isotope. The higher vibrational frequency of the tetrahedral sites means it is more favourable for the deuterium atoms to make octahedral-octahedral jumps via the tetrahedral site, as opposed to hydrogen atoms. In the palladium-hydrogen lattice, the energy difference between the ground state and the activated state decreases with increasing isotopic mass, in the case of octahedral-octahedral jumps (i.e. diffusion). In the case of tetrahedral-tetrahedral jumps, increasing isotopic mass requires more energy to diffuse through the lattice [16]. Despite this interesting phenomenon, the diffusion rates of H and D do cross-over at high temperature, that is, H diffuses faster than D.

Fick’s laws (in particular, the diffusion coefficient) are of practical interest when dealing with the palladium-hydrogen system because they allow determination of the time required to load a palladium sample with hydrogen. Fick’s first law defines the diffusive flux assuming the system is at steady state. The diffusive flux, \( J \) is calculated from the product of the diffusion coefficient (diffusivity) and the concentration gradient. Fick’s first law in one dimension is given below:

\[
J_i = -D \frac{\partial C_i}{\partial x}
\]  

[2-9]

Where, \( J \) is the diffusive flux (mol m\(^2\) s\(^{-1}\))

\( D \) is the diffusion coefficient (diffusivity) (m\(^2\) s\(^{-1}\))

\( C_i \) is the concentration of species i (mol m\(^{-3}\))

\( x \) is the length (m)
Fick’s second law can be used to predict how the concentration of a species changes with time due to diffusion. Fick’s second law, in one dimension, can be represented by the following equation:

$$\frac{∂c_i}{∂t} = D \frac{∂^2c_i}{∂x^2}$$ \hspace{1cm} [2-10]

Here, \(t\) is the time (s).

For the Pd-H(D) system, Fick’s diffusion coefficient is given by:

$$D(n) = D^* \left( \frac{d\ln a}{d\ln n} \right) = D^* \frac{r}{RT} \left( \frac{d\mu_H}{dn} \right)$$ \hspace{1cm} [2-11]

where \(n\) is the H/Pd atom ratio, \(D^*\) is the concentration independent (Einstein’s) diffusion constant, \(a\) is the activity of the hydrogen, and \(\mu_H\) can be obtained from the equation for chemical potential using \(p_{H_2}\), discussed in earlier sections. Fick’s diffusion coefficient is dependent on the non-ideality of the dissolved hydrogen [15]. In the \(β\)-phase its value is some 4.5 times greater than in the dilute phase (\(α\)-phase) at 298 K.

### 2.10 Hydrogen Isotope Exchange

It has been known for over a century that diatomic hydrogen (and, hence, its isotopomers, deuterium and tritium) interacts with solid palladium by effectively dissociating into atoms which are incorporated within the solid lattice of the metal. The result of this process is a non-stoichiometric palladium hydride (PdH\(_x\); \(0 < x < 0.8\)) in which new bonding associations are made between the hydrogen atoms and the palladium framework atoms. Deuterium and tritium also form hydrides with the palladium metal, called palladium deuteride and tritide, respectively. Because of the difference in zero-point energy (as discussed in Section 2.3.6) of the isotopically different species, significant isotope effect arises in the stabilities of the different hydride species (e.g. hydride, deuteride and tritide) and the rates of reaction of their formation. This differential behaviour of hydrogen, deuterium and tritium towards palladium can be usefully exploited: there are a number of chromatographic and membrane separation techniques using palladium hydride that have been studied to date. These experimental techniques have been developed to efficiently separate mixtures of \(H_2\), \(D_2\) and \(T_2\). These are discussed in more detail in the Section 2.5 of this thesis.
Hydrogen isotope exchange involves the exchange of an element in the gas phase with a solid containing that element, representing a fundamental gas-solid interaction. This heterophase exchange reaction can be applied to isotope separation for enrichment of the heavier hydrogen isotopes [1]. The hydrogen isotope exchange reaction has been postulated as occurring through the following reaction mechanism [1, 60]:

1. Diffusion of the diatomic gas phase hydrogen molecule through the bulk gas
2. Diffusion of the diatomic gas phase hydrogen molecule to the metal surface
3. Adsorption of the diatomic gas phase hydrogen molecule
4. Dissociation of the diatomic gas phase hydrogen molecule into atomic form
5. Surface diffusion of atomic hydrogen species
6. Diffusion from the surface to the bulk metal
7. Diffusion through the metal lattice
8. Movement of atomic hydrogen from the subsurface lattice to the surface
9. Recombination of atomic species to diatomic molecular hydrogen
10. Desorption of diatomic hydrogen molecule
11. Diffusion of the diatomic hydrogen molecule away from metal surface
12. Diffusion of diatomic hydrogen molecule into the bulk gas

In this thesis, the exchange reaction in β-phase palladium hydride will be discussed because of its relevance to the current project but it is important to point out that exchange reactions of isotopic species can occur in a range of transition metals. Palladium and its alloys are by far the most extensively studied systems, but some authors have reported exchange in metal hydrides containing lanthanum, nickel, copper, magnesium and boron [61, 62]. Studies relating to the palladium-hydrogen system have mainly focussed on their thermodynamic nature. The thermodynamics and inherent properties of the palladium-hydrogen systems are discussed in detail by Flanagan and Oates, Alefeld and Volk, Sicking, Wicke and Nernst and Santadrea and Behrens [9, 15, 16, 59]. The kinetic aspects of the systems have been investigated in less depth. Few literature sources exist that discuss the kinetic aspects of the individual steps of the reaction mechanism.

One of the main reasons for the lack of literature regarding the kinetics of the reaction steps is the difficulty in elucidating the key parameters relating to the individual steps of the reaction mechanism. These parameters are affected strongly by varying
experimental design and material characteristics. Generalisations of the kinetics of isotope exchange are difficult to make, as each investigator has focussed on a particular substrate morphology and parameter space. Furthermore, the study of exchange kinetics is a complicated task due to a number of factors such as adsorption and desorption mechanisms on the surface, diffusion mechanisms from surface to bulk palladium hydride lattice, metal hydride surface properties, effects of temperature, pressure, flowrate and presence of impurities in the gas supplies. Available literature has therefore focussed on finding the “overall” rate of exchange, encompassing the various steps in the reaction mechanism. Some consideration has been made to the rate limiting step, with the majority of investigators concluding that the surface steps are rate limiting [2, 3]. A kinetic model for the exchange process over describing effects of temperature, pressure and flowrates is a requirement of the current PhD project; the next sections will describe previous efforts to describe the kinetics and mechanisms of exchange by a number of different investigators.

2.10.1 Hydrogen Isotope Exchange Kinetics Review

The seminal study in the area of isotope exchange was published by Foltz and Melius in 1987 [1]. They investigated the exchange of one isotope on a palladium hydride sample (in the β-phase) for another isotope under hydrogen or deuterium flow. This was performed for both exchange directions, i.e. PdDₓ to PdHᵧ and PdHₓ to PdDᵧ, whereby the PdDₓ to PdHᵧ exchange is thermodynamically favourable and the reverse in unfavourable. Their studies will be discussed, including their developed model because of its relevance to the current PhD project. Foltz and Melius used an open experimental apparatus (similar to the IsoEx rig being used in this project) which consisted of a simple flow tube in which a palladium powder sample pellet was compressed in the centre, see Figure 2-13. The pellet was 20.3 cm long and 1 cm in diameter, and was packed to a density of 7.5g cm⁻³. The average particle diameter was 106-124 µm. The average porosity, εₚ, was 0.38. The particle bed (pellet) was initially loaded with one isotope to β-phase hydride stoichiometry by admitting a measured amount of gas over a period of several hours. After measuring the gas overpressure in the flow tube, an initial stoichiometry for each hydride was determined as PdH₀.₆₅ and PdD₀.₆₁, for the palladium hydride and palladium deuteride, respectively. After bed preparation a fast-acting high-conductance valve was used to introduce gas flow of the other isotope. Gas composition
leaving the pellet was monitored by Raman spectroscopy via a window located in the side of the flow tube. Raman spectroscopy allowed real-time, non-destructive monitoring of the outlet gas stream.

Their study focussed on a packed palladium bed geometry, with no variation in temperature, pressure or flowrates. Their study was confined to a single particle morphology compressed to a specific density. Input pressure for the PdDx to PdHy exchange was set to ~1187 Torr (~1.58 bar) and for the PdHx to PdDy exchange it was set at ~1124 Torr (~1.48 bar). Flowrates, Q, in each exchange were 0.83 ± 0.02 L min⁻¹ and 0.71 ± 0.02 L min⁻¹, respectively. The single temperature investigated was 299 K.

2.10.1.1 Development of Rate Equations and Isotope Exchange Rate

Foltz and Melius developed a parameterised rate-equation model to describe the exchange reaction in their chosen geometry, flowrate, temperature and pressure. In an effort to simplify the multiple step exchange reaction, the authors broke the overall exchange mechanism into three different processes: the solid-, surface- and gas- phase. They assumed the solid- and gas- phase processes were fast compared to the surface processes, which they assumed to be rate limiting. Their main aim therefore was to focus on the surface processes and compare them to experimental data obtained from both exchange directions (PdDx to PdHy and PdHx to PdDy). They developed a plug flow with pressure drop model assuming constant stoichiometry and separation factor,
and external mass transfer control with no net gas uptake in the palladium hydride, therefore, upon absorption of an atom of hydrogen into the substrate, one atom is desorbed. The model describes the case where deuterium is initially sorbed into the palladium pellet and hydrogen gas is flowed through the bed. The authors start by developing rate equations in terms of the atomic densities of H and D, in moles per unit volume, for the solid and gas phases:

\[
\frac{\partial n_{SD}}{\partial t} = -R_{exch} \tag{2-12}
\]

\[
\frac{\partial n_{SH}}{\partial t} = R_{exch} \tag{2-13}
\]

These first two equations (Equations 12 and 13) define the rate of change of the two hydrogen species in the solid phase. The isotope exchange rate is shown as \( R_{exch} \). Rate of change of the atomic species (H or D) in gas phase is given by:

\[
\frac{\partial n_{gD}}{\partial t} = \left[ \frac{1 - \varepsilon_p}{\varepsilon_p} R_{exch} \right] - \frac{\partial (n_{gD} v_f)}{\partial x} \tag{2-14}
\]

\[
\frac{\partial n_{gH}}{\partial t} = - \left[ \frac{1 - \varepsilon_p}{\varepsilon_p} R_{exch} \right] - \frac{\partial (n_{gH} v_f)}{\partial x} \tag{2-15}
\]

Where \( \left[ \frac{1 - \varepsilon_p}{\varepsilon_p} \right] \) is the solid-to-void volume ratio and \( v_f \) is the flow velocity in the x direction (axial direction).

The above equations form four coupled rate equations for; \( n_{SD} \), \( n_{SH} \), \( n_{gD} \), \( n_{gH} \), where subscripts ‘s’ and ‘g’ denote the solid and gas phases, and subscripts ‘H’ and ‘D’ correspond to the hydrogen and deuterium atoms respectively. Equations 2-15 and 2-12 represent hydrogen atom loss from the gas phase, and subsequent deuterium atom loss from the solid phase, respectively. Equations 2-13 and 2-14 represent the gain in hydrogen atoms in the solid phase and the subsequent gain in deuterium atoms in the gas phase, respectively. The second term in Equations 2-14 and 2-15 contain a term for the flow velocity, which arises from one-dimensional equation of continuity as discussed by Bird [63].

Next, the authors focussed on solving the rate of the surface exchange reaction by analysing a general set of exchange reactions for a “single exchange mechanism” where only one atom of incident gas is exchanged, shown below:
\[ D_2(g) + H_s \xrightarrow{k_1} HD(g) + D_s \quad [R1] \]
\[ HD(g) + H_s \xrightarrow{k_2} H_2(g) + D_s \quad [R2] \]

The rate of surface reaction (exchange), \( R_{\text{exch}} \), was found to be:

\[
R_{\text{exch}} = \frac{1}{4} k \left( n_{g_D} + n_{g_H} \right) \left( \frac{8RT}{\pi M} \right)^{\frac{1}{2}} S_0 N_{\text{surf}} \left\{ \left( \alpha \right)^{\frac{1}{2}} x_{H_D} x_{D_S} - \left( \alpha \right)^{-\frac{1}{2}} x_{D_D} x_{H_S} \right\} \quad [2-16]
\]

Where, \( k \) is the isotope exchange coefficient, and the constant of proportionality. It arises from a series of manipulations of the forward and reverse kinetic rate constants (identified in Equations 10 and 11) using the separation factor, \( \alpha \). \( x_{i,g} \) is the mole fraction of isotope ‘i’ in the gas phase and \( x_{i,s} \) is the mole fraction of isotope ‘i’ in the solid phase. \( \left( \frac{8RT}{\pi M} \right)^{\frac{1}{2}} \) is the thermal velocity, \( v_t \), of a gas molecule of molar mass \( M \) at temperature \( T \). \( R \) is the molar gas constant. \( N_{\text{surf}} = ([H_S] + [D_S]) \) is the total surface density of hydrogen and deuterium atoms on the surface. \( S_0 \) is used in the equation to convert the exchange rate from moles per second per unit surface area, to moles per second per unit volume as required by Equations 14 and 15. Substituting Equation 16 into Equations 12 and 13 indicates that deuterium is lost from the solid palladium, and hydrogen gained, when \( \left( \alpha \right)^{-\frac{1}{2}} \) times the product of the hydrogen impingement rate [given by \( \frac{1}{4} (n_{g_D} + n_{g_H}) v_t x_{H_D} \) ] and the deuterium surface density [given by \( N_{\text{surf}} f_{D_D} \) ] is greater than \( \left( \alpha \right)^{\frac{1}{2}} \) times the product of the deuterium impingement rate [given by \( \frac{1}{4} (n_{g_D} + n_{g_H}) v_t x_{D_D} \) ] and the hydrogen surface density [given by \( N_{\text{surf}} x_{H_S} \) ]. If this inequality is reversed then hydrogen is lost from the solid palladium, and deuterium gained.

At equilibrium \( \left\{ \left( \alpha \right)^{\frac{1}{2}} x_{H_D} x_{D_S} - \left( \alpha \right)^{-\frac{1}{2}} x_{D_D} x_{H_S} \right\} = 0 \) and therefore

\[
\alpha = \frac{\left( x_{H_S} \right) / \left( x_{H_D} \right)}{\left( x_{D_S} \right) / \left( x_{D_D} \right)} = \frac{\left( x_{D_D} \right) / \left( x_{D_S} \right)}{\left( x_{H_D} \right) / \left( x_{H_S} \right)} \quad [2-17]
\]

Equation 17 is the same as the standard definition for the separation factor as discussed in Section 2.3.8 of this thesis. In the H-D-Pd system the value of \( \alpha \) is >1, meaning that
hydrogen has a higher affinity for the metal than deuterium. The exchange reaction which forms the hydride phase is, therefore, the favourable reaction. This feature is evident in the mathematical structure of Equation 16.

The isotope exchange coefficient, $k$, has units of cm$^2$/mole. To define this parameter better Foltz and Melius breakdown the parameter into the following equation to describe the external mass transfer controlled process:

$$k = p_{exch}\sigma$$

[2-18]

Here, $\sigma$ is defined as the surface area occupied by a mole of adsorbed H or D atoms such that $\sigma = (N_{surf})^{-1}$. The quantity $p_{exch}$ is therefore interpreted as the probability that an isotopic exchange event occurs during a collision of a gas phase atom with the surface. Thus, $p_{exch}$ is called the isotope exchange probability and it constitutes a fundamental parameter of Foltz and Melius’s model. The temperature dependence of $p_{exch}$ is found via an Arrhenius equation:

$$p_{exch} = p_0 \exp\left(-\frac{E_a}{RT}\right)$$

[2-19]

Where, $E_a$ is the activation energy for the exchange reaction.

The process which establishes the equilibrium in the gas phase can be described by the reaction:

$$H_2 + D_2 \rightleftharpoons 2HD$$

[R3]

At any location in the bed and at any time, it is assumed that equilibrium between the isotopic molecular species in the gas holds at all points in space and time within the pellet. The equilibrium constant, $K_{eq}$ for this reaction is given by:

$$\log K_{eq} = -\left(\frac{155}{4.57T}\right) + 0.6276 \quad K_{eq} = \frac{[HD]^2}{[H_2][D_2]}$$

[2-20]

$K_{eq} \sim 4$ at high temperatures because the maximum HD concentration is achieved with a 50:50 mix of $H_2$ and $D_2$; therefore the denominator of the right hand side part of equation 2-20 becomes 1/4. The molecular mole fractions: $x_{HD}$, $x_{H_2}$, $x_{D_2}$ are related to their atomic mole fractions by the following equation:
\[ x_{HD} = -\left[ \frac{K_{eq}}{4-K_{eq}} \right] + \left[ \frac{2}{4-K_{eq}} \right] \left\{ (K_{eq}^2/4) + 4K_{eq}[1 - \left( \frac{K_{eq}}{4} \right)x_{Hg}x_{Dg}] \right\}^{\frac{1}{2}} \]  
\[ x_{H_2} = x_{Hg} - \frac{1}{2}x_{HD} \]  
\[ x_{D_2} = x_{Dg} - \frac{1}{2}x_{HD} \]

Their experimental results were modelled using the above equations and a series of equations solved for \( n_S(x, t) \) and \( n_g(x, t) \) for H and D by using a stiff ordinary differential equation (ODE) integrator. \( n_g(x, t) \) is converted from atomic to molecular composition to give results similar to those recorded during the experiments. The authors compared the time resolved molecular composition of the gas (in terms of partial pressure) at the exit of the pellet with experimental results. \( p \) was allowed to vary freely in the model calculations, and was evaluated by fitting the model results to experiment. The experimental conditions of temperature and pressure were used to constrain the model, and an average stoichiometry \((H/D)/Pd\) of 0.62 was used. In order to calculate the 1-dimensional (1D) gas flow velocity, \( v_f \) through the pores of the palladium pellet, the following modified Darcy’s Law equation is used:

\[ v_f = \frac{(K_{eq}) \Delta p}{\mu \Delta x} \]  
\[ Q = \left( \frac{kA}{\mu L} \right) \left( \frac{\Delta p}{L} \right) \]

Here,

\( Q \) = the unidirectional, steady flow rate

\( k \) = the permeability

\( A \) = cross-sectional area of the pellet

\( \mu \) = the fluid viscosity

\( \Delta P \) = pressure drop along the pellet

\( L \) = length of the pellet
Darcy’s Law (Equation 25) has been modified using the Dupuit-Forchheimer assumption, which can be obtained by dividing Equation 24 by the porosity $\varepsilon_p$. It is used to define the average interstitial velocity.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2-14.png}
\caption{Composition of gas exiting palladium pellet versus time for deuteride-to-hydride (PdD$_x$ to PdHy) exchange process (left) and hydride-to-deuteride (PdH$_x$ to PdD$_y$) exchange process (right). Reprinted from [1]}
\end{figure}

Figure 2-14 shows the experimental results and modelling (lines in figure) for both exchange reaction directions obtained by Foltz and Melius. It can be seen that the D-H exchange is a much faster process, whilst the H-D exchange is much slower overall. This is a direct result of the relative stability of isotopes on the solid and in the gas phase [15, 47]. Their model achieved good description of the process for the D-H exchange, but a poorer fit with the less favourable H-D exchange process. Reasonable agreement with both exchange directions was achieved using an $\alpha$ value of 2.4, which the authors obtained from the work of Wicke and Nernst [9] and a value of $p_{exch} = 2.6\times10^7$. In attempting to model the H-D exchange better, the authors ran a simultaneous fit to both sets of data allowing their values of $p$ and $\alpha$ to vary. No real improvement on the model accuracy was achieved. The authors assume the discrepancy between model results and experimental data for the H-D exchange to increased channelling (or by-pass) gas flow as a result of differential powder volume expansion.
between the hydride and the deuteride. In simple terms, the volume of the palladium pellet reduces in transition from hydride to deuteride, creating extra flow paths for the gas phase. They also admit that, in reality, the gas exiting the pellet does deviate to a small degree from an equilibrium mixture (contrary to the assumption of equilibrium isotopic composition in the gas phase at all points in the pellet). The effect is particularly noticeable for the PdH$_x$ to PdD$_y$ exchange, suggesting an alternate reaction sequence driving the composition away from equilibrium could be possible.

This observation lead Foltz and Melius [1] to propose a “multiple exchange mechanism”, where both atoms of the incident gas species are exchanged, as shown below (Note: subscript ‘s’ denotes a surface species):

\[
\begin{align*}
D_2 + H_s + H_s & \rightleftharpoons H_2 + D_s + D_s & [R4] \\
D_2 + H_s + D_s & \rightleftharpoons HD + D_s + D_s & [R5] \\
HD + H_s + H_s & \rightleftharpoons H_2 + H_s + D_s & [R6]
\end{align*}
\]

One thing that is clearly evident from these equations is that HD will be produced in significantly smaller quantities than the equilibria described in Reactions R1 and R2. Model calculations utilising this reaction mechanism were found to underestimate the HD amount at the bed exit, implying that the multiple exchange mechanism plays only a minor role in the overall observed exchange process.

In an attempt to further the studies of Foltz and Melius, Outka and Foltz [2] considered the role of the substrate surface in the exchange process. The experimental setup was the same as that of Foltz and Melius [1]. Their studies used the inclusion of small amounts of CO in the hydrogen gas flows, to block surface sites thereby inhibiting any reactions on the surface. The presence of these impurities in the gas stream provides more information to deduce a suitable exchange reaction mechanism (i.e. the role of the surface becomes much more apparent). The authors developed a \textit{surface-exchange} model which uses a microscopic mechanism which specifically considers the role of the surface in the exchange. Outka and Foltz divided the overall exchange process into three phases, gas, bulk, and surface; a schematic of the surface-exchange process in shown in Figure 2-15 and developed specific rate equations for each step of the reaction mechanism to include in their model. Two reactions exist that link the gas to the surface: adsorption (step 1) and desorption (step 3), and 1 which links the surface to the
bulk (step 2). This mechanism was developed upon the typical chemistry observed for hydrogen on surfaces of metals. As identified previously, hydrogen molecules undergo dissociation upon contact with the palladium surface. Absorption of hydrogen into the bulk palladium proceeds via chemisorbed hydrogen atoms. The elementary reactions of dissociative adsorption (step 1 in Figure 2-15) and recombinative desorption (step 3 in Figure 2-15) are therefore also included in the model.

![Figure 2-15: Surface-exchange mechanism. Reprinted from [2]](image)

Step 2 is the least well understood from a fundamental point of view, and is not an elementary reaction because the movement of hydrogen atoms from the surface to the bulk and vice-versa are not elementary reactions like the steps of adsorption and desorption.

Outka and Foltz used the impurity CO to validate their surface-exchange model. When CO is present in the gas stream it adsorbs to the surface of the palladium, therefore blocking surface sites. A reduction in the exchange reactions accompanies CO adsorption because CO has a much longer residence time on the surface than H₂. The calculated residence time, \( \tau \), for H₂ was \( \tau_{\text{H}_2} \sim 2 \text{ ms} \), while the residence of CO was calculated as \( \tau_{\text{CO}} \sim 2500 \text{ s} \). This means less H₂ in the gas phase can collide with the surface to take part in exchange reactions. CO poisons the surface, but can be removed since the adsorption is reversible. CO completely inhibits the exchange process once a monolayer had formed on the surface of the palladium. This indicates that the whole surface takes part in the exchange reactions and no special or defect sites are needed under normal conditions [2]. However, Outka do stress that special sites may become important as the system temperature is lowered. At lower temperatures, the small differences in energetic of the different parts of the surface may have large effects on the exchange process.
The characteristic time of the exchange process was also investigated, and found to be $\tau_{exch} \sim 0.32$ ms initially. As the deuteride to hydride (D-H) process of exchange is dependent on the amount of deuterium on the surface, $[D(b)]$ the characteristic time of exchange increases as the concentration of deuterium on the surface falls, see equation below (for D-H exchange):

$$\tau_{exch} = \left( k_{exch}^* \sqrt{\alpha \frac{[D(b)]}{[D(b)]_{max}}} \right)^{-1}$$

[2-26]

As can be seen in the equation used by Outka and Foltz [2] the characteristic time of the exchange process is inversely proportional to the amount of deuterium in the bulk palladium. It can therefore be deduced from this equation that the surface exchange and desorption steps contribute significantly to the overall rate of the exchange.

It must be noted that there are a number of assumptions made in the work of Outka and Foltz [2] that need addressing. There is a lack of isotope-specific dependence for the rates of various reaction steps and there is no consideration to how the exchange process is affected by temperature. Also, no activation energies are determined. The key findings from the work of Outka and Foltz [2] are that the overall rate of isotope exchange is dependent on two surface processes: (1) desorption of $H_2/D_2$ from the surface; and (2) the exchange process between surface hydrogen isotopes and bulk $\beta$-phase palladium hydride.

In order to address some of the shortfalls of the work of Outka and Foltz [2] and Foltz and Melius [1], Carstens and Enicias [3] conducted experiments over a range of temperatures, in order to obtain rate constants $k$, and activation energies, $E_a$, for both exchange directions. Quantification and identification of isotopic species was achieved via Raman spectroscopy of the gas phase. Similar to the work of Outka and Foltz [2], the effects of impurity gases were also studied and their effects on the rate constants determined. Details of the palladium ‘compact’ used by the authors were not reported, specifically the dimensions and density of the pellets. This is important information to know when trying to compare the work with other studies, particularly when trying to determine porosity $\varepsilon_p$ of the bed/pellet, and hence its flow characteristics. The authors do not model their experimental findings, instead they compute a number of parameters from their exchange results, assuming first-order kinetic behaviour. Activation energies were determined from Arrhenius-type plots. The experiments were performed over a
range of temperatures between -100°C (173 K) and room temperature, with an input gas flowrate of 2 L min⁻¹. The pressure was maintained at 7 bar.

Figure 2-16 ln(k) vs. 1/T for PdDₓ to PdDᵧ (D-H) exchange over palladium metal (left) and PdHₓ to PdDᵧ (H-D) exchange over palladium metal (right). Filled circles and lines represent best data obtained with pure gases. The dashed lines and open diamonds indicate results found for cylinder gas with no purification. Reprinted from [3]

A value for the rate constant was determined for each temperature investigated and these were plotted in order to determine the activation energy via a simple Arrhenius analysis:

\[ k = A₁ \exp\left(-\frac{E_a}{RT}\right) \]  \[ 2-27 \]

\( A₁ \) is the pre-exponential factor which has units of s⁻¹ for a first order process; \( E_a \) represents the (Arrhenius) activation energy in kJ mol⁻¹ for the reaction (with \( R \) in kJ K⁻¹ mol⁻¹).

Plots of ln(k) vs. 1/T from Carstens and Encinias [3] are shown in Figure 2-16 for the D-H and H-D exchange directions. What is clearly evident in both plots, is that as temperature is decreased the rate is observed to decrease. The rate of D-H exchange is significantly faster, as would be expected in the thermodynamically favourable exchange direction.
Figure 2-17 Plots of ln(k) vs. 1/T for the PdDₓ to PdHᵧ (D-H) exchange over palladium metal (left) and PdHᵧ to PdDₓ (H-D) exchange over palladium metal (right) in the presence of different 100ppm impurities: CH₄ (filled circles), CO₂ (open squares), H₂O (open diamonds), and CO (filled triangles). Reprinted from [3]

The effect of impurities on the rate constants of both exchange directions can be seen in Figure 2-17. The reduction in the rate of exchange increases in the CO>H₂O>CO₂>CH₄. CO causes the most dramatic decrease in the observed exchange rate because of its blocking effect on surface sites, and lengthy residence time on the surface (as discussed previously). An important result of the work of Carstens and Encinias [3] is that any impurities present in the gas streams will have a significant effect on the recorded exchange rates, particularly CO. It is therefore important to use gas purifiers in the study of exchange kinetics because the rate of exchange will be affected by residual quantities of impurities on the Pd surface. This thesis took note of this information and commercial purifiers capable of reducing impurity levels to sub ppb levels were purchased. Examining the activation energy of the exchange reaction in the presence of impurities allows one to see the detrimental effect of their presence, see Table 2-1.

Table 2-1 Activation energies $E_a$ (kJ mol$^{-1}$) and pre-exponential factors $A_1$ (s$^{-1}$) for hydrogen isotope exchange over -phase palladium hydride/deuteride in both exchange directions. The +/- values represent the experimental uncertainty. Reprinted from [3]

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>PdDₓ to PdHᵧ</th>
<th>PdHᵧ to PdDₓ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_a$ (kJ mol$^{-1}$)</td>
<td>$A_1$ (s$^{-1}$)</td>
</tr>
<tr>
<td>None</td>
<td>8.8 ± 0.4</td>
<td>7.4</td>
</tr>
<tr>
<td>CH₄</td>
<td>8.4 ± 0.4</td>
<td>5.1</td>
</tr>
<tr>
<td>CO₂</td>
<td>18 ± 0.8</td>
<td>370</td>
</tr>
<tr>
<td>H₂O</td>
<td>33 ± 3</td>
<td>3.6</td>
</tr>
<tr>
<td>CO</td>
<td>96 ± 13</td>
<td>2.9</td>
</tr>
</tbody>
</table>
It is clear to see from the activation energies that the presence of impurities, particularly CO and H₂O, increase the activation energy of the exchange reaction in both exchange directions. Under clean conditions (i.e. with commercial purifiers on the gas streams) the activation energy of the process is calculated to be 8.8±0.4 kJ mol⁻¹ for the D-H exchange and 12±1 kJ mol⁻¹ for the less favourable H-D exchange.

A negative aspect about the studies of Carstens and Encinias [3] was that there was no pressure variation during experimentation, and their results for gas composition leaving the palladium pellet (or ‘compact’) were not published. Therefore, conclusions on the pressure dependence of the rate kinetics could be drawn.

In 1992, Powell [64] attempted to address the lack of published pressure and temperature data on the exchange reaction by investigating exchange kinetics under varying pressure and temperature. His method was quite different from the previous studies of Foltz and Melius, and Carstens and Encinias [2, 3] and involved measuring the surface conductance of the palladium hydride/deuteride during isotope exchange. Similar to Foltz and Melius, he also calculated $p_{\text{exch}}$ (defined as the “isotope exchange probability” by Foltz and Melius). However, unlike previous investigations he related $p_{\text{exch}}$ to temperature, pressure and the specific isotopes. In Powell’s studies [64] $p_H$ is the probability that an atom of H, D or T will penetrate bulk palladium following a collision of a H₂, D₂ or T₂ molecule with the surface. Strictly speaking, this probability is not related to the exchange of β-phase palladium hydride, it is more related to the probability of hydrogen/deuterium sorption into the bulk palladium. Powell [64] found that the following Arrhenius-type expressions could describe the reaction (sorption) probability that an atom of hydrogen or deuterium will penetrate the film surrounding the particle and reach bulk palladium (after a gas molecule-surface collision event):

$$p_H = 286P_H^{-0.5} e^{(-\frac{3935K}{T})} \quad [2-28]$$

$$p_D = 286P_D^{-0.5} e^{(-\frac{4120K}{T})} \quad [2-29]$$

$$p_T = 286P_T^{-0.5} e^{(-\frac{4223K}{T})} \quad [2-30]$$

Where $P_x$ is in Pascals (Pa).
Using the experimental conditions of Foltz and Melius [1] (i.e. 299 K and 101.325 kPa) the following probabilities are obtained:

\[ p_H = 1.7 \times 10^{-6} \]
\[ p_D = 1.1 \times 10^{-6} \]
\[ p_T = 1 \times 10^{-6} \]

The value of \( p_H \) obtained by Powell was directly compared to the \( p_H \) value obtained by Foltz and Melius (\( p_H = 0.26 \times 10^{-6} \)). The values are remarkably similar, indicating some link between the two probabilities. In the case of Foltz and Melius [1] this is the probability an exchange event will occur when an atom of hydrogen/deuterium collides with the surface, and in the case of Powell [64] it represents the probability that an hydrogen/deuterium/tritium atom will penetrate into the bulk palladium. Powell’s value can be thought of as including both the surface steps and transition into the bulk palladium whilst Foltz and Melius’ value is for the surface exchange reaction only. The difference in values suggest that the probability of bulk penetration is higher than an exchange event occurring, where different isotope species must reside on neighbouring sites in order for exchange to take place. The author concludes that the exchange reaction is a second-order process involving the gas molecule and the entire Pd surface. The process is therefore highly dependent on surface-area, and thus very dependent on the specific nature of the palladium powder used, and whether it has extra pores within its structure (providing extra flow channels). These results also suggest that the density of the pellet/bed/compact used will greatly affect the exchange process. Therefore, in this thesis it was essential to characterise the palladium powder as best as the AWE non-disclosure agreements allowed and compress the pellets to specific densities.

In 1999, Charton [65] proposed a number of improvements to the model of Foltz and Melius [1]. The discrepancies between experimental and modelled results obtained by Foltz and Melius were reduced by the inclusion of terms for axial dispersion (neglected by Foltz and Melius), variation in temperature (due to the exothermic and endothermic nature of the D-H and H-D exchange directions, respectively), separation factor and stoichiometry (all of which Foltz and Melius assumed to be constant). Charton [65] also removed the “exchange probability” parameter \( p_{exch} \) from their model, and advantageously described the external mass transfer control of the process by
accounting for diffusion of atoms in the $\beta$-phase using a known diffusivity obtained from Volkl and Alefeld [59]. The model developed by Charton [65] did not contain any adjustable parameters as in the work of Foltz and Melius, where values of the isotope exchange probability, $p_{exch}$, and the isotope separation factor, $\alpha$ were allowed to vary in order to match experimental data. Charton [65] compared the results of Foltz and Melius and their model which also assumed local equilibrium ($H_2 + D_2 \rightleftharpoons 2HD$). They commented that the parameter $p_{exch}$ in Foltz and Melius’ model is most likely a lumped parameter taking into account dispersion factors in the axial and radial direction and film mass-transfer processes. Even with the inclusion of axial dispersion in the local equilibrium model, it was still not sufficient in describing the unfavourable PdH$_x$ to PdD$_y$ (H-D) exchange process. These findings, and those of Foltz and Melius, both point to the fact that the simple equilibrium assumption (in all points of the bed) is incorrect due to cooling effects caused by the endothermic nature of the H-D exchange. This causes the diffusivity in the Pd/PdH$_x$ lattice to change, i.e. reduce, meaning equilibrium establishment is inhibited.

When Charton [65] included mass transfer resistances, particularly those of internal diffusion (which was accounted for by the linear driving force model), the model fit to the data of Foltz and Melius was improved, but discrepancies still existed. This again pointed to the need to accurately account for the temperature processes occurring in each exchange direction. The temperature is seen to greatly affect the solid diffusion rates, and hence the establishment of equilibrium (which both models assume). They reported a temperature difference of 35 K between the exothermic and endothermic exchange reactions, which equates to an internal diffusion coefficient 3.5 times larger for the exothermic processes. In future models it may be advantageous to determine whether the deviation from equilibrium is because of poor understanding of the kinetics of atom-dissociation and recombination or over-simplification whilst describing key processes in the exchange reaction. An example would be the use identical diffusivities when clearly the different isotopes of hydrogen will have different diffusivities.

Leardini [66] investigated the desorption kinetics of mixed hydride palladium foil ($\beta$-PdH$_x$D$_y$) in order to elucidate a surface recombination mechanism. They studied transition state energies of H$_2$, HD and D$_2$ recombination below 420 K and concluded that the calculated activation energies of desorption for each isotopic species. The values of activation energies found by the authors imply the existence of an activation
barrier for surface recombination, because they are higher than the formation enthalpies of β-phase palladium hydride and deuteride [17]. For comparison the activation energies of desorption calculated by Leardini [66] and the β-phase palladium hydride and deuteride formation enthalpies are shown below:

\[ E_{\text{desorb}}(H_2) = 84.7 \pm 0.4 \text{ kJ mol}^{-1} \]
\[ E_{\text{desorb}}(HD) = 79.3 \pm 0.4 \text{ kJ mol}^{-1} \]
\[ E_{\text{desorb}}(D_2) = 78.9 \pm 0.4 \text{ kJ mol}^{-1} \]
\[ \Delta H^{\alpha \rightarrow \beta}(PdH) = -37.4 \pm 0.3 \text{ kJ mol}^{-1} \]
\[ \Delta H^{\alpha \rightarrow \beta}(PdD) = -33.6 \pm 0.6 \text{ kJ mol}^{-1} \]

As can be seen from the values above, the enthalpy of β-phase formation is much lower than the activation energy of desorption of all hydrogen isotopomers. This suggests that desorption steps may be the rate limiting step in the overall rate of the exchange reaction. Although, the authors do highlight varying surface conditions in the samples they used in experiments. The presence of oxides on the surface would increase the recorded activation energy of desorption.

The authors summarised the steps occurring in the desorption process as:

a.) Diffusion of H and D atoms through β-PdH\textsubscript{x}D\textsubscript{y} 

b.) Transformation of β-PdH\textsubscript{x}D\textsubscript{y} into α-Pd 

c.) Diffusion of H and D atoms through α-Pd 

d.) Transition of H and D atoms from bulk to surface states 

e.) Surface recombination of H and D atoms to form H\textsubscript{2}, HD and D\textsubscript{2} physisorbed isotopomers. 

f.) Desorption of physisorbed molecules into the gas phase.

In 1995, Fukada [4] discussed the isotopic exchange rate in conjunction with the isotope separation factor (\(\alpha\)) during the chromatographic separation of T\textsubscript{2}, D\textsubscript{2} and H\textsubscript{2} over a palladium substrate. They used an experimental apparatus (Figure 2-18) consisting of cylinder 6.35 mm in diameter and 205 mm in length packed with “spongy” palladium particles (diameter 0.174 mm to 0.295 mm). These particles were quite different from the powders used by other investigators [1-3], in that they had internal pore structure
creating an additional porosity to that created by normal pellet compaction. Experiments were conducted over a temperature range of 223 K to 363 K with a gas flowrate of 20 cm$^3$ min$^{-1}$ to 200 cm$^3$ min$^{-1}$.

Figure 2-18 Schematic diagram of experimental apparatus used by Fukada [67].

After bed preparation and hydrogenation was completed, a pulse change of 5 cm$^3$ D$_2$ was admitted to the bed (equivalent to a 5% D$_2$ step change in the H$_2$ gas stream). Upon introduction of D$_2$, isotope exchange occurred within the bed. Only HD concentration in the outlet of the bed was monitored. Values for the rate constant $k$, and isotope separation factor, $\alpha$, were determined by fitting numerical calculations to experimental results. Numerical calculations were based on material balance equations through the pellet and the equation for diffusion in the solid state.

The isotope exchange reaction was studied using a $\beta$-phase palladium hydride bed (pellet) and the rate-controlling step was considered to be diffusion in the pores within the “spongy” palladium particles. The authors specify that above 300 K diffusion in the internal pores of the palladium particles is rate-limiting, and below 300 K the limiting process is diffusion in the bulk $\beta$-phase palladium hydride lattice. This is in contrast to the work of Foltz and Melius [1] who concluded that the surface processes are rate-limiting. Since the work was aimed at improving chromatographic separations of hydrogen isotopes, the height equivalent to a theoretical plate (HETP) model was used. Here, the palladium hydride bed is broken down into a series of plates in which
equilibrium between H and D is assumed to exist between the solid and gaseous phases. This process allows column efficiency to be determined; an important parameter in the design of an efficient chromatographic separation column.

The main processes considered in the study by Fukada [4] were,

1. Differential material balance equation of deuterium in the bed
2. The diffusion equation in spongy particles
3. The overall isotope exchange rate equation on palladium solid surfaces.

A material balance equation of HD in the metal hydride bed for a low deuterium concentration including the diffusion equation and overall isotope exchange rate was developed following on from previous studies by Fukada [67, 68]. This was transformed and using Laplace transformations into the following expression describing the effluent HD concentration:

\[ \mathcal{L}[c_{HD}(t, h)] = \frac{\exp\left(\frac{y h}{2D_L}\right)}{\left(1 + \frac{y^2}{2(1+y)}\right) \sinh\left(\frac{y h (1+y)}{2D_L}\right) + \cosh\left(\frac{y h (1+y)}{2D_L}\right)} \]

\[ y(s) = \sqrt{1 + \frac{4D_L s (1 + h(s))}{\nu^2}} - 1 \]  \hspace{1cm} [2-32]

\[ h(s) = \frac{\gamma K_D}{\nu s} \left( \frac{1}{k_g a_\nu} + \frac{1}{k_r a_\nu} \right) + \frac{1}{3\gamma K_D D_s \left( \frac{3}{\nu s} \coth\left(\frac{3}{\nu s}\right) - 1 \right) \left( \frac{3}{\nu s} \coth\left(\frac{3}{\nu s}\right) - 1 \right)} \]  \hspace{1cm} [2-33]
Table 2-19 Nomenclature for equations 2-31, 2-32 and 2-33. Source: [4]

<table>
<thead>
<tr>
<th>Term</th>
<th>Description</th>
<th>Dimension</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_g$</td>
<td>Gas-phase mass transfer coefficient</td>
<td>L/t</td>
<td>m s⁻¹</td>
</tr>
<tr>
<td>$k_p$</td>
<td>Mass-transfer coefficient for the pore diffusion</td>
<td>L/t</td>
<td>m s⁻¹</td>
</tr>
<tr>
<td>$k_r$</td>
<td>Modified exchange rate constant</td>
<td>L/t</td>
<td>m s⁻³</td>
</tr>
<tr>
<td>$a_s$</td>
<td>Specific surface area</td>
<td>L⁻²</td>
<td>m²</td>
</tr>
<tr>
<td>$K_D$</td>
<td>Capacity coefficient of deuterium</td>
<td>L³/mol</td>
<td>m³ mol</td>
</tr>
<tr>
<td>$D_s$</td>
<td>Diffusion coefficient in solid phase</td>
<td>L²/t</td>
<td>m² s⁻¹</td>
</tr>
<tr>
<td>$s$</td>
<td>Laplace parameter</td>
<td>t⁻¹</td>
<td>s⁻¹</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Void ratio of Pd bed</td>
<td>dimensionless</td>
<td>-</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Radius of particle</td>
<td>L</td>
<td>m</td>
</tr>
<tr>
<td>$D_L$</td>
<td>Longitudinal dispersion coefficient</td>
<td>L²/t</td>
<td>m² s⁻¹</td>
</tr>
<tr>
<td>$v$</td>
<td>Interstitial fluid velocity</td>
<td>L/t</td>
<td>m s⁻¹</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>The molar density of the Pd bed</td>
<td>mol/L³</td>
<td>mol m⁻³</td>
</tr>
<tr>
<td>$k$</td>
<td>Overall mass transfer capacity coefficient</td>
<td>L/t</td>
<td>m s⁻¹</td>
</tr>
</tbody>
</table>

The terms in the denominator of the final equation shown above (Equation 2-33) represent: the resistance of the fluid-film diffusion (first term), the pore diffusion in particles (second term) and the exchange reaction on the surface (third term). The final term represents diffusion in the solid palladium lattice. The authors use numerical analysis by Fast Fourier Transforms (FFT) to solve these complex equations since it is difficult to inversely transform the solutions shown above [68]. After doing this, the authors found that a few lumped parameters control the extent and rate of exchange:

a.) \( \frac{\gamma K_D}{\varepsilon} \) (the dimensionless deuterium capacity)

b.) \( k \) or \( \gamma K_D k \)

c.) \( \frac{v^2}{D_L} \)

\( \frac{\gamma K_D}{\varepsilon} \) and \( k \) were determined from fitting of the numerical results to the experimental data. \( D_L \) was separately determined as a function of temperature, based on moment analysis (see [68]), and the values were correlated to the tortuosity \( \tau_L \):
\[
D_L = \frac{D_m}{\tau_L + \nu a}
\]  

[2-34]

\(\tau_L\) was found to be 1.4, regardless of temperature and fluid velocity.

Numerical calculations for \(D_L\) and \(k\) were found to match experimental recorded values well at all temperatures and interstitial fluid velocities. Also, excellent agreement between model and experiments was observed for the HD effluent concentration. Fukada [4] also calculated the separation factor, \(\alpha\), during their experiments. They found values in good agreement with other investigators using similar experimental conditions similar (i.e. deuterium concentration at the inlet), in particular with the values of Wicke and Nernst [9]. The separation factor was found to the relatively independent of the total hydrogen pressure (0 - 12 bar).

Height equivalent to a theoretical plate (HETP) based methods are appropriate for assessing the separation ability of chromatographic separations of hydrogen isotopes. Fukada [4] determined that HETP values were dependent on 3 parameters:

- interstitial fluid velocity;
- column temperature; and
- pressure.

Figure 2-20 shows the HETP vs. interstitial fluid velocity obtained by Fukada [4]. The plot shows the experimentally determined values (symbols) and the calculated model results (lines). The minimum HETP value was 4.4 cm s\(^{-1}\) at 275 K and 295 K. It was found to be lower at higher temperatures, corresponding to an increased interstitial fluid velocity associated with higher temperatures. A good fit to results was achieved in model calculations, which used the mean values of \(D_L\) and \(k\) found from experimentation.
The HETP value was found to be the sum of two contributions from:

- axial dispersion \(2D_L/v\); and
- the overall mass transfer resistance (given by
  \[2 \left(\frac{\gamma K_D v}{\varepsilon_p k}\right) \left(1 + \frac{\gamma K_D}{\varepsilon_p}\right)^{-2}\])

This finding suggests that when modelling the exchange process in β-phase palladium hydride, a term for axial dispersion should be included. Since axial dispersion is dependent on the interstitial fluid velocity, it is important to determine this parameter during experimentation. In order to optimise an isotope separation process, knowledge of the interstitial fluid velocity is crucial. The second parameter contributing to the HETP value, the overall mass transfer resistance, is another important consideration. Fukada [4] considered the effects of temperature on the overall mass transfer capacity coefficient \((\gamma K_D k)\) and found a boundary condition around 300 K (Figure 2-21). Above 300 K, small temperature dependence was observed; whilst below 300 K a strong dependence was observed. At temperatures above 300 K a small Arrhenius-type activation energy for the overall mass transfer capacity coefficient (4.28 kJ mol\(^{-1}\)) was calculated. At low temperatures the activation energy increases to 17.1 kJ mol\(^{-1}\). The \(\gamma K_D k\) term is used when the rate-limiting step is pore diffusion or external diffusion, and is considered to be the fluid-phase concentration difference. \(k\) is used when the rate-
limiting step is solid diffusion through the palladium lattice. It is another overall mass-transfer coefficient, and is defined in terms of the solid phase concentration difference.

![Temperature dependence of overall mass-transfer coefficient](image)

Figure 2-21 Temperature dependence of overall mass-transfer coefficient defined by gaseous phase concentration difference $K_{D}k$. Reprinted from [4].

Fukada [4] also investigated pressure dependence of the two mass-transfer parameters ($\gamma K_{D}k$ and $k$). He found an inverse dependence, i.e. higher pressure gives a lower value of the mass-transfer coefficient. This is accredited to external diffusion resistance through the gaseous film (gaseous diffusion) and/or gaseous diffusion in the pores of the palladium particles (in “spongy” palladium). Using the established correlation of Wakao and Funazkri [69], Fukada [4] concluded the rate determining step above 300 K was molecular diffusion in the pores of their “spongy” palladium powder. The overall mass-transfer coefficient related to solid diffusion was found to have little pressure dependence. They suggest this could be because the exchange reaction proceeds via the Bonhoeffer-Farcus mechanism (see below):

$$\text{HD} + 2(-S) = \begin{array}{c}
\text{H} \\
\text{S}
\end{array} \begin{array}{c}
\text{D} \\
\text{S}
\end{array} = \begin{array}{c}
\text{H-S} \\
\text{S}
\end{array} + \begin{array}{c}
\text{D-S} \\
\text{S}
\end{array}$$

Where $S$ represents a surface atom.
The dependence of $k$ on total hydrogen pressure disappears when the surface coverage of hydrogen is large. Another reason for this lack of dependence on pressure is accredited to the activation energy of the overall mass-transfer coefficient. The experimentally determined value of 17.1 kJ mol$^{-1}$ is close to the activation energy of hydrogen diffusion determined by Wicke and Nernst (23.8 kJ mol$^{-1}$) [9]. Therefore, these studies suggest the presence of a thick surface hydride phase/bulk phase, requiring the activation energy equivalent to $\beta$-phase palladium hydride diffusion in order for a hydrogen atom to overcome this and take part in an exchange event. Evidence is therefore present suggesting that $\beta$-phase diffusion is the rate-determining step, although the authors state that the isotope exchange reaction could also be the rate-determining step because the effects of palladium particle diameter on the overall mass-transfer coefficient $k$ was not investigated. Fukada [4] were unable to prepare uniform “spongy” palladium particles of different diameters. Also, they were unable to determine the specific surface area of the “spongy” palladium particles due to the internal pore structure. This information shows the need for experimentation using different particle sizes and morphology to make more conclusive statements on the rate-determining step of the isotope exchange reaction. Also, it is imperative to know the characteristics of the palladium powder used in any experimentation in order to accurately model results.

In 2009, Luo [60] investigated hydrogen-deuterium exchange in $\beta$-phase palladium hydride using a Sieverts’ apparatus coupled to a residual gas analyser (RGA). Their experiments were able to determine thermodynamics and kinetics of the exchange reaction, in particular the rates of the two exchange directions (D-H, and H-D) and the equilibrium constant $K_{eq}$. They also investigated the exchange rate, $k_1$ for the reactions identified by Foltz and Melius [1] (Reactions R1 and R2).

Luo [60] were the first investigators to publish values for the equilibrium constant, $K_{eq}$ for the H-D-Pd system. They found values equivalent to model values published in previous literature and validated the result against equilibrium measurements made on the H-D-Pt system, of which experimental values are known. The authors examined the equilibrium constant $K_{eq}$ over a number of temperatures, ranging from 173 - 298 K, and found that their values agreed well for the H-D exchange ($D_2 + PdH_x$), but less well for the opposite D-H exchange ($H_2 + PdD_x$). They accredited this difference to the fact that their results were recorded when the system was not in equilibrium. Less scatter was
observed in their data for the H-D exchange $K_{eq}$ values because of smaller error associated with the experiments due to the larger equilibrium partial pressure of deuterium, with respect to hydrogen. The magnitude of the experimental error was ~700 Pa, and the experimental partial pressures recorded for the H-D exchange were as low as 1000 Pa, making the proportional error significant. In comparison, the partial pressure values during the D-H exchange were in the order ~6000 Pa.

In comparing their experimentally determined $K_{eq}$ values with the separation factor, $\alpha$, the authors found that $\alpha$ would reach equilibrium first in at all experimental temperatures investigated. They also determined the dependence of $\alpha$ on the degree of exchange and found no correlation at all temperatures. This is an interesting finding since it shows that the separation factor stays relatively constant regardless of ‘how far’ the exchange reaction has proceeded. Activation energies of both exchange directions were also determined and compared with literature values from Carstens and Encinias [3]. The authors found much lower activation energies; 2 kJ mol$^{-1}$ and 3.5 kJ mol$^{-1}$ and 8.8 kJ mol$^{-1}$ and 12 kJ mol$^{-1}$, for the D-H and H-D exchanges, respectively for each author. They accredited this difference to the different apparatus used by each study. Carstens and Encinias used a flow based apparatus, similar to Foltz and Melius, whilst Luo used a dosing (Sievert’s) apparatus. The authors assumed the difference is caused by a larger build-up of impurities on the palladium surface in the flow based device, increasing the activation energy. This would appear consistent with the findings of Outka and Foltz [2] and Carstens and Encinias [3], who both observed a large dependency of activation energies on impurities.

Luo [60] constructed a comprehensive kinetic model which was able to model the experimental results of both exchange directions reasonably well. Experimentally determined separation factors were close to those previously reported in the literature. However, it must be noted that the study was performed over a limited pressure range due to limitations of the apparatus. Experiments seemed to be not diligent enough, with insufficient equilibration time being a common theme throughout the experiments. Also, there was no investigation into flow effects or effects of particle morphology. Furthermore, no consideration was made to the individual steps of the reaction mechanism, the exchange rates determined were “overall” exchange rates and no consideration to rate-limiting step was made.
Larson et al [70] attempted the first comprehensive kinetic based model of the hydrogen isotope exchange process considering the adsorption and desorption of all the individual species. They again returned to the results of Foltz and Melius and fitted their model to their results. Their model was a one-dimensional isobaric reactor model that solved the transient set of governing equations including the overall mass balance for the gas phase, material balances for all of the gas-phase and surface species, and an ideal gas equation of state. The code was coupled to with the Chemkin package to facilitate the incorporation of arbitrary multistep reaction mechanisms into the simulations. This was used to test and optimize the basic mechanism describing the surface chemistry at or near the interface between the gas phase and the palladium particle. The kinetic description included mechanisms for reversible dissociative adsorptions of the three gas phase species on the particle surface as well as the atomic migrations between the surface and the bulk.

The following reversible reactions were considered in the model:

\[
\begin{align*}
H_2 + 2V_s & \rightleftharpoons 2H_s & \text{[R7]} \\
HD + 2V_s & \rightleftharpoons H_s + D_s & \text{[R8]} \\
D_2 + 2V_s & \rightleftharpoons 2D_s & \text{[R9]} \\
CO + 2V_s & \rightleftharpoons CO_s & \text{[R10]} \\
H_s + V_b & \rightleftharpoons H_b + V_s & \text{[R11]} \\
D_s + V_b & \rightleftharpoons D_b + V_s & \text{[R12]}
\end{align*}
\]

The forward and reverse rate constants for the above reactions are \( k_i \) and \( k_{-i} \), respectively. \( V_s \) represents the surface concentration of vacant sites. \( H_s \) is the concentration of surface H atoms (mol m\(^{-2}\)). \( D_s \) is the concentration of surface D atoms (mol m\(^{-2}\)). \( H_b \) is the bulk concentration of H atoms (mol m\(^{-3}\)). \( D_b \) is the bulk concentration of D atoms (mol m\(^{-3}\)).

After fitting Foltz and Melius’ [1] experimental data the authors presented a number of kinetic rate constants for the adsorption and desorption of H\(_2\), D\(_2\) and HD:
The rate constants for surface to bulk transfer steps were derived from the thermochemistry of dissolution studied by Santandrea and Behrens [47]. To maintain thermodynamic consistency, only the forward and reverse rate constants were specified for the reactions involving $H_2$ and $D_2$. Additionally to this the forward kinetic rate constant for the HD reaction mechanism was specified arbitrarily. The reverse rate constant for the formation of H$_2$D was determined from the known equilibrium constant ($K_{eq}$) for the equilibration reaction ($H_2 + D_2 \rightleftharpoons 2H_D$) between mixed hydrogen isotope gas species and Pd. The reverse rate constants for movement of the atomic species from the bulk to complete desorption from Pd were adapted from the work of Santandrea and Behrens and Charton et al [65]. All the remaining forward rate constants were specified arbitrarily until the experimental data of Foltz and Melius [1] was fitted satisfactorily.

Upon applying the model to Foltz and Melius’ experimental data Larson et al found that the model was capable of reproducing the data quite satisfactorily for the D-H exchange. For the H-D exchange, the model suffered from the inability to reproduce the experimental data that Foltz and Melius encountered. They noted their disappointment that the model, despite having a large number of adjustable parameters could not fit the Foltz and Melius’ experimental results. They implied their model and that of Foltz and Melius shared a common flaw and that it probably was down to some aspects of the physics of the exchange being not adequately modelled. They also alluded that this may

### Table 2-2 Larson et al’s [70] kinetic rate constants elucidated from fitting unpoisoned experimental data from Foltz and Melius [1]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Estimated value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$ (cm$^5$ mol$^{-2}$ s$^{-1}$)</td>
<td>$1.155 \times 10^{18}$</td>
</tr>
<tr>
<td>$k_1$ (cm$^2$ mol$^{-1}$ s$^{-1}$)</td>
<td>$2.290 \times 10^7$</td>
</tr>
<tr>
<td>$k_2$ (cm$^5$ mol$^{-2}$ s$^{-1}$)</td>
<td>$4.390 \times 10^7$</td>
</tr>
<tr>
<td>$k_2$ (cm$^2$ mol$^{-1}$ s$^{-1}$)</td>
<td>$1.263 \times 10^7$</td>
</tr>
<tr>
<td>$k_3$ (cm$^5$ mol$^{-2}$ s$^{-1}$)</td>
<td>$4.385 \times 10^7$</td>
</tr>
<tr>
<td>$k_3$ (cm$^2$ mol$^{-1}$ s$^{-1}$)</td>
<td>$5.593 \times 10^6$</td>
</tr>
<tr>
<td>$k_5$ (cm$^5$ mol$^{-2}$ s$^{-1}$)</td>
<td>$4.505 \times 10^6$</td>
</tr>
<tr>
<td>$k_5$ (cm$^2$ mol$^{-1}$ s$^{-1}$)</td>
<td>$7.482 \times 10^3 \exp(18.05x_{H} + 17.79x_{D})$</td>
</tr>
<tr>
<td>$k_6$ (cm$^5$ mol$^{-2}$ s$^{-1}$)</td>
<td>$2.895 \times 10^5$</td>
</tr>
<tr>
<td>$k_6$ (cm$^2$ mol$^{-1}$ s$^{-1}$)</td>
<td>$1.499 \times 10^5 \exp(17.79x_{H} + 18.05x_{D})$</td>
</tr>
</tbody>
</table>
be the internal diffusion of hydrogen isotopes within the Pd particles, although the work of James et al suggests this is not correct [71].

Similarly to Outka and Foltz [2], Larson also investigated the effect of impurities on the exchange process. They found by including the reactions involving surface poisoning by CO into their model they could fit Foltz and Melius’ data remarkably well. This again suggests that Foltz and Melius’ original work may have been significantly affected by impurities. An interesting aspect of Larson’s work was the analysis of the apparent equilibrium constant ($K_{app}$) (or concentration ratio) during Foltz and Melius’ experimental data. They found that Foltz and Melius’ assumption of equilibrium at all times and at all points in the bed appeared incorrect and the effluent concentrations leaving Foltz and Melius’ reactor were not in equilibrium. In fact the effluent data showed that $K_{app}$ was a long way from the $K_{eq}$ values determined from static Sievert’s type measurements [4, 9, 40, 58, 60, 72].

Larson et al [70] also applied their model to a ‘blowdown’ D-H isotope exchange experiment carried out at 300 K in a flow apparatus with an inlet pressure of 2 bar. They found that HD was under-produced and the experimental concentrations of HD were much smaller than those that would be expected at equilibrium. They noted that there may be some experimental error as a consequence of HD not being directly measured. Their model significantly overestimated the amount of HD by a factor of 2. Furthermore, the shape of the HD curve was asymmetric and did not align with that of the experiment. Due to the failings of a model with a significant amount of complexity and adjustable parameters, Larson et al [70] argue that some important physical processes occurring in Pd had been overlooked in the model development and there was a requirement to develop a multi-dimensional, multiphysics modelling capability in conjunction with data from carefully planned and executed isotope exchange experiments at various temperatures.

### 2.11 Hydrogen Isotope Separation Techniques

This section of the thesis summarises a number of other techniques for separating hydrogen isotopes. The main focus of the background study was in the previous section ‘Hydrogen Isotope Exchange’ as this is the subject of the PhD. It was felt by the author
that it is important to outline the available methods of hydrogen isotope separation to
give context to the potential uses of hydrogen isotope exchange.

2.11.1 Cryogenic Distillation

Distillation separates components by difference in boiling points. Cryogenic distillation
of hydrogen isotopes is a relatively new technology. A team of researchers led by J. R.
Bartlit from the Los Alamos National Laboratory in the US were first to discuss
cryogenic distillation of hydrogen isotopes for fusion reactors [73]. Their design
featured four interlinked, cryogenic and fractional distillation columns capable of
separating a mixed isotope feedstream of hydrogen, deuterium and tritium into four high
purity feed streams needed for thermonuclear fusion reactors, HD, HT, H₂, D₂ and T₂.
The technique has continued to be refined in a number of international facilities
dedicated to fusion research, particularly the fuel-cycle. Kinoshita[74] developed a
model to accurately simulate cryogenic distillation column cascades, whilst Yamanishi
[75] investigated mass transfer effects, also with a computer simulation, before later
investigating the control characteristics of a distillation column [76]. Yamanishi
validated the simulation model against experiments and found it capable of describing
the composition distribution within a cascade of distillation columns [77]. He also
considered the effect of a feedback stream on the process and developed an extended
model to include this effect. Iwai [78] demonstrated the reliability of a cryogenic
systems by operating a column without mechanical trouble for 2 years. Reliability will
be essential for efficient operation of a practical fusion reactor. Cryogenic columns for
this purpose often packed, and subsequently, the effect of different packing materials
has also been considered, with a common choice being Dixon Rings. Cryogenic
distillation units are energy intensive because of the extreme temperature required for
separation. Despite this, they are now widely regarded as the technique of choice for
large-scale separation of hydrogen isotopes. This is because of a number of reasons, as
outlined by Yamanishi [76, 79]:

1. Large processing flow rate.
2. Compact unit size – small internal diameters can be used.
3. High separating performance – high separation factors are achieved.
4. Ability to process varying feed compositions.
5. High purity hydrogen isotope product streams.
6. Negligible tritium permeation – owing to the cryogenic temperature of operation.

Cryogenic distillation is seen as the key component of the proposed ISS at ITER because of its ability to deal with varying gas composition in the feed stream [78] from the fusion reactor. Other systems involving chromatographic separations have been proposed to deal with varying feed compositions, but most have been deemed difficult requiring complex control systems. There are some disadvantages with cryogenic distillation systems, however. Startup/shutdown procedures can be difficult and, as previously mentioned, operation at cryogenic temperature is energy intensive.

2.11.2 Chromatographic Separation

Gas chromatographic separations of hydrogen isotopes use differences in isotopic affinity for the surface of active materials as the means of separation. Different isotopes of hydrogen can therefore be separated by differences in speed of travel through a material. Materials typically used are adsorbents, metal hydrides or alloys of hydride forming materials. The most extensively investigated hydride material is palladium because of its remarkable isotope effect, rapid exchange kinetics and ability to store large quantities of hydrogen isotopes. It is, however, expensive and this has driven other investigators to investigate more exotic hydride forming metal compounds (such as AB₅ types), and less expensive hydride forming metals (such as vanadium).

This section aims to give an overview of metal hydride and adsorbent based processes. The author points the reader towards the following additional sources [80-102].

2.11.3 Metal Hydride Separations

Metal hydride based separation of hydrogen isotopes has been investigated for over half a century. Typical experimental setup involves metal hydride packed bed columns which are exposed to a hydrogen isotope gas mixture. Palladium hydride has been by far the most investigated hydride for these type of separations, although a number of different hydride materials have been characterised by Aldridge [103]. He investigated approximately 60 different alloy hydride materials, mainly based on lanthanum and calcium AB₅ type hydrides using alloy materials of nickel and copper. He concluded that hydrogen isotope separation would be feasible using metal hydride chromatography if materials were synthesised with a separation factor of 1.3 or more and suitably rapid
equilibrium characteristics. He notes that if a material was found with separation qualities matching palladium, commercial separation would be achieved without question. Rutherford [104] performed an extensive review of metal hydride separations in 1988. This included discussion of other metal hydride materials other than palladium and should be referred to alongside the studies of Aldridge. Separations based on hydrogen-absorbing metals or alloys require a large isotope separation factor (see Section 2.3.6). Palladium has a remarkably high separation factor at room temperature and this can be used to enact efficient separations of isotopic mixtures of hydrogen using chromatographic techniques. Due to the relevance of palladium to the current PhD project, further discussion in this section will relate to palladium hydride and palladium-alloy hydride systems.

A number of different chromatographic techniques have been developed; displacement, self-displacement, elution, and frontal. Separation of hydrogen isotopes by displacement chromatography was first investigated by Glueckauf and Kitt [105] in 1957. They reported high enrichment of D₂ (ca. 99.5 % purity) in the outlet of the column using palladium black supported on asbestos. Displacement technique using palladium has also been investigated by Fukada [106]. He found that 100% D₂ purity could be achieved in a small column, with approximately 60 % recovery from the initial mixture. The procedure involves loading the metal hydride bed with a hydrogen isotopic mixture, then flow a displacement gas with greater affinity for the metal surface. In the case of a palladium hydride system, hydrogen has a higher affinity (discussed in section 2.9) for the metal than deuterium or tritium and is, therefore, suitable for use as the displacement gas. Upon introduction of a mixed H₂-D₂ feed, hydrogen adsorbs to the surface preferentially and forms an interstitial hydride phase near the inlet part of a column, leaving the deuterium to adsorb (and subsequently absorb into the metal lattice) further down the column. When the displacement gas is flowed through the column the hydrogen displaces the deuterium and causes an enriched band of deuterium to exit the column first, followed by HD (formed due to the catalytic nature of Pd) and finally hydrogen. Displacement chromatography using hydrogen has been found to offer the highest enrichment ratio and recovery ratio of deuterium, when compared to other techniques [107]. The separation is, however, inherently batch in nature.

Self-displacement chromatography uses a similar principal to the displacement technique, but in this case the hydrogen in the initial gas mixture is used as the
displacement gas. Glueckauf and Kitt [105] also investigated this technique during their experiments in 1957 and found it capable of producing D$_2$ product purity of 99.7 %. Columns are sorbed with an isotopic mixture at room temperature, followed by progressive heating from the column inlet. This causes the hydrogen absorbed at the inlet to desorb and flow towards the column outlet due to pressure difference. As the hydrogen passes through the column it displaces the absorbed deuterium from the metal causing an enriched band of deuterium to arrive at the outlet of the column first. Twin column systems are often used to reach the required enrichment via a number of cycles through the two columns [108] (see Figure 2-22). The self-displacement technique has the advantage of needing no displacement or carrier gases. Glueckauf and Kitt also noted that in this technique there is less chance of deuterium remaining irreversibly adsorbed to the palladium surface. The self-displacement technique is considered useful for separating small amount of deuterium from isotopic mixtures because of its high enrichment ratio but moderate recovery ratio [107] and requirement for no carrier gas. This was confirmed by Watanabe [109] who investigated Pd-Pt alloys using the self-displacement method. He reported of ~97.5 % D$_2$ purity obtained from a starting mixture of 90 % H$_2$ – 10 % D$_2$, with a recovery ratio of 60 %. The alloy materials were also tested with a 50:50 mix of H$_2$:D$_2$ and found to enrich D$_2$ to similar levels with an even higher recovery ratio of 80 %. Self-displacement separations are again batch in nature.
Elution chromatography is the most simplified technique of separating hydrogen isotope mixtures. In elution chromatography a mixed isotope feed is introduced into a column containing metal hydride particles and allowed to equilibrate. An inert gas (i.e He or Ar) is then fed into the column inlet to purge the hydrogen isotopes from the particle bed. Optimum operational temperatures for elution chromatographic separation are often higher than displacement techniques, which are effective at room temperature. Fukada [110] has used numerical modelling to simulate elution chromatography of hydrogen isotopic mixtures containing H₂-HD-D₂ and found the optimum temperature to be approximately 323 K. Elution chromatography is the least promising technique for separating hydrogen isotopes because of large amount of tailing (or overlap) in the recorded chromatograms of each isotopic species. The recovery ratio is, therefore, poor when compared to other displacement techniques.

The frontal (or breakthrough) technique requires the feed gas mixture to be continuously fed to the metal hydride bed. In this method the feed gas acts as the displacing gas and also as a carrier, therefore only a deuterium-rich band is formed in the palladium bed [107]. The rest of the bed is near the feed gas composition and no resolution of the other components can be achieved. This technique can be effective for enriching deuterium from natural hydrogen. Fukada [107] found that recovery ratio of 60% could be
achieved using natural hydrogen feed, which corresponds to an enrichment ratio of over 100.

Botter and co-workers [111] investigated a number of packing materials for displacement chromatographic separations of H-D mixtures. Hugony [112] also investigated packing materials, but in this case for resolution of H-T mixtures. Both investigators concluded that α-alumina was the best packing material, particularly when mixed in a ratio 1:3 of Pd to alumina, respectively. This material produces a small height equivalent to a theoretical plate (HETP), or equilibrium stage height, value of approximately 1 mm. This compares admirably to some of the aforementioned column packing materials which typically have a HETP value of 3-6cm. Rutherford [104] also studied palladium packing materials and came to the same conclusion as Botter and Hugony. They accredited this good performance to the low specific surface area of the α-alumina material (ca. 1 m² g⁻¹) causing the ‘tailings’ between isotopic bands to be suppressed.

Metal hydride chromatographic separations using palladium and its alloys are promising and relatively easy methods of separating hydrogen isotopes when compared to other available technologies, such as cryogenic distillation which needs extreme temperatures and continual cooling from cryogenic liquids such as argon. One downside is the cost of palladium. On a large-scale it would be prohibitively expensive. Glueckauf and later Fukada [105, 107] both conclude that chromatographic techniques are useful techniques for concentrating the heavier isotopes from mixtures, but in no more than laboratory or small batch scale processes. Separating deuterium from natural hydrogen using chromatography is considered by Glueckauf to be not viable. The discontinuous nature of the process and the large quantities of palladium required to store the more abundant hydrogen make the process extremely uneconomical.

Some continuous processes using metal hydrides have been discussed in the literature [113]. These involve countercurrent processes, equivalent in principle to distillation, which are setup to allow the solid metal hydride bed in a chromatographic column to move. Typically, hydrogen is stripped from the metal hydride at the bottom of the column using heat. The solid is then sent back to the top of the column and the hydrogen gas is recycled to bottom of the column to begin rising through the column once again. This is a form of reflux. Inert gases are usually used to transport the solid
metal hydride material through the column circuit. Metal hydride forming materials, such as palladium, are usually loaded onto support materials (i.e. zeolites). Significant difficulties arise in the transport of absorbent material through the column without causing degradation by attrition.

2.12 Comparison of hydrogen isotope exchange against other isotope separation techniques

The above sections regarding hydrogen isotope separation techniques will now be compared to hydrogen isotope exchange, the subject of investigation herein. Hydrogen isotope exchange offers a number of advantages over the other separation techniques outlined above. The main advantage is the ability to produce pure hydrogen isotopes from mixed isotope feed streams. Furthermore, the separation can be achieved in a simple flow based packed powder bed process at ambient conditions. The column lengths needed to achieve the separation are significantly shorter in length than those required for chromatographic separations involving palladium doped substrates. This makes the separation ideal for laboratory/small scale operations in which mixed isotope streams need to be purified.

The main disadvantages of the hydrogen isotope exchange process revolve around the high cost of Pd and the potential for Pd degradation under continued exposure to varied isotopic atmospheres. Degradation occurs when the Pd particles (making up the packed bed) undergo swell and shrink by differing amounts under exposure to the different hydrogen isotopes. This causes packed powder bed to eventually degrade due to formation of cracks and fissures in the bed structure. The other major disadvantage of the process, and the main inhibitor to large scale processes involving hydrogen isotope exchange, is the inherent batch nature of the process. Continuous processes are possible but require challenging process setups involving moving beds.

While cryogenic distillation offers the ability to produce continuous high purity hydrogen isotopes (and their isotopomers) at high throughputs, the initial capital cost and continued operating costs are significant. Moreover, by the nature of the process the operating temperatures need to be < 40 K requiring, for example, liquid helium. Membrane processes generally offer a means of separating hydrogen isotopes from inert/process gas streams. It is more challenging to obtain pure hydrogen isotope without the use of thick palladium/palladium alloy membranes combined with high feed
gas pressure to encourage differences in the diffusion characteristics between the isotopes to produce a separation. They do, however, offer the ability for process scale up and can be produced of palladium alloys which are resilient to Pd degradation and poisoning by impurities in the feed gas streams.

In order to summarise these, the following table has been produced (Table 2-3).
<table>
<thead>
<tr>
<th>Technique</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen isotope exchange in packed powder Pd</td>
<td>• Ambient separation conditions (i.e. temperature and pressure).</td>
<td>• High cost of pure Pd powder</td>
</tr>
<tr>
<td></td>
<td>• High separation efficiency in small columns.</td>
<td>• Impurity contamination of Pd powder</td>
</tr>
<tr>
<td></td>
<td>• Pure hydrogen isotopes can be produced.</td>
<td>• Multiple columns required to achieve high purity isotopic gases</td>
</tr>
<tr>
<td></td>
<td>• Ideal for laboratory scale separations.</td>
<td>• Batch operation.</td>
</tr>
<tr>
<td></td>
<td>• Easy equipment setup.</td>
<td>• Palladium susceptible to degradation through bed cracking.</td>
</tr>
<tr>
<td>Cryogenic distillation</td>
<td>• High purity gases can be obtained in a single column.</td>
<td>• High economic cost of separation equipment.</td>
</tr>
<tr>
<td></td>
<td>• Cryogenic distillation columns can handle varied feed gas compositions.</td>
<td>• High operating costs due to extreme low temperatures required for separation.</td>
</tr>
<tr>
<td></td>
<td>• High throughput.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Different hydrogen isotopomers can be separated.</td>
<td></td>
</tr>
<tr>
<td>Chromotographic separation of hydrogen isotopes</td>
<td>• Lower palladium inventory required for separation.</td>
<td>• Batch processes; multiple columns required for semi-continuous operation.</td>
</tr>
<tr>
<td></td>
<td>• Multiple displacement techniques available.</td>
<td>• Long column lengths required for separation.</td>
</tr>
<tr>
<td></td>
<td>• Easy equipment setup.</td>
<td>• Poor separation efficiency in single column.</td>
</tr>
<tr>
<td></td>
<td>• Low operating and capital cost.</td>
<td>• Difficult to produce pure hydrogen isotopes from mixed feed gases.</td>
</tr>
<tr>
<td>Palladium based membranes (pure and alloy types)</td>
<td>• Easy scale up by numbering up of membrane modules.</td>
<td>• High cost of palladium and alloying materials.</td>
</tr>
<tr>
<td></td>
<td>• Palladium alloy membranes offer improved resistance to degradation and poisoning.</td>
<td>• Production of pure hydrogen isotopes difficult.</td>
</tr>
<tr>
<td></td>
<td>• Membranes can be tailored to application through alloying with other metals.</td>
<td>• High pressure required for membrane processes.</td>
</tr>
<tr>
<td></td>
<td>• Most applicable to purifying hydrogen isotopes from inert/process gases.</td>
<td></td>
</tr>
</tbody>
</table>
2.13 Summary of key background information

Hydrogen isotope separation has been investigated thoroughly over the past one hundred years. However, the process of hydrogen isotope exchange, which occurs during isotope separations involving Pd have received less attention. The study of hydrogen isotope exchange in Pd will allow a better understanding of isotope separations this media, and allow an insight into the production of HD which in most cases is an undesirable intermediate species. Studying the isotope exchange reaction, as is undertaken herein, will allow improved isotope separation processes involving Pd to be designed and the current understanding of the system enhanced. The key points regarding the background information are summarised below:

- An extensive amount of information exists regarding the palladium-hydrogen system, but little information exists for the hydrogen isotope exchange process occurring in a flow device.

- The kinetics of the hydrogen isotope exchange process have not been characterised in detail previously. While a handful of studies have been performed on the kinetics of the isotope exchange process in a flowing device, they have focussed on a single temperature and pressure only.

- These studies have been performed under the assumption that equilibrium is achieved between gas and solid phases in the palladium-hydrogen-deuterium system.
Chapter Three

Materials and Methods
Chapter 3. Materials and methods

3.1 Introduction

As previously discussed, hydrogen isotope exchange occurs when one isotope of hydrogen (e.g. deuterium) is replaced by another isotope in solid storage media, such as palladium. It was first studied by Foltz and Melius in 1987 [1] in a simple flow based apparatus using Raman spectroscopy to analyse the gaseous composition leaving the bed (H₂, D₂ and HD). They formed a pure palladium powder bed and exposed it to both isotopes (protium and deuterium) and observed the subsequent exchange reaction. As discussed in the Background chapter of this work, there have been a number of investigations published in the literature involving different experimental geometries, bed morphology and palladium structures [1, 3, 4, 56, 113-118]. However, none have comprehensively covered the effects of temperature, pressure and flowrate on the exchange process. The seminal study by Foltz [1] used only one flowrate and operated at room temperature only. Future studies by Fukada [4, 106] investigated the isotope exchange reaction during chromatographic separations of tritium, deuterium and protium. No comprehensive study has been performed investigating the effects of inlet pressure, temperature and flowrates on the exchange process. To this end, a unique and custom-built apparatus was commissioned by AWE, Aldermaston and constructed by Hiden Isochema, Warrington to study the exchange process over a wide range of experimental conditions. The apparatus was installed in laboratory 1.04, 9w University of Bath. The following section will discuss the commissioning work undertaken during this work, as well as the experimental procedure and methods required to produce valid, repeatable isotope exchange results.

3.2 Materials and Methods

3.2.1 Materials

The solid storage media used for the study of the exchange process presented in this chapter is powdered palladium black (Pd). This material has been supplied by AWE, Aldermaston and has an average particle size between 500 nm – 1.5 µm. The powder was 99.9 % pure. Exact details of the powder are of a sensitive nature and subject to a non-disclosure policy as dictated by the UK Ministry of Defence (MoD). Ultra-pure
hydrogen gas (H₂) (99.999 %, purchased from Air Products and Chemicals Inc.) and deuterium gas (D₂) (99.99 %, purchased from BOC) were used in the exchange and hydriding reactions. Other non-reactive gases used were nitrogen (99.9999 %, purchased from Air Products and Chemicals Inc.) to activate the valves and helium (99.9999 %, purchased from Air Products and Chemicals Inc.) as a carrier gas, inert atmosphere during sample preparation and a means of quantifying the background levels in the mass spectrometer. Argon (99.99 %, purchased from BOC) has also been used in the latter months due to a worldwide shortage of helium gas.

3.2.2 Gas purification

In order to further purify the two reactive gases (H₂ and D₂) in line gas purifiers were purchased. These purifiers were fitted below the regulators delivering gas to the inlet section of the IsoEx rig (see section 3.3.1). The purchased purifiers were Entegris Gatekeeper in line high pressure hydrogen purifiers (model number: 500KFHP). They are claimed to remove impurities in hydrogen gas streams to sub-ppb levels by adsorption onto a number of solid sorbents contained within the purifier. These purification units have a long life of up to three years of continuous use and can be recharged by the manufacturers. It was deemed necessary to further purify the reactive gas streams to remove impurities to the lowest practical levels because they poison the surface of Pd powder, rendering it unusable for exchange reactions. Carbon monoxide (CO) and water (H₂O) are the main impurities to remove with respect to their ability to poison the Pd surface. CO is known to adsorb strongly to Pd and remains on the Pd surface for a significant residence time [2, 3]. Impurities also increase the activation energies of the surface interactions between Pd and H₂/D₂. Carstens and Encinias quantified this effect during exchange reactions on a Pd powder not dissimilar to that used in this work [3].

In order to characterise and record the most accurate exchange data possible it was deemed very important to maximise the purity of the gas streams. There was also an economic driver with respect to high purity D₂ gas. High purity D₂ gas carries a significantly increased cost compared to ‘standard’ purity (99.9 %) D₂ gas. The cost of the highest purity H₂ gas was also significant compared to the ‘ultra pure’ H₂ purchased in this project. After performing a cost analysis comparing the cost of the purchasing
high purity D₂ and H₂ and the cost of the in line purifiers it was deemed economically beneficial to purchase the purifiers.

3.3 Commissioning and Use of Hydrogen Isotope Exchange (IsoEx) Apparatus

3.3.1 Hydrogen Isotope Exchange Apparatus

The apparatus used to study the phenomenon of exchange is shown in Figure 3-1. The equipment was designed by AWE, Aldermaston and constructed by Hiden Isochema, Warrington. It consists of an inlet section, reactor section, exhaust section and mass spectrometer. The inlet section features parallel pipework to carry either hydrogen isotope gas (H₂ or D₂) to the reactor independently. After the inlet section is a reactor tube where the palladium compact is contained. Here hydrogen isotopes (H₂ or D₂) are exposed to a hydrided (PdHₓ) (or deuterided (PdDᵧ)) palladium bed to enact the exchange reaction. After the reactor section the gases flow towards the exhaust where a sampling point is located to divert exiting gases from the Pd bed to the mass spectrometer for analysis. Gas flow is controlled by two Bronkhorst mass flow controllers (MFC) located on both inlet gas streams (H₂ and D₂). The reactor can be heated directly by a coil heater surrounding the tube (max. 300 °C). Lower temperatures (min. -65 °C) can be achieved using the environmental chamber surrounding the reactor section (blue ‘box’ in Figure 3-1). A PC workstation is connected to the apparatus to allow control of apparatus. IsoEx software was supplied which controls valve operation, reactor temperature, gas flowrates and pressure. This software also allows for sequences to be written so that experiments can be designed and carried out automatically. Engineering drawings for the apparatus can be found in the Electronic Supplementary Information that accompanies this work. This is in addition to the Supplementary Information shown at the end of the thesis. This was necessary to enable all of the A3 format engineering drawings (> 10) to accompany the work.
Figure 3-1 IsoEx apparatus installed in Laboratory 1.04, 9West, University of Bath

Figure 3-2 Flow diagram of IsoEx apparatus

Figure 3-3 Block flow diagram of IsoEx apparatus
3.3.2 Mass Spectrometry

The IsoEx apparatus is equipped with a bespoke Hiden Analytical type HAL3F-RC quadrupole mass spectrometer (QMS) commissioned by AWE, Aldermaston. It is capable of analysing gases within the mass range of 1 to 50 amu using two available detectors, Faraday and secondary electron multiplier (SEM) (see below). The device is fitted with a triple ion filter and dual oxide coated iridium filaments. Two software packages have been supplied to control the mass spectrometer. Basic scan functions can be accessed through the apparatus control software, IsoEx, allowing the user to monitor gas composition leaving the reactor in real-time via multiple ion tracking. Advanced scan options can be accessed through the optional MASsoft software. This software allows selection of a number of different scan types: Bar, Profile and Multiple Ion Detection (MID).

![Figure 3-4 Hiden Analytical HAL3F-RC Quadrupole Mass Spectrometer](image)

Each of these modes is useful for obtaining different information about the gas stream. When selecting BAR mode, a histogram will be produced showing the selected scan range, in amu, on the x-axis and the mass spectral peak intensities on the y-axis (in microTorr). Each mass will have its own distinct peak showing the quantity of each component in the gas stream. BAR mode is useful for qualitative assessments of the components in the gas stream; it is not to be used as a definitive representation of the quantities of each component in a gas stream. To achieve this, MID mode must be used.
MID mode tracks the ionic species of interest in real-time and produces a graph of time (min) vs. recorded pressure (Torr). It was used to accurately calculate the quantities of each component in the gas stream. The software formed an integral part of the research into hydrogen isotope exchange because it allowed observation of the exchange reaction in real-time. Using the recorded values of gaseous pressure, the amounts of H₂, D₂ and HD in the gas stream was calculated and the mass balance over the surface of the palladium was solved.

Some experiments during the research project required helium and deuterium in the gas stream. Deuterium and helium only differ in mass by a very small amount; helium (He) has a standard atomic mass of 4.002602 amu and deuterium (D₂) has a mass of 4.028204 amu. It was therefore difficult to determine accurate quantities of each gas when both were present in the gas stream. To overcome these difficulties, Profile mode was selected in MASsoft. Whilst BAR mode scans measure and display a single reading for each mass, a Profile mode scan takes a series of measurements for each mass. This leads to a bell-curve of all the detected masses around mass 4 amu, giving a profile. By careful manipulation of the variables in MASsoft, two peaks, corresponding to He and D₂, were separated enabling quantification of each component.

Each of these modes was used during the commissioning period. The software of choice was MASsoft because it gave a far greater flexibility in changing scan and instrument environment parameters within the software. Much of the work during the first 6 months of the project involved trying to understand the importance/significance of each of the scan and environmental parameters. A list, and short description, of the scan parameters within MASsoft is shown in the Supplementary Information.

Manipulation of these scan and environmental parameters allows the instrument to be correctly setup, specific to each experiment that will be performed on the IsoEx rig. For example, if it is known that a gas will be in small quantities the dwell and settle times, along with electron emission and auto zero can be used to increase the sensitivity and therefore accuracy of the scan. The dwell and settle times can be increased, causing the instrument to search for the ion of interest for longer and also allow the electronic longer to settle. This, along with a boosted electron output via changes to electron emission voltage and emission level, increase the sensitivity of the instrument to detect ions in smaller quantities.
3.3.3 Detectors

The mass spectrometer is fitted with dual detectors: Faraday and SEM (Secondary Electron Multiplier). The Faraday detector can operate at any pressure within the range $10^{-5}$ to $10^{-10}$ Torr. The SEM detector gives higher sensitivity with low background noise compared with the Faraday detector. It does, however, have a lifetime unlike the Faraday detector. The lifetime of the SEM detector is determined by the total ion current (charge) it measures. For example, the lifetime of a SEM detector monitoring a partial pressure of $1 \times 10^{-8}$ Torr will be one hundred times longer than the same detector monitoring a peak at $1 \times 10^{-6}$ Torr. Therefore, SEM detector lifetime will be extended if only large peaks are monitored, either by using the Faraday detector, or if they must be detected by the SEM, keeping the time monitoring high partial pressure gas species to a minimum.

The SEM detector was calibrated to give a gain of x1000 by selecting the operating voltage. SEM detectors must be calibrated with respect to the Faraday detector. The ideal situation is to calibrate the SEM using the mass in greatest quantity in the experiments, i.e protium or deuterium in the case of exchange. This procedure should be done approximately once a month.

3.3.4 Commissioning the IsoEx Apparatus

Initial construction and commissioning of the IsoEx rig began early September 2010 in the presence of engineers from AWE (Dr Tim Barnes) and HidenIsochema (Richard Murden) and lasted for approximately two weeks. During this time, the rig was unpacked following shipping and constructed in laboratory 1.04 in the Department of Chemical Engineering, building 9West at the University of Bath. The rig consists of four main sections: the inlet section, consisting of the inlet pipework for H$_2$, D$_2$ and He and associated control valves; the reactor chamber, comprising an environment chamber and reactor; the mass spectrometer, a QMS with fast acting capillary; and finally, an exhaust section where all gases are vented into the department’s waste gas stack.

Commissioning aimed to solve any initial ‘snagging’ issues and leave the rig fully operational. After initial construction, commissioning continued for a number of months until experiments could be carried out without problems. During initial stages of the PhD, a number of operational issues became clear whilst using the apparatus. These
needed to be solved in order for the apparatus to function efficiently and without problems. The first objective was to develop an accurate ‘Events’ sequence within the MASsoft mass spectrometer software. This is a key part of the mass spectrometer setup. An accurate ‘Events’ sequence is needed to ‘tell’ the mass spectrometer what functions to perform (and in what order) during sampling and recording data. The ‘Events’ sequence was developed by Richard Murden (Hiden Isochema) and the software team from Hiden Analytical, the mass spectrometer suppliers. It was required in all experiments on the IsoEx rig.

Another major area of focus during this period was in testing the fast switching of gases, from H\textsubscript{2} to D\textsubscript{2}. Considering the nature of the experiments, this aspect of the control system had to function correctly and give smooth transitional flow curves between flow set-points for each gas. It was noticed during commissioning that the transition period whilst beginning to flow each gas was noisy; resulting in large fluctuations in the recorded flowrates, rather than a smooth transition from no-flow to flow.

To solve this problem some re-calibration software from Bronkhorst (the mass flow controller manufacturers (MFCs)) was used to bring the controllers back into calibration. In order to use the associated software, one must first connect the MFCs to a computer via a VGA cable. Control of the MFCs can then be achieved through the software installed on the PC. To alter the flow transition profile the user must alter the three parameters in the PID control of the MFCs; the proportional value, the integral value and the derivative value. By altering these parameters the user can adjust the MFCs to provide a more smooth flow transition. Upon changing settings within the PID control, smooth flow transition was achieved.

Further issues during commissioning were regarding the hydrogen gas sensors installed in the IsoEx. Two sensors are associated with the rig; a ceiling-mounted funnel type hydrogen sensor above the rig, and a Crowcon Xgard flammable gas sensor fitted into the extract system for the chemical engineering building. During the first year of the studentship the ceiling-mounted sensor has performed well. The extract system sensor, however, has suffered from significant drift in detected levels of H\textsubscript{2}, leading to the sensor needing re-calibration twice in the first 6-months despite a manufacturers guarantee that the sensor should last 4-6 months without need for re-calibration.
Engineers from Pollution Monitors, the sensor suppliers, highlighted problems whilst calibrating the sensor due to its location in an exhaust system with gas flow. Despite the department’s ventilation being shutdown, there was still sufficient flow of gas to prevent an accurate calibration of the H₂ sensors. There was also a possibility that the sensor was poisoned by sealant during installation into the ventilation system in building 9West. After consultation with Cleanroom Design and Construction Ltd (CDC) and Pollution Monitors a more robust sensor was purchased and installed in a separate cabinet away from the ducting. Sampling is achieved via a sampling tube inserted into the side of the extraction ducting within the laboratory. Since the re-design, no further problems were experienced and the sensor was stable.

Pd compact preparation (as discussed in Section 3.5.1 of this report) was initially attempted using a G-clamp supplied by the department. This method for compressing Pd powder compacts was found to be unsatisfactory. Required Pd compact densities were achieved but in an unsafe manner. Because of the nature of the G-clamp, one end of the reactor was able to move, allowing the reactor and compression pins to ‘pop’ out of the clamp. The method was then modified so that the Pd compact was prepared using a robust and stable T-Bar sash clamp.

In order to hydride the Pd compact correctly and minimise pressure changes upon introduction of gas flow, a number of pressure vs. flow calibrations were performed. These allowed accurate pressure dosing to be performed before exchange experiments, creating a pressure in the reactor similar to that expected when gas flow is introduced.

3.3.5 Correction of H₃⁺ contributions in Hydrogen Isotope Mass Spectrometry

During the first 6 months operation of the IsoEx rig an anomalous mass 3 amu signal was detected by the mass spectrometer whilst flowing H₂ through the system. The signal was present during initial gas composition tests and also during exchange and breakthrough experiments.

It is important to remove this mass 3 signal from the scan when trying to monitor for HD, which also has a mass of 3 amu. Otherwise, recorded pressures for HD would be anomalous, potentially altering the findings of the isotope exchange experiments. In order to address this issue, a program was written in MASsoft which can be appended to the main scan program to remove the influence of the H₃⁺ from any future experiments.
Under typical operating conditions, 5 – 30 % of the mass 3 signal can be due to H$_3^+$ [119].

After a literature search, the problem was identified as coming from the ion source, i.e. the filament. The H$_3^+$ signal is formed in the ion source of the mass spectrometer by the reaction [119]:

$$H_2^+ + H_2 \rightarrow H_3^+ + H$$ \hspace{1cm} [R13]

As can be seen from the above equation, the molecular hydrogen molecule (H$_2$) is ionised to H$_2^+$ in the ion source of the mass spectrometer. Subsequent to this, further molecular hydrogen entering the mass spectrometer reacts with charged molecular hydrogen (H$_2^+$), forming H$_3^+$ and a proton, i.e. atomic hydrogen. The abundance of H$_2^+$ is proportional to the partial pressure of H$_2$ entering the mass spectrometer. The production of H$_3^+$, is therefore, proportional to the second power of the partial pressure of H$_2$:

$$p_{H_3} = K.(p_{H_2})^2$$ \hspace{1cm} [3-1]

where K is an experimentally determined proportionality constant. In terms of the IsoEx rig, a BAR mode scan was performed to obtain the peak intensities (in microTorr) of mass 2 and mass 3. Using the above equation, the true isotope ratio of the gas stream can then be calculated from the following equation:

$$R = \frac{p_3}{p_2} = \frac{p_{HD} + p_{H_3}}{p_{H_2}} = \frac{p_{HD}}{p_{H_2}} + K.p_{H_2} = R^* + K.p_{H_2}$$ \hspace{1cm} [3-2]

where, $p_2$ and $p_3$ are the observed mass-2 and mass-3 partial pressures (or intensities) and R and $R^*$ represent the measured and corrected partial pressures, respectively.

The above equation was then fed back into theMASsoft via a short ‘Events’ sequence which was appended to the mass spectrometer scan program within the ‘Scan Editor’ sub-menu. The small section of code performs a simple calculation and removes the H$_3^+$ signal from the recorded mass 3 (HD) signal. The program outputs a corrected HD partial pressure signal, $p_{HD}$ in ppm.
3.3.6 Calibrating the relative sensitivities (R.S.) of H₂, D₂ and HD

When sample gas species are fed to the mass spectrometer through the capillary tube they are ionised in order for detection to occur. The gas species must be ionised in order to interact with the detectors in the mass spectrometer. However, not all of the incoming gas species are ionised leaving some of the gas molecules to pass through the mass spectrometer undetected. To accurately quantify the actual amount of gas present in a sampled gas stream the detected ion signal must be divided by a factor which represents the ability of the filament to ionise the particular gas species of interest. Each gas species has a specific value (factor) by which the ion signal (number of counts on the detector) is divided. These factors are called Relative Sensitivities or R.S. values. For instance, the R.S. value for H₂ is 0.44. So the ion current value is divided by this value to ‘boost’ the detected value to represent the actual quantity of H₂ that entered the detection chamber. The mass spectrometer uses R.S. values to provide an accurate representation of the actual quantity of gas entering the detection chamber through the capillary.

The mass spectrometer was supplied with a library of R.S. values for a number of different gases, including H₂, He, Ar and N₂ which were used in this project. Unfortunately, the manufacturer’s library did not contain values for D₂ and HD. Considering these two gases, along with H₂, form the majority of the gas stream in hydrogen isotope exchange reactions it was very important to determine the correct R.S. values for these species in order to ensure the detected values were representative of the actual quantity of gas entering the mass spectrometer. When any new species (such as D₂ and HD) were entered into the mass spectrometer they were automatically assigned the same R.S. value of H₂ (i.e. 0.44). This needed to change in order to another value specific to D₂ or HD. In order to determine these values pure D₂ and HD gas were needed. Pure D₂ gas was readily available from BOC. Pure HD gas was more difficult to source, and carried a significant cost. Once the two gases were sourced the following calibration procedure was performed.

H₂ gas was used as the reference gas in which to compare the ‘pure’ D₂ and HD signals to. This was because the H₂ R.S. value was already known from the manufacturer’s library. A flow of 100 % H₂ revealed a certain detected partial pressure within the mass spectrometer. This detected pressure was therefore the level the D₂ and HD needed to
equal when each was flowing at 100 %. The experimental procedure for determining the D₂ R.S. value involved first flowing H₂ gas to record the partial pressure in the mass spectrometer using a 100% H₂ flow. After the H₂ signal had stabilised the H₂ gas flow was shut off and pure (100 %) D₂ gas was introduced into the mass spectrometer. The D₂ partial pressure value was recorded and adjusted to match the 100 % H₂ partial pressure by reducing the R.S. value. The recorded D₂ partial pressure value was multiplied by 0.44 to give the value of the ‘actual’ detected partial pressure considering imperfect ionisation. This value was the divided by a different R.S. value until the D₂ partial pressure signal matched that of pure 100 % H₂ flow. The exact same procedure was performed for HD.

Once the new R.S. values for D₂ and HD were determined the author was confident that the recorded H₂, D₂ and HD partial pressures were accurate.

3.3.7 Removal of background levels

In all the purchased gases there were so called ‘background levels’ of impurities. Furthermore, low levels of impurities were also detected inside the mass spectrometer detection chamber itself due to an imperfect vacuum created by the scroll pump. The scroll pump did create a very low vacuum in the region of 10⁻⁹ Torr, however, despite this there still existed certain quantities of impurities such as H₂O, N₂, O₂, Ar and CO₂. These impurities were also detected in the purchased gases, even after passing them through the in line purifiers. In order to ensure highly accurate results during the exchange reactions performed in this work these background levels must be removed. In particular, it was important to quantify the levels of D₂ in the incoming H₂ gas stream and vice versa to ensure accurate exchange results. It was also important to detect any mass 2 and mass 4 species arising in the mass spectrometer from cracking of impurity species entering the detection chamber from the scroll pump seals.

This was done by recording the background levels of impurities coming from the gas cylinders (with in line purifiers in place) using the mass spectrometer and an empty reactor chamber. Additionally to this, the background levels of impurities arising from imperfect vacuum were quantified by sealing the mass spectrometer sample capillary with a ‘blank’ cap and recording only the species present in the ‘sealed’ detection chamber of the mass spectrometer. These two methods allowed the levels of impurities
from the gas cylinders and imperfect vacuum to be quantified. Background levels of H$_2$ evolved from the stainless steel of the IsoEx rig have not been quantified.

### 3.4 Characterisation of Pd powder

#### 3.4.1 Scanning Electron Microscope (SEM)

A scanning electron microscope (SEM) was used to characterise the palladium black powder received from AWE, Aldermaston. [The nature of the powder is confidential and not for dissemination to other parties, other than the specified readers of this report]. A used palladium sample which was exposed to a number of cycles of protium and deuterium loadings in the apparatus has also been observed under SEM. The purpose of this was to identify changes to the structure of the powder and whether impurities (present in the ‘as received’ gases) had accumulated at the surface. As received powder and used samples were taken to the SEM and prepared in an Edwards S150B Sputter Coater under vacuum of 0.2 mbar for ~4 minutes. This sputter coater deposited a thin layer of gold on the sample to enhance their conductivity. The SEM was operated in the 10-20 kV range and micrographs were taken of a number of areas on each sample. Quantity maps were also scanned on the used palladium sample to reveal impurities on the surface.

Unfortunately, the SEM results cannot be published due to MoD non-disclosure policy around the sensitive nature of the Pd powder used in this work. However, the author wanted to highlight that powder characterisation techniques were initially trialled and not ignored. Only due to the aforementioned reasons were the results from these tests omitted.

### 3.5 Pre-experimental procedure

#### 3.5.1 Pd compact preparation

Preparation of the Pd sample was very important when investigating hydrogen isotope exchange over palladium. The morphology of the bed can significantly influence the reaction, leading to a faster or slower exchange profile. Bed density used in this work was 3 g cm$^{-3}$. 
Pd beds were situated in the reactor using a set of two push-rods. These rods were used to compress the sample powder into the centre of the reactor (see diagram above). Each push-rod is manufactured so that a seal is formed between the rod and the wall of the reactor tube.

The procedure for situating the powder in the reactor is as follows:

- First, one push-rod was placed inside the reactor to act as a base onto which powder was to be poured.
- Second, a small diameter plastic funnel was placed into the mouth of the reactor.
- Third, the weighed Pd powder was poured into reactor.
- Fourth, the other push-rod is placed in the reactor tube at the pouring end.
- Finally, the push-rods were used to compress the Pd powder using a T-Bar sash clamp.

The density of the Pd powder can be varied by applying different forces to the push-rods, via the T-Bar sash clamp. The density of the Pd compact can be calculated using the following method:

**Bed density, ρ_{bed}, method:**

Firstly, the target compact density and mass of compact must be chosen. For this example calculation a density of 3 g cm$^{-3}$ is used and a mass of 3 g of Pd. The density of pure palladium metal is $\rho_{Pd} = 12.023$ g cm$^{-3}$.

Reactor dimensions:
After choosing the target density and the mass of sample the following equation was used to determine the required volume of the Pd compact:

$$\rho_{\text{target}} = \frac{m_{\text{exp}}}{V}$$

[3-3]

where:

- $\rho_{\text{target}}$: target Pd powder density (g/cm$^3$)
- $m_{\text{exp}}$: mass of sample (g)
- $V$: volume of compact (cm$^3$)

Example calculation:

$$\frac{3 \text{ g}}{\text{cm}^3} = \frac{3 \text{ g}}{V}$$

$$V = 1 \text{ cm}^3$$

This volume was used to determine the required length of the compact, via the equation:

$$V = AL$$

where:

- $V$: volume of compact (cm$^3$)
\[
A \quad \text{internal area of reactor tube (cm}^2 \text{)} \quad [A = \pi r^2] \\
L \quad \text{required length of compact (cm)}
\]

Using this equation, the required length of the Pd compact (using the identified target density and mass) is: \( L = 3.54 \text{ cm} \).

### 3.5.2 Sample cleaning

Pd is easily contaminated by impurities coming from the ‘as received’ gas cylinders, such as carbon monoxide (CO), carbon dioxide (CO\(_2\)), oxygen (O\(_2\)), nitrogen (N\(_2\)) and methane (CH\(_4\)). These impurities are common to all the gases used on the IsoEx rig and adhere to the surface of the palladium powder, inhibiting the exchange reaction by blocking active sites and therefore preventing hydrogen from being absorbed into the Pd lattice. CO is perhaps the most significant impurity with a residence time on the surface of \(~2500\text{ s at NTP}\) \([2]\). Considering this, and the number of quoted impurities in the ‘as received’ gases, it was necessary to develop an efficient and consistent cleaning method for the Pd samples.

Two cleaning methods were trialled to ensure a clean sample; \( \alpha \)-clean and a \( \beta \)-clean. These names denote the phase the palladium powder is in during the cleaning, i.e. \( \alpha \)- and \( \beta \)- phase. Both methods involve introducing hydrogen to the sample followed by an outgassing step to remove H\(_2\) and impurities from the surface. In the \( \alpha \)-clean the reactor chamber is heated to 150 °C (423 K). The palladium powder is then given a low loading of hydrogen (H atoms distributed over the surface in such a way that interactions between them are low/inconsequential) by introducing a low hydrogen pressure to the reactor chamber. The sample is left for a period of 10 minutes to equilibrate and reduce any impurities present on the surface. After equilibration, the reactor chamber is exposed to a vacuum (outgas) for a period of 25 minutes. This procedure is repeated for 5 cycles and then evacuated under vacuum for >12 hours (overnight) whilst maintaining the reactor temperature at 150 °C. When a fresh Pd compact is put into the IsoEx rig, a \( \alpha \)-clean procedure is performed to remove any impurities built up during storage in air [the samples are received in plastic bottles/plastic sealed bags].

**\( \alpha \)-clean:**

- Evacuate the compact for 1 hour while the temperature of the reactor was brought up to 150°C.
After evacuating the reactor section for 1 hour, hydrogen at a pressure of 600 Torr (~0.8 bar) was introduced to the compact for a period of 10 minutes.

The temperature of the compact remained at 150°C for the remainder of the process.

After 10 minutes, the compact was evacuated for 25 minutes.

The process of introducing hydrogen followed by evacuation was repeated for 5 cycles.

At the end of the 5th cycle, the compact was evacuated for a period of 12 hours.

The compact remained heated for the duration of this period.

At the end of 12 hours, the heater was switched off and the compact was allowed to cool.

The compact was now ready for loading.

The β-clean was a similar procedure to that of the α-clean. The difference being the Pd compact was kept in the β-phase during the entire cleaning process. This was achieved by maintaining a low temperature in the reactor chamber, allowing the hydride phase to remain with minimal changes to the lattice parameter (swelling), therefore, preserving the compact integrity for further exchange experiments. The β-clean was a much faster process and could be completed in a couple of hours, depending on the number of cycles of outgassing that were performed. The procedure is shown below:

**β-clean:**

- The procedure assumes the palladium bed starts as manufactured, pressure tested and at a vacuum.
- ‘Cold degas’ at room temperature; here the bed/compact was evacuated at < 10^{-2} mbar.
- ‘Bed hydriding’ – the bed was slowly but fully hydrided, and the overpressure left at 1.5 bar.
- ‘Cleaning’ – hydrogen was flowed through the bed at 1 slpm for 30 minutes.

An alternative β-clean process features cycles of cold degas and hydrogen loading. This static clean process involves forming a β-phase hydride compact by introducing a known pressure (ca. 1.5 bar) of H₂, then performing a cold degas to remove and
impurities from the surface of the palladium using vacuum only. This cycle was repeated a number of times to ensure the Pd compact was clean. It is important to note that this alternative cleaning methodology can cause significant degradation in a Pd compact structural integrity due to repeated swelling and shrinking of the Pd lattice.

### 3.6 Experimental procedure

A number of different experimental procedures were carried out on the IsoEx rig in order to investigate hydrogen isotope exchange reactions occurring within solid storage media such as Pd. Two specific experimental techniques were used during this project. The first ‘switchover’ type experiments were used early on in this work. The second ‘non pre-flow’ type of experiments were used for the majority of experiments that followed because of the reproducibility of results and less difficult setup. In fact, all the experimental data published here was obtained by using ‘non pre-flow’ methodology. Despite this, the author believes it necessary to record both experimental procedures for any future investigators of hydrogen isotope exchange using the IsoEx rig. The procedure to find the permeability (κ) of a Pd bed is also described below. This was an important technique used for providing a starting κ value from which modelling efforts could proceed. Furthermore, the very important initial hydriding procedure is described and explained below.

#### 3.6.1 Initial hydriding/deuteriding

Hydriding (or deuteriding) the packed powder Pd bed prior to any experiments was vital to prevent failure of the bed. The Pd beds were hydride/deuterided by administering a controlled pressure dose of either H\(_2\) or D\(_2\) after sample loading and cleaning (see Section 3.5.1 and 3.5.2). This causes the Pd to absorb H\(_2\) or D\(_2\) in a controlled manner, reducing the likelihood of cracks and fissures appearing due to lattice expansion in the Pd under hydrogen isotope loading. Pd is known to swell by ~10 % upon hydrogen (deuterium) absorption. This swelling causes the particles in a Pd bed to bind tightly together. Upon hydrogen desorption the Pd lattice shrinks, causing particles in a Pd bed to move apart which opens up cracks. Repeated cycling of hydrogen loading and desorption can even cause Pd beds to disintegrate. It is therefore imperative that Pd beds are kept under a hydrogen atmosphere to prevent the unwanted effects of lattice expansion and contraction.
If initial hydriding (or deuteriding) of the Pd sample was not carried out and \( \text{H}_2 \) or \( \text{D}_2 \) gas flowed onto an unhydrided sample the integrity of the Pd bed was found to drop. The incoming \( \text{H}_2/\text{D}_2 \) gas reacts with the fresh Pd causing the upstream portions of the Pd bed to swell while the downstream areas remain static. This upstream swelling caused cracks in the Pd bed between the hydried and unhydried sections of the bed. In some cases the Pd bed would simply fail and be blown out of the middle of the reactor, colliding with the gaskets at the end of the reactor tube. This represented a significant waste of Pd.

The initial hydriding was performed by gradually administering pressure doses until the desired experimental pressure was reached. For example, if an upstream pressure of 7 bar was to be used the pressure doses were built up in 1 bar steps until 7 bar was reached. This ensured the Pd hydried in a controlled manner rather than under extreme upstream pressure.

### 3.6.2 Permeability determination

In order to determine the permeability the Pd bed must be loaded into the reactor and cleaned following the instructions set out in Sections 3.5.1 and 3.5.2. Following this the Pd compact (packed bed) was hydried or deuterided by administering a pressure dose of \( \text{H}_2 \) or \( \text{D}_2 \). The Pd bed was then left for 30 minutes to equilibrate with the gas overpressure. After this a low flow of 800 ml min\(^{-1}\) of the same gas as the initial hydriding was begun (i.e. \( \text{H}_2 \) if the bed was PdH\(_x\), and \( \text{D}_2 \) if the bed was PdD\(_y\)). The flow was then allowed to stabilise for some minutes. Finally, the pressure drop over the packed Pd bed was recorded using the pressure sensors upstream and downstream of the reactor. The pressure drop value can be used in conjunction with other known parameters of the Pd bed and incoming \( \text{H}_2 \) gas, such as viscosity and porosity, to determine the permeability of the Pd bed by using the Darcy equation (Dupuit-Forchheimer modified version).

### 3.6.3 Switchover experiments

Here the reactor was loaded with the Pd compact following the procedure outlined in Section 3.5.1. After sample loading and cleaning the Pd packed bed was hydried or deuterided depending on the exchange direction to be investigated using the pressure dose function within the IsoEx software. The Pd bed was then left for 30 minutes to
ensure complete hydriding (deuteriding). Following this a sequence was created in the IsoEx software to automatically control the experiment. This involved specifying time intervals between each experimental function. The following description will describe the procedure to enact a D-H exchange, i.e. going from a deuterided Pd bed (PdDx) to a hydride Pd bed (PdHx). To perform the reverse H-D exchange the procedure should be followed using the other hydrogen isotope to that described here.

The first experimental function was to turn on the mass spectrometer software (MASsoft) in preparation for gas sampling. The next step was to open the mass spectrometer sample valve to allow gas to pass into the detection chamber via the capillary connected to the exhaust section of the IsoEx rig. Following this D₂ gas flow was initiated and allowed to flow until the signal in the mass spectrometer had stabilised. Immediately after this H₂ gas flow was initiated. This began the exchange reaction within the Pd bed. H₂ gas was allowed to flow until the mass spectrometer showed the exchange was complete and no more D₂/HD was detected.

After the exchange was complete a pressure dose of H₂ was administered into the reactor and the H₂ gas flow was shut off. This H₂ gas dose ensured the Pd remained in a hydride state, therefore preventing the appearance of cracks and fissures due to hydrogen desorption. The mass spectrometer sampling was then shut and the MASsoft software was stopped and the results saved. After this the hydride Pd bed could be used for the next H-D exchange.

3.6.4 Non pre-flow experiments

Similarly to the switchover experiments, the Pd bed was loaded into the reactor and cleaned thoroughly before any experiments were carried out. The Pd beds were then hydrided (or deuterided depending on the hydrogen isotope exchange experiment) into the β-phase with a controlled pressure dose into the reactor. The pressure within the reactor was gradually built up to that of the proposed experiment. For example, for a 1 L min⁻¹ exchange pressure doses were administered to the reactor in 1 bar increments until ~7 bar was held within the reactor. The Pd beds were then left for at least 30 minutes to ensure complete hydriding had occurred and the bed was in the β-phase. After this the experiment was ready to proceed. The difference between the non-pre-flow and switchover type experiments was that the system begins in a ‘static’ state. That is, the opposite isotope to that loaded on the Pd bed was flowed into the reactor to start
the exchange. For example, for a D-H exchange the Pd bed was initially deuterided into the β-phase (PdD$_{>0.55}$) and the experiment was started by beginning flowing H$_2$ gas into the reactor to enact the exchange.

The exact experimental procedure for a D-H exchange will now be discussed in detail. Again the first experimental procedure was turning on the mass spectrometer software (MASsoft) in preparation for gas sampling. The next step was to open the mass spectrometer sample valve to allow gas from the exhaust of the IsoEx rig into the capillary tube to deliver gas to the detection chamber. The inlet MFC on the H$_2$ line was then initiated at the correct flow set point and H$_2$ gas was admitted to the IsoEx reactor, starting the exchange. The effluent gas concentration was then recorded by means of the mass spectrometer. The exchange experiment was run until no more HD was detected in the effluent gas stream and H$_2$ gas had completely broke through and saturated the Pd bed. The experiment was finished by administering a pressure dose of H$_2$ that match the upstream pressure in the reactor, recorded on pressure sensor P3. This ensured the Pd bed remained in the β-phase and would not suffer from cracking/degradation from hydrogen desorption. At this point the Pd bed was in the hydride state ready for the reverse H-D exchange experiment. All exchange data from the IsoEx software and MASsoft was recorded and saved for post experimental analysis and modelling.

To perform the reverse H-D exchange any future user should carry out the same experimental procedure but using a initially hydried Pd bed (PdH$_{>0.5}$) and flow in D$_2$ gas rather than H$_2$.

3.6.5 Low pressure experiments

Low pressure experiments were necessary to confirm the findings of other studies in the literature investigating hydrogen isotope exchanges over Pd packed powder beds (for example, Foltz and Melius [1]) To perform low pressure experiments (< 2 bar) on the IsoEx rig in its current state an additional experimental procedure was developed. This was because the MFCs installed on each inlet line were incapable of flowing at gas below 800 ml min$^{-1}$, as this was the minimum flow setpoint. Even a flowrate of 800 ml min$^{-1}$ created an upstream pressure of ~ 5 bar due to the highly dense nature of the Pd bed and small particle size. Furthermore, the pressure regulators prior to the inlet section of the IsoEx rig had a minimum pressure upon opening of ~10 bar. This meant that despite careful opening of the regulators a pressure of ~ 10 bar was created
upstream of the MFCs. Consequently, upon flowing at the minimum flowrate of 800 ml min\(^{-1}\) a pressure of \(~5\) bar was realised on the upstream side of the Pd bed.

To work around this problem, some additional pressure regulators were fitted to the pressure cylinders outside of laboratory 1.04 to control pressure to the low values required for these types of experiments. The low experimental pressure (ca. 1.5 bar) was set on the cylinder mounted pressure regulators. The additional pressure regulators associated with the IsoEx rig were then opened fully to allow the low pressure gas to pass through unrestricted. The experiment was setup in the exact same manner as the non-pre-flow type experiments. That is, the Pd bed was loaded, cleaned and hydrided (or deuterided depending on the exchange direction). The mass spectrometer software was then switched on ready for data recording. Then the sample valve to the mass spectrometer was opened in preparation for effluent gas sampling and delivery to the mass spectrometer detection chamber. The inlet gas (either H\(_2\) or D\(_2\)) was then allowed to flow into the reactor by setting the relevant MFC (MFC-1 or MFC-2) to its maximum flowrate (50 L min\(^{-1}\)). This caused the MFC valve to open fully and allow the low pressure gas stream through to the reactor unrestricted. The effluent gas concentration was recorded until no more HD was detected and the MASsoft software showed complete saturation of the Pd bed by the incoming gas (i.e. complete breakthrough). Note: these experiments took significantly longer than the higher pressure exchange experiments. The penultimate experimental function was to administer a pressure dose of the incoming gas into the reactor (that matched the upstream pressure observed during experiment) to keep the Pd bed in the \(\beta\)-phase and ready for the reverse experiment. Finally, after the exchange was complete, the sample valve was closed, MASsoft turned off and all data was recorded and saved for post experimental analysis and modelling.

### 3.6.6 Experimental conditions

Hydrogen isotope exchanges have been carried out in both directions, D-H and H-D using two pressure regimes. Firstly, low pressure exchanges were investigated using the experimental methodology described in Section 3.6.5. These experiments were carried out at \(~1.5\) bar. However, due to difficulties with pressure control in the IsoEx system at low pressure not all low pressure experiments were carried out at exactly the same pressure. The pressure setpoint was always set at 1.5 bar on the cylinder mounted.
regulators, but due to the large volume of pipework fitted to the IsoEx rig, complex valve arrangement and influence of dead volumes in the system, it was not always possible to achieve 1.5 bar during low pressure experiments. Because of these experimental artefacts, the upstream pressure in the low pressure experiments varied somewhat between each experimental repeat. The range of upstream pressures in the four experimental repeats was 1.3 – 1.6 bar. As will be explained in the following Results chapter, this had an influence on the post processing of data.

Despite this the experiments were deemed valid and carried out at a number of temperatures that represented the extremes of the temperature matrix which could be investigated on the IsoEx rig. The temperatures investigated were 208 K, 293 K and 373 K. The maximum range of the rig was 208 K – 573 K.

Secondly, high pressure exchanges were investigated. The high pressure exchanges were carried out using an inlet gas (either H₂ or D₂) flowrate of 1 L min⁻¹. This corresponded to an upstream pressure of 5.5 – 8 bar, depending on the inlet gas stream and the temperature. The upstream pressures in these experiments were always consistent and comparable. The high pressure exchanges were investigated at the same temperatures as the low pressure experiments so that comparisons could be made and the effect of pressure on the exchange could be determined.

### 3.7 Experimental matrix

The following two tables present the upstream pressures used during both the low pressure and high pressure (1 L min⁻¹ flowrate) exchanges. The differences in pressure arise from the changing reactor temperatures used. The associated temperatures at which the exchange experiments were carried out are also presented.
Table 3-1 Experimental matrix for the D-H exchanges carried out in this work

**D-H exchange**

<table>
<thead>
<tr>
<th>Upstream pressure (P₃)</th>
<th>208 K</th>
<th>293 K</th>
<th>373 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 bar</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.6 bar</td>
<td></td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>1.7 bar</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>5.5 bar</td>
<td></td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>6.3 bar</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>7.5 bar</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
</tbody>
</table>

Table 3-1 shows the completed D-H hydrogen isotope exchange experiments carried out in this thesis. For the low pressure (< 2 bar) experiments, the upstream pressure was controlled by setting the pressure on a regulator. For the higher pressure (> 5.5 bar) experiments, the upstream pressure was dictated by specifying the gas flowrate to 1 L min⁻¹. Table 3-2 shows the completed H-D hydrogen isotope exchange experiments carried out in this thesis. The H-D 1 L min⁻¹ experiments (>7.5 bar) had significantly higher upstream pressures due to the increased viscosity and mass of the flowing D₂ gas.

Table 3-2 Experimental matrix for the H-D exchanges carried out in this work

**H-D exchange**

<table>
<thead>
<tr>
<th>Upstream pressure (P₃)</th>
<th>208 K</th>
<th>293 K</th>
<th>373 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 bar</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.6 bar</td>
<td></td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>1.7 bar</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>7.5 bar</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8 bar</td>
<td></td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>8.3 bar</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
</tbody>
</table>
Chapter Four

Results and Discussion
Chapter 4. Results and Discussion

4.1 Introduction

This section of the thesis presents the hydrogen isotope exchange results obtained using the experimental procedures outlined in the previous chapter. Both exchange directions (D-H and H-D) have been investigated using high (1 L min\(^{-1}\)) and low pressure (ca. 1.5 bar upstream pressure) inlet gas streams over a wide range of temperatures. The raw experimental data in the form of effluent gas pressures in the mass spectrometer (in Torr) have been converted into effluent gas mole fractions and plotted as a function of time. The resulting charts, shown in the next sections of this chapter, demonstrate the effect of pressure and temperature on the hydrogen isotope exchange process occurring within hydrided (and deuterided) Pd packed powder beds.

In the later sections of this chapter the experimental observations including differences and similarities between the various exchange reactions are discussed. These are compared to existing exchange data taken from the literature.

4.2 Experimental results

This section of the chapter will present the results for the low and high pressure hydrogen isotope exchange experiments carried out during the course of the research project. Data for both D-H and H-D exchange directions is presented for three experimental temperatures, 208 K, 293 K and 373 K. The low pressure hydrogen isotope exchange experiments were carried out at ~1.5 bar. The higher pressure exchanges were carried out using a flowrate of 1 L min\(^{-1}\). This corresponded to an upstream pressure of between 5.5 – 8 bar depending on temperature and the incoming hydrogen isotope gas stream.

The low pressure exchange experiments are presented without uncertainty because of problems with pressure control. Large differences between the timings of the experimental repeats (for example the arrival of the gaseous species) made it very difficult to provide meaningful uncertainty values because the repeats were not comparable. For this reason only data for the experimental repeat with an upstream pressure of 1.5 bar has been presented. The other three experimental repeats for the low
pressure exchanges had upstream pressures of 1.3 bar, 1.4 bar and 1.6 bar, respectively. Despite there only being 0.1 – 0.2 bar difference in the upstream pressure, this was enough to affect the breakthrough times of these experiments significantly, causing a large difference in the appearance times of the exchange features. The author stresses that the experimental findings in each experiment were very similar (in terms of HD production and breakthrough curve shapes), however upon post processing of the results these small differences in upstream pressure caused unrealistic and extreme uncertainty bars that dominated the appearance of the low pressure exchange data because the results were not comparable in terms of experimental conditions. For this reason uncertainty bars have been left off the low pressure exchange charts for both exchange directions. If suitably improved mass flow controllers and regulators could be sourced for the rig this problem would be removed and comparable, repeatable results would be obtained. Refer to the Future Work section (Section 7.3) of this work for more discussion on this recommendation.

The 1 L min\(^{-1}\) isotope exchanges are presented with uncertainty bars because each of the three repeats of these experiments was entirely comparable. The experimental uncertainty was calculated using the standard deviation arising from the experimental repeats. All the hydrogen isotope exchange results are presented in groups. For example, the D-H exchanges are shown in sets of three charts showing the different temperatures investigated. The reverse H-D exchanges are also shown in the same manner. This format is repeated for both the low and 1 L min\(^{-1}\) exchanges. The experimental data points have been plotted versus time and dot-dash lines have been added to the charts to aid the reader in following the experimental exchange features.

4.2.1 Low pressure PdD to PdH exchanges

Figure 4-1(a) – (c) presents the low pressure D-H hydrogen isotope exchange experimental data obtained at 208 K, 293 K and 373 K, respectively. The effluent gas mole fractions of H\(_2\), D\(_2\) and HD are plotted as a function of time. The mole fractions were calculated from the detected partial pressures of each gas species in the mass spectrometer. The exchange reactions experimental data are plotted up to the point where the exchange was deemed complete for all intents and purposes. In reality the exchange experiments were carried on for some time after the times plotted on the following charts. However, to maintain chart clarity for the reader only the necessary
Figure 4-1 Low pressure PdD to PdH exchange data obtained at: (a) 208 K; (b) 293 K; (c) 373 K
data points have been plotted (i.e. the point where the detected gas species concentrations were constant; representing the end of the exchange reaction).

4.2.2 Low pressure PdH to PdD exchanges

Figure 4-2(a) – (c) presents the low pressure H-D hydrogen isotope exchange experimental data obtained at 208 K, 293 K and 373 K, respectively. The effluent gas mole fractions of H$_2$, D$_2$ and HD are plotted as a function of time. The mole fractions were calculated from the detected partial pressures of each gas species in the mass spectrometer. There were significantly more experimental data points recorded in this exchange direction compared to the low pressure D-H exchange. This was because the mass spectrometer sample rate remained the same but the overall time to complete the exchange was longer. As such, the data points appear closer to each other in the H-D exchanges compared to those in the D-H exchanges. The H-D exchange reactions are plotted up to the point where the reaction could be deemed complete for all intents and purposes.

4.2.3 1 L min$^{-1}$ PdD to PdH exchanges

Figure 4-3(a) – (c) presents the 1 L min$^{-1}$ D-H hydrogen isotope exchange experimental data obtained at 208 K, 293 K and 373 K, respectively. The effluent gas mole fractions of H$_2$, D$_2$ and HD are plotted as a function of time. The mole fractions were calculated from the detected partial pressures of each gas species in the mass spectrometer. The charts plot data up to 30 seconds. This was not, however, the end of the experimental run. The experiment was carried out for >100 seconds. The data has been cut off at 30 seconds because the exchange was deemed sufficiently complete at this point, and it allows the reader to visualise the exchange features clearly. Figure 4-3(b) shows the experimental data for the 1 L min$^{-1}$ D-H exchange carried out at 293 K. The chart plots data up to 20 seconds in this case. This was because it was difficult to identify the exchange features when the maximum x-axis value was 30 seconds. Furthermore, in this particular exchange, the reaction is almost complete at 20 seconds so there was little need to plot additional points beyond 20 seconds.
Figure 4-2 Low pressure PdH to PdD exchange data obtained at: (a) 208 K; (b) 293 K; (c) 373 K
Figure 4-3 1 L min⁻¹ PdD to PdH exchange data obtained at: (a) 208 K; (b) 293 K; (c) 373 K.
4.2.4 1 L min⁻¹ PdH to PdD exchanges

Figure 4-4(a) – (c) presents the 1 L min⁻¹ H-D hydrogen isotope exchange experimental data obtained at 208 K, 293 K and 373 K, respectively. The effluent gas mole fractions of H₂, D₂ and HD are plotted as a function of time. The mole fractions were calculated from the detected partial pressures of each gas species in the mass spectrometer. Similarly to the low pressure data, the timescales of the 1 L min⁻¹ H-D exchanges were longer compared to the D-H exchanges. As such, the maximum value on the x-axis of the following charts is 100 seconds. At this time all the different temperature H-D exchanges carried out at 1 L min⁻¹ were deemed complete.
Figure 4-4 1 L min⁻¹ PdH to PdD exchange data obtained at: (a) 208 K; (b) 293 K; (c) 373 K.
4.3 Equilibrium analysis – Apparent equilibrium constant (K\textsubscript{app})

An important assumption during early hydrogen isotope exchange investigations was the formation of an instantaneous equilibrium between the gas and solid phases in all points in the Pd bed [1]. To assess this assumption by Foltz and Melius the effluent concentrations leaving the Pd bed as a function can be manipulated to give the apparent equilibrium constant or concentration ratio (K\textsubscript{app}). K\textsubscript{app} takes the following form, which is the same as the traditional description of the equilibrium constant:

\[
K_{\text{app}} = \frac{[\text{HD}]^2}{[\text{H}_2][\text{D}_2]} \tag{4-1}
\]

Here the effluent concentrations of HD, H\textsubscript{2} and D\textsubscript{2} are used to give the apparent equilibrium constant as a function of time during hydrogen isotope exchange experiments. This section presents the results of this equilibrium analysis for both low pressure and 1 L min\textsuperscript{-1} hydrogen isotope exchange experiments. Each chart plots K\textsubscript{app} for the three experimental temperatures (208 K, 293 K and 373 K) as a function of time. For reference the equilibrium constant values found from static Sievert’s type experiments reported in the literature are also plotted on the charts.

4.3.1 Low pressure PdD to PdH equilibrium analysis

Figure 4-5 shows the variation in the apparent equilibrium constant (K\textsubscript{app}) as a function of time for each to the low pressure D-H hydrogen isotope exchanges carried out at 208 K, 293 K and 373 K (solid black, red and green lines on Figure 4-5, respectively). The dashed black, red and green lines on Figure 4-5 represent the equilibrium constant value for 208 K, 293 K and 373 K, respectively. These equilibrium constant values were calculated using the empirical relationships described by Foltz and Melius and other authors in the literature [1, 4, 9, 15, 40, 60, 120].
4.3.2 Low pressure PdH to PdD equilibrium analysis

Figure 4-6 shows the variation in the apparent equilibrium constant ($K_{app}$) as a function of time for each of the low pressure H-D hydrogen isotope exchanges carried out at 208 K, 293 K and 373 K (solid black, red and green lines on Figure 4-6, respectively). The dashed black, red and green lines on Figure 4-6 represent the equilibrium constant value for 208 K, 293 K and 373 K, respectively.
4.3.3 1 L min⁻¹ PdD to PdH equilibrium analysis

Figure 4-7 shows the variation in the apparent equilibrium constant ($K_{app}$) as a function of time for each to the 1 L min⁻¹ D-H hydrogen isotope exchanges carried out at 208 K, 293 K and 373 K (solid black, red and green lines on Figure 4-7, respectively). The dashed black, red and green lines on Figure 4-7 represent the equilibrium constant value for 208 K, 293 K and 373 K, respectively.

![Figure 4-7 Apparent equilibrium constant ($K_{app}$) as a function of time for the 1 L min⁻¹ D-H exchanges carried out at 208 K, 293 K and 373 K](image)

4.3.4 1 L min⁻¹ PdH to PdD equilibrium analysis

Figure 4-8 shows the variation in the apparent equilibrium constant ($K_{app}$) as a function of time for each to the 1 L min⁻¹ H-D hydrogen isotope exchanges carried out at 208 K, 293 K and 373 K (solid black, red and green lines on Figure 4-8, respectively). The dashed black, red and green lines on Figure 4-8 represent the equilibrium constant value for 208 K, 293 K and 373 K, respectively.
4.4 Discussion and analysis

4.4.1 Introduction

This section of the Chapter will discuss the direct experimental observations of the low pressure and 1 L min$^{-1}$ hydrogen isotope exchange experiments. The findings of the equilibrium analysis are also discussed in detail. Furthermore, additional post experimental analysis and comparison of the apparent equilibrium constant is performed. The main aim of the discussion is to critically analyse the experimental data whilst referring to existing hydrogen isotope exchange studies performed by other authors in the literature.

The main features and differences of the exchange directions are discussed, with regards to the low and high pressure regimes individually. The discussion then analyses specific differences observed at different temperatures within the two pressure regimes. Finally, comparisons are made between the two pressure regimes to derive the influence of pressure on the hydrogen isotope exchange reaction.

4.4.2 Comparison of HD production in 1 L min$^{-1}$ and low pressure exchanges

In order to aid the reader in the following discussion sections the following HD comparison charts have been produced. Figure 4-9 presents the HD production during...
the 1 L min\(^{-1}\) and low pressure D-H exchanges. Figure 4-10 presents the HD production during the 1 L min\(^{-1}\) and low pressure H-D exchanges. As can be seen from the figures, the HD production differs greatly when moving from the low pressure to high pressure (1 L min\(^{-1}\)) experimental regimes. HD was generally produced for far longer in the low pressure exchanges corresponding to the lower inlet gas pressure, and *vice versa* for the 1 L min\(^{-1}\) exchanges. These figures show that pressure had a significant impact on the exchanges. These phenomena will be discussed in more detail in the following sections. These figures will be referred to in the later sections of the discussion in order to support the hypotheses being discussed.

![Figure 4-9 Comparison of D-H 1 L min\(^{-1}\) and low pressure HD production.](image)

![Figure 4-10 Comparison of H-D 1 L min\(^{-1}\) and low pressure HD production](image)
4.4.3 Discussion and analysis of experimental data

Figure 4-1 and Figure 4-2 show the experimental data for the low pressure D-H and H-D hydrogen isotope exchanges, respectively. Figure 4-1(a) – (c) show the D-H isotope exchange experiments carried out at 208 K, 293 K and 373 K, respectively. Figure 4-2(a) – (c) show the H-D isotope exchange experiments carried out at 208 K, 293 K and 373 K, respectively. Significant differences were found between the two exchange directions (D-H and H-D). First of all, the timescale of the two different directions was significantly different. The low pressure D-H exchanges were found to complete in less time compared to the H-D exchanges. This observation was found at all temperatures and during each experimental repeat.

The difference can be accredited to the difference in thermodynamic favourability of each exchange direction. Pd has a greater affinity for H atoms. This phenomenon arises from differences in the zero-point energy of the respective isotopes (see Background chapter) [17, 37, 38, 121]. As such, the PdD to PdH exchange (D-H), where H atoms exchange places with the surface bound D atoms, is favoured over the reverse exchange direction, H-D, where D atoms exchange places with surface bound H atoms. Another way to view this greater affinity is in terms of the Gibb’s free energy of the system. There is a greater Gibb’s free energy for H atom absorption into the Pd lattice compared to D atom absorption. This drives the preference for H atom absorption. Therefore the more favourable D-H exchange takes place over a shorter time period and D atoms are exchanged quickly by the incoming H\textsubscript{2} species.

Another immediate difference between the two exchange directions carried out at low pressure was the HD production. HD production during the H-D exchanges was greater than in the D-H exchanges. This can again be accredited to differences in the zero-point energies of the isotopic species. The zero-point energy change for substitution of H atoms for D atoms in the gas phase (ΔE = 35 meV) is larger than the zero-point energy change for substitution of H atoms for D atoms in the hydride phase (ΔE = 27 meV). This means that it is more favourable thermodynamically to form HD in the gas phase than form palladium deuteride (PdD). Because of this a greater quantity of HD gas was observed in the H-D exchanges carried out at low pressure.

A further difference between the low pressure D-H and H-D exchanges was the initial periods of ‘pure’ gas. These can be viewed by referring to Figure 4-1 and Figure 4-2. In
particular the initial period of D$_2$ in the D-H exchanges and the initial period of H$_2$ in the H-D exchanges. By comparing these features it was clear that the length of time that pure gas was evolved from the Pd bed was greater in the D-H exchanges. Therefore, D$_2$ gas was displaced in an efficient manner by incoming H$_2$ gas in the D-H exchanges. In comparison, the length of time of pure H$_2$ in the H-D exchanges was shorter. This demonstrates that there was a period at the start of the exchange experiment where H$_2$ was displaced efficiently by incoming D$_2$ gas (bearing in mind that a small period of pure H$_2$ would arise from the gaseous overpressure held in the reactor at the start of the experiment). However, this pure H$_2$ production was short lived and HD production begins to dominate. This observation was found during all the exchange temperatures investigated here.

4.4.4 Low pressure PdD to PdH exchanges

Figure 4-1(a) – (c) show the D-H isotope exchange data obtained at low pressure and three temperatures, 208 K, 293 K and 373 K, respectively. Temperature has a significant effect on the hydrogen isotope exchange process. Figure 4-1(a) shows the data for the 208 K exchange. Here there was a period of ~100 seconds where pure D$_2$ gas was evolved from the Pd bed. Admittedly, some of this gas can be accredited to the initial gas overpressure within the IsoEx reactor, however, the effect of this was minimal because the initial gas in the reactor cleared quickly (< 2 seconds) to the exhaust and passed the mass spectrometer sampling point once the downstream valve P4 was opened just prior to initiation of the H$_2$ gas flow into the reactor. It should be noted that at 208 K the inlet H$_2$ gas pressure (and overall mixed gas pressure in the Pd bed) was lower than at the higher temperature exchanges. This causes a lower gas velocity in the Pd bed; therefore the time for the gas to permeate through the Pd bed was greater compared to the higher temperature exchanges. The result would be a longer period of pure D$_2$ gas at the start of the experiment. Furthermore, the higher initial D atom loading within the Pd would cause a longer period of observed pure D$_2$ gas. This is because there was a greater number of moles of D atoms to be exchanged, and therefore the desorption of D$_2$ gas continues for longer as the incoming H$_2$ gas has more surface (and bulk) sites to fill to complete the exchange.

This period of pure D$_2$ gas evolution from the Pd bed represents an efficient exchange of incoming H$_2$ gas for surface D species with little HD production. This is relatively
surprising considering the temperature of the exchange. At 208 K one would expect the exchange reaction to be less efficient due to fewer gas collisions with the Pd surface at this low temperature and pressure. Furthermore, the probability of these collisions overcoming the activation energy needed for the reaction to proceed would be less. The significant period of pure D\textsubscript{2} gas evolution from the Pd bed must therefore be accredited to the dynamic gas inlet conditions at the start of the experiment and the localised heating associated with the exothermic adsorption of H\textsubscript{2} gas in the D-H exchange direction. Upon starting the 208 K exchange a pressure of \(~1.5\) bar was admitted to the upstream side of the Pd bed. This higher pressure front colliding with the Pd bed appears to be sufficient, even at very low temperature, to cause efficient exchange of surface D atoms for incoming H\textsubscript{2} gas with little or no HD production initially. Any HD that was produced during the initial interactions was consumed and did not pass through the Pd bed. This finding could suggest a direct exchange of incoming H\textsubscript{2} for D\textsubscript{2} without production of the intermediate HD molecule during the initial periods of the D-H exchange. A direct exchange event would be more likely in the higher temperature conditions associated with the D-H exchange. The D-H exchange is an exothermic process and it therefore causes significant localised temperature rise in the vicinity of the exchange front \[65\]. This would increase the probability of an incoming H\textsubscript{2} gas molecule directly displacing D\textsubscript{2} gas from the Pd surface, resulting in a longer period of pure D\textsubscript{2} observed at the start of the experiment.

Another possible explanation could be that the desorbed D\textsubscript{2} gas molecules, produced by H\textsubscript{2} adsorption, are progressing through the Pd bed ahead of the exchange front displacing D atoms or causing them to diffuse through the Pd lattice towards the downstream side of the Pd bed. This can be viewed as the desorbed D\textsubscript{2} species colliding with the deuterided Pd surface causing additional downstream D\textsubscript{2} desorption by enhancing (or triggering) the D atoms to diffuse through the Pd lattice. This diffusion would cause enhanced bulk to surface transfer of D atoms which would increase the amount of D\textsubscript{2} being desorbed downstream. Moreover, this phenomenon would also create additional vacant sites for the incoming H\textsubscript{2} gas to adsorb onto. In addition, it is possible that the dynamic pressure conditions at the start of the experiment could have affected the D atoms bound to the surface and within the Pd lattice structure. The sharp change in pressure could cause D atoms to migrate through the Pd lattice to the lower pressure downstream side of the Pd bed (near the reactor exhaust) leaving some of the
upstream portions of the Pd bed with more vacant sites for H\textsubscript{2} to adsorb directly without HD production.

Furthermore, the higher viscosity of D\textsubscript{2} gas causes it to progress through the Pd bed at a slower velocity compared to the two other gas species. Coupling this with greater diffusion rates of D atoms in Pd compared to H atoms [59], and the localised heating which increases the gas viscosity further still, means that D\textsubscript{2} species would be detected for a greater length of time initially because it would take longer to permeate the Pd bed, while HD and H\textsubscript{2}. These species would also be slowed down by reaction with the Pd surface. All these hypotheses would go some way to explaining the length of the pure D\textsubscript{2} gas period and the small amounts of HD produced. However, more investigation is needed using the IsoEx rig alongside complementary in-situ characterisation techniques to probe the quantum nature of the Pd surface and bulk.

After 100 seconds, HD gas was detected in the 208 K exchange. The profile of the HD curve is sharp, rising to a peak mole fraction of 0.4 before falling sharply in line with the falling D\textsubscript{2} curve. This shows that a significant quantity of HD (with respect to the other gas species) was produced in the exchange front moving through the Pd bed directly behind the plug of pure D\textsubscript{2} gas. Furthermore, the sharpness of the HD curve suggests that the exchange front was confined to a small area within which HD was produced. It appears that at 208 K HD was produced in a narrow band where exchange reactions were occurring, with little production outside this band. Had there been HD production over a wider exchange front the HD curve would appear more spread out. The narrow band of HD production would be due to the low temperature and therefore lower gas velocity of the gas species. This would prevent the exchange front from spreading into larger portions of the Pd bed. These findings show that even at low temperature the D-H exchange was efficient and there appears to be significant amounts of direct hydrogen isotope exchange of D atoms for H atoms without HD production. The reason for this finding was likely due to the D-H exchange being favoured thermodynamically, the dynamic conditions at the start of the experiment, low gas velocity, quantum affects within the Pd lattice and diffusion of atomic species.

Comparing the 208 K exchange data with the 293 K D-H exchange (Figure 4-1(b)) it can easily be seen that the initial period of pure D\textsubscript{2} gas was longer in the 293 K exchange. Furthermore, the peak height of the HD curve in the 293 K data was lower,
indicating a lower HD production in the exchange front. The period of pure D_2 production was found to occur for approximately double the length of time compared to the 208 K exchange. This was despite a lower initial loading of D atoms within the Pd bed. At 293 K the initial loading was PdD_{0.65} compared with PdD_{0.7} for the 208 K exchange. Again, very little HD was detected during this initial period of D_2 gas, indicating that any HD that was produced was consumed by additional reaction with the deuterided Pd surface. The HD peak was found to be depressed compared to the 208 K and 373 K exchanges (Figure 4-1(a) and (c)) indicating a lower quantity of HD in the exchange front. This depression of the HD curve has been observed before by Larson et al. in a ‘blowdown’ experiment involving upstream pressures of 2 bar [70]. They also came to the conclusion that more investigation is needed to conclusively determine the explanation behind this observation. Later sections of this chapter will present additional experimental data which sheds light on these observations.

The reason for the increased period of D_2 was difficult to explain. The 293 K data was quite anomalous in this respect. At 293 K the length of the pure D_2 period would be expected to be less than found at 208 K due to the increased temperature. Higher temperature causes faster gas velocities through the Pd bed and increased diffusion of the D atoms species within the Pd lattice. Alongside this there would have been higher exchange reaction rates because more H_2 gas molecules would be colliding with the Pd surface. Moreover, a greater proportion of these molecules would have sufficient energy to overcome the energy barrier for reaction (activation energy). These phenomena combined would reduce the length of time pure D_2 was observed because the stored D atom capacity would be exhausted sooner than was observed for the 208 K exchange. However, this was not the case.

One important finding from modelling the 293 K exchange was that the Pd bed permeability was significantly less compared to the 208 K and 373 K exchange. This result will be discussed in detail in Chapter 5 of this work. However, the author believed it was relevant to discuss this particular finding in relation to these results. The lower permeability value means that the incoming H_2 gas takes longer to permeate through the Pd bed and features of the exchange (such as the pure D_2 period) would be observed for longer. The reason why the permeability was lower for the 293 K exchange is unknown at present. It could be due to increased compaction of the Pd bed during experimental setup of the 293 K experiment, therefore making the result anomalous. Another
possibility, if the result is found to be repeatable in future, is the influence of additional areas within the Pd lattice, for instance the subsurface layers. It has been found that under certain conditions these areas of the Pd structure can influence the exchange [122-124]. If these regions were available at 293 K and not the other temperatures it would slow the progress of the incoming gas species because additional vacant sites would be present for absorption and diffusion of atomic species. Another interesting finding relating to these subsurface regions is that they can influence the desorption activation energy. When subsurface regions are populated they have been shown to lower the activation energy of desorption of molecular isotope species [122-124].

A lower activation energy for desorption would favour direct desorption of \( \text{D}_2 \) gas from the Pd surface rather than HD production. Consequently, a lower proportion of HD would be observed in the exchange front. This was what was found during the low pressure 293 K exchange data. While direct exchange events are certainly possible, more investigation will be needed coupled with additional modelling to prove conclusively whether these hypotheses are true. Another important consideration with the low pressure 293 K D-H exchange was the temperature rise associated with the exothermic adsorption of \( \text{H}_2 \) gas [65]. This would increase the localised rates of surface reactions involving \( \text{H}_2 \) and desorption rates of \( \text{D}_2 \) gas from the Pd surface. This would go some way to explain the longer period of \( \text{D}_2 \) observed at the start of the 293 K experiment. It would also increase the probability of direct exchange events which would certainly increase the period of \( \text{D}_2 \) found at the start of the run.

Referring to the 373 K exchange data (Figure 4-1(c)) it was clear that the 373 K data returns to the expected trend set out by the 208 K data. The time of the initial \( \text{D}_2 \) period was less than the 208 K data and this was to be expected. One would expect the 293 K \( \text{H}_2 \) breakthrough to occur somewhere in between the times found for the 208 K and 373 K data. The \( \text{H}_2 \) breakthrough occurs sooner in the 373 K exchange data than the 208 K exchange. This was expected due to the increased pressure of the gas species, increased reaction rates and diffusion rates associated with the higher temperature and the lower initial loading of D atoms within the Pd bed (PdD\(_{0.5}\)). One noticeable difference in the 373 K data was the HD production. HD was produced in larger quantities compared with the two other low pressure D-H exchanges. The HD curve was found to be broad and HD was detected some time before \( \text{H}_2 \) breakthrough. The exchange front was therefore spread out with exchange reactions occurring over a larger portion of the Pd
bed. This can also be viewed by referring to the gradient of the H\textsubscript{2} and D\textsubscript{2} signals. The gradients were found to be shallower indicating the exchange front was smeared compared to the lower temperature exchanges during which the gradients were found to be sharp. This smearing was likely due to the increased temperature of this exchange. The incoming H\textsubscript{2} gas species had a higher pressure and therefore velocity through the Pd bed. This coupled with enhanced diffusion rates would mean that the H\textsubscript{2} gas front would penetrate further into the Pd bed and have sufficient energy to react with ‘fresh’ PdD, producing additional D\textsubscript{2} and HD species.

Moreover, HD was produced in greater proportions for longer during the exchange. This suggests that HD production was favoured at this temperature. This is because of the higher energy in the Pd-H(D) system at higher temperature. It is thermodynamically favourable to produce more HD at high temperature. This can be viewed by referring to the equilibrium constant (\(K_{eq}\)) whose value increases with increased temperature. The increase in HD production arises from favourable system energy changes with respect to differences in the zero point energies of the gas and solid phase species (see Background chapter) [37, 70].

4.4.5 Low pressure PdH to PdD exchanges

Figure 4-2(a) – (c) show the low pressure H-D exchange data obtained at 208 K, 293 K and 373 K, respectively. Immediately it can be seen that the exchange profiles are significantly different to the D-H exchanges. All three temperatures exhibited much greater quantities of HD production during the hydrogen isotope exchanges. This arises from the thermodynamically unfavourable nature of the H-D exchange process compared to the D-H direction. Pd has a greater affinity for H atoms over D atoms. This means that during an exchange H atoms persist within the Pd structure and consequently more HD was produced as a direct result of this. This phenomenon also explains the large difference in the overall exchange completion time.

Figure 4-2(a) shows the experimental data for the low pressure H-D exchange carried out at 208 K. The reaction can be seen to continue for approximately 1200 seconds which was double the length of time required to complete the exchange to occur compared to the D-H exchange at 208 K. Another immediate difference between the H-D and D-H exchanges at 208 K was the quantity of HD produced. The HD profile found during the H-D exchange was broad and HD was detected in large quantities for the
majority of the exchange. The length of HD production coincides with the slow breakthrough of D₂ gas observed during this exchange. Compared to the D-H exchange (Figure 4-1(a)) the breakthrough of the incoming D₂ gas took far longer than the breakthrough of H₂ gas. This indicates that the H-D exchange at 208 K was less efficient than the D-H exchange at 208 K. The explanation of this finding arises from the greater affinity Pd has for H atoms. H atoms therefore persist in the Pd lattice and it takes longer for the incoming D₂ gas to exchange the H atoms completely. Another consequence of this is the increased likelihood of HD production during the exchange reaction. Because H atoms persist in the Pd lattice and there was a large quantity of D₂ in the gas phase the system ‘prefers’ to form HD instead of H₂ because of differences in zero point energy of the gas- and solid-phase species [17, 37, 121].

Figure 4-2(a) also shows there was a short period initially (~ 75 seconds) where pure H₂ was detected. Some of this pure H₂ was due to the initial gas overpressure in the IsoEx reactor. The remainder was H₂ gas displaced by the incoming D₂ gas species. This period of pure H₂ suggests that during the initial dynamic conditions (associated with introducing D₂ gas to the system) some direct exchange could be occurring, whereby incoming D₂ directly displaces H₂ species from the Pd surface with little HD production. This also indicates that the exchange of H atoms for incoming D₂ was efficient in the initial stages of the reaction. After 75 seconds the HD gas signal rises sharply, appearing before the arrival of D₂. This indicates that after the initial period of H₂ gas there was a period of HD detected before the appearance of D₂. The detection of HD occurs directly after the initial period of pure H₂ gas indicating the arrival of the mixed gas front. This mixed gas front consists of the three gas species and represents the tailings of the advanced H₂ gas front, significant quantity of HD and the forward portion of the D₂ gas moving through the Pd bed. HD was produced in large amounts during this exchange representing a less efficient exchange than the D-H exchange carried out at 208 K. The efficiency of the exchange would also be affected by the endothermic nature of the adsorption reaction. Upon adsorption of D atoms energy was consumed, lowering the temperature in the vicinity of the exchange front. This would cause lower reaction kinetics, diffusion rates and gas velocity. The probability of a successful exchange event would therefore be reduced according to the kinetic theory of gases which relates the number of collisions to the subsequent observed reaction rate.
Fewer collisions with the Pd surface reduce the number of collisions with the correct orientation, and therefore, the observed reaction rate.

Figure 4-2(b) shows the low pressure H-D exchange carried out at 293 K. The general shape of the isotope exchange was very similar to that found at 208 K. There was a longer initial period of pure H\textsubscript{2} and the HD curve arrived later than in the lower temperature exchange. The longer period of H\textsubscript{2} at the start of the exchange represents an efficient exchange of incoming D\textsubscript{2} gas for H atoms on the Pd surface. More H\textsubscript{2} gas, in comparison with the 208 K exchange, was displaced from the Pd bed during the initial period of the reaction. This could be due to the higher inlet pressure of the 293 K exchange (1.6 bar compared with 1.5 bar for the 208 K exchange) causing an increased period of dynamic conditions whereby the Pd bed was exposed to rapidly changing pressure. As discussed previously, this could trigger enhanced H\textsubscript{2} desorption compared to what would be expected under steady state conditions. Trentin [50] also observed a similar period of efficient exchange at the start of a H-D exchange carried out at 1 bar and 298 K. The author does however recognise that during modelling of this exchange a lower permeability value (\(\kappa\)) was found (see Modelling chapter). This lower \(\kappa\) value reduces the gas velocity through the Pd bed, and consequently the initial period of H\textsubscript{2} would be detected for longer. However, the length of the pure period was significantly longer than the 208 K exchange so the author believes there was indeed enhanced H\textsubscript{2} desorption during this period; most likely due to the dynamic conditions at the start of the experiment.

After this dynamic period (when the gas pressure changes had settled HD) production was found to increase. HD production increases because the initial pressure conditions have settled and the system returns to favouring retention of H atoms in the solid phase. The incoming D\textsubscript{2} gas was therefore less likely to displace H\textsubscript{2} gas directly because of the difference in zero point energy of the solid and gaseous species. When there are high concentrations of D\textsubscript{2} in the gas phase an increase in the thermodynamic effect is observed [17, 37, 38] (discussed in Chapter 2, Section 2.9.6)

The low pressure 293 K H-D exchange continued for longer than the 208 K exchange. This is counterintuitive because of the lower initial loading of H atoms on the Pd bed compared with the 208 K exchange (293 K = PdH\textsubscript{0.8}; 208 K = PdH\textsubscript{0.7}). Furthermore, the higher pressure of the gas phase and increased Pd bed permeability during the 293 K
exchange would mean the gas velocity through the bed would be increased compared to the 208 K exchange. These two effects should reduce the time needed to complete the exchange. However, as stated above, this was not found. The author highlights the lower permeability found during experimental modelling of the 293 K H-D data. This result is discussed in full in the Modelling Chapter in the later parts of this work. The 293 K κ value was found to be lower than the 208 K and 373 K H-D exchanges. The permeability values should in reality increase with temperature. A similar finding was found for the low pressure 293 K D-H exchange. The reason for the lower κ value was unclear. It is possible that different regions within the Pd structure have an effect at this temperature, causing the progress of the gas phase to be slowed. These subsurface regions may also play a role in the longer initial period of H₂ found during the 293 K exchange. For instance, when these regions are populated they are known to lower the desorption activation energies \( E_a \) of the surface H atoms. This would cause an increase H₂ signal to be found during the exchange because there would be a higher probability of H₂ being desorbed.

Figure 4-2(c) shows the low pressure H-D exchange carried out at 373 K. This exchange showed significant departure from what was observed during the two lower pressure exchanges. The time for completion of the exchange reaction was significantly less than in both the 208 K and 293 K exchanges. The time to completion was approximately half the other two low pressure H-D exchanges. This was because of the lower initial loading of H atoms on the Pd bed. Coupling this with the enhanced reaction rates arising from the increased temperature mean that the H atom capacity of the PdHₓ would be exhausted sooner. The increased temperature of the system improves the probability of a successful exchange interaction. Moreover, the gas pressure at 373 K was the highest of the three low pressure H-D exchanges. The gas velocity through the Pd was therefore at a maximum during the 373 K exchange meaning the time to completion would be shorter. Since the probability of an exchange event is directly linked to the number of collisions [63, 125], a higher gas pressure/velocity would increase the number of collisions and the associated energy, increasing the number of events. This would exhaust the H atom capacity within the Pd bed faster than at lower temperatures. Finally, the inlet gas pressure was at a maximum for the 373 K exchange. This would also assist in lowering the overall exchange completion time and improve the probability of successful exchange event.
Another interesting finding was the period of pure H\textsubscript{2} at the start of the experiment. It was found to be comparatively shorter than the 293 K H-D exchange. As discussed above, the length of this initial efficient exchange period was in part due to the lower $\kappa$ value found subsequently from modelling efforts. If this lower permeability was indeed true then the length of the 373 K initial H\textsubscript{2} period would have in fact been longer than the 293 K exchange. This was to be expected considering the increased temperature and subsequent enhanced reaction rates/gas collisions with the Pd surface.

The overall shape of the HD signal during the 373 K exchange was different to that observed at 208 K and 293 K. The total length of time HD was produced was also significantly shorter than the other two temperature exchanges. Again, this was most likely because of the lower initial loading (PdH\textsubscript{0.6}) and higher inlet gas pressure. HD was again found to be produced in large amounts during in between the advancing displaced H\textsubscript{2} front and the incoming D\textsubscript{2} gas front. Again, this was because of Pd’s increased affinity for H atoms over D atoms. Moreover, the high inlet gas concentration of D\textsubscript{2} would favour an even greater enhancement of the thermodynamic effect favouring HD production [17, 37]. This can physically be seen by observing the HD peak height on Figure 4-2(c). The peak height was the highest of the three low pressure H-D exchanges.

### 4.4.6 1 L min\textsuperscript{-1} PdD to PdH exchanges

Figure 4-3(a) – (c) show the experimental data for the 1 L min\textsuperscript{-1} D-H isotope exchange reactions carried out at 208 K, 293 K and 373 K, respectively. The three temperatures were carried out with upstream pressures ($P_{in}$) of 5.8 bar, 6.3 bar and 8 bar, respectively. The downstream pressure ($P_{out}$) during all the experiments was atmospheric pressure (1 bar). These exchanges therefore occurred under significantly higher pressure conditions than the low pressure exchanges discussed in the two previous sections. The initial hydrogen isotope loadings were PdD\textsubscript{0.7}, PdD\textsubscript{0.65} and PdD\textsubscript{0.55}, respectively.

First of all it was clear that pressure has a significant effect on the exchange. This can be observed by comparing the low pressure D-H exchanges to the 1 L min\textsuperscript{-1} D-H exchanges. For example, the total time for complete exchange in the low pressure 208 K D-H exchange was ~1200 seconds. In the 1 L min\textsuperscript{-1} D-H exchange carried out at 208 K the time was 30 seconds. The author notes that the Pd bed length was 0.02105 m and
0.0316 m for the 1 L min\(^{-1}\) D-H exchanges and low pressure D-H exchanges, respectively. This would certainly affect the total time of the exchange but, in the author’s opinion, not enough to cause a 40 fold increase in the exchange completion time associated with the low pressure exchange. It therefore appears that upstream pressure has a large effect on the exchange process. This was because of the increased pressure driving force, higher gas velocities through the Pd bed (and therefore number of molecular collisions with the Pd surface) and the sheer number of mols of H\(_2\) gas entering the system. It also suggests that the surface reaction rates are heavily influenced by the upstream (driving) gas pressure.

Figure 4-3(a) shows the experimental data obtained at 208 K, the lowest temperature exchange carried out at 1 L min\(^{-1}\). Out of the three temperatures this exchange took the longest to complete. The exchange was complete at 30 seconds, compared with 20 seconds for the 293 K exchange and 15-20 seconds for the 373 K exchange. This result was expected because of the low temperature of the exchange and the higher initial loading of D atoms on the Pd bed. The low temperature reduces the energy of the gas molecules. Subsequently the number of collisions with the Pd surface was reduced and therefore the probability of a successful exchange event was diminished according to the kinetic theory of gases \([63, 125]\). HD was produced in significant quantities following the initial period of pure D\(_2\) gas and before complete breakthrough of the incoming H\(_2\) gas species. This demonstrates that the equilibrium reaction \(\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}\) between the gaseous species and the Pd surface was occurring producing HD. The lower pressure of the incoming H\(_2\) gas causes a lower gas velocity through the Pd bed compared with the other two temperature exchanges. This essentially allows the advancing gas species more time to interact with the Pd surface, producing more HD as a consequence of the equilibrium reaction. Furthermore, it is likely that localised heating affects in the vicinity of the isotope exchange front enhanced the surface reaction rates in the 208 K exchange, increasing the production of HD and generally helping the exchange to complete in less time. Charton et al \([65]\) showed that there was an approximate 60 K rise in temperature within the exchange front for D-H reactions.

Similar to the low pressure exchange carried out at 208 K, there was an initial period where pure D\(_2\) gas was detected. Some of this gas can be accredited to the initial gas pressure in the IsoEx reactor (5.5 bar). However, this overpressure would clear the reactor in < 2 seconds because of the differential pressure between the upstream and
downstream areas of the Pd bed. Some of the pure D\textsubscript{2} must therefore arise from efficient exchange of the incoming H\textsubscript{2} species for D atoms on the Pd surface. This was to be expected, even at these low temperatures, for the D-H exchange because of the reasons discussed in Chapter 2, Section 2.9.6. Moreover, as was postulated in the low pressure D-H exchanges, the high pressure dynamic conditions at the start of the experiment are likely to encourage/trigger desorption of D\textsubscript{2} species. Coupling this with Pd’s greater affinity for H atoms compared with D atoms means the 1 L min\textsuperscript{-1} 208 K D-H exchange showed efficient exchange of PdD\textsubscript{3} species for incoming H\textsubscript{2} gas, despite the low temperature. Moreover, the initial efficient exchange of D atoms for incoming H\textsubscript{2} gas is likely to be in some part to the rise in temperature associated with adsorption of H\textsubscript{2} molecules on the Pd surface. As discussed before, this temperature rise was of the order of 60 K [65]. This would encourage additional D\textsubscript{2} gas to desorb from the Pd surface because more energy was available to overcome the \( E_a \) for desorption. Another point to consider is that the hydrogen isotope heat effects modelling completed by Charton et al [65] were only at one temperature (298 K) and were based on the results of Foltz and Melius [1]. It is quite possible that at 208 K the localised increase in temperature was greater than 60 K due to the higher initial stoichiometry of the Pd bed (PdD\textsubscript{0.7}). Essentially this would mean there were more D atoms to exchange and therefore there may have been even more heat released during the initial period of the exchange which would cause significantly enhanced D\textsubscript{2} desorption rates, materialising as a longer pure D\textsubscript{2} gas period at the start of the exchange experiment.

Figure 4-3(b) shows the experimental exchange data for the 1 L min\textsuperscript{-1} 293 K D-H exchange. This exchange showed the largest departure from what would be expected looking at the shape of the other two temperatures D-H exchanges. Firstly, the initial period of pure D\textsubscript{2} was significantly longer than was found during the other two temperatures. Secondly, the shape of the HD curve was drastically different to all the other exchanges carried out during this work. The HD curve was sharp, rising quickly in line with the falling D\textsubscript{2} signal and the breakthrough H\textsubscript{2} signal. Furthermore, the HD peak height was depressed compared to what was found during the low pressure D-H 293 K exchange and both the other two temperatures investigated at higher pressure (1 L min\textsuperscript{-1}). Finally, the total time for complete exchange was \( \sim 12 \) seconds and significantly less than was found during the low pressure 293 K D-H exchange.
The long initial period of pure $\text{D}_2$ demonstrates that the incoming $\text{H}_2$ species in the 293 K D-H exchange was very efficient at displacing the surface D atoms. No HD was detected during this period indicating that there may be direct exchange events occurring whereby incoming $\text{H}_2$ gas was directly displacing $\text{D}_2$ gas, with no HD production. Outka and Foltz [2] considered additional reaction pathways, including a direct exchange of $\text{H}_2$ for $\text{D}_2$ without the formation of intermediate HD, and found that HD was ‘chronically under-produced’. If any HD was produced during this period it underwent additional reactions with the Pd bed, displacing more $\text{D}_2$ gas before being consumed. Larson et al [70] also observed this depressed HD signal and efficient initial period during a D-H exchange carried out in blowdown conditions similar to those used in this work. As discussed in previous sections of this work, a possible explanation could be the existence and influence of additional regions within the Pd structure [33, 122, 124]. For instance, it is known that subsurface regions exist within the Pd and that these can reduce the $E_a$ value for desorption of surface species. If these subsurface regions are being populated at 293 K and not the other temperatures it would certainly explain the enhanced $\text{D}_2$ desorption rates observed at the start of the experiment. Another possible explanation for these observations at 293 K is a change in surface reaction mechanism, for example a move from Langmuir-Hinshelwood to Eley-Rideal, at this temperature. This could be due to the influence of subsurface or bulk regions within Pd. A change in surface reaction mechanism has been found by some authors [122], although these investigations were done at near vacuum condition using an ion beam technique. Moreover, referring to the other exchanges, both D-H and H-D, carried out at 293 K it is clear that some unexplained phenomena or reactions are occurring which were effecting the exchange process significantly at this particular temperature.

Subsurface regions could be influencing the production of HD, causing a depressed detected HD signal. For example, if $\text{H}_2$ was efficiently exchanging $\text{D}_2$ species by direct exchange events the mixed gas front (where HD was produced) would be sharpened and less HD would be produced because less D atoms would be remain within the Pd bed, and therefore fewer D atoms would desorb with adsorbed H atoms to form HD. This hypothesis was further reinforced by the fact the HD signal remained low and ended quickly after the crossing of the $\text{H}_2$ and $\text{D}_2$ signal. This indicates that D atoms remained in low quantities after the $\text{H}_2$ breakthrough, again pointing towards an efficient $\text{H}_2$ exchange front moving through the Pd bed directly exchanging D atoms. Of course, the
author recognises that more investigation is needed to prove these hypotheses and definitively assess the influence of subsurface regions and subsequently describe the 293 K D-H exchange in terms of physical and chemical phenomena.

Figure 4-3(c) shows the experimental data for the 1 L min\(^{-1}\) D-H exchange carried out at 373 K. The exchange completion time was the lowest of the three temperatures investigated. The exchange was found to complete after approximately 11 seconds. This was to be expected due to the higher temperature of the exchange. This caused increased surface reaction rates, higher gas velocity through the Pd bed which reduced the completion time of the exchange reaction. Furthermore, the higher inlet pressure of the 373 K exchange would further enhance the exchange reaction rates. Additionally to this the lower initial loading means that the reserve of D atoms within the Pd bed would be exhausted sooner, reducing the overall time of the exchange reaction. The Pd bed permeability was also at its highest during the 373 K exchange and this would effectively increase the speed of the exchange reaction.

The initial period of D\(_2\) was longer than that found at 208 K, but less than the 293 K exchange which, as discussed previously, was out of the trend expected from the other two temperatures. The gradients of the falling D\(_2\) signal and breakthrough H\(_2\) signal are steeper than the 208 K exchange, but less than the 293 K exchange. A steeper gradient represents a sharper exchange front. The H\(_2\) front was therefore moving through the Pd bed like a plug of gas. HD production was confined entirely between the tail end of the D\(_2\) signal and the breakthrough of the H\(_2\) gas. HD was therefore produced in large amounts ahead of the advancing H\(_2\) gas front and little overlap was found. The sharp nature of the HD curve suggests that the D atoms contained in the Pd bed were efficiently exchanged by the incoming H\(_2\) gas species. Because the HD signal does not continue for long beyond the completion of the H\(_2\) breakthrough it means that few D atoms remained within the Pd. This suggests that there was a significant amount of direct exchange of D atoms by the incoming H\(_2\) species during the initial period of the exchange. This finding is reinforced by the length of the pure D\(_2\) gas period at the start of the experiment. The HD peak height was similar to the 208 K exchange, peaking at a mole fraction value of \(y = 0.4\). This indicates that the equilibrium reaction was occurring quickly in the mixed gas zone between the falling D\(_2\) signal and rising H\(_2\) signal. Therefore, after the initial dynamic conditions the reaction profile moves to
produce more HD and the equilibrium reaction dominates in the regions immediately ahead of the advancing H$_2$ gas front.

Another factor to bear in mind with the 373 K exchange was the temperature rise upon adsorption of H$_2$ gas. As discussed before this was likely to be of the order of 60 K, although it is certainly possible that the value could be higher which would alter the exchange profile even further, creating sharper exchange fronts and affecting HD production.

4.4.7 1 L min$^{-1}$ PdH to PdD exchanges

Figure 4-4(a) – (c) show the experimental 1 L min$^{-1}$ H-D exchanges carried out at 208 K, 293 K and 373 K, respectively. The upstream pressures were 7.5 bar, 8 bar and 8.3 bar, respectively. The initial H atom loadings on the Pd bed were PdH$_{0.8}$, PdH$_{0.7}$ and PdH$_{0.6}$ for the 208 K, 293 K and 373 K exchanges, respectively. The experimental uncertainty was calculated from the repeat experimental data. Similarly to what was found during the low pressure exchanges, the H-D exchanges at 1 L min$^{-1}$ flowrate took significantly longer to complete. This again demonstrates the greater affinity Pd has for H atoms compared with D atoms. H atoms therefore persist in the Pd system and it takes significantly longer for the incoming D$_2$ gas to displace the H atom capacity. As explained previously, this greater affinity arises from differences in zero point energy of the gas and solid phase species (see Background section of this work).

Figure 4-4(a) shows the experimental data for the 208 K exchange carried out using a flowrate of 1 L min$^{-1}$. Here the most noticeable feature was the breakthrough of the D$_2$ gas before the arrival of the HD gas signal. This demonstrates that the D$_2$ gas permeated through the Pd bed rapidly without significantly reacting with the Pd bed. The reason for this was likely to be the high inlet gas pressure and the low temperature of the exchange. Moreover, Charton et al [65] calculated an ~ -60 K temperature drop during an endothermic H-D exchange. This reduction in temperature upon adsorption of incoming D$_2$ species would lead to a significant drop in the adsorption rate constant in the localised area of the exchange front, lowering the probability of further exchange events involving D$_2$ which explains to gas passing through the Pd bed with little reaction. This aligns with the findings of Carstens and Encinias [3] who found that below 210 K the exchange process was limited by the microscopic processes occurring on the surface or within Pd. The author notes that the localised cooling would reduce
the gas viscosity, increasing the gas velocity and therefore decreasing the residence time of the gas species in proximity to the Pd surface. This effect was however deemed insignificant in comparison to the reduction in the kinetic rate constant for D₂ adsorption and the lower thermal energy of the gas species. Overall, these phenomena would combine to prevent the D₂ gas from reacting significantly with the Pd surface. The initial period of pure H₂ in this experiment was most likely also due to the 7.5 bar overpressure at the start of the experiment at 208 K. The high pressure in the reactor would take longer to evacuate the reactor once the downstream valve was opened at the start of the experiment.

HD was produced for the remainder of the exchange after the D₂ gas had begun to break through the Pd bed. This shows that HD was being produced while there was a high concentration of D₂ flowing through the Pd bed. The H atoms were therefore persisting in the solid phase even in a nearly pure D₂ gas environment. It appears that the low temperature was suppressing the exchange of D₂ for H atoms and the higher pressure conditions coupled with the unfavourable nature of the H-D exchange were not allowing the gas to significantly react with the Pd surface. The probability of an exchange event was significantly lower at 208 K and therefore the number of successful exchange collisions was reduced. When this is combined with the higher gas velocity of the 1 L min⁻¹ exchange the HD signal was low, suggesting the equilibrium reaction between H₂, D₂ and Pd was skewed. Comparing the 1 L min⁻¹ exchange data with the low pressure exchanges it was clear that the higher pressure conditions affected the production of HD (see Figure 4-10) and the breakthrough time of the D₂ gas.

Figure 4-4(b) shows the significant change in the H-D exchange profile at 293 K. The exchange completed in less time than the 208 K exchange; the exchange was complete in ~ 45 seconds compared to the > 100 seconds for the 208 K H-D exchange. The exchange profile was more akin to that found during the low pressure 293 K H-D exchanges. There was again an initial period of pure H₂ gas. It is believed that this is due to the initial 8 bar overpressure in the IsoEx reactor as well as some efficient exchange of the surface H atoms for the incoming D₂ gas. As mentioned in the discussion of the low pressure H-D exchanges, Trentin [50] also observed the same initial period of efficient exchange during a H-D exchange carried out at 1 bar and 298 K. There was some low level production of HD in this period which indicates that alongside the efficient ‘direct’ exchange there was some exchange via production of
intermediate HD. HD was detected beyond 80 seconds in low levels suggesting that H atoms were persisting in the solid phase even after the majority of the solid phase was saturated with D atoms. The HD peak was significant and demonstrated that the equilibrium reaction was occurring within the mixed gas zone in between the tailing H₂ gas and the advancing D₂ gas front. Unlike the 208 K exchange the HD peak was found to coincide with the crossing over of the H₂ and D₂ signal as would be expected and was seen in the majority of the other exchange experiments.

Figure 4-4(c) shows the experimental data for the 1 L min⁻¹ H-D exchange carried out at 373 K. The exchange completion time was the shortest of all the three H-D exchanges investigated. This indicates that the 373 K exchange was the most efficient (slightly more so than the 293 K exchange). The exchange was complete in ~40 seconds; indicated by the complete breakthrough of D₂ gas and the diminished HD signal. Unlike the 208 K and 293 K H-D exchanges the HD signal was found to reach zero. The HD signal reached zero at approximately 75-80 seconds compared to > 100 seconds for the 293 K exchange and >130 seconds for the 208 K exchange. This indicates that during the 373 K exchange there was significant desorption to exhaust the H atom reserve in the Pd bed quickly, despite the unfavourable nature of the exchange. Another reason for the slightly faster depletion of H atoms was the lower initial loading on the Pd compared to the lower temperature exchanges (PdH₀.₆ compared with PdH₀.₈ and PdH₀.₇ for the 208 K and 293 K exchanges, respectively.) Coupling this with the enhanced reaction rates encountered at high temperature, due to increased molecular collisions with the Pd surface, means the exchange completed in less time than the other exchanges. However, the reduction in temperature caused by the endothermic nature of the H-D exchange direction cools the local area to the exchange front [65]. This cooling acts to maintain the stoichiometry of the Pd at a higher level which partially negates the increase in the kinetic rate constant at the higher temperature of the 373 K exchange. This explains why there was not a marked difference in exchange completion time between the 293 K and 373 K experimental data [126].

Another noticeable feature of the 373 K was the similarity of the exchange profile to the 293 K exchange and the sharp gradient of the falling H₂ signal/breakthrough D₂ signal. The steep gradient of the H₂ and D₂ signals indicates a sharp gas fronts, both for the incoming D₂ gas and the displaced H₂ gas. This was to be expected because of the higher driving pressure during this exchange. Higher pressure causes the gas velocity to
increase compared to the lower pressure exchanges. This physically means that convection dominated the process and there was less time for molecular diffusion to spread the gas fronts due to reaction with the surface. It consequently meant that HD production was confined to a narrow zone in between the H₂ gas tail and D₂ gas front. Moreover, the similarity between the high temperature exchanges can be accredited to appreciably similar flow conditions (in terms of pressure and viscosity). Carstens and Encinias [3] showed that at temperatures above 210 K diffusion in the free gas was rate limiting and that the exchange process (both H-D and D-H) were limited by flow effects. It was also shown in a paper written in the course of this project that despite an increase in exchange probability at higher temperatures other effects, such as stoichiometry changes, influence the overall apparent exchange efficiency more significantly than increases in kinetics [126].

4.4.8 Discussion of equilibrium analysis – Apparent equilibrium constant (K_{app})

The apparent equilibrium constant (K_{app}) has been used to analyse the extent of the equilibrium reaction (H₂ + D₂ ⇌ 2HD) during the hydrogen isotope exchange reactions. It was found by analysing the effluent gas concentrations of H₂, D₂ and HD. The apparent equilibrium constant was plotted as a function of time for the low pressure and 1 L min⁻¹ exchanges carried out in this work. The resulting plots demonstrate when the equilibrium reaction becomes prominent. Figure 4-5- Figure 4-8 show the results of the apparent equilibrium constant analyses. Each of the plots also present the equilibrium constant (K_{eq}) values obtained from static measurements using a Sievert’s type apparatus [9, 47]. This allows the reader to compare the time dependent K_{app} values to those recorded previously in the literature and assess the extent of the equilibrium reaction. Table 4-1 and Table 4-2 present the experimentally determined peak apparent equilibrium constant values (K_{app}). These tables should be used as a reference point for the following discussion. The empirical K_{eq} values reported in the literature from static measurements are K_{eq} = 2.91, K_{eq} = 3.24 and K_{eq} = 3.44 for 208 K, 293 K and 373 K, respectively [9].
Table 4.1 Comparison of low pressure peak apparent equilibrium constant, \( K_{\text{app, peak}} \), values to those found empirically [9].

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Table 4.2 Comparison of low pressure peak apparent equilibrium constant, \( K_{\text{app, peak}} \), values to those found empirically [9].

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Figure 4-5 shows the \( K_{\text{app}} \) values for the low pressure D-H exchanges carried out at 208 K, 293 K and 373 K (solid black, red and green lines, respectively). It was clear from the data that none of the exchanges achieved equilibrium in the reaction front. There is no doubt that under static conditions equilibrium would have been achieved between the Pd surface and the isotopic species, however during the dynamic conditions of the flow experiments carried out in this work equilibrium was not achieved in the reaction front in any of the experiments. The 373 K exchange came closest with a peak value of \( K_{\text{app}} = 3 \). This was to be expected considering that HD production is favoured at higher temperature, as discussed in the previous sections and the Background chapter. The 293 K D-H exchange showed the most significant departure from equilibrium, with a peak value of \( K_{\text{app}} = 1 \) and the 208 K \( K_{\text{app}} \) value was also significantly lower than the \( K_{\text{eq}} \) value (\( K_{\text{app}} = 2 \) compared to \( K_{\text{eq}} = 2.91 \); see Table 4-1). The peaks in the \( K_{\text{app}} \) plots coincide directly with the peaks in the HD signals detected during the exchange experiments, as would be expected.

The \( K_{\text{app}} \) value recorded for the 208 K exchange was low but still significant. It represented approximately 70 % of the value recorded during empirical static measurements. HD was therefore produced in appreciable amounts in the reaction front despite the dynamic flow conditions associated with the inlet gas pressure. The reason
for this could be due to the lower gas pressure at this temperature. This would decrease the gas velocity through the Pd bed, allowing the gas species more residence time in the vicinity of the Pd surface. Another possible explanation could be the influence of additional surface-subsurface-bulk processes occurring in Pd at low temperature. Ludwig et al [122] observed enhanced HD production at low temperatures through additional processes in Pd. It should, however, be noted that these measurements were performed at near vacuum conditions so their applicability here is not known at present without additional investigation involving complementary experimental techniques.

The $K_{app}$ value for the 293 K exchange was only 30% of the empirical value reported in the literature (see Table 4-1). The reason for such a low $K_{app}$ value during the D-H 293 K exchange is not fully understood at present. However, as was discussed in the previous sections, the occurrence of additional reaction pathways, such as direct exchange events, would affect the $K_{app}$ value significantly. If direct exchanges of incoming H$_2$ for D$_2$ gas were occurring there would be far less HD present in the gas phase, resulting in a lower $K_{app}$ value. Outka and Foltz [2] investigated a direct exchange without the formation of intermediate HD and noted that HD was ‘chronically under-produced’.

Figure 4-6 shows the apparent equilibrium constant analysis for the low pressure H-D exchanges carried out in this work. The $K_{app}$ values for each of the 208 K, 293 K and 373 K are plotted as a function of time (solid black, red and green lines on Figure 4-6). The $K_{eq}$ values are the same as described at the start of this section. The first noticeable feature was that all the exchanges achieved equilibrium between the gas species and the solid phase Pd. All three plots show that the general shape of $K_{app}$ were similar. The peaks were high and broad indicating HD was produced in significant quantities during each exchange temperature. The $K_{app}$ peaks coincide directly with the peaks in the HD signals recorded during experimentation.

The reason for the high $K_{app}$ values during the low pressure H-D exchanges comes down to the lower affinity Pd has for D atoms [16, 37, 56] (previously discussed in Background chapter; Section 2.9.6). This means that it is more favourable to form HD (energetically) in the gas phase than form PdD. Therefore more HD gas was formed during the H-D exchanges, compared to the D-H exchanges. This manifested in the
higher recorded $K_{\text{app}}$ values which equalled the empirical $K_{\text{eq}}$ values reported in the literature. Furthermore, because of this thermodynamic effect HD was produced for longer and therefore the $K_{\text{app}}$ plots were broader and continued for significantly longer in the low pressure D-H exchanges.

Figure 4-7 shows the $K_{\text{app}}$ plots for the 1 L min$^{-1}$ D-H exchanges carried out at 208 K, 293 K and 373 K (solid black, red and green lines, respectively). Again, the empirical $K_{\text{eq}}$ values are the same as those described for the low pressure exchanges. Firstly, similarly to the low pressure D-H exchange, equilibrium was not achieved in any of the 1 L min$^{-1}$ D-H exchanges. All the $K_{\text{app}}$ plots are appreciably lower than the empirical $K_{\text{eq}}$ values (dashed black, red and green lines on Figure 4-7). The peak 208 K $K_{\text{app}}$ value was $\sim$1.4. This was approximately 50% of the empirical $K_{\text{eq}}$ value (Table 4-2). The equilibrium reaction was therefore diminished in comparison to what was observed during static measurements of the equilibrium constant. The cause of this was the higher inlet pressure of the exchange. The highly dynamic conditions are likely to be the reason for the depressed HD production below those found during static measurements. The gas has physically less time to interact and equilibrate because of the pressure driving force.

The $K_{\text{app}}$ plot (and experimental data plot) does, however, show that HD was still produced in appreciable quantities. The reason for this was similar to what was discussed for the low pressure D-H exchange. The low temperature means the gas pressure was lower and therefore the residence time of the gas molecules in the vicinity of the Pd surface is greater. This improves the probability of a successful exchange event. Moreover, studies in the literature have shown enhanced HD production at low temperature due to additional surface- subsurface-bulk processes [33, 122-124]. It is also probable that the exothermic nature of the $\text{H}_2$ adsorption increased the production of HD, and therefore increased the $K_{\text{app}}$ value. The localised increase in temperature would improve the reaction kinetics and subsequently enhance the production of HD further. The 208 K $K_{\text{app}}$ plot was broad and continued for the majority of the total exchange time. This was most likely due to the increased initial stoichiometry of the Pd bed. Because there were physically more D atoms to exchange it would mean that HD production would continue for longer, as was found here, and this means the $K_{\text{app}}$ plot broadens and is apparent for the majority of the exchange.
The 293 K $K_{app}$ plot is dramatically lower than the empirical $K_{eq}$ value. The peak value was $K_{app} = 0.25$. This was only 8 % of the empirical value (see Table 4-2). This again points towards an exchange reaction proceeding without significant production of HD, i.e. by a direct exchange mechanism. Significantly lower HD production (and therefore a lower $K_{app}$) was also observed by Larson et al [70]. They found a depressed HD signal during a blowdown exchange carried out at 2 bar and 298 K. The results from their experiment were very similar to those found herein during the low pressure D-H exchange at 293 K. The 1 L min$^{-1}$ D-H exchange at 293 K involved significantly higher pressure to that used by Larson and it appears that pressure causes an increased depression of the HD curve. The equilibrium reaction occurring in the exchange reaction front was therefore diminished significantly. Again this indicates that at this particular temperature and exchange direction there was additional surface reaction processes at work. As discussed previously, this could be a direct exchange process, or indeed a consequence of additional regions in Pd. Subsurface regions have been shown to lower the activation energy ($E_a$) for desorption of surface species. It is also worth pointing out that these subsurface regions would be more populated at higher pressure (as is the case for the 1 L min$^{-1}$ exchanges), therefore their effect on the exchange process would be increased. This would aid in lowering the amount of HD produced because it would be more energetically favourable to desorb D$_2$ rather than HD. Both these hypotheses would severely affect the apparent equilibrium reaction observed during experimentation.

The 373 K D-H exchange at 1 L min$^{-1}$ had a $K_{app}$ value of ~1.75. This represents 50 % of the empirical $K_{eq}$ value (Table 4-2). Again, the high inlet gas pressure causes very dynamic conditions within the Pd bed in terms of gas velocity. These conditions cause HD production to remain lower during the length of the exchange. The peak $K_{app}$ value was still the highest of the three exchange temperature here, indicating the reaction front was closest to achieving equilibrium. As discussed previously, HD production is enhanced with increasing temperature and this is what was observed during the 373 K exchange experiment. The higher temperature improves the reaction kinetics and therefore the probability of producing HD under these dynamic conditions.

Figure 4-8 shows the apparent equilibrium constant analysis as a function of time for the 208 K, 293 K and 373 K H-D exchanges carried out using a 1 L min$^{-1}$ flowrate.
Similarly to the low pressure exchange $K_{app}$ values, the peak $K_{app}$ values during the H-D exchanges were again higher than the D-H exchanges, indicating a closer approach to the static equilibrium $K_{eq}$ values. The peak $K_{app}$ value for the 1 L min$^{-1}$ H-D 208 K exchange was similar to the peak value found in the 1 L min$^{-1}$ D-H 208 K exchange, indicating that both processes appear to be affected by the low temperature. This explanation for this could reside in the findings of Carstens and Encinias [3]. They found that the exchange process was limited by surface processes at temperatures below 210 K. This would inhibit the equilibrium reaction and reduce the quantities of HD gas formed, as was found during the two 1 L min$^{-1}$ exchange reactions.

The 1 L min$^{-1}$ H-D exchange carried out at 293 K had a peak $K_{app}$ value of 3.3. This was actually higher than the empirical $K_{eq}$ values reported in the literature for 293 K, though this may be due to noise in the plots of $K_{app}$ associated with the sampling of the effluent gas concentrations. It is likely that the peak $K_{app}$ was of the order of the empirical $K_{eq}$ value ($K_{eq} = 3.25$). Equilibrium was therefore achieved in the reaction front moving through the Pd bed. The explanation for this could again fall on the existence of additional regions in Pd. Subsurface regions, when populated, are known to reduce the activation energy for desorption. Although it has not been shown conclusively as of yet, the subsurface regions could be assisting in H atom desorption via formation of HD. Considering that the quantity of D atoms on the Pd surface (in the exchange front) would be low due to the low affinity for D atoms compared with H atoms, any desorption that did occur would be either additional H$_2$ and HD; although HD desorption would be favoured thermodynamically. This would increase the amount of HD in the gas phase which would increase the $K_{app}$ value found from analysis of the effluent gas concentrations.

The $K_{app}$ plot for the 373 K H-D exchange carried out at 1 L min$^{-1}$ flowrate has a peak value of 2.3. This represents ~65 % of the empirical $K_{eq}$ value for a mixed hydrogen isotope system held at 373 K (Table 4-2). Equilibrium was therefore not fully realised in the exchange reaction front. This can also be viewed by referring to the HD peak height in the experimental data from this temperature. The HD curve was less than would be expected had complete equilibrium been achieved. It is probable that the high inlet gas pressure ($P_{in} = 8.3$ bar) of the inlet D$_2$ gas. Under these conditions the gas velocity would be at its highest and therefore the residence time in the vicinity of the Pd surface...
would be reduced. Furthermore, the temperature increase due to adsorption would increase the localised temperature to ~450 K. This would be sufficient to encourage additional H2 desorption without the formation of HD. Moreover, because of the temperature increase the Pd stoichiometry would potentially lower to below that required for the β-phase (PdH < PdH0.5). There would therefore be far less H atom capacity for formation of HD via desorption of surface H and newly adsorbed D atoms. The effect of this would be a reduced $K_{app}$ value below that expected from empirical relationships for the equilibrium constant as a function of temperature.

Figure 4-11 plots the peak $K_{app}$ values for the low pressure and 1 L min$^{-1}$ isotope exchanges carried out at 208 K, 293 K and 373 K. This allows the reader to visualise which exchanges depart the greatest from equilibrium. While the author acknowledges that more experiments will need to be completed to draw firm conclusions on whether the features eluded here are indeed correct. However, the departure from the empirical $K_{eq}$ values reported in the literature was significant in some of the exchanges, particular the 1 L min$^{-1}$ experiments. The change in the trends of the peak $K_{app}$ values was greatest at 293 K in all cases. At 293 K the $K_{app}$ values diverge significantly from the approximate linear trend set out by the $K_{eq}$ values. This demonstrates that there was a consistent change in behaviour of the exchange processes, whether at low or high pressure, around ambient conditions (293 K). The reason for this has been postulated previously to be because of the influence of additional processes within Pd. For instance, the role and effect of the subsurface regions may be having a significant impact on the formation of equilibrium within the reaction front. Their existence appears to skew the gas phase concentration towards larger concentrations of H2 and D2, which in turn lowers the apparent equilibrium constant ($K_{app}$). The peak equilibrium values were even more pronounced during the 1 L min$^{-1}$ exchanges, both D-H and H-D, suggesting that pressure has a serious impact on the formation of equilibrium in the reaction front (see Table 4-2). The effect of pressure on the peak $K_{app}$ values can be understood by referring to the low pressure D-H and 1 L min$^{-1}$ D-H peak $K_{app}$ plots (black and green lines on Figure 4-11, respectively) alongside Table 4-1 and Table 4-2. The pressure diminishes the recorded peak $K_{app}$ value further. As discussed previously, this is hypothesised to be due to more populated subsurface sites. The effect of this
would be to increase desorption of D$_2$ and consequently reduce the amount of HD, moving the gas phase further away from equilibrium.

![Graph showing peak apparent equilibrium constant values for both the low pressure and 1 L min$^{-1}$ isotope exchanges carried out at 208 K, 293 K and 373 K.](image)

At 1 L min$^{-1}$ the peak $K_{app}$ value plots were mirrored. This suggests that the additional processes occurring in Pd at 293 K affect the two different exchange directions in a contrasting manner. For instance, during the D-H exchanges these additional processes reduced the recorded $K_{app}$ values by reducing the concentration of HD in the gas phase, while in the H-D exchange they appear to assist the equilibrium reaction by encouraging the formation of additional HD. This skews the trend of $K_{app}$ for the 1 L min$^{-1}$ H-D exchange towards the empirical $K_{eq}$ values (see yellow and blue lines, respectively).

With regards to the 1 L min$^{-1}$ D-H exchanges these additional (at present unknown) processes skew the trend further away from the equilibrium values (see green line on Figure 4-11). The 1 L min$^{-1}$ H-D peak $K_{app}$ values at 208 K and 373 K were significantly lower than the $K_{eq}$ values for these temperatures. This indicates that at
these temperatures pressure effects the equilibrium reaction significantly and suppresses the formation of HD. This effect can also be viewed by referring to the low pressure H-D exchanges which all achieve the expected peak $K_{app}$ values.

The only exchanges whose peak $K_{app}$ values matched the empirical values for the equilibrium constant ($K_{eq}$; blue line on Figure 4-11) was the low pressure H-D experiments (red line on Figure 4-11). The reason for this has been eluded previously in prior discussions. The cause was likely to be the low pressure, lower gas velocity and Pd’s greater affinity for H atoms. Because of differences in zero point energy of the gas and solid phase species, H atom adsorption/absorption is thermodynamically favourable compared to D atom adsorption/absorption. This causes H atoms to persist in the solid phase and HD desorption is favoured over formation of PdD species. This therefore caused the peak $K_{app}$ values to be in line with those found from Sievert’s type static dosing experiments.
Chapter Five

Modelling hydrogen isotope exchange
Chapter 5. Modelling hydrogen isotope exchange

5.1 Introduction

This chapter describes the modelling undertaken to analyse the experimental data displayed in Chapter 4. The chapter will present modelling results using two different modelling software tools. The first part of the chapter will describe the model of hydrogen isotope exchange written in MATLAB. This model is based on the model developed by Foltz and Melius in their seminal paper in 1987 [1]. Because of instabilities in the formulation of Foltz and Melius’ model in MATLAB, COMSOL Multiphysics was utilised to provide a platform for a modified version of the model providing more stable solutions at higher pressure and varied temperature. In the later parts of the chapter the full kinetic COMSOL Multiphysics model will be discussed.

Descriptions of each model will be discussed in following sections of this chapter. These aim to give the reader a fundamental understanding of the assumptions and mathematical models used, as well as the numerical schemes employed to solve the differential equations that arise from describing the system mathematically. More thorough descriptions of the models, including the foundations, solvers and some of the issues during development, are presented in the Supplementary Information.

Results obtained from the various models are presented alongside the curve fitting parameters, as well as the failures of each model.

5.2 Validation of the Foltz and Melius model using MATLAB

5.2.1 Introduction

Considering the success of Foltz and Melius’ [1] model, initial efforts to model hydrogen isotope exchange focussed on recreating the single-exchange Foltz and Melius model. The resulting model was then applied to Foltz and Melius’ original data to validate the model, before applying it to the exchange data obtained in this work. Due to the relative simplicity of the single-exchange mechanism, this model was an attractive proposition in the early stages of modelling experimental data. Despite there being a
plethora of computational packages available for computing such a problem, MATLAB was chosen due to its suitability for solving systems of equations, easy coding and superior calculation speed.

A numerical model that is able to simulate both the PdD to PdH and PdH to PdD exchange has been developed based on the model described in Foltz and Melius’ [1] paper. In order to achieve this, the following objectives were completed.

- The rate equations that Foltz and Melius used to describe the exchange are derived from first principles.
- An appropriate numerical method to approximate the solutions to these equations was selected.
- The equations were written into a MATLAB format and a model was built comprising script and function files.
- The model was developed to describe the change in gas species (H$_2$, HD and D$_2$) mole fraction as a function of time. This included necessary optimisation to ensure the model did not require excessive computational time.

The completed model was then used to simulate Foltz and Melius’ results, as well as new isotope exchange data obtained on the IsoEx rig.

5.2.2 Derivation of the Foltz and Melius model

Since Foltz and Melius did not derive or provide adequate explanations for the rate equations used in their model, it was necessary to derive the equations from first principles. As in Foltz and Melius’ original work, the MATLAB model deals with the gaseous species in terms of atomic species. The original authors took this approach to simplify the equations that arise from analysis of the system. The following equations are for the D-H exchange process assuming one-dimensional axial flow along the palladium bed. The original notation used by Foltz and Melius has been retained in order to differentiate this model from additional models presented later in this chapter.

Solid-phase atom balance

Firstly, an atom balance is performed for the surface protium ($n_{S_H}$) over a simple control volume ($dV$) around a palladium particle.
The atom balance follows the standard equation to perform a material balance.

\[ \text{input} - \text{output} + \text{generation} = \text{accumulation} \]  \hspace{1cm} [5-1]

Since no surface protium crosses the control boundary, the input and output terms are equal to zero. During an exchange it is assumed that only the isotope exchange reaction changes the quantity of \( n_{\overset{\circ}{\text{H}}} \), and such, the rate of change of surface protium is equal to the isotope exchange rate \( R_{\text{exch}} \).

\[ \text{generation} = \text{accumulation} \]  \hspace{1cm} [5-2]

\[ R_{\text{exch}} \ dV = \frac{\partial n_{\overset{\circ}{\text{H}}}}{\partial t} \]  \hspace{1cm} [5-3]

\[ R_{\text{exch}} \ dV = \frac{\partial (n_{\overset{\circ}{\text{H}}} V)}{\partial t} \]  \hspace{1cm} [5-4]

The control volume \( (dV) \) is constant. The product rule can therefore be used to convert equation 5-4 to equation 5-5.

\[ R_{\text{exch}} \ dV = V \frac{\partial n_{\overset{\circ}{\text{H}}}}{\partial t} \]  \hspace{1cm} [5-5]

\( dV \) and \( V \) both represents the control volume, and such, are cancelled from equation 5-3. This leads to equation 5-6 which is the format of the equation used by Foltz and Melius to describe the rate of change of the atomic density of surface protium \( (n_{\overset{\circ}{\text{H}}} ) \).

\[ R_{\text{exch}} = \frac{\partial n_{\overset{\circ}{\text{H}}}}{\partial t} \]  \hspace{1cm} [5-6]

During an exchange event, Foltz and Melius assumed that there was no net gas sorption. This meant that the loss of surface deuterium \( (n_{\overset{\circ}{\text{D}}} ) \) is equal to the rate of surface protium generation. Using this assumption, a similar atom balance can be performed on the surface deuterium species (equation 5-7).
\[-R_{\text{exch}} = \frac{\partial n_{SD}}{\partial t}\]  \[[5-7]\]

**Gaseous-phase atom balance**

The atom balance considers only atomic species, and such only gaseous protium and deuterium atoms are considered, \(n_{GH}\) and \(n_{GD}\), respectively. The balance for the gaseous species is performed over a control volume of the palladium packed powder bed.

We again consider the standard material balance equation (equation 5-1) in order to develop the atom balance for the gas species. The input term in this equation is given by \(v_f n_{gh}\). This describes the atomic flux of gaseous protium into the control volume (\(dV\)) through the cross sectional area (\(A\)). The gas velocity is given by \(v_f\). It then follows that the gas flux crossing the output boundary of the control volume is equal to the original flux plus a given change in \(n_{GH}\) that occurred over the control length \(dx\). The consumption of gaseous protium was assumed to equal the rate at which surface protium was generated. Hence the rate of gaseous protium consumption is accounted for by the same isotope exchange rate term \((R_{\text{exch}})\). Since the model assumes one dimensional axial flow, gas flux in other directions is ignored.

\[v_f n_{gh} A - \left(v_f n_{gh} + \frac{\partial (v_f n_{gh})}{\partial x} \right) A - R_{\text{exch}} dV = \frac{\partial n_{gh}}{\partial t}\]  \[[5-8]\]

The atomic balance for gaseous protium is given by equation 5-8, in accordance with the format of equation 5-1.

\[dx A = dV\]  \[[5-9]\]

Equation 5-8 can be expanded and combined with equation 5-9 to give equation 5-11.
\[ v_f n_{gH} A - (v_f n_{gH} A + \frac{\partial (v_f n_{gH})}{\partial x} dV) - R_{exch} dV = \frac{\partial n_{gH}}{\partial t} \]  \[ 5-10 \]

\[-R_{exch} dV = \frac{\partial (v_f n_{gH})}{\partial x} dV + \frac{\partial n_{gH}}{\partial t} \]  \[ 5-11 \]

In a similar fashion to the solid phase balance, the \( N_{gH} \) term is expanded and the product rule is applied to equation 5-11 followed by cancellation of the control volume terms.

\[-R_{exch} \frac{\partial (v_f n_{gH})}{\partial x} = \frac{\partial n_{gH}}{\partial t} \]  \[ 5-12 \]

Because the same isotope exchange rate is used to describe the change in surface and gaseous species, the term must be multiplied by a factor which accounts for the solid to void ratio within the palladium packed bed. The solid to void ratio is included as follows.

\[ \frac{V_{Solid}}{V_{Void}} = \frac{V_{Total} - V_{Void}}{V_{Void}} = \left( \frac{V_{Total}}{V_{Void}} - 1 \right) = \left( \frac{1}{\varepsilon_p} - 1 \right) = \left( \frac{1 - \varepsilon_p}{\varepsilon_p} \right) \]  \[ 5-13 \]

The atom balance for gaseous protium across the palladium bed is therefore represented by equation 5-14, as originally used described by Foltz and Melius [1].

\[-R_{exch} \left( \frac{1 - \varepsilon_p}{\varepsilon_p} \right) - \frac{\partial (v_f n_{gH})}{\partial x} = \frac{\partial n_{gH}}{\partial t} \]  \[ 5-14 \]

The mass balance for the gaseous deuterium is therefore found to be equivalent to equation 5-15.

\[ R_{exch} \left( \frac{1 - \varepsilon_p}{\varepsilon_p} \right) - \frac{\partial (v_f n_{gD})}{\partial x} = \frac{\partial n_{gD}}{\partial t} \]  \[ 5-15 \]

The above two partial differential equations (equations 5-14 and 5-15) describing the change in gaseous species with space and time are coupled with the two differential equations describing the change in solid phase protium and deuterium (equations 5-6 and 5-7) and solved using MATLAB.

Isotope Exchange Rate

One important variable yet to be discussed is the isotope exchange rate \( R \). The single-exchange model can be represented by Reactions R13 and R14.
Traditional reaction engineering analysis of the above equation results in rate equations for the change in concentration of the various species involved in the single-exchange model. An example of this would be the rate equation for the change in solid phase deuterium (equation 5-16).

\[
\frac{\partial[D_S]}{\partial t} = k_1[D_2][H_S] - k_{-1}[HD][D_S] + k_2[HD][H_S] - k_{-2}[H_2][D_S]
\]  

[R5-16]

Rates of change of the other species (H\(_2\), D\(_2\), HD and H\(_s\)) are described in a similar manner. Foltz and Melius used a series of manipulations of these rate equations to derive the isotope exchange rate \(R_{\text{exch}}\). This term was presented by Foltz and Melius \[1\] in the form of equation 5-17.

\[
R_{\text{exch}} = \frac{1}{4} k \left( n_{gD} + n_{gH} \right) \left( \frac{8RT}{\pi M} \right)^{1/2} S_o N_{\text{Surf}} \left\{ \alpha^{1/2} x_{Hg} x_{Ds} - \alpha^{-1/2} x_{Dg} x_{Hs} \right\}
\]  

[R5-17]

The term includes an “overall isotope exchange rate constant” \(k\). Using statistical correlations and the isotope separation factor \(\alpha\), Foltz and Melius derived relationships between the individual rate constants of the two steps in the single-exchange model. Unfortunately, no further reference was given describing the details of the statistical correlations used by Foltz and Melius so it was difficult to validate the method. However, Larson et al \[70\] did attempt to assess the accuracy of these correlations. Larson et al used empirical equations for the thermochemistry of dissolution found by Santandrea and Behrens \[47\], and the known equilibrium constant for the \(H_2 + D_2 \rightleftharpoons 2HD\) equilibration reaction \[9, 40, 41, 60\] to compare the rate constants used by Foltz and Melius to those found from experimentation. The values used by Foltz and Melius were not too dissimilar to the values found from known thermodynamic relationships. Larson et al \[70\] therefore deemed that the inaccuracy of Foltz and Melius’ “statistical correlations” was not significant. Because of this finding,
the MATLAB model presented in the following sections follows the Foltz and Melius formulation.

Equation 5-17 can, however, undergo further rearrangement to assist in simplifying the calculations that are made in the MATLAB model. Upon rearrangement, equation 5-18 is found. This is the isotope exchange rate used in the model.

\[
R_{\text{exch}} = \frac{1}{4} \ k \ \left( \frac{8RT\alpha}{\pi M} \right)^{\frac{1}{2}} \left\{ n_{gH} n_{sD} - \frac{n_{gD} n_{sH}}{\alpha} \right\} \tag{5-18}
\]

Here, \( k \) forms the fundamental fitting parameter in the MATLAB model. \( k \) is varied to fit experimental data through manipulation of the “isotopic exchange probability”, \( p_{\text{exch}} \), that is, the probability of a gaseous molecule colliding with the palladium surface and causing an isotope exchange event.

\[
k = \left( \frac{S_n}{s_{do}} \right) p_{\text{exch}} \tag{5-19}
\]

\( p_{\text{exch}} \) was simply adjusted arbitrarily to allow the model to obtain the best fit to experimental data. Full derivations of the isotope exchange rate and accompanying equations can be found in Supplementary Information.

5.2.3 MATLAB Model

This section will aim to outline how MATLAB was used to provide solutions to the sets of rate equations described previously. The basic structure of the MATLAB files will be discussed alongside the numerical methods used to provide solutions to the 4 coupled differential equations. For listings of the full MATLAB script and function files please refer to the Supplementary Information that accompanies this thesis. The reader will also find a short MATLAB guide which introduces some fundamentals of using MATLAB as modelling software.

Creating matrices, specifying initial conditions and defining physical properties used in the model

Firstly, when using MATLAB it is imperative that all the necessary parameter values are specified in the master script file prior to any further coding. This ensures that MATLAB has all the data stored in its memory prior to any computation. It is also important to ensure all of the units associated with these parameters are correct since
MATLAB has no internal unit checking service. Necessary data specific to the H-D-Pd system was taken from Foltz and Melius [1], while physical properties of palladium and hydrogen isotopes were taken from literature [10, 11, 127-129]. In the early stages of modelling in MATLAB, the gas viscosity was assumed constant throughout the exchange. The chosen value for the viscosity was an average of the values for H$_2$ and D$_2$. A full list of the data used in the model can be found in the Supplementary Information that accompanies this thesis.

Next, matrices were setup in MATLAB to store the solutions to the coupled partial differential equations (PDEs) (for the gas phase species) and ordinary differential equations (ODEs) (for the solid phase species). These solution matrices are created for the species concentrations, both gas- and solid-phase, as well as the isotope exchange rate. An extract of the MATLAB code to achieve this is shown below.

```matlab
sd_sol = zeros(n+1,m+1);   % Solution Matrix for Surface Deuterium
sh_sol = zeros(n+1,m+1);   % Solution Matrix for Surface Protium
gd_sol = zeros(n+1,m+1);   % Solution Matrix for Gaseous Deuterium
gh_sol = zeros(n+1,m+1);   % Solution Matrix for Gaseous Protium
```

Equations 5.14 and 5.15 show that the solutions to the PDEs for the gas phase H and D atomic species vary with axial distance along the Pd bed (space) and time. MATLAB was therefore coded with solution matrices capable of accommodating the values arising from solving the spatial and time dependent terms in the PDEs. It can be seen from the above extract from the MATLAB code that each matrix for the gas- and solid-phase atomic species was made up of ‘n+1’ rows and ‘m+1’ columns. ‘n’ represents the number of spatial steps and ‘m’ represents the number of time steps used during the calculation. These values describe how large the solution matrices were and, therefore, define how many calculations are carried out to solve the model.

For example, if ‘n’ is equal to five and ‘m’ equal to four, the solution matrices would contain six rows and five columns. The differential equations are solved at five equally spaced points in time (the total time is specified to match that of the particular experiment that is to be modelled) and six equally spaced points along the Pd bed; one at each end of the Pd bed, and four points that divide the remaining bed length equally. This example is, of course, far from the actual values of ‘n’ and ‘m’ that are required to approximate a complex problem such as the single-exchange model. In the final
MATLAB model ‘n’ and ‘m’ were much larger, meaning the coupled differential equations for the gas- and solid-phase species were solved a great number of times more, at small intervals in axial distance and time. Because of the nature of the numerical scheme used to solve equations 5-6, 5-7, 5-14 and 5-15, the solutions in theory become more accurate the larger the values used for ‘n’ and ‘m’.

\[
\text{sd sol} = \begin{bmatrix}
a & \cdots & b \\
\vdots & \ddots & \vdots \\
c & \cdots & d
\end{bmatrix}
\]

Figure 5-3 Solution matrix for surface deuterium used in the MATLAB model

After the solution matrices have been established in MATLAB, the initial conditions for the calculation need to be introduced. These values represent the points at which MATLAB will begin the calculation and subsequently begin populating the solution matrices. The essential initial conditions in the model describe the concentration of each of the four atomic species at the start of the experiment/modelling run. If we take the D-H exchange as an example, at the start of the D-H exchange the whole Pd bed is saturated with deuterium atoms at a known concentration of ‘sd0’, which is found from literature Pd-H/Pd-D phase relationships. The other species were specified according to
the isotope exchange experiment to be simulated. One caveat to initial condition specification in MATLAB was that zeros could not be specified. Specifying zero as an initial value for any of the species in MATLAB causes a ‘not a number’ (NaN) error as it begins to read the code and perform mathematical operations (such as division) with the initial conditions. For this reason, a small value for each minor species (for example H atoms when the Pd bed was initially loaded with D atoms) was specified, i.e. 0.0001.

Following correct initial specification of the initial conditions and model variables the MATLAB model was initiated for hydrogen isotope exchange simulation.

5.2.4 Validation of MATLAB Model

In order to validate the model developed based on the work of Foltz and Melius, the MATLAB model has been used to simulate their original data. The experimental data from Foltz and Melius was loaded into the MATLAB model, alongside the specific conditions used by Foltz and Melius. These included the Pd bed length, Pd bed density, experimental pressures and initial Pd loading characteristics. The upstream pressure used by Foltz and Melius was ~1.5 bar. The initial Pd loading in the D-H and H-D exchange were PdD₀.₆₁ and PdH₀.₆₅, respectively. Foltz and Melius used a Pd bed length of 20.3 cm, with a density of 7.5 g cm⁻³ and subsequent porosity of 0.31 taking into account the effect of Pd swelling under hydrogen isotope loading. The isotope exchange probability, p was specified to the same value used in Foltz and Melius’ work (p = 2.6e-7). To provide a stable solution the model was setup with 150,000 timesteps (m = 150,000) and 10 spatial steps (n = 10) at which the differential equations were solved via an implicit backward difference numerical method. Upon running the model with these conditions the following results were obtained for both exchange directions (D-H and H-D).
Figure 5-5 MATLAB model results using original Foltz and Melius experimental data; D-H exchange. Data points are from the work of Foltz and Melius; lines represent the MATLAB model results.

Figure 5-5 shows the MATLAB model results for the D-H exchange compared to the experimental data obtained by Foltz and Melius. As can be seen, the model fit is good and certainly on par with the original model results of Foltz and Melius.

Figure 5-6 MATLAB model results using original Foltz and Melius experimental data; H-D exchange. Data points are from the work of Foltz and Melius; lines represent the MATLAB model results.
Figure 5-6 shows the MATLAB model fit to Foltz and Melius’ experimental data. Similarly to their original work, the model fit to the H-D exchange data is not good. The model cannot satisfactorily reproduce experimental data at the later stages of the experiment. Experimentally, the HD ceases detection after approximately 2250 seconds, while the model predicts HD production to continue until after the Foltz and Melius experiment finished (> 2600 seconds). A similar trend is observed in the D2 model data which shows a slower rate of breakthrough from the Pd bed compared to that observed in experiment.

While the Foltz and Melius based MATLAB model suffers from the same problems in the H-D exchange as the original model, the fit in the D-H exchange is more than satisfactory. For this reason the MATLAB model was selected to model exchange data obtained on the IsoEx apparatus. The next section describes the outcome of the modelling efforts on the IsoEx data obtained at elevated pressures and different temperatures compared to the work of Foltz and Melius.

5.2.5 Application of MATLAB exchange model to IsoEx experimental data

The MATLAB model was applied to exchange data obtained on the IsoEx apparatus using a flowrate of 1 L min⁻¹. Both exchange direction experiments were carried out at elevated pressure and different temperatures to Foltz and Melius’ experiments. For the D-H exchange the upstream pressures were 5.8, 6.3 and 8 bar for the exchanges performed at 208, 293 and 373 K, respectively. For the H-D exchange the upstream pressures were 7.5, 8 and 8.3 bar for the exchanges performed at 208, 293, and 373 K, respectively. The Pd bed length and density used was 2.105 cm and 3 g cm⁻³, respectively. This corresponds to a porosity of εp = 0.775 accounting for Pd swelling under hydrogen loading.

To begin the model was loaded with initial conditions that matched those of experiments. Upon running the Foltz and Melius derived MATLAB model, it was found to be incapable of reproducing IsoEx experimental data. This was the case for both D-H and H-D exchanges. The model exhibited large instabilities in both exchange direction models. These instabilities were such that despite significant variation in the isotope exchange probability (p) and numerical scheme (by manipulation of the number of time (m) and spatial steps (n)) no satisfactory fits were found for the IsoEx 1 L min⁻¹ experiments. The available memory on the computer used for these simulations was not

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sufficient to allow for any further refinement of the numerical scheme beyond what was used to match Foltz and Melius’ experimental data (Figure 5-5 and Figure 5-6). It must be noted that, in the author’s opinion, even with an increase in computing power, the model in this formulation would not be capable of reproducing high pressure exchange data. The Foltz and Melius derived model was constrained by the isotope exchange probability and only ran to completion over a certain range of p values from ~1e-8 to 3e-7. Outside of this range, the numerical scheme was not refined enough to provide stable solutions and resulted in the MATLAB model crashing. For the IsoEx exchange experiments, these p values were not suitable and therefore no meaningful data could be obtained from the MATLAB model for these experiments.

This finding suggests that this formulation of the Foltz and Melius model is only suitable for low pressure exchange data. In order to model higher pressure isotope exchange data robustly a new mathematical modelling tool was chosen. The chosen software was COMSOL Multiphysics which was purchased alongside a significantly more powerful computer with large amounts of memory, storage and multiple processors. Details of COMSOL Multiphysics and the purchased computer are detailed in the next section.

5.3 COMSOL Multiphysics

5.3.1 Introduction

In order to address the issues with the MATLAB version of the Foltz and Melius derived model. A new model was created in COMSOL Multiphysics. This software is a finite element analysis (FEA), solver and simulation package developed in Sweden in 1986. The software was originally called FEMLAB (pre-2005) before being renamed COMSOL. The software allows entry of coupled systems of partial differential equations (PDEs) that describe physical phenomena. COMSOL Multiphysics offers the user a number of independent ‘modules’ that encompass the equations and numerical solvers necessary to provide solutions to specific physics and engineering problems. These modules are provided alongside the basic COMSOL Multiphysics module which contains options for direct entry of specific PDEs and other mathematical equations.

The modules used in this work were the default COMSOL Multiphysics module and the Chemical Reaction Engineering (CRE) module. The CRE module analyses
computational fluid dynamics (CFD), mass and energy balances and couples these to chemical reaction kinetics. It incorporates various models via the ‘Chemical Species Transport Interfaces’ relevant to the field of transport phenomena, including multi-component diffusion, fluid flow and species transport in porous media. These transport phenomena models can be coupled to additional models describing chemical reactions, whether they occur in the free fluid or at a surface.

To develop a model in COMSOL Multiphysics one must first specify the dimensions of interest, whether this be a 1D, 2D or 3D model of the process. The user must then select whether the model is to be solved in steady state or dependent on time. This is done by selecting either a ‘Stationary’ or ‘Time-dependent’ within COMSOL’s user interface. After this the specific physics required in the model must be chosen. Within the CRE module there are physics interfaces for fluid flow, species transport in porous media, concentrated species transport, diluted species transport, ionic species transport or chemical reaction engineering. Alongside these there are complementary physics interfaces for heat transfer, whether through conduction, convection or radiation. It is the user’s responsibility to select necessary physics interfaces to describe the process to be modelled.

To describe hydrogen isotope exchange a number of physics interfaces are chosen, namely ‘Species Transport in Porous Media’, ‘Darcy’s Law’, ‘Free and Porous Media Flow’ and ‘Reaction Engineering’. The necessary combination of these is subject to the dimensions of the specific model. For instance, for 1D models of hydrogen isotope exchange only the ‘Species Transport in Porous Media’, ‘Darcy’s Law’ and ‘Reaction Engineering’ are required. The capability and use of these interfaces will now be discussed in more detail in the following sections.

5.3.2 The Chemical Species Transport interfaces

The transport and conversion of material is denoted chemical species transport in the CRE module. This includes the simulation of chemical reactions, and mass or material transport through diffusion and convection. COMSOL Multiphysic’s chemical species interfaces include the following physics sub-branches:

- The Reaction Engineering interface
- The Transport of Diluted Species interface
- The Transport of Concentrated Species interface
- The Nernst-Planck Equations interface
- The Species Transport in Porous Media interface

As described in the previous section, for hydrogen isotope exchange modelling only the Reaction Engineering and Species Transport in Porous Media are required to describe the species transport. The flow through the packed Pd bed is described by the fluid flow interfaces, which are described in more detail in the next section.

The mechanisms for chemical species transport in each physics sub-branch are defined by the relevant mass transfer equations describing diffusion and convection. The Reaction Engineering branch is used to describe the chemical reactions occurring within a system, and the kinetics that properly describe them. The interface includes all the tools required to simulate chemical reaction kinetics in well-defined environments. This includes the simulation of reversible, equilibrium and irreversible reactions in volumes of on surfaces. The behaviour of chemical reactions in real environments, or indeed in dynamic processes such as isotope exchange as is investigated here, is often not adequately described by assumptions of perfect mixing or controlled environments. This means, therefore, that the transport of material through both space and time need to be considered in order to provide acceptable simulations of dynamic systems.

While the chemical reactions occurring in the Pd packed bed can be dealt with in the Reaction Engineering interface, the species transport within the porous material is solved via the Species Transport in Porous Media interface. This physics sub-branch is tailored for modelling solute transport in porous media. The interface is ideal for modelling species transport in porous systems where the substrate is immobile, as is the case for hydrogen isotope exchange over compacted Pd powder beds. This interface also has the capability of including reaction kinetics, as well as material sources and sinks (i.e. formation and consumption of species due to reactions). The Species Transport in Porous Media interface can be coupled to the Reaction Engineering interface, which subsequently sets up the mass balances and source terms within the transport interface.

The relevant physics chemical species transport interfaces are now described in more detail.
5.3.2.1 The Reaction Engineering interface

The Reaction Engineering interface is used to simulate and optimize chemical reacting systems where spatial variations can be neglected or are well controlled. The mass and energy balance equations describing these systems assume perfect mixing in the reacting system. For this reason, when setting up models of hydrogen isotope exchange, the Reaction Engineering (RE) interface is used only to define the equilibrium reaction occurring within the reactor \((H_2 + D_2 \leftrightarrow 2HD)\) prior to introduction of the opposite isotope to initiate exchange. By doing this the model is setup in such a way that equilibrium holds in the reactor prior to introduction of any other species. This technique produces significantly improved stability during simulations.

The Reaction Engineering interface sets up a 0D model of the reacting system and describes the instantaneous equilibrium reaction occurring between Pd and the three isotopic species \((H_2, D_2\text{ and } HD)\). The three species are specified in the Reaction Engineering interface. This includes inputting the molecular mass of each species, the density and the initial concentration of each species.

To address additional instability issues the equilibrium reaction is described in the interface by a fast reversible reaction by specifying a large forward rate constant \((k_f)\) and defining the desorption rate by the known equilibrium constant for the isotope exchange process, \(K_{eq}\). The Reaction Engineering interface is then coupled to the Species Transport in Porous Media interface. This is achieved by instructing the software that the mass balance for the system is performed in the Species Transport in Porous Media interface. The three species alongside the reaction rate law for the equilibrium reaction are then transferred into the Species Transport in Porous Media interface to enable space- and time-dependent models of the system to be formed. Once complete, the rate of change of each of the three species (due to the equilibrium reaction) appear in ‘Reactions’ nodes within the transport physics interface.

Prior to this method, isotope exchange models were found to be numerically unstable during the initial timesteps of the simulation. Instabilities arose because the model was not in equilibrium at the start of the simulation. Essentially the equations describing the rate of change of the chemical species were in conflict with the equilibrium equation. This caused the solution time to be greatly increased because the numerical stepsize had to be reduced to provide a solution that met the set tolerances.
The Reaction Engineering interface is based on the Mass Action Law. The interface is used in hydrogen isotope exchange modelling to describe the equilibrium reaction that occurs between Pd and hydrogen isotopic species. As described in the previous section, difficulties were encountered when specifying the reaction within COMSOL Multiphysics as a pure equilibrium reaction. For this reason the equilibrium reaction was setup as a rapid reversible reaction using the known equilibrium constant $K_{eq}$. This value can be found in the literature and varies with temperature, and to a small extent pressure. The equilibrium reaction that is accounted for in the interface is as follows:

$$H_2 + D_2 \rightleftharpoons 2HD$$  \[R15\]

The forward and reverse reactions have the rate constants $k_f$ and $k_r$, respectively. The overall reaction rate is formulated as:

$$r = k_f c_{H_2} c_{D_2} - k_r c_{HD}^2$$ \[5-20\]

where $c_{H_2}$, $c_{D_2}$ and $c_{HD}$ are the concentrations of $\text{H}_2$, $\text{D}_2$ and $\text{HD}$, respectively (mol m$^{-3}$). The net rate expressions for the three species are:

$$R_{H_2} = -k_f c_{H_2} c_{D_2} + k_r c_{HD}^2 = -r$$  \[5-21\]

$$R_{D_2} = -k_f c_{H_2} c_{D_2} + k_r c_{HD}^2 = -r$$  \[5-22\]

$$R_{HD} = k_f c_{H_2} c_{D_2} - k_r c_{HD}^2 = r$$  \[5-23\]

The subsequent material balances for $\text{H}_2$, $\text{D}_2$ and $\text{HD}$ are as follows:

$$\frac{\partial c_{H_2}}{\partial t} + \nabla \cdot N_{H_2} = R_{H_2} = -r$$  \[5-24\]

$$\frac{\partial c_{D_2}}{\partial t} + \nabla \cdot N_{D_2} = R_{D_2} = -r$$  \[5-25\]

$$\frac{\partial c_{HD}}{\partial t} + \nabla \cdot N_{HD} = R_{HD} = r$$  \[5-26\]

where $N_{H_2}$, $N_{D_2}$ and $N_{HD}$ are the molar flux vectors for $\text{H}_2$, $\text{D}_2$ and $\text{HD}$, respectively. The rate of consumption of $\text{H}_2$ and $\text{D}_2$ is equal to the production rate of $\text{HD}$. The reaction
rate in the above equations is not explicitly known. However, the relationship between
the forward and reverse reaction rates in Reaction R15 is given by the following ratio:

\[ K_{eq} = \frac{k_f}{k_r} \] [5-27]

By knowing the equilibrium constant \( K_{eq} \) for the equilibration reaction, the reverse rate
constant can be specified by arbitrarily picking the forward rate constant.

### 5.3.2.2 The Species Transport in Porous Media interface

The Species Transport in Porous Media interface describes species transport between
the fluid, solid and gas phases in saturated and variably saturated porous media. It
applies to one or more species that move primarily within a fluid filling the voids in a
solid porous medium. The interface has the equations, boundary conditions, reaction
rate expressions, and species sources for modelling of species transport solving for the
species concentrations. The main nodes that can be utilised within this interface are:

- Free Flow
- Mobile Fluid, Immobile Solid

These nodes add the equations for the species concentrations, provides an interface for
defining the properties of the porous media (Pd), as well as additional properties
governing diffusion, adsorption and the velocity field which is a model input and comes
from the physics interfaces describing fluid flow (discussed in Section 5.3.3). As
discussed previously, this interface can be coupled to the RE interface and describes the
mass balance on the system.

**Theory of the Species Transport in Porous Media interface**

The ‘Free Flow’ physics node implements the Navier-Stokes equations to describe the
fluid flow in free flowing areas such as an open pipe. The specific equation sets and
principles of this physics node are discussed further in Section 5.3.3.2. The ‘Mobile
Fluid, Immobile Solid’ physics node contains the necessary equations to describe
species transport in porous media, and is discussed further herein. The transport of
chemical species in porous media occurs through diffusion and convection. The mass
balance implemented by this interface is described by the following equation:
\[(\varepsilon_p + \rho_b k_{P,i}) \frac{\partial c_i}{\partial t} + (c_i - \rho_p c_{i_s}) \frac{\partial \varepsilon_p}{\partial t} + \nabla \cdot (c_i \mathbf{u}) = \nabla \cdot \left[ (D_{D,i} + \theta \tau_{F,i} D_{F,i}) \nabla c_i \right] + R_i + S_i \]

[5-28]

where:

- \(\varepsilon_p\) is the porosity of the porous medium
- \(\rho_b\) is the density of the bulk fluid (gas) (kg m\(^{-3}\))
- \(\theta\) is the fluid volume fraction (-)
- \(c_i\) is the concentration of species \(i\) in the gas phase (mol m\(^{-3}\))
- \(\rho_p\) is the solid phase density (kg m\(^{-3}\))
- \(\mathbf{u}\) is the velocity field (m s\(^{-1}\))
- \(c_{i_s}\) is the concentration of species \(i\) sorbed to the solid phase (mol m\(^{-3}\))
- \(R_i\) is a reaction rate expression which accounts for reactions in the solid and gas phase
- \(S_i\) is an arbitrary source term, which can be used to include the effects of a fluid source or sink.
- \(\tau_{F,i}\) is the tortuosity factor for species \(i\) (-) and accounts for the reduced diffusivities due to the fact that the solid grains in the solid phase impede the Brownian motion of the species. [for saturated porous media \(\theta = \varepsilon_p\) and therefore: \(\tau_F = \varepsilon_p^{1/3}\)]
- \(D_{F,i}\) is the single phase diffusivity of species \(i\) (m\(^2\) s\(^{-1}\))
- \(D_{D,i}\) is the dispersion tensor (m\(^2\) s\(^{-1}\)) [no dispersion is accounted for in this work]
- \(k_{P,i}\) is the adsorption isotherm for species \(i\) on the solid phase \([k_{P,i} = \partial c_{i_s} / \partial c_i]\)

Here the reaction rate term \(R_i\) comes from the Reaction Engineering interface or, alternatively, from user specified reaction rates. When modelling hydrogen isotope exchange the user specified reaction rates have been utilised extensively to describe the rate of change of the three species, H\(_2\), D\(_2\) and HD. The dispersion tensor \(D_{D,i}\) has not been implemented as the fluid flow is assumed to suffer from negligible dispersion. This is a reasonable assumption considered the relatively high pressures and small Pd bed size used in experiments. The adsorption isotherm term is also neglected in favour of specified reaction kinetics describing the adsorption and desorption of the species.

The effective diffusivity of each gas species in porous media is defined by:
\[ D_e = \theta \tau F_i D_{F,i} \]  

which appears in the right hand side of equation 5-28. For hydrogen isotope exchange modelling \( \theta = \varepsilon_p \).

The convection term \((c_i u)\) describes the movement of species due to the bulk fluid velocity. The velocity \(u\) used in this interface is inputted via the fluid flow interfaces used in the model. For example, in a 1D model of isotope exchange in a porous Pd bed \(u\) comes from the Darcy’s Law interface. This model input couples the two physics interfaces together. All the other parameters in equation 5-28 are inputted by the user into COMSOL Multiphysics’s ‘Global Parameters’ node. This node applies to all interfaces used in a model.

### 5.3.3 The Fluid Flow interfaces

The CRE module models the transport and conversion of material in chemical reactors. In many of these applications, this includes transport through convection. The module includes a number of physics interfaces for the simulation of fluid flow; both in free channels and in porous media. Fluid Flow interfaces are used to simulate the fluid flow occurring in a system and can be coupled to any other physical process occurring within the system to be modelled. The Fluid Flow branch (contained within the CRE module) has a number of sub-branches to describe the momentum transport. These include:

- The Laminar Flow interface
- The Darcy’s Law interface
- The Free and Porous Media Flow interface

For isotope exchange modelling, only the latter two of these are necessary depending on the geometry of the system to be modelled. The Darcy’s Law interface is used for modelling fluid movement through the interstices in a porous medium where a homogenization of the porous and fluid media into a single medium is done. Together with the continuity equation and equation of state for the pore fluid (gas) this interface can be used to model low velocity flows, for which the pressure gradient is the major driving force. Darcy’s law can be used in porous media where the fluid is mostly influenced by the frictional resistance within the pores.

If the system to be modelled involves transitions between the slow flow in porous media, governed by Darcy’s law, and fast flow in channels described by the Navier-
Stokes equations the Free and Porous Media Flow interface must be used. This interface contains the equations and boundary conditions necessary to describe these types of phenomena. This interface is useful when the geometry of the system is 2D or 3D where there are likely to be areas of free gas flow and areas of porous media flow. In 1D the Darcy’s law interface is sufficient to describe a porous system.

5.3.3.1 The Darcy’s Law interface

The Darcy’s Law interface has the equations, boundary conditions, and mass sources for modelling fluid movement through interstices in a porous medium using Darcy’s law. The main feature is a ‘Fluid and Matrix Properties’ node. This can be specified and provides an interface for defining the fluid material and the porous medium properties such as porosity (\( \varepsilon \)) and permeability (\( \kappa \)).

Theory of the Darcy’s Law interface

In a porous medium, the global transport of momentum by shear stress in the fluid is often negligible because the pore walls impede the momentum transport to the fluid in the space outside the pores. The two phases (porous media and fluid) are therefore treated as a single homogenous phase. Darcy’s law together with the equation of state for the gas and the continuity equation provide a complete mathematical model suitable for applications involving porous media flows, where pressure is the main driving force.

Darcy’s law states that the velocity field of the fluid phase is determined by the pressure gradient, the fluid viscosity and the characteristic structure of the porous medium [63]:

\[
\mathbf{u} = -\frac{\kappa}{\mu} \nabla p
\]  

[5-30]

where \( \kappa \) is the permeability (m\(^2\)), \( \mathbf{u} \) is the velocity field (m s\(^{-1}\)), \( \mu \) is the viscosity (Pa.s) and \( p \) is the pressure (Pa).

The Darcy’s Law interface combines Darcy’s law with the continuity equation in the following manner:

\[
\frac{\partial}{\partial t} (\rho \varepsilon_p) + \nabla \cdot (\rho \mathbf{u}) = Q_m
\]  

[5-31]

where \( \rho \) is the fluid density (kg m\(^{-3}\)), \( \varepsilon_p \) is the porosity of the porous medium and \( Q_m \) is the mass source term (kg m\(^{-3}\) s\(^{-1}\)). The fluid density is described by the ideal gas law:
\[ \rho = \frac{pM}{RT} \]  \hspace{1cm} \text{[5-32]}

where \( R \) is the molar gas constant (J mol\(^{-1}\) K\(^{-1}\)), \( M \) is the molecular mass of the gas, and \( T \) is the temperature of the system (K).

### 5.3.3.2 The Free and Porous Media Flow interface

The Free and Porous Media Flow interface contains the equations and boundary conditions necessary to describe a system where there is free gas and porous media flow areas. The interface uses a combination of the Navier-Stokes equations and the Brinkman equations to describe the momentum transport in each of the two regions. At the interface between the two regions, the implemented boundary condition enforces continuity for the velocity field and the pressure.

**Theory of the Free and Porous Media Flow interface**

In order to describe the free flowing gas section within a model the Navier-Stokes equations for fluid flow are utilised. The Navier-Stokes equations describe the motion of fluid substances. They arise from applying Newton’s second law to fluid motion, together with the assumption that the stress in the fluid is the sum of the diffusing viscous term, which is proportional to the velocity gradient, and pressure term. Solving the Navier-Stokes equations for a particular flow problem reveals the velocity field. This field is a description of the velocity of a fluid at a given point in space and time. The Navier-Stokes equations in their most general form are [63]:

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \tag{5-33}
\]

\[
\rho \frac{\partial \mathbf{u}}{\partial t} + \rho (\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot [-p \mathbf{I} + \tau] + \mathbf{F} \tag{5-34}
\]

\[
\rho C_p \left( \frac{\partial T}{\partial t} + (\mathbf{u} \cdot \nabla) T \right) = - (\nabla \cdot \mathbf{q}) + \mathbf{S} - \tau \frac{\partial p}{\partial T} \mid_{\rho} \left( \frac{\partial p}{\partial t} + (\mathbf{u} \cdot \nabla) p \right) + Q \tag{5-35}
\]

where

- \( \rho \) is the density (kg m\(^{-3}\))
- \( \mathbf{u} \) is the velocity vector (m s\(^{-1}\))
- \( p \) is the pressure (Pa)
- \( \tau \) is the viscous stress tensor (Pa)
• $F$ is the volume force vector (N m$^{-3}$)
• $C_p$ is the specific heat capacity at constant pressure (J kg$^{-1}$ K$^{-1}$)
• $T$ is the absolute temperature (K)
• $q$ is the heat flux vector (W m$^{-2}$)
• $Q$ contains the heat sources (W m$^{-3}$)
• $I$ is a 3x3 identity matrix
• $S$ is the strain-rate tensor:

$$S = \frac{1}{2}(\nabla u + (\nabla u)^T) \quad [5-36]$$

The operation “:” denotes a contraction between tensors defined by:

$$a : b = \sum_n \sum_m a_{nm} b_{nm} \quad [5-37]$$

which can be referred to as the double dot product.

Equation 5-33 is the continuity equation and represents the conservation of mass. Equation 5-34 is a vector equation and represents the conservation of momentum and Equation 5-35 describes the conservation of energy, formulated in terms of temperature.

To close the Navier-Stokes equation system (Equation 5-33 through Equation 5-35), some constitutive relations are needed. If the fluid can be considered Newtonian and the Stoke’s assumption can be applied then the viscous stress tensor becomes:

$$\tau = 2\mu S - \frac{2}{3} \mu (\nabla \cdot u) I \quad [5-38]$$

where the dynamic viscosity $\mu$ (Pa.s) depends on the thermodynamic state of the fluid but not on the velocity field, i.e. the dynamic viscosity does not vary at different points in the velocity field.

In order to describe the flow in porous media, the Free and Porous Media Flow interface employs the Brinkman equations. The flow in porous media is governed by a combination of the momentum balance equation and the continuity equation. These two equations, once combined, form the Brinkman equations:

$$\frac{d}{dt} (\varepsilon \rho) + \nabla \cdot (\rho u) = Q \quad [5-39]$$
\[
\frac{\partial}{\partial t} \left( \rho \left( \frac{\partial u}{\partial t} + (u \cdot \nabla) \frac{u}{e} \right) \right) = -\nabla p + \nabla \cdot \left[ \frac{1}{\rho} \left\{ \mu (\nabla u + (\nabla u)^T) - \frac{2}{3} \mu (\nabla \cdot u) I \right\} \right] - \left( \frac{\mu}{\kappa} + Q \right) u + F
\]

[5-40]

When the flow has variable density, as is the case with gases, the above equations must be solved together with the equation of state which describes the density as a function of temperature and pressure. For gases, the ideal gas law can be used (equation 5-32). The \( Q \) term is the mass source which accounts for mass deposit and creation in domains of the geometry that form the model.

5.3.4 The Heat Transfer in Porous Media Interface

The Heat Transfer in Porous Media interface has been used to describe heat transfer in the porous Pd bed. The interface uses the following form of the heat equation:

\[
\left( \rho C_p \right)_{eq} \frac{\partial T}{\partial t} + \rho G C_{Pg} u \cdot \nabla T = \nabla \cdot (k_{eq} \nabla T) + Q
\]

[5-41]

where:

- \( \rho_G \) is the fluid density (kg m\(^{-3}\)).
- \( C_{pg} \) is the molar fluid heat capacity at constant pressure (J K\(^{-1}\) mol\(^{-1}\)).
- \( (\rho C_p)_{eq} \) is the equivalent volumetric heat capacity at constant pressure.
- \( k_{eq} \) is the equivalent thermal conductivity (W m\(^{-1}\) K\(^{-1}\)).
- \( u \) is the fluid velocity field (m s\(^{-1}\)). \( u \) is the Darcy velocity (described by the Darcy’s Law and Free and Porous Media Flow interfaces) and is the volume flow rate per unit cross sectional area. The average linear velocity (the velocity in the pores) can be calculated as \( u_L = u/\varepsilon \), where \( \varepsilon \) is the fluid’s volume fraction (the porosity of the porous Pd).
- \( Q \) is the heat source (or sink) (W m\(^{-3}\))

The equivalent conductivity of the solid-fluid system, \( k_{eq} \) relates the conductivity of the solid \( k_p \) and the conductivity of the fluid, \( k_G \) by:

\[
k_{eq} = \varepsilon_p k_p + \varepsilon_G k_G
\]

[5-42]

The equivalent volumetric heat capacity of the solid-fluid system is calculated by:

\[
(\rho C_p)_{eq} = \varepsilon_p \rho_p C_{pd} + \varepsilon_G \rho_G C_{pg}
\]

[5-43]
where $\varepsilon_p$ is the solid material’s (Pd) volume fraction, which is related to the volume fraction of the fluid $\varepsilon_G$ (porosity) by:

$$\varepsilon_p + \varepsilon_G = 1$$  \hspace{1cm} [5\text{-}44]

The Heat Transfer in Porous Media interface was used in the kinetic based models described in later sections of this chapter. Heat transfer was not considered in the Foltz and Melius derived COMSOL Multiphysics models based on equilibrium assumptions.

### 5.4 Details of computer purchased for COMSOL Multiphysics

In order to model hydrogen isotope exchange thoroughly and in multiple dimensions a new workstation was needed to compute the model solutions in an acceptable time. The computer purchased for the task was a Dell Precision T5600. The workstation featured dual Intel Xeon E5-2650 processors and had 128 GB of memory (128 GB 1600MHz RAM). Each processor had eight cores, giving a total number of cores available for computation of sixteen. COMSOL Multiphysics has the ability to segregate the number of cores and assign a particular number of cores to each computation. This allowed multiple simulations to be run simultaneously without effecting the overall computation time significantly. The productivity of the workstation was therefore maximised using this technique.

### 5.5 COMSOL Multiphysics Equilibrium Hydrogen Isotope Exchange Model

#### 5.5.1 Introduction

The model developed by Foltz and Melius was extended using COMSOL Multiphysics with the aim of improving modelling results for exchanges performed at higher pressures and temperatures. The model was setup using a 1D geometry representing the packed Pd bed only. Three COMSOL Multiphysics physics interfaces are used in the model: Species Transport in Porous Media, Darcy’s Law and a second Species Transport in Porous Media. The first Species Transport in Porous Media interface is used to describe the transport and reactions occurring on the gas phase species $\text{H}_2$, $\text{D}_2$ and HD. The second Species Transport in Porous Media interface is used to describe the surface species $\text{H}_s$ and $\text{D}_s$ used in this extended version of Foltz and Melius’ model. The
Darcy’s Law interface describes the fluid flow through the porous Pd bed. As described in previous sections, the velocity calculated in this interface is coupled to the two other physics interface, where it is used to calculate the rate of change of the three gas species and two surface species due to convection, diffusion and reactions with the surface of the Pd. The mass balances on the five species are solved to give the change in species as a function of time.

Because the geometry is essentially a straight line (1D) representing the porous media, there is no need for the Free Flow physics nodes to describe the motion of free gas by solving the Navier-Stokes equations. The beginning and end of the geometry represent the boundaries where gas inflow and outflow conditions are specified, respectively.

For the 1 L min\(^{-1}\) sets of experiments the gas inlet pressure ranges from 5.8 – 8 bar. The temperature range for these experiments was 208 – 373 K. The Pd bed length is 0.02105 m and the porosity \(\varepsilon\) was 0.777, accounting for Pd swelling under hydrogen (deuterium) dosing. This swelling occurs in the individual particles that make up the packed Pd bed and represents approximately 10% increase in diameter. The permeability \(\kappa\) value used in the model is varied to fit experimental data. The other fitting parameters are the isotope exchange probability, \(p\) and the equilibrium constant \(K_{eq}\). As identified in the Results section of this work, the concentration ratio \(K_{app}\) (or apparent equilibrium constant) obtained from analysis of experimental gas species concentrations as a function of time, reveals that in flowing experiments occurring at high pressure the reaction \(H_2 + D_2 \rightleftharpoons 2HD\) does not achieve instantaneous equilibrium. The calculated \(K_{app}\) values are significantly less than the \(K_{eq}\) values published in the literature, which are generally obtained through static dosing measurements [9, 40, 47, 60]. Furthermore, Larson et al [70] analysed the concentration ratio for Foltz and Melius’ raw experimental data and found the exiting gas stream from their Pd bed was not in equilibrium at any point in both exchange directions. The calculated \(K_{app}\) values from IsoEx experiments are used as a starting point in each of the COMSOL Multiphysics hydrogen isotope exchange models. These values are then varied to provide improved fits to experimental data.

In the model, the Pd bed is loaded with the appropriate isotope for each exchange direction. The amount of isotope within the Pd bed is specified using known phase relationships [6, 8, 9, 15]. The isotope loading was as follows:
The H₂, D₂ and HD viscosity values used in the model are calculated from the Sutherland equation (equation 5-45) based on the temperature of the exchange reaction:

\[ \mu_i = \mu_0 \frac{T_0 + C}{T + C} \left( \frac{T}{T_0} \right)^{3/2} \]  

where:
\[ \mu_i \text{ is the dynamic viscosity of the gas species at the temperature of the reactor (Pa.s)} \]
\[ \mu_0 \text{ is the reference viscosity at the reference temperature } (T_0) \text{ (Pa.s)} \]
\[ T \text{ is the reactor temperature (K)} \]
\[ T_0 \text{ is the reference temperature (K) } [T_0 = 293.85 \text{ K}] \]
\[ C \text{ is Sutherland’s constant for the gaseous species} \]

The \( \mu_0 \) value for hydrogen is \( \mu_0 = 8.76E-6 \text{ Pa.s} \). Finding the reference viscosity, Sutherland constant and temperature values for D\(_2\) was somewhat difficult. Because of this, the D\(_2\) viscosity was taken from literature [130]. The viscosity of HD was found from the average of the H\(_2\) and D\(_2\) viscosities.

### 5.5.2 COMSOL Multiphysics equilibrium model formulation

The main difference between the model described herein and the MATLAB model described earlier is the treatment of the gaseous species. In the COMSOL Multiphysics equilibrium based model, the gases are treated as molecular rather than atomic species. The Foltz and Melius model has been adapted in this way to provide a more stable model for solution by COMSOL Multiphysics. It also provides a model that is more realistic and comparable to what is occurring within the IsoEx reactor. The formulation of the model is now discussed in more detail. The initial conditions, flow variables and inlet conditions are presented alongside the equations that are used in the model to calculate the reaction rate of each species at each spatial and time point in the Pd bed.

#### Initial conditions

The initial conditions for the three gas species (H\(_2\), D\(_2\) and HD) are as follows:

\[ x_{H2initial} = 0.0001 \]  
\[ x_{D2initial} = \left[ \left( 1 + \left( x_{H2initial} \left( \frac{K_{eq}}{4} - 1 \right) \right) \right)^{1/2} - \left( x_{H2initial} \left( \frac{K_{eq}}{4} \right) \right)^{1/2} \right]^2 \]  
\[ x_{HDinitial} = \left( K_{eq} x_{H2initial} x_{D2initial} \right)^{1/2} \]

For the D-H exchange models the gas phase initial conditions are derived from a known \( x_{H2initial} \) value of 0.0001; specifying that the quantity of free gaseous H\(_2\) in the reactor is
very low. \( x_{D2\text{initial}} \) and \( x_{HD\text{initial}} \) values are derived from the assumption that the gas phase is in equilibrium with the Pd within the reactor. Through algebraic manipulation of the equation for the equilibrium constant \( K_{eq} \) (equation 5-49) the above equations are obtained (equations 5-46 to 5-48).

\[
K_{eq} = \frac{[HD]^2}{[H_2][D_2]} = \frac{x_{HD}^2}{x_{H2}x_{D2}}
\]  

[5-49]

Similarly, for the H-D exchange models the gas phase initial conditions are specified by inputting \( x_{H2\text{initial}} = 0.9999 \).

These initial mole fractions are then combined with the ideal gas law and the initial pressure in the reactor to calculate the initial concentrations of \( H_2 \), \( D_2 \) and \( HD \):

\[
c_{H2\text{initial}} = x_{H2\text{initial}} \left( \frac{P_{\text{initial}}}{RT} \right)
\]  

[5-50]

\[
c_{D2\text{initial}} = x_{D2\text{initial}} \left( \frac{P_{\text{initial}}}{RT} \right)
\]  

[5-51]

\[
c_{HD\text{initial}} = x_{HD\text{initial}} \left( \frac{P_{\text{initial}}}{RT} \right)
\]  

[5-52]

The initial surface concentrations \( H_s \) and \( D_s \) (mol m\(^{-3}\)) are calculated from the following relationships:

\[
c_{Hs\text{initial}} = \left( \frac{K_1 c_{H2\text{initial}} c_{s\text{total}} + K_2 c_{HD\text{initial}} c_{s\text{total}}}{1 + K_1 c_{H2\text{initial}} c_{Hs\text{initial}} + K_2 c_{HD\text{initial}} c_{Hs\text{initial}}} \right)
\]  

[5-53]

\[
c_{Hs\text{initial}} = \left( \frac{c_{HD\text{initial}} c_{s\text{total}} + c_{D2\text{initial}} c_{s\text{total}}}{K_1 c_{H2\text{initial}} + K_2 c_{HD\text{initial}}} \right)
\]  

[5-54]

In the above equations \( K_1 \) and \( K_2 \) are correction factors identified by Larson et al [70]. These corrections were derived from thermodynamic assessments of the statistical relationships Foltz and Melius used to derive the rate constants used in their original model. In their work they related the forward and reverse rate constant for each species to the forward rate constant of hydrogen adsorption and the known separation factor, \( \alpha \). Larson et al [70] found that the relationships derived by Foltz and Melius were not
thermodynamically consistent. They therefore proposed the correction factors $K_1$ and $K_2$ as a means of addressing these inconsistencies:

$$K_1 = \frac{\phi}{\alpha} \quad [5-55]$$

$$K_2 = \frac{1}{\phi \alpha} \quad [5-56]$$

where $\phi = 1.81$ and $\alpha = 2.51$. Thus, in this manner, thermodynamic consistency is achieved while retaining the symmetry of the Foltz and Melius relationships (see Larson et al [70]).

**Inlet conditions**

The inlet conditions describe the characteristics of the gas species entering the reactor. This includes the inflowing concentration of the gas species and the pressure. For improved stability and solution time, the gas entering the reactor is assumed to be in equilibrium. The inlet gas mole fractions therefore take a similar form to Equations 5-46, 5-47 and 5-48:

$$x_{H_2\text{inlet}} = 0.9999 \quad [5-57]$$

$$x_{D_2\text{inlet}} = \left[ \left( 1 + \left( x_{H_2\text{inlet}} \left( \frac{K_{eq}}{4} - 1 \right) \right) \right)^{1/2} - \left( x_{H_2\text{inlet}} \left( \frac{K_{eq}}{4} \right) \right)^{1/2} \right]^2 \quad [5-58]$$

$$x_{HD\text{inlet}} = \left( K_{eq} x_{H_2\text{inlet}} x_{D_2\text{inlet}} \right)^{1/2} \quad [5-59]$$

For the D-H exchange models the inlet $H_2$ mole fraction is specified as $x_{H_2\text{inlet}} = 0.9999$ (as shown above), representing pure $H_2$ flowing into the reactor. For the H-D exchange models, $x_{H_2\text{inlet}} = 0.0001$ representing pure $D_2$ flowing into the reactor. And the subsequent inlet gas concentrations are found in the same way as equations 5-50, 5-51 and 5-52:

$$c_{H_2\text{inlet}} = x_{H_2\text{inlet}} \left( \frac{P_{\text{in}}}{RT} \right) \quad [5-60]$$

$$c_{D_2\text{inlet}} = x_{D_2\text{inlet}} \left( \frac{P_{\text{in}}}{RT} \right) \quad [5-61]$$
\[ c_{HD_{\text{inlet}}} = x_{HD_{\text{inlet}}} \left( \frac{P_{\text{in}}}{RT} \right) \]  

Here, \( P_{\text{in}} \) is the inlet pressure into the reactor. The inlet pressures used in the low pressure and 1 L min\(^{-1}\) isotope exchange experiments are as follows:

**Table 5-5 Inlet gas pressures used in the low pressure D-H exchange COMSOL Multiphysics models**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>208</td>
<td>1.5</td>
</tr>
<tr>
<td>293</td>
<td>1.6</td>
</tr>
<tr>
<td>373</td>
<td>1.7</td>
</tr>
</tbody>
</table>

**Table 5-6 Inlet gas pressures used in the low pressure H-D exchange COMSOL Multiphysics models**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>208</td>
<td>1.5</td>
</tr>
<tr>
<td>293</td>
<td>1.6</td>
</tr>
<tr>
<td>373</td>
<td>1.7</td>
</tr>
</tbody>
</table>

**Table 5-7 Inlet gas pressures used in the 1 L min\(^{-1}\) D-H exchange COMSOL Multiphysics models**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>208</td>
<td>5.8</td>
</tr>
<tr>
<td>293</td>
<td>6.3</td>
</tr>
<tr>
<td>373</td>
<td>8.0</td>
</tr>
</tbody>
</table>

**Table 5-8 Inlet gas pressures used in the 1 L min\(^{-1}\) D-H exchange COMSOL Multiphysics models**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>208</td>
<td>7.5</td>
</tr>
<tr>
<td>293</td>
<td>8.0</td>
</tr>
<tr>
<td>373</td>
<td>8.0</td>
</tr>
</tbody>
</table>

**Flow variables**

During simulations, the mole fractions of the three gas species (\( H_2 \), \( D_2 \) and HD) are calculated as follows:

\[ x_{H_2} = \frac{c_{H_2}}{c_{H_2} + c_{D_2} + c_{HD}} \]  

[5-63]
\[
\begin{align*}
  x_{D_2} &= \frac{c_{D_2}}{c_{H_2} + c_{D_2} + c_{HD}} \\
  x_{HD} &= \frac{c_{HD}}{c_{H_2} + c_{D_2} + c_{HD}}
\end{align*}
\]

[5-64] [5-65]

These mole fraction are subsequently used to calculate the physical properties of the gas in each point in space and time within the COMSOL Multiphysics model. In order to accurately describe the viscosity and density of the gas mixture during the simulations the following equations are used:

\[
\begin{align*}
  \mu_{mix} &= \mu_{H_2}x_{H_2} + \mu_{D_2}x_{D_2} + \mu_{HD}x_{HD} \\
  \rho_{mix} &= \frac{(x_{H_2}M_{H_2} + x_{D_2}M_{D_2} + x_{HD}M_{HD})p}{RT}
\end{align*}
\]

[5-66] [5-67]

where \(M_{H_2}, M_{D_2}\) and \(M_{HD}\) are the molecular masses of \(H_2, D_2\) and \(HD\), respectively.

Reaction rate expressions

COMSOL Multiphysics allows custom reaction rate expressions to be inputted via ‘Reactions’ nodes within the Species Transport in Porous Media interfaces. These Reactions nodes have been utilised in setting up the equilibrium based isotope exchange model. The reaction rate expressions for each of the three gas species and two surface species are now presented. The gas and solid phase reaction rate expressions are derived from the work of Foltz and Melius [1]. However, rather than combine the rate of change of each species into an overall isotope exchange rate the expressions are kept separate. Because the model has been setup to consider molecular species, unlike Foltz and Melius, there is a rate expression for HD.

COMSOL Multiphysics treats species in the Species Transport in Porous Media interface as having volumetric concentrations (mol m\(^{-3}\)) for the purpose of unit consistency while solving the mass balances during model calculations. For this reason, the surface species in the second Species Transport in Porous Media interface, \(H_s\) and \(D_s\), have concentration values in mol m\(^{-3}\). Strict surface reaction expressions require these species to be considered using concentrations per unit area (mol m\(^{-2}\)). In order to convert the volumetric concentrations into surface concentrations the following equations are used:
\[ c_{H_{surface}} = \frac{c_{H_s}}{S_0} \quad [5-68] \]

\[ c_{D_{surface}} = \frac{c_{D_s}}{S_0} \quad [5-69] \]

where \( S_0 \) is the specific surface area of the Pd particles in the packed powder bed (m\(^2\) m\(^{-3}\)). \( c_{H_s} \) and \( c_{D_s} \) are the volumetric concentrations of \( H_s \) and \( D_s \), respectively (mol m\(^{-3}\)). \( c_{H_{surface}} \) and \( c_{D_{surface}} \) are the surface concentrations used in the reaction rate expressions (mol m\(^{-2}\)).

The resulting surface concentrations are used in the reaction rate expressions for the change in gaseous and surface species as a function of time. The rate expressions for the five species considered in the model are shown below:

\[
R_{H_{surface}} = \frac{1}{4} k \left( \frac{8RTa}{\pi M} \right)^{1/2} \left( \frac{\alpha}{\phi} c_{H_{D_{surface}}} + \frac{1}{2} \alpha \phi c_{H_s} c_{D_{surface}} - c_{D_s} c_{H_{surface}} - \frac{1}{2} c_{H_D} c_{D_{surface}} \right) \quad [5-70]
\]

\[
R_{D_{surface}} = \frac{1}{4} k \left( \frac{8RTa}{\pi M} \right)^{1/2} \left( c_{D_2} c_{H_{surface}} + \frac{1}{2} c_{H_D} c_{H_{surface}} - \frac{\alpha}{\phi} c_{D_2} c_{D_{surface}} - \frac{1}{2} \alpha \phi c_{H_2} c_{D_{surface}} \right) \quad [5-71]
\]

\[
R_{H_2_{surface}} = \frac{1}{4} k \left( \frac{8RTa}{\pi M} \right)^{1/2} \left( c_{H_D} c_{H_{surface}} - \frac{\alpha}{\phi} c_{H_2} c_{D_{surface}} \right) \quad [5-72]
\]

\[
R_{D_2_{surface}} = \frac{1}{4} k \left( \frac{8RTa}{\pi M} \right)^{1/2} \left( \frac{\alpha}{\phi} c_{H_D} c_{D_{surface}} - c_{D_2} c_{H_{surface}} \right) \quad [5-73]
\]

\[
R_{HD_{surface}} = \frac{1}{4} k \left( \frac{8RTa}{\pi M} \right)^{1/2} \left( c_{D_2} c_{H_{surface}} + \frac{\alpha \phi}{2} c_{H_2} c_{D_{surface}} - \frac{\alpha}{\phi} c_{H_D} c_{D_{surface}} - \frac{1}{2} c_{H_D} c_{H_{surface}} \right) \quad [5-74]
\]

where \( k \) is the isotope exchange rate constant, \( \alpha \) is the separation factor and \( M \) is the average molecular mass of the three gas species (\( H_2 \), \( D_2 \), and HD); \( M = 3 \) g mol\(^{-1}\). \( \left( \frac{8RT}{\pi M} \right)^{1/2} \) is the thermal velocity \( v \) of a gas molecule and is found from the kinetic theory.
of gases [63, 125]. The above equations can be found through manipulation of the Foltz and Melius equations by expanding the mole fraction descriptions.

The separation factor is known to vary with the gas and solid phase concentrations of the isotopic species [4, 45, 95, 131, 132]. For this reason, this variation is accounted for in the COMSOL Multiphysics models in order to provide a more accurate solution. The variation in the separation factor is different depending on the isotope exchange direction that is being investigated. Two equations are used to account for situations where there is high or low concentrations of deuterium on Pd. These correspond to high initial loadings of deuterium or hydrogen, respectively, and are used accordingly in the D-H or H-D exchange models. The variation in $\alpha$ is incorporated into the model via the following equations:

$$\alpha_{highD} = \frac{4}{\alpha} \left( 1 - \left( \frac{4-K_{eq}}{K_{eq}} \right) \left( \frac{c_{H_2}+\frac{1}{2}c_{HD}}{c_{H_2}+c_{D_2}+c_{HD}} \right) \right)$$  \hspace{1cm} [5-75]

$$\alpha_{highH} = \left( \frac{4}{K_{eq}} + \frac{2c_{H_2}/c_{HD}}{1+2c_{H_2}/c_{HD}} \right) \alpha$$  \hspace{1cm} [5-76]

where $\alpha_{highD}$ and $\alpha_{highH}$ are the separation factors used in D-H and H-D exchange experiments, respectively. These values replace the $\alpha$ values in equations 5-70, 5-71, 5-72, 5-73 and 5-74. As can be seen from the formulation of the above equations, the value of $\alpha_{highD}$ and $\alpha_{highH}$ vary with the concentration of the gas species. The appropriate value of the separation factor can therefore be calculated at each point in space and time during the exchange models, providing an improved and thermodynamically consistent solution. In the above equations $\alpha$ represents the separation factor value based on static measurements. Wicke and Nernst [9] have performed such measurements and subsequently derived an empirical expression to describe the variation in the static separation factor with temperature:

$$ln \alpha = \frac{245}{T} - 0.055$$  \hspace{1cm} [5-77]

The isotope exchange rate constant $k$ used in equations 5-70 - 5-74 follows the same formulation used by Foltz and Melius. $k$ (m$^3$ mol$^{-1}$) is a product of the isotope exchange probability $p$ (-) and the area occupied by a mole of adsorbed H or D atoms, $\sigma$. Therefore:
\[ k = p\sigma \]  
\[ \sigma = \frac{1}{c_{H_{\text{surface}}} + c_{D_{\text{surface}}}} \]

The isotope exchange probability, \( p \) refers to the probability that an isotope exchange event occurs during the collision of a gas phase molecule with the surface. \( p \) is the fundamental kinetic parameter in the COMSOL Multiphysics equilibrium model.

### 5.5.3 Equilibrium based model results

The results of the equilibrium based Foltz and Melius derived modelling using COMSOL Multiphysics are now presented alongside the experimental data obtained on the IsoEx apparatus. Both low pressure (ca. 1.5 bar) and higher pressure (1 L min\(^{-1}\)) exchange experiments are now presented alongside the modelling data. The 1 L min\(^{-1}\) experimental and modelling data have been published in the literature [126] and the author directs the reader to this for additional information regarding these results.

#### 5.5.3.1 Low pressure PdD to PdH exchange modelling results

Figure 7(a) - (c) shows the modelling results for the D-H exchange performed at 208 K, 293 K and 373 K. The modelling data is presented alongside raw experimental data for comparison.
Figure 5-7 Model results for low pressure PdD to PdH isotope exchange experiments; (a) 208 K; (b) 293 K; (c) 373 K
5.5.3.2 Low pressure PdH to PdD exchange modelling results

Figure 8(a) - (c) shows the modelling results for the H-D exchange performed at 208 K, 293 K and 373 K. The modelling data is presented alongside raw experimental data for comparison.
Figure 5-8 Model results for low pressure PdH to PdD isotope exchange experiments: (a) 208 K; (b) 293 K; (c) 373 K
5.5.3.3 1 L min⁻¹ PdD to PdH exchange modelling results

Figure 9(a) – (c) show the modelling results for the D-H exchange performed at 208 K, 293 K and 373 K. The model data are presented alongside the raw experimental data for comparison.
Figure 5-9 Model results for 1 L min$^{-1}$ PdD to PdH isotope exchange experiments; (a) 208 K; (b) 293 K; (c) 373 K
5.5.3.4 1 L min⁻¹ PdH to PdD modelling results

Figure 10(a) – (c) show the modelling results for the D-H exchange performed at 208 K, 293 K and 373 K. The model data is presented alongside the raw experimental data for comparison.
Figure 5-10 Model results for 1 L min\(^{-1}\) PdH to PdD isotope exchange experiments; (a) 208 K; (b) 293 K; (c) 373 K
5.5.3.5 Discussion and analysis of equilibrium based model results

In order to avoid confusion the equilibrium based model (derived from Foltz and Melius [1]) results are now discussed. What is immediately apparent is the differing ability of the model to describe hydrogen isotope exchange at different pressures. The modelling fits to experimental data for the low pressure data are good, particularly for the D-H exchange. The low pressure H-D exchange fits are satisfactory; however, there are evidently issues with matching the later stages of the exchange as well as the HD curves. The low pressure 208 K H-D exchange model data does not fit the later stages of the HD and D₂ signals (Figure 5-8(a)) and the 293 K H-D exchange model data (Figure 5-8(b)) exhibits a significant departure from experimental data, despite significant efforts to manipulate the model variables. Despite these shortcomings, considering the simplicity of the equilibrium based model the low pressure model fits are deemed more than satisfactory.

The fits to the higher pressure 1 L min⁻¹ exchanges are less good, particularly for the H-D exchange. The equilibrium model is incapable of reproducing the higher pressure experimental data. The model consistently over estimates HD production for the 1 L min⁻¹ exchanges. Furthermore, in the H-D exchanges the initial period of near pure H₂ production is not realised in the model data. The model fits to the 1 L min⁻¹ D-H exchanges are better, but still differ from experimental data significantly. Again, HD production is significantly over estimated and the general shape of the curves does not match experimental data. Moreover, in most of the 1 L min⁻¹ exchanges the crossover point of the falling H₂/D₂ signal and rising H₂/D₂ does not match what was observed experimentally.

The main reason for these failings was the inherent instabilities in the model setup. Despite efforts to vary the exchange probability (p), permeability (κ) and the equilibrium constant (K_eq) in order to match experimental data, good fits to experimental data were not possible. Firstly, difficulties were encountered when trying to vary p. Outside a narrow band of values (p = 10⁻⁶ - 10⁻⁷) the model became highly unstable and would not solve to completion, despite trying various numerical solvers available in COMSOL Multiphysics. In some of the 1 L min⁻¹ exchange models it would have been advantageous to vary p beyond these values in order to improve the fits to experimental data. The magnitude of p was found to directly influence the shape
of the HD curve, crossover points of the breakthrough curves and the size of the initial period of ‘pure’ gas (either H\textsubscript{2} or D\textsubscript{2} depending on the exchange direction) at the start of the exchanges. Higher \( p \) values caused a sharpening of the calculated HD curve. If \( p \) values outside the narrow band identified earlier could have been used the model fits may have been improved.

Numerical instabilities were also encountered whilst attempting to vary \( \kappa \) and \( K_{eq} \). \( K_{eq} \) proved particularly troublesome. The author found that when trying to adjust \( K_{eq} \) to the values obtained from analysis of the concentration ratio \( (K) \) (or apparent equilibrium constant) in most of the 1 L min\(^{-1} \) models the values drove the model unstable and subsequently no solution could be obtained. It has been found that adjusting to \( K_{eq} < 2.1 \) causes the equilibrium model to fail. For this reason, the \( K_{eq} \) values used in the equilibrium models were often higher than the \( K \) values calculated from analysis of the effluent gas concentration. \( K_{eq} \) is the variable in the equilibrium model which determines the height of the HD curve. Therefore, using larger \( K_{eq} \) values causes the magnitude of the HD curve to increase, and consequently HD production is over estimated in the models.

It is the author’s opinion that even if these instability issues could be overcome the equilibrium based model would not be sufficient in describing high pressure exchange data. The main problem is the assumption of equilibrium in all spatial and time points in the Pd bed. The assumption of equilibrium is the main driver of the unsatisfactory fits to experimental data. The model does not include a finite treatment of the surface processes and offers no flexibility to trial different adsorption mechanisms, for example Langmuir-Hinshelwood or Eley-Rideal. Furthermore, there is no ability to adjust the kinetics of the individual surface processes to match experimental data. The kinetics of the two step reaction mechanism considered in the model were lumped into an ‘overall isotope exchange rate constant’ \( (k) \), reducing the flexibility of the model to adapt to varied experimental conditions. Because of these reasons, a more advanced and flexible kinetic based model is needed to describe the D-H and H-D exchange processes (particularly for the high pressure).
5.6 COMSOL Multiphysics kinetic hydrogen isotope exchange model

5.6.1 Introduction

In order to try and improve the hydrogen isotope exchange modelling results a new model was developed considering the reaction kinetics for the individual steps in an exchange event. Various studies in the literature have identified individual reaction steps as rate limiting \([2, 3, 32, 70, 133, 134]\). Using the rigorous kinetic model of the exchange process, derived herein, has allowed for the individual rate constants for each reaction step to be elucidated.

Note: The heat effects presented in Chapter 6 are not directly coupled to the kinetics of the exchange process at present. Please refer to the Future Work section for further discussion.

5.6.2 Kinetic model formulation

The following reactions are considered in the kinetic model:

\[
\begin{align*}
H_2 + 2V_s & \rightleftharpoons 2H_s & \text{[R16]} \\
HD + 2V_s & \rightleftharpoons H_s + D_s & \text{[R17]} \\
D_2 + 2V_s & \rightleftharpoons 2D_s & \text{[R18]}
\end{align*}
\]

The above reactions are derived based on the Langmuir-Hinshelwood surface reaction mechanism \([135]\). As identified in the Background chapter of this work, there are a significant number of reaction steps contributing to the overall exchange mechanism. These include: bulk diffusion in the free gas, diffusion in the pores of the Pd packed bed, adsorption of molecular gas species (H\(_2\), D\(_2\) or HD), dissociation of molecular gas species to atomic surface species (H or D), surface diffusion of atomic species, surface to bulk Pd transfer steps (where the atomic species are absorbed into the Pd lattice), bulk diffusion of atomic species within Pd, bulk to surface transfer steps of atomic species, recombination of atomic species to molecular species, and finally, desorption of molecular species.
Due to small nature of the Pd particles used in this study (< 1 µm) the bulk transfer processes bulk diffusion in the Pd lattice are not considered. These processes are known to be rapid [15, 59] and their effect on the overall process can therefore be considered negligible when the particle diameter is small. Other processes not considered in the kinetic model are the dissociation and recombination of molecular species at the Pd surface. These are also considered sufficiently rapid as not to significantly affect the overall exchange process. The main processes considered by the model are the adsorption and desorption steps for each of the molecular gas species (H₂, D₂ and HD). Adsorption and desorption rates are manipulated in the model by varying the forward and reverse kinetic rate constants (k₁, k₁₋₁, k₂, k₂₋₁, k₃ and k₃₋₁) for each of the three reactions identified above. As identified by [33, 66], these processes are generally considered to be the rate limiting steps of the exchange process. In particular, desorption processes have been identified as the most significant in limiting the isotope exchange rate [66]. While it has been noted earlier that the dissociation and recombination processes have not been directly considered, it is important to note that the rates of these processes will be lumped into the forward and reverse rate constants (k_i and k_i₋₁) which are manipulated to fit experimental data.

The model also has the ability to consider surface diffusion of atomic species. However, a sensitivity analysis was performed and this parameter in the model was found to not greatly influence the process, unless very unrealistic values of the surface diffusion coefficient (D₀, surface) were specified, i.e. >10⁻³ m² s⁻¹. Differences in the bulk gas diffusion coefficients of each of the three species (H₂, D₂, and HD) can also be included in the model analysis. Again, however, variation in the individual diffusion coefficient of H₂ (D₇₂), D₂ (D₇₂) and HD (D_HD) had little effect on the model outcome, unless extreme values were specified. Specifying largely different diffusion coefficients for the three species did have some effect, but it is known that the free gas diffusion of the three species is not too dissimilar. D₇₂, D₇₂ and D_HD were thus specified as the same value of 5x10⁻⁶ m² s⁻¹. This simplification is verified further by the knowledge that the isotope exchange model, as setup herein, is a convection driven process where individual diffusion coefficients have little effect on the overall process; the main driver for mass transfer is the momentum and pressure driving forces of the bulk isotopic gas flow into the reactor.
**Rate law expressions**

The following section will identify the rate law expressions used in the COMSOL Multiphysics kinetic model. The reaction rates for the adsorption and desorption steps of R1, R2 and R3 are displayed below:

\[ R_{1\text{ads}} = k_1 c_{H_2} c_{V_2}^2 \quad [5-80] \]

\[ R_{1\text{des}} = k_{-1} c_{H_2}^2 \quad [5-81] \]

\[ R_{2\text{ads}} = k_2 c_{HD} c_{V_2}^2 \quad [5-82] \]

\[ R_{2\text{des}} = k_{-2} c_{H_2} c_{D_2} \quad [5-83] \]

\[ R_{3\text{ads}} = k_3 c_{D_2} c_{V_2}^2 \quad [5-84] \]

\[ R_{3\text{des}} = k_{-3} c_{D_2}^2 \quad [5-85] \]

where \( c_{H_2}, c_{D_2} \) and \( c_{HD} \) are the concentrations of \( H_2, D_2 \) and HD, respectively (mol m\(^{-3}\)). \( c_{H_2}, c_{D_2} \) and \( c_{V_2} \) are the surface concentrations of H, D and vacant sites within Pd (mol m\(^{-3}\)). \( k_i \)'s and \( k_{-i} \)'s are the forward and reverse kinetic rate constants for each reaction, respectively. Strict treatment of surface reactions requires the concentrations \( c_{H_2}, c_{D_2} \) and \( c_{V_2} \) to have units of mol m\(^{-2}\). This was achieved by dividing the volumetric surface concentrations by the specific surface area of the Pd particles, \( S_0 \):

\[ c_{H_{\text{surface}}} = \frac{c_{H_2}}{S_0} \quad [5-86] \]

\[ c_{D_{\text{surface}}} = \frac{c_{D_2}}{S_0} \quad [5-87] \]

\[ c_{V_{\text{surface}}} = \frac{c_{V_2}}{S_0} \quad [5-88] \]

The subsequent surface concentrations \( c_{H_{\text{surface}}}, c_{D_{\text{surface}}} \) and \( c_{V_{\text{surface}}} \) (with units of mol m\(^{-2}\)) are used in the rate law expressions for change of surface species. The reaction rates considering the surface concentrations are shown below:

\[ R_{1\text{ads, surface}} = k_1 c_{H_2} c_{V_{\text{surface}}}^2 \quad [5-89] \]

\[ R_{1\text{des, surface}} = k_{-1} c_{H_{\text{surface}}}^2 \quad [5-90] \]
Combining the above expressions reveals the rate law expressions for each surface species:

\[ R_{H_{surf}} = 2 \left( R_{1_{adsurface}} - R_{1_{desurface}} \right) + \left( R_{2_{adsurface}} - R_{2_{desurface}} \right) \]  
\[ R_{D_{surf}} = 2 \left( R_{3_{adsurface}} - R_{3_{desurface}} \right) + \left( R_{2_{adsurface}} - R_{2_{desurface}} \right) \]  
\[ R_{V_{surf}} = 2 \left( R_{1_{desurface}} + R_{2_{desurface}} + R_{3_{desurface}} - R_{1_{adsurface}} - R_{2_{adsurface}} - R_{3_{adsurface}} \right) \]  

The rate of change of the molecular species H₂, D₂ and HD are therefore:

\[ R_{H_{surf}} = R_{1_{adsurface}} - R_{1_{desurface}} \]  
\[ R_{D_{surf}} = R_{2_{adsurface}} - R_{2_{desurface}} \]  
\[ R_{V_{surf}} = R_{3_{adsurface}} - R_{3_{desurface}} \]  

Species described in COMSOL Multiphysics must have units of mol m⁻³ for the model to run satisfactorily. The overall volumetric rate expressions (in mol m⁻³) for the six species considered in the model can then be found by the following expressions:

\[ R_{H_2} = R_{H_{surf}} S_0 \]  
\[ R_{D_2} = R_{D_{surf}} S_0 \]  
\[ R_{V_2} = R_{V_{surf}} S_0 \]  
\[ R_{H_2} = R_{H_{2surf}} S_0 \]  
\[ R_{HD} = R_{HD_{surf}} S_0 \]
\[ R_{D_2} = R_{H_2 \text{surface}} S_0 \]  

**Kinetic rate constants**

In order to fit experimental data obtained on the IsoEx apparatus the six kinetic rate constants \( (k_1, k_{-1}, k_2, k_{-2}, k_3, k_{-3}) \) are varied accordingly. The initial values of these are chosen arbitrarily for each exchange direction, apart from \( k_{-2} \) (the desorption rate constant for HD) whose value is found according to the equilibrium constant, \( K_{eq} \):

\[ k_{-2} = \frac{k_2}{k_{HD}} \]  

\[ K_{HD} = \sqrt{\frac{K_1 K_3}{K_{eq}}} \]

and

\[ K_1 = \frac{k_1}{k_{-1}} \]

\[ K_3 = \frac{k_3}{k_{-3}} \]

Strict thermodynamic treatment of the model reaction system requires that the rate constant for desorption of HD \( (k_{-2}) \) be specified from the arbitrarily chosen rate constants for the adsorption and desorption of H\(_2\) and D\(_2\) \( (k_1, k_{-1}, k_3, k_{-3}) \). This reduces the fitting parameters in the kinetic model from six to five. It is important to note at this point that in modelling experimental data from the IsoEx apparatus \( K_{eq} \) was also varied in accordance with post experiment analysis of this parameter. After analysing the low pressure and 1 L min\(^{-1}\) IsoEx experiments, as was discussed in the Chapter 4 of this work, it was discovered that \( K_{eq} \) deviated from the statically measured values reported previously in the literature [9]. This variation has been included in the kinetic COMSOL model of the isotope exchange process by specifying \( K_{eq} \) to the value calculated from experimental analysis of the apparent equilibrium constant \( (K_{app}) \) (see chapter 4). The author directs the reader to additional publications in the literature which discuss observations of differing \( K_{eq} \) values in flowing systems [70, 126].
Initial conditions and model setup

The initial conditions for the kinetic model are setup in a similar manner to the equilibrium based model. The H\textsubscript{2} inlet mole fraction \(x_{H_2\text{inlet}}\) is specified appropriately for the exchange direction to be modelled by using the known composition of the gas flowing into and out of the reactor at \(t = 0\), i.e. for D-H exchange \(x_{H_2\text{inlet}} = 0.9999\) and \(x_{H_2\text{out}} = 0.0001\); and for the H-D exchange \(x_{H_2\text{inlet}} = 0.0001\) and \(x_{H_2\text{out}} = 0.9999\). A ramping function \((\text{step}1\left(\frac{t}{t_{\text{step}}}\right))\) is also used in the kinetic model. This ramps the inlet mole fraction function towards the maximum inlet value over a short time \((t_{\text{step}} = 0.1\text{s})\) to avoid dramatic changes in the model initially, which create shocks to the numeric system and cause the solver in COMSOL Multiphysics to make large reductions in the timestep in order to resolve the equations within the specified tolerance. This artificial ramping is deemed acceptable because in reality there would be a short period of time where the inlet conditions would stabilise.

\[x_{H_2\text{inlet}} = x_{H_2\text{out}} + \left(x_{H_2\text{in}} - x_{H_2\text{out}}\right)\text{step}1\left(\frac{t}{t_{\text{step}}}\right)\]  \[5-111\]

The inlet mole fractions of HD and D\textsubscript{2} \((x_{HD\text{inlet}}\) and \(x_{D_2\text{inlet}}\), respectively) are derived from the assumption of equilibrium in the gas phase at entry to the reactor. While in reality this is not strictly true, for model stability it was found that setting the inlet conditions in this manner significantly improved the model solution time.

\[x_{HD\text{inlet}} = \gamma \sqrt{ \left(1 + \left(\frac{2(1-x_{H_2\text{inlet}})}{\gamma}\right)\right)} - 1 \]  \[5-112\]

\[x_{D_2\text{inlet}} = 1 - x_{H_2\text{inlet}} - x_{HD\text{inlet}} \]  \[5-113\]

where \(\gamma = \frac{x_{H_2\text{inlet}}K_{eq}}{2}\) and \(K_{eq}\) is the equilibrium constant for the hydrogen isotope-Pd system \((H_2 + D_2 \rightleftharpoons 2HD)\). Full derivations of the above two equations for the inlet mole fractions can be found in the Supplementary Information supporting this work.

The inlet concentrations of the gaseous species \(([H_2\text{inlet}], [D_2\text{inlet}], \text{ and } [HD_{\text{inlet}}])\) are found from the ideal gas law in the same manner as the equilibrium model. The initial concentrations of the gas species are assumed to be in equilibrium with the Pd at the
start of the model. Therefore, the expressions describing these are similar to those describing the inlet gas conditions (above).

5.6.3 COMSOL Multiphysics kinetic hydrogen isotope exchange model results

The results of the kinetic based COMSOL Multiphysics model are now presented alongside the experimental data obtained on the IsoEx apparatus. Both low pressure (ca. 1.5 bar) and higher pressure (1 L min\(^{-1}\)) exchange experiments are now presented alongside the modelling data.

Note: The model fits to experimental data are subjective. More comprehensive methods of judging the quality of fit was envisaged, but due to time constraints towards the end of the project, this was not possible. The reader should bear in mind the need for model validation and a prescribed method of judging the model fit to experimental data, for example a least squares analysis.

5.6.3.1 Low pressure PdD to PdH exchange kinetic COMSOL Multiphysics modelling results

Figure 5-11(a) – (c) show the kinetic COMSOL Multiphysics modelling results in fitting IsoEx experimental data for the low pressure D-H experiments carried out at ca. 1.5 bar upstream pressure. The modelling data presented below is for the low pressure experiments carried out on a 3 g Pd packed powder bed with bulk density of 3 g cm\(^{-3}\).
Figure 5-11 Kinetic COMSOL model results for low pressure D-H exchanges; (a) 208 K; (b) 293 K; (c) 373 K
5.6.3.2 Low pressure PdH to PdD exchange kinetic COMSOL Multiphysics modelling results

Figure 5-12(a) – (c) show the kinetic COMSOL Multiphysics modelling results in fitting IsoEx experimental data for the low pressure H-D experiments carried out at ca. 1.5 bar upstream pressure. The modelling data presented below is for the low pressure experiments carried out on a 3 g Pd packed powder bed with bulk density of 3 g cm$^{-3}$. 
Figure 5-12 Kinetic COMSOL model results for low pressure H-D exchanges; (a) 208 K; (b) 293 K; (c) 373 K
5.6.3.3 1 L min\(^{-1}\) PdD to PdH exchange kinetic COMSOL Multiphysics modelling results

Figure 5-13(a) – (c) show the kinetic COMSOL Multiphysics modelling results in fitting IsoEx experimental data for the 1 L min\(^{-1}\) D-H experiments carried out at 5.8 bar, 6.3 bar and 7.5 bar upstream pressure for the 208 K, 293 K and 373 K, respectively. The modelling data presented below is for the experiments carried out on a 2 g Pd packed powder bed with bulk density of 2 g cm\(^{-3}\).
Figure 5-13 Kinetic COMSOL model results for 1 L min\(^{-1}\) D-H exchanges; (a) 208 K; (b) 293 K; (c) 373 K
5.6.3.4 1 L min⁻¹ PdH to PdD exchange kinetic COMSOL Multiphysics modelling results

Figure 5-14(a) – (c) show the kinetic COMSOL Multiphysics modelling results in fitting IsoEx experimental data for the 1 L min⁻¹ H-D experiments carried out at 7.5 bar, 8 bar and 8 bar upstream pressure for the 208 K, 293 K and 373 K, respectively. The modelling data presented below is for the experiments carried out on a 2 g Pd packed powder bed with bulk density of 2 g cm⁻³.
Figure 5-14 Kinetic COMSOL model results for 1 L min\(^{-1}\) H-D exchanges: (a) 208 K; (b) 293 K; (c) 373 K
5.6.4 Discussion of COMSOL Multiphysics kinetic modelling results

The results presented in Figure 5-11 - Figure 5-14 show that the COMSOL Multiphysics kinetic based model is more than satisfactory at reproducing experimental data. The effluent concentrations (H₂, D₂ and HD) leaving the reactor as a function of time has been modelled effectively. The overall quality of the fits is remarkable. Very few discrepancies between the experimental and model data are found in any of the above figures. Unlike the equilibrium based model (discussed earlier), the kinetic based model is capable of predicting the effluent concentration leaving the reactor in low and high pressure isotope exchange experiments at varied temperatures. The main variables in the kinetic model were the six rate constants (\(k_i\) and \(k_{-i}\)), the Pd bed permeability (\(\kappa\)) and the equilibrium constant (\(K_{eq}\)). These eight variables were varied in order to provide the best fit to experimental data. The obtained values of these are discussed in the next section of this work.

Despite the overall quality of the kinetic model fits, there are some features of the exchange profiles that could not be recreated by varying the model parameters. Figure 5-11(a) shows the results for the low pressure D-H exchange carried out at 208 K. The timescales of H₂, D₂ and HD appearance have been matched very well; however, the tail of the HD experimental data could not be fitted exactly. The HD signal drops sharply after the peak and follows the diminishing signal of D₂ closely. This sharp decline following the tail end of the D₂ signal could not be recreated despite significant variance of the HD adsorption and desorption rate constants (\(k_2\) and \(k_{-2}\), respectively).

The model fit to the experimental data from the low pressure 293 K is deemed excellent and the author believes little more could be done to improve the fit. Figure 5-11(c) presents the results for the low pressure D-H exchange carried out at 373 K. Again, the kinetic model fit to this data is good. The timescales of the effluent concentrations are good, but the shape of the model HD curve is not quite right. The model curve is too sharp in comparison to the experimental data. The author is confident a better fit could be obtained by further manipulation of the rate constants, particularly those relating to HD production and consumption; \(k_2\) and \(k_{-2}\), respectively. Due to time constraints these additional adjustments could not be carried out.

Figure 5-12 presents the modelling results for the low pressure H-D exchanges. The overall quality of the fits is again remarkable, perhaps even better than the low pressure
D-H exchanges. This is a significant achievement over the equilibrium based (Foltz and Melius derived) model which was incapable of reproducing experimental data for these exchanges both using MATLAB and COMSOL Multiphysics. This alone proves the validity and applicability of the kinetic based model to isotope exchange modelling. There are, like the D-H data, some features of the H-D exchanges which could not be reproduced. Figure 5-12(a) shows the kinetic model data alongside experimental data for the H-D 208 K exchange. The overall fit is again very good. It is only in the later stages of the exchange where the model diverges from experiment data. Both the HD and D₂ curves show slight divergence after ~300 seconds. The author believes this does not indicate any failings in the kinetic model. Additional manipulation of the six rate constants would, almost certainly, bring the model in line with experimental data.

Figure 5-12(b) and (c) show that the kinetic model is capable of reproducing experimental data at increased temperatures and pressures. Similar to the low pressure 208 K these two plots also show there is a small amount of discrepancy between the model results and experimental data in some areas of the exchange profile. It is again the belief of the author that these discrepancies could be removed given time to adjust the rate constants, permeability and $K_{eq}$ values accordingly.

Figure 5-13(a) – (c) show the modelling results for the 1 L min⁻¹ D-H exchanges carried out at 208 K, 293 K and 373 K, respectively. The experimental data for each exchange is reproduced well by the kinetic model again validating the ability of the model to fit data obtained at higher pressure. The model fit for the 208 K exchange is good (Figure 5-13(a)), but there was again some discrepancies in some areas of the exchange profile. For example, in some area the model diverges away from the experimental data. Initially the model data exhibits some anomalous behaviour, which can be observed in the slight bulge on the HD data between 1 – 3 seconds into the exchange. Coinciding with this was a dip in the D₂ model data. These features can be accredited to small instabilities in the numerical solution of the model equations initially, and perhaps a lack of refinement in the spacing of the timesteps at which the equations were solved. These features could be removed by reducing the default spacing of the timesteps used in the model and refining the kinetic rate constants and $K_{eq}$ values.

Figure 5-13(b) shows the model fit to the D-H experimental data obtained at 293 K. The fit is again very good. This was a particularly good achievement due to the nature of the
experimental data recorded at 293 K. As can be seen on the figure the exchange profile is dramatically different to the others. HD production is greatly suppressed compared with the exchanges carried out at low pressure and those at 208 K and 373 K using a flowrate of 1 L min\(^{-1}\). This complicated the fitting procedure and required significantly different rate constant values compared to those used for 208 K and 373 K, including arbitrary specification of the reverse rate constant for HD (\(k_{-2}\)). Considering the difficulty encountered during fitting the experimental data the fit is deemed more than adequate with little scope for improvement.

The model fit to the 1 L min\(^{-1}\) D-H exchange carried out at 373 K is shown in Figure 5-13(c). Again the fit is good. The only significant difference between the model and experimental data is on the tail end of the HD curve (immediately after the peak). Here the experimental data is observed to drop sharply and the model has not reproduced the effect. However, given time to manipulate the rate constants the author believes this feature could be reproduced. If the HD curve could be matched closely it would also likely bring the slight deviation in the model H\(_2\) breakthrough curve into line with the experimental H\(_2\) data.

Figure 5-14(a) – (c) show the modelling results for the 1 L min\(^{-1}\) H-D exchanges carried out at 208 K, 293 K and 373 K, respectively. All the fits are good considering this has been traditionally (according to Foltz and Melius [1]) the exchange direction most difficult to model due to its unfavourable thermodynamic nature. Of all the exchange data discussed previously, however, the largest departure of the model from experiment occurs in the 1 L min\(^{-1}\) 208 K H-D exchange (Figure 5-14(a)). At approximately 10 seconds into the exchange the experimental data was observed to show the ‘crossover’ of the D\(_2\) and H\(_2\) signals occurring before the appearance of HD. The ‘crossover’ of the model data occurs at ~16 seconds and corresponds with the peak of the HD curve, as was observed in all other exchange data. After significant manipulation of the model parameters this experimental feature could not be reproduced. The remainder of the exchange profile was model very well, for instance the HD experimental data is fitted almost perfectly and the later stages of the H\(_2\) and D\(_2\) signals match very well. The author believes there are two possible explanations for the early appearance of the ‘crossover’ of H\(_2\) and D\(_2\) in the experiment: (1) the Pd bed was damaged allowing free H\(_2\) and D\(_2\) gas to permeate through the bed faster; (2) there is a real phenomenon
occurring which is not accounted for in the model. Further experiments and investigation will be required to firmly conclude which explanation is correct.

Figure 5-14(b) shows the ability of the COMSOL Multiphysics kinetic model in reproducing experimental data from the 1 L min\(^{-1}\) 293 K H-D exchange. While the fit is good there are 3 areas that could be improved. Firstly, the model HD data does not fit the initial signals found during experiment. The model HD curve also fails to reproduce the continued low level production of HD observed experimentally after 40 seconds. Furthermore, because of this failure to reproduce the later HD signals the model D\(_2\) curve does not match that observed experimentally. These failures could be removed by further (small) adjustments to the rate constant values and possibly \(K_{eq}\). The focus should be on adjusting \(k_2\), \(k_{-2}\) and \(k_{-3}\).

Finally, Figure 5-14(c) presents the models ability to reproduce the experimental data obtained at 373 K and 1 L min\(^{-1}\) flowrate (\(P_{in} = 8\) bar). The fit was again more than satisfactory. Similarly to the improvements identified previously, slight modifications to the kinetic rate constants and \(K_{eq}\) would cause the model data to fit experiment even closer. It is only due to time constraints that these improvements have not been implemented. Overall, the kinetic model fits to experimental data for the various exchanges was considered good and achieves the project outcomes.

### 5.7 Kinetic Analysis

#### 5.7.1 Introduction

This section outlines the findings from the kinetic analysis of experimental isotope exchange data. By fitting experimental data from low pressure and 1 L min\(^{-1}\) isotope exchange experiments it has been possible to extract kinetic parameters (rate constants) for the various adsorption and desorption reactions considered in the COMSOL Multiphysics kinetic model (Reactions R16, R17 and R18).

The rate constant values, Arrhenius plots and calculated activation energies (\(E_A\)) for each forward and reverse reaction step are now presented.

#### 5.7.2 Kinetic rate constants

Table 5-9 to Table 5-12 show the kinetic rate constants for each of the forward and reverse reactions steps that make up the reversible reactions described shown in earlier
sections of this chapter (Reactions R16, R17 and R18). The rate constants were found by fitting the COMSOL Multiphysics kinetic model to experimental data. Alongside the permeability value (κ), the six rate constants form the only parameters to be varied to fit experimental data.

The kinetic rate constants were derived from subjectively fitting the average experimental data obtained over 3-5 runs. The author therefore notes the potential for inaccuracies and that more experimental work and validation is needed to conclusively determine the surface reaction kinetics. Due to insufficient time during the end of the experimental programme, the kinetic rate constants presented herein could not be actively validated. The proposed validation procedure would involve running a kinetic COMSOL model at a temperature not yet investigated using predicted rate constants from known activation energies (see following discussion sections). Any following investigations using the models derived herein should aim to carry out these validation exercises early in the experimental campaign.

In order to debate the following results without making repeated reference to the above point the kinetic rate constants elucidated here are discussed in a definitive manner. Potential causes of the observed phenomena are presented with the aim of aiding future investigators into the hydrogen isotope exchange process.

The experimentally fitted rate constants used in the kinetic model were as follows.
5.7.2.1 Low pressure exchange rate constants

Table 5-9 Kinetic rate constants obtained from model fitting of low pressure D-H exchange experimental data

<table>
<thead>
<tr>
<th>DtoH 208 K</th>
<th>DtoH 293 K</th>
<th>DtoH 373 K</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
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<td>$k_1$</td>
<td>3.0</td>
</tr>
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<tr>
<td>$k_6$</td>
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<td>$k_3$</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Table 5-10 Kinetic rate constants obtained from model fitting of low pressure H-D exchange experimental data

<table>
<thead>
<tr>
<th>HtoD 208 K</th>
<th>HtoD 293 K</th>
<th>HtoD 373 K</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
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</tr>
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</table>

Table 5-9 and Table 5-10 show the rate constants elucidated from the kinetic model for the low pressure exchange experimental data. All the kinetic rate constants exhibit roughly linear behaviour and increase with temperature, as would be expected from an Arrhenius type relationship.

Table 5-9 shows the majority of the D-H exchange $k_i$ values increase with increasing temperature. The $k_i$ value that didn’t exhibit this behaviour was the $k_{-2}$ values which varied across the temperature range. Table 5-10 shows the fitted rate constant data from the low pressure H-D exchanges carried out at 208 K, 293 K and 373 K. Similarly to the D-H data, the $k_i$ values that do not follow the expected trend with increasing temperature were the $k_{-2}$ values, particularly the value found for the 293K H-D exchange.
5.7.2.2 1 L min⁻¹ exchange rate constants

Table 5-11 Kinetic rate constants obtained from model fitting of 1 L min⁻¹ D-H exchange experimental data

<table>
<thead>
<tr>
<th></th>
<th>DtoH 208 K</th>
<th>DtoH 293 K</th>
<th>DtoH 373 K</th>
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<tbody>
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<td>k₂</td>
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<td>k₃</td>
<td>30.0 m⁻² mol⁻¹ s⁻¹</td>
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</table>

Table 5-12 Kinetic rate constants obtained from model fitting of 1 L min⁻¹ H-D exchange experimental data

<table>
<thead>
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<th>HtoD 208 K</th>
<th>HtoD 293 K</th>
<th>HtoD 373 K</th>
<th>Units</th>
</tr>
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</tr>
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<td>k₂</td>
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<td>k₂</td>
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<td>k₂</td>
<td>15.0 m⁻² mol⁻¹ s⁻¹</td>
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<td>20.0 m⁻² mol⁻¹ s⁻¹</td>
</tr>
</tbody>
</table>

Table 5-11 and Table 5-12 show the rate constants elucidated from the kinetic model for the D-H and H-D 1 L min⁻¹ exchange experimental data. In these data sets some of the \( k_{-2} \) rate constants have the value \( k_2/K_{HD} \). This was because while fitting the kinetic rate constants it was possible to achieve a satisfactory fit to experimental data by only specifying the rate constants of the hydrogen and deuterium adsorption and desorption \( (k_1, k_{-1}, k_3 \text{ and } k_{-3}) \) arbitrarily, and thus being thermodynamic consistent. The value of \( k_{-2} \) (given by \( k_2/K_{HD} \)) for the D-H exchange at 208 K was 3.18. The value of \( k_{-2} \) (given by \( k_2/K_{HD} \)) for the H-D exchange at 293 K was 12.4. In the majority of \( k_{-2} \) values, however, the best fits were achieved by also specifying \( k_{-2} \) arbitrarily until an improved fit was achieved to the experimental data.

Similarly to the low pressure data, many of the rate constant values do exhibit the expected behaviour with respect to temperature.

Table 5-11 and Table 5-12 demonstrate that in both exchange directions at 1 L min⁻¹ flowrate, similarly to the low pressure exchanges, only the \( k_{-2} \) values exhibit non-linear trends with respect to temperature. A likely explanation for this is the fact that HD formation (desorption) is driven entirely by the adsorption of H and D atoms into the Pd
bed. HD formation is therefore technically an intermediate process. Such processes will be more affected by the previous surface processes.

5.7.3 Arrhenius plots

In order to further analyse the elucidated kinetic rate constants Arrhenius plots have been produced in order to determine the activation energies of forward (adsorption) and reverse (desorption) reactions involved in Reactions (R16, R17 and R18). The Arrhenius equation is as follows:

\[ k = Ae^{-Ea/RT} \]  

[5-114]

The Arrhenius equation gives the dependence of the reaction rate constant \((k)\) of a chemical reaction on the absolute temperature \((T)\). Arrhenius plots can be constructed by taking the natural logarithm of the above equation and plotting \(\ln k\) vs. \(1/T\) (or 1000/T). The resulting plot usually takes the form of a straight line with slope \(-Ea/R\). The activation energy \((Ea)\) can therefore be easily determined alongside the pre-exponential factor \((lnA)\). This factor is called the ‘frequency factor’ and represents the number of collisions (which result in a reaction or not) per second.

The author highlights the inevitable inaccuracies in the derived Arrhenius plots due to the lack of experimental data beyond three temperatures and a limited number of experimental repeats. The following discussion sections treat the derived Arrhenius plots in a definitive manner with the aim of highlighting observed trends and potential causes (i.e. reaction mechanisms, pressure and temperature effects), however, the reader should be aware that further experimental validation is required to ensure the activation energies are indeed accurate. The results and discussion presented herein offer a good starting point for further investigation into the kinetics and activation energies of the hydrogen isotope exchange process.

The Arrhenius plots for \(k_1, k_{-1}, k_2, k_{-2}, k_3\) and \(k_{-3}\) for the low pressure and 1 L min\(^{-1}\) exchange experiments are presented below.

5.7.3.1 Low pressure PdD to PdH exchange: plots of \(k_1, k_{-1}, k_2, k_{-2}, k_3\) and \(k_{-3}\)

Figure 5-15(a) – (c) show the Arrhenius plots for the forward and reverse rate constants associated with the low pressure D-H exchange experiment carried out at 1.5 – 1.7 bar. The majority of the plots, namely \(\ln k_1, \ln k_{-1}, \ln k_3,\) and \(\ln k_{-3}\), are linear as would be
expected from an Arrhenius type relationship. The plots for $lnk_2$ and $lnk_{-2}$ do exhibit non-linearity. Figure 5-15(a) – (c) also show that the Arrhenius plots for the forward and reverse rate constants in each of Reactions R16, R17 and R18 have similar trends around the 293 K point. For example, all the plots exhibit a slight ‘kink’ around 293 K, indicating the rate constants at this temperature do not follow a linear trend. However, the magnitude of the deflection in the plots of $lnk_1$, $lnk_{-1}$ $lnk_3$ and $lnk_{-3}$ was insignificant.

The author notes that firm conclusions cannot be drawn until additional experiments at temperatures between those investigated here have been carried out. There is a need for a comprehensive set of experiments, carried out at varied temperatures (whilst keeping the pressure constant) to produce conclusive Arrhenius plots with significant quantification of experimental uncertainties. However, the magnitude of the shift away from linear in the case of the $lnk_2$ and $lnk_{-2}$ plots was significant. In both plots the non-linearity (or anomalous point) occurs at 293 K. This was similar to what was inferred from analysis of the ‘apparent concentration ratio’ in chapter 4 of this work. Here, a shift away from what would be expected from empirical relationships of $K_{eq}$ was also observed at 293 K. The author points the reader to this earlier chapter for a thorough discussion of this observation. The Arrhenius plots of $lnk_2$ and $lnk_{-2}$ have an overall trend exhibiting a positive gradient. This is a recognised feature of an intermediate component in a multistep reaction mechanism, as is the case for HD in hydrogen isotope exchange over Pd. A positive gradient suggests a negative activation energy and a decrease in reaction rate with temperature. Another possibility is that the surface reaction mechanism considered here (Langmuir-Hinshelwood) is incorrect. To address this, the kinetic COMSOL model could be easily modified to consider other mechanisms, such as the Eley-Rideal mechanism. Again, further experimental validation of the findings here would allow firm conclusions to be drawn.
Figure 5-15 Arrhenius plots for (a) $k_1$ and $k_1^{-1}$; (b) $k_2$ and $k_2^{-1}$; and (c) $k_3$ and $k_3^{-1}$ for low pressure D-H exchange.
5.7.3.2 Low pressure PdH to PdD exchange: plots of $k_1$, $k_{-1}$, $k_2$, $k_{-2}$, $k_3$ and $k_{-3}$

Figure 5-16(a) – (c) show the Arrhenius plots for the forward and reverse rate constants associated with the low pressure H-D exchange experiments carried out at 1.5 – 1.7 bar. Similarly to the D-H exchange Arrhenius plots the plots of of $\ln k_1$, $\ln k_{-1}$, $\ln k_3$ and $\ln k_{-3}$ (Figure 5-16(a) and (c)) can be considered linear. The plots of $\ln k_2$ and $\ln k_{-2}$ were non-linear. Moreover, the shift (or temperature value causing the shift) was 293 K as was the case for the low pressure D-H Arrhenius plots. In this case (H-D exchange) the plots of $\ln k_2$ and $\ln k_{-2}$ exhibited a negative trend, suggesting an increase in the reaction rate with increased temperature and a positive activation energy, contrary to that found for the low pressure D-H exchange. Such behaviour around 293 K could also point towards a “jump” in activation energy in a narrow span around this temperature, which would give rise to two connected almost straight line portions on the Arrhenius plots [136]. Further experimentation at a number of other temperatures would be needed to confirm/disprove this hypothesis.
Figure 5-16 Arrhenius plots for (a) $k_1$ and $k_{-1}$; (b) $k_2$ and $k_{-2}$; and (c) $k_3$ and $k_{-3}$ for low pressure H-D exchange.
5.7.3.3 1 L min⁻¹ PdD to PdH exchange: plots of $k_1$, $k_{-1}$, $k_2$, $k_{-2}$, $k_3$ and $k_{-3}$

Figure 5-17(a) – (c) show the Arrhenius plots for the forward and reverse rate constants associated with the 1 L min⁻¹ D-H exchange experiment carried out at 5.5 – 8 bar. Figure 5-17(a) shows the Arrhenius plots for $k_1$ and $k_{-1}$. Both $\ln{k}_1$ and $\ln{k}_{-1}$ can be considered linear and therefore exhibit the expected behaviour with respect to temperature. Furthermore, the plots Arrhenius plots relating to the rate constants for the adsorption/desorption of D₂ ($\ln{k}_3$ and $\ln{k}_{-3}$, respectively) also exhibit the expected Arrhenius behaviour with respect to temperature. Figure 5-17(b) and (c) show the Arrhenius plots for $k_2$ and $k_{-2}$, respectively. The plots of $\ln{k}_2$ and $\ln{k}_{-2}$ had trends which were highly irregular and non-linear, similar to that found from the low pressure exchanges for the rate constants relating to HD production/consumption. The likely cause of these non-linear Arrhenius plots is the intermediate nature of the HD molecule and its surface reactions [136].
Figure 5-17 Arrhenius plots for (a) $k_1$ and $k_{1i}$; (b) $k_2$ and $k_{2i}$; and (c) $k_3$ and $k_{3i}$ for 1 L min$^{-1}$ D-H exchange
5.7.3.4 1 L min⁻¹ PdH to PdD exchange: plots of \( k_1, k_{-1}, k_2, k_{-2}, k_3 \) and \( k_{-3} \)

Figure 5-18(a) – (c) show the Arrhenius plots for the forward and reverse rate constants associated with the 1 L min⁻¹ H-D exchange experiment carried out at 5.5 – 8 bar. Like the 1 L min⁻¹ D-H exchange Arrhenius plots, the logarithmic data for the \( H_2 \) and \( D_2 \) forward and reverse rate constants (\( k_1, k_{-1}, k_3, k_{-3} \), respectively) exhibit linear behaviour with respect to temperature. Figure 5-18(b) shows the Arrhenius plots for \( k_2 \) and \( k_{-2} \). Here, the plots of \( \ln k_2, \ln k_{-2} \), had roughly linear trends with only a slight deflection, again around the 293 K \( k_2 \) and \( k_{-2} \) values.
Figure 5-18 Arrhenius plots for (a) $k_1$ and $k_{i1}$; (b) $k_2$ and $k_{i2}$; and (c) $k_3$ and $k_{i3}$ for 1 L min$^{-1}$ H-D exchange.
5.7.4 Activation energies ($E_a$)

The activation energy ($E_a$) of a chemical reaction represents the energy barrier that must be overcome for the reaction to proceed. The concept was first introduced by Swedish scientist Svante Arrhenius in 1889 [137]. This section introduces the calculated $E_a$ and pre-exponential factor ($A$) values derived from the experimental data obtained on the IsoEx apparatus. The pre-exponential factor represents the total number of collisions with the Pd surface, whether they lead to a reaction or not. Linear trendlines have been plotted through the data displayed on Figure 5-15 - Figure 5-18 in order to elucidate the activation energy ($E_a$) of each forward and reverse reaction considered in the COMSOL Multiphysics model (Reactions R16, R17 and R18). The logarithmic form of the Arrhenius equation has been applied to the linear trendlines through the three points associated with each rate constant to elucidate the activation energies. The resulting $E_a$ values and pre-exponential factors ($A$) are shown below.

The following sections present the derived activation energies obtained from linear fits to the Arrhenius plots presented in the previous sections. As was highlighted previously, the kinetic constants found herein cannot be considered definitive due to the possibility of experimental inaccuracies arising from potential artefacts arising from the experimental setup, and lack of numerous experimental repeats. Further investigation at other temperatures to those investigated here (and more repeats) would allow a thorough suit of data to be produced permitting detailed quantification of the experimental uncertainty. The following analysis has been written with respect to the available data and do go into detail. The reader is advised to treat the data with caution until further investigation has been carried out to validate the findings presented herein.
5.7.4.1 Low pressure exchange activation energies

Table 5-13 Activation energies and pre-exponential factors for the low pressure (a) D-H and (b) H-D exchanges

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Ea (kJ mol⁻¹)</th>
<th>A (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>k₁ (H₂ + 2Vₛ → 2Hₛ)</td>
<td>2.5</td>
<td>10.0</td>
</tr>
<tr>
<td>k₁ (2Hₛ → H₂ + 2Vₛ)</td>
<td>2.6</td>
<td>6.4</td>
</tr>
<tr>
<td>k₂ (HD + 2Vₛ → Hₛ + Dₛ)</td>
<td>-2.1</td>
<td>0.7</td>
</tr>
<tr>
<td>k₂ (Hₛ + Dₛ → HD + 2Vₛ)</td>
<td>-1.9</td>
<td>0.9</td>
</tr>
<tr>
<td>k₃ (D₂ + 2Vₛ → 2Dₛ)</td>
<td>7.2</td>
<td>33.0</td>
</tr>
<tr>
<td>k₃ (2Dₛ → D₂ + 2Vₛ)</td>
<td>3.4</td>
<td>14.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Ea (kJ mol⁻¹)</th>
<th>A (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>k₁ (H₂ + 2Vₛ → 2Hₛ)</td>
<td>12.1</td>
<td>26.0</td>
</tr>
<tr>
<td>k₁ (2Hₛ → H₂ + 2Vₛ)</td>
<td>5.8</td>
<td>4.9</td>
</tr>
<tr>
<td>k₂ (HD + 2Vₛ → Hₛ + Dₛ)</td>
<td>11.1</td>
<td>65.0</td>
</tr>
<tr>
<td>k₂ (Hₛ + Dₛ → HD + 2Vₛ)</td>
<td>3.3</td>
<td>1.9</td>
</tr>
<tr>
<td>k₃ (D₂ + 2Vₛ → 2Dₛ)</td>
<td>5.3</td>
<td>15.0</td>
</tr>
<tr>
<td>k₃ (2Dₛ → D₂ + 2Vₛ)</td>
<td>3.6</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 5-13 (a) shows the activation energies and pre-exponential factors (or frequency factor) for the forward and reverse reactions involved in the low pressure D-H exchange. $E_a$ values for each of the reaction steps is shown in kJ mol⁻¹. The H₂ adsorption and desorption ($k₁$ and $k₋₁$) $E_a$ values are 2.5 kJ mol⁻¹ and 2.6 kJ mol⁻¹, respectively. This demonstrates that the forward and reverse reactions have similar activation energies, with a slightly higher value calculated for the desorption $E_a$. The $A$ value for these two reaction steps are 10 and 6.4, respectively. The overall frequency of H₂ colliding with the Pd surface was therefore greater than the frequency of H₂ desorption events, as would be expected in this exchange direction. However, the $A$ value for $k₋₁$ was relatively large in comparison to the value for $k₁$. This suggests that there was still significant H₂ desorption events occurring; possibly due to continued H₂ adsorption on the Pd surface causing neighbouring Hₛ species to desorb.

The D₂ adsorption and desorption ($k₃$ and $k₋₃$) $E_a$ values were 7.2 kJ mol⁻¹ and 3.4 kJ mol⁻¹, respectively. This indicates that for adsorption of D₂ to occur a larger energy barrier must be surpassed compared to that of the desorption $E_a$ value. An explanation for this is Pd’s increased affinity for H₂. H₂ is preferentially adsorbed over D₂, and therefore the probability of further D₂ adsorption/absorption in this exchange would be reduced significantly (and hence, a larger $E_a$ value was calculated). The lower $E_a$ value for H₂ adsorption supports this hypothesis. The $k₃$ and $k₋₃$ $A$ values were 33 and 14, respectively. This suggests there were a large number of potential adsorption and desorption collisions (involving D₂) occurring during this exchange direction. The author highlights the good fit to the experimental data in all exchanges, however, the
dynamic (non-steady state) nature of the experiments will have introduced inevitable inaccuracies in the elucidated $E_a$ values.

The calculated $E_a$ values for the adsorption and desorption of HD are negative. This indicates a decrease in reaction rate with increasing temperature. This suggests that both adsorption and desorption reactions are slower/occur less frequently at increased temperature. A possible explanation of this could be that higher temperatures favour direct formation of H$_2$ and D$_2$ rather than HD. While firm conclusions on the HD activation energies cannot be made due to the non-linear shape of the Arrhenius plots, when a linear trend line was fitted to the data displayed on Figure 5-15(b) a rough overall positive trend was found and enabled approximate $E_a$ values for the HD forward and reverse reactions to be elucidated. Negative activation energies (resulting from a positive gradient Arrhenius plot) can also be interpreted as an indication that there exists a more complicated mechanism than a single activated energy barrier. For example, the activation energy may be temperature dependent or not constant [136]. Furthermore, negative $E_a$ values can also be an indication of a more complicated reaction mechanism (i.e. there are several mechanisms that are active at the same time) not considered in the COMSOL Multiphysics model. In some reactions involving multistep reaction mechanisms the $E_a$ value has been shown to “jump” over a narrow temperature span, resulting in an Arrhenius plot with two connected straight line portions [136]. The low pressure D-H Arrhenius plots do show signs of this behaviour, but more experimentation would be needed to confirm these observations. One possible explanation for the change in $E_a$ could be the influence of sub-surface and bulk sites within the Pd powder. Mavrikis [138-140] found that the sub-surface sites within Pd can act to lower the activation energy of surface processes under certain conditions.

Comparing the calculated $E_a$ values for the low pressure H-D exchange it can be seen in Table 5-13(b) that the energies are significantly higher than those found for the low pressure D-H exchange. H-D exchange is less favourable thermodynamically since Pd has a greater affinity for hydrogen, and this is a likely explanation for these findings. Less easily explained are the high $E_a$ values for the adsorption reactions of H$_2$ and HD (from $k_1$ and $k_2$), 12.1 kJ mol$^{-1}$ and 11.1 kJ mol$^{-1}$, respectively. These are significantly higher than the calculated values for desorption of H$_2$ and HD, 5.8 kJ mol$^{-1}$ and 3.3 kJ mol$^{-1}$, respectively. The initial loading of the Pd could affect the calculated activation
energies. The Pd was initially loaded at its maximum possible uptake due to H loading and therefore there would be fewer sites available for additional hydrogen adsorption, creating a higher calculated energy barrier. Alternatively, the incoming D$_2$ flow coupled with the high porosity of the Pd bed could be sufficient to swamp the desorbing H$_2$ and HD species, driving them through the bed with low quantities of additional adsorption, and hence a higher calculated $E_a$ value. However, the author refers the reader to Figure 5-16(b) and stresses the apparent non-linear shape of the Arrhenius plots relating to HD adsorption/desorption kinetics. Figure 5-16(a) and (c) can be considered linear, but some non-linearity may still exist since the plots do appear to have two straight line regions. In both cases, this could imply that the Arrhenius equation is not applicable in this situation, or there are more complicated reaction pathways at work that have not been accounted for in the COMSOL Multiphysics kinetic model.

Figure 5-16(c) shows the Arrhenius plot for the adsorption and desorption rate constants for D$_2$ in the low pressure H-D exchange. The two plots ($k_3$ and $k_{-3}$) are linear and therefore show Arrhenius behaviour with respect to temperature. The derived $E_a$ values for adsorption and desorption are 5.3 kJ mol$^{-1}$ and 3.6 kJ mol$^{-1}$, respectively. Here the $E_a$ value for adsorption of D$_2$ is significantly lower than the values calculated for H$_2$ and HD. This is surprising given the preferential adsorption of H$_2$ over D$_2$ in Pd [9, 15, 56]. Due to the dynamic nature of the experiments, the increased pressure of the incoming gaseous D$_2$ could affect the apparent preferential adsorption of H$_2$ and HD over D$_2$ observed in static Sievert’s type experiments [9, 15, 56, 132]. The D$_2$ flowing into the packed bed had a higher pressure than the isotopic species contained within the Pd bed, and was flowing into the reactor at significantly higher amounts. It is probable that the large, instantaneous influx of high pressure D$_2$ and the reduction in bed overpressure (due to opening the reactor outlet valve) allowed greater quantities of D$_2$ to adsorb on the Pd bed. This would explain the increased D$_2$ rate constant values ($k_3$ and $k_{-3}$) and subsequent low $E_a$ values elucidated for the low pressure H-D exchange. The desorption $E_a$ value calculated from fitting a linear trend line to the $k_{-3}$ data was similar in magnitude to the value derived for desorption of HD. Both values are comparable smaller than the desorption $E_a$ value for H$_2$ ($k_{-1}$). This suggests that HD and D$_2$ desorption are more likely to occur than H$_2$ desorption. This agrees with the earlier findings that show the H-D exchange occurring over a longer time period as D$_2$ ‘struggles’ to displace the entire H atom reserves in the Pd bed.
Overall the magnitude of the activation energies calculated from fitting the low pressure experimental data are of the order of those found by Luo et al [60]. They found significantly lower activation energies while investigating hydrogen isotope exchange in a Sievert's type apparatus. They compared their findings to those of Carstens and Encinias [3] and concluded their values were lower because of a lower build-up of impurities in their static dosing apparatus compared to the flow apparatus used by Carstens and Encinias and Foltz and Melius [1]. Considering the IsoEx rig was already supplied with ultra-pure gases which were passed through additional in line gas purification, it is reasonable to assume that at the low pressures of these experiments impurity build-up was also kept to a minimum during the low pressure experiments. Consequently, the activation energies found here are more comparable to those found by Luo [60].

### 5.7.4.2 1 L min⁻¹ exchange activation energies

Table 5-14 Activation energies and pre-exponential factors for the 1 L min⁻¹ (a) D-H and (b) H-D exchanges

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Ea (kJ mol⁻¹)</th>
<th>A (s⁻¹)</th>
<th>Reactions</th>
<th>Ea (kJ mol⁻¹)</th>
<th>A (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>k₁ (H₂ + 2Vₛ → 2Hₛ)</td>
<td>15.3</td>
<td>26984.0</td>
<td>k₁ (H₂ + 2Vₛ → 2Hₛ)</td>
<td>9.3</td>
<td>61.0</td>
</tr>
<tr>
<td>k₁ (H₂ → H₂ + 2Vₛ)</td>
<td>13.4</td>
<td>11772.0</td>
<td>k₁ (2Hₛ → H₂ + 2Vₛ)</td>
<td>8.4</td>
<td>198.0</td>
</tr>
<tr>
<td>k₂ (HD + 2Vₛ → Hₛ + Dₛ)</td>
<td>15.4</td>
<td>6539.0</td>
<td>k₂ (HD + 2Vₛ → Hₛ + Dₛ)</td>
<td>5.0</td>
<td>128.0</td>
</tr>
<tr>
<td>k₂ (Hₛ + Dₛ → HD + 2Vₛ)</td>
<td>12.2</td>
<td>1592.0</td>
<td>k₂ (Hₛ + Dₛ → HD + 2Vₛ)</td>
<td>11.2</td>
<td>638.0</td>
</tr>
<tr>
<td>k₃ (D₂ + 2Vₛ → 2Dₛ)</td>
<td>12.2</td>
<td>390.0</td>
<td>k₃ (D₂ + 2Vₛ → 2Dₛ)</td>
<td>3.6</td>
<td>87.0</td>
</tr>
<tr>
<td>k₃ (2Dₛ → D₂ + 2Vₛ)</td>
<td>5.5</td>
<td>73.0</td>
<td>k₃ (2Dₛ → D₂ + 2Vₛ)</td>
<td>2.7</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Table 5-14 shows the calculated activation energies from fitting linear trendlines through the Arrhenius plots (Figure 5-17 and Figure 5-18) for the 1 L min⁻¹ D-H exchange (labelled (a)) and the H-D exchanges (labelled (b)).

The activation energies for the 1 L min⁻¹ D-H exchange (Table 5-14(a)) were significantly higher than those obtained from the low pressure experiments (Section 5.7.4.1). The range of $E_a$ values here are similar to those calculated by Carstens and Encinias [3] who performed their experiments at pressures similar to those used in this work (ca. 6 bar). However, they did not analyse the individual rate constants of the complex reaction mechanism and only calculated overall activation energies for the two exchange directions. The Arrhenius plots for $k₁$ and $k₋₁$ (Figure 5-17(a)) were linear
and therefore the calculated $E_a$ values from the Arrhenius equation are more reliable. The adsorption $E_a$ was (like the low pressure exchanges) higher than the value for desorption. This was a consistent finding for all gas species ($\text{H}_2$, HD and $\text{D}_2$) in the D-H exchange. Conversely, the $\text{D}_2$ adsorption $E_a$ value was lower than that of $\text{H}_2$ and HD. The Arrhenius plots for $\text{H}_2$ and $\text{D}_2$ (Figure 5-17) were linear which adds weight to these findings, while the plot for the HD adsorption/desorption rate constants were non-linear but exhibited a negative trend. Furthermore, the $\text{D}_2$ desorption $E_a$ was significantly lower than any other calculated values for the D-H exchange. This was to be expected considering the direction of exchange and the higher affinity Pd has for H atom loading compared with D atoms. It is probable that this causes the low $E_a$ for $k_{-3}$. The author highlights the slightly non-linear Arrhenius plots (Figure 5-17(c)) as a source of uncertainty, however, it appears that under the conditions investigated here (i.e. high pressure) and the dynamic nature of the experiments that $\text{D}_2$ adsorption/desorption faces a lower energy barrier for surface interactions to occur, compared with $\text{H}_2$ and HD. Large amounts of $\text{H}_2$ adsorption from the incoming gas would cause increased $\text{D}_2$ desorption as the $\text{H}_2$ front moved through the Pd bed. This displaced $\text{D}_2$ front may adsorb to the Pd surface further along the axial distance ($z$) of the bed, occupying vacant sites. The author believes it may be possible that additional $\text{D}_2$ adsorption may encounter a lower energy barrier on, or at neighbouring, sites where D atoms are already adsorbed. There is the possibility that this additional $\text{D}_2$ adsorption may be occurring on the ‘transitional’ tetrahedral sites in the Pd bed. There was also uncertainty about the affect the bulk Pd sites have on the adsorption/desorption $E_a$ values. Surface to bulk transfer (and vice-versa) steps were not considered in the COMSOL Multiphysics model. Additionally, bulk diffusion within the Pd lattice was not considered in the model. It is known that D atoms diffuse at a faster rate through Pd than H atoms [15, 59] and it is probable that this would have an effect on this exchange reaction where $\text{D}_2$ and D atoms were being displaced by incoming $\text{H}_2$.

The $E_a$ values for individual rate constants for the 1 L min$^{-1}$ H-D exchange are shown in Table 5-14(b). What was immediately obvious was the magnitude of the calculated $E_a$ values for this exchange direction. They were significantly lower than those found for the 1 L min$^{-1}$ D-H exchanges. Another noticeable finding was the frequency factor, $A$, which was found to also be lower (for all the kinetic rate constants) than the 1 L min$^{-1}$ D-H exchanges. This suggests that the number of successful (or unsuccessful) collisions
with the Pd surface was lower in the H-D exchange direction; which would be expected considering the thermodynamically unfavourable nature of this exchange. This finding would also contribute to the increased timescale of the 1 L min\(^{-1}\) H-D exchanges compared to the 1 L min\(^{-1}\) D-H exchanges.

The lower \(E_a\) values were more difficult to explain with the most probable explanation being the differing experimental conditions between the 1 L min\(^{-1}\) D-H and 1 L min\(^{-1}\) H-D exchanges. The 1 L min\(^{-1}\) H-D exchange experiments were carried out at a higher upstream pressure compared to the D-H exchanges due to the difference in viscosity of H\(_2\) and D\(_2\). This would have caused a number of differences in the experimental regime, for example, with regards to gas velocity through the Pd bed, molecular collision frequency with the Pd surface and the overall pressure differential over the Pd bed (driving force). Furthermore, one must not ignore the influence of the heat effects occurring during the two exchange directions. During the endothermic H-D exchange direction the localised bed temperature decreases significantly, while in the D-H exchange the localised bed temperature increases sharply. It is probable that the decrease in bed temperature in the vicinity of the Pd surface encourages adsorption of both H and D atoms, which may manifest itself in a lower calculated \(E_a\) value in dynamic (non-steady state) experiments such as those investigated here. The reverse would be true for the D-H exchange direction, whereby localised heating would reduce adsorption rates and thereby increase the recorded \(E_a\) values. The author notes that additional experimentation would be needed to confirm if these hypotheses are true. In particular, it would be advisable to carry out some steady state experiments (at low gaseous concentrations) to reduce the influence of temperature fluctuations on the fitted rate constants.

In the 1 L min\(^{-1}\) H-D exchanges the \(k_{-2} E_a\) value (HD desorption) was found to be noticeably larger than the other surface reaction processes. This was surprising since HD production was significant during the experiments. However, the \(E_a\) value is found from the slope of the Arrhenius plot. A large \(E_a\) value results from a steep slope on the Arrhenius plot, which arises if the surface process was significantly affected by temperature. Referring to Figure 5-14, it is evident that there was a significant change in HD production with increasing temperature (refer to the profile in each figure). The \(k_3\) and \(k_{-3} E_a\) values were found to be appreciably less than those for the
adsorption/desorption of H\textsubscript{2} (\(k_1\) and \(k_{-1}\)). This indicates that the surface processes involving D\textsubscript{2} had a smaller energy barrier to overcome compared with those involving H\textsubscript{2}. This was again surprising considering the thermodynamically unfavourable nature of the H-D exchange direction, and Pd’s preference for H atom adsorption/absorption. The dynamic nature of the experimental methodology and the subsequent high pressure influx of D\textsubscript{2} molecules could be the explanation for the low adsorption \(E_a\) value. The author highlights the increasing inlet pressure and higher viscosity of the D\textsubscript{2} gas during the 1 L min\textsuperscript{-1} H-D exchanges. These conditions would affect the model fitted rate constants and therefore the elucidated \(E_a\) values. Moreover, there may be some variance in the adsorption/desorption kinetic rate constants due to pressure, i.e. the rate constants are pressure dependent. If this was the case, the rate constants would be significantly affected under the dynamic conditions of the IsoEx experiments. Another possible explanation, which would need significant additional investigation to prove, is the influence of additional sites in the Pd lattice. Tetrahedral sites could offer additional sites for D\textsubscript{2} molecules to adsorb which would also result in lower \(E_a\) values being elucidated from the COMSOL Multiphysics model. Furthermore, it is probable that these additional sites may become more influential as the localised temperature of the Pd bed is reduced during the endothermic H-D exchange direction. The low desorption \(E_a\) value for D\textsubscript{2} was less surprising considering the thermodynamics of the Pd-H-D system. Qualitatively, one would expect the desorption \(E_a\) value for D\textsubscript{2} to be lower due to Pd’s greater affinity for H atoms.

The \(k_1\) and \(k_{-1}\) \(E_a\) values were found to be the highest of all the surface processes in the 1 L min\textsuperscript{-1} H-D exchanges. It is likely that this was due to a number of factors. Firstly, the adsorption \(E_a\) value was the highest. The explanation of this could reside in the fact that initially the Pd was saturated with H atoms meaning there were fewer available sites for H\textsubscript{2} adsorption during the exchange. This phenomenon would be further confounded by the lack of availability of transitional sites (tetrahedral) for H atom adsorption. The high desorption \(E_a\) value for H\textsubscript{2} arises from the thermodynamics of the Pd-H-D system. H atoms are preferentially adsorbed/absorbed into the Pd lattice over D atoms. Desorption of H atoms therefore encounters an energy penalty, resulting in a greater calculated \(E_a\) value for \(k_{-1}\).
The magnitude of the activation energies found for the 1 L min⁻¹ exchanges were more comparable to those found by Carstens and Encinias [3] and Outka and Foltz [2]. This was despite the inlet gas pressure being significantly higher in the current work. The explanation for this could reside in the fact that even though impurities were removed to sub-ppb levels in the IsoEx rig, the build-up over time due to higher pressure would affect the activation energies. In essence, although the gases were ultra-pure, impurities still exist, which under higher pressure would be colliding with (and adsorbing to) the Pd surface in greater quantities. This enhanced build-up of impurities on the surface would increase the activation energies akin to those found by Carstens and Encinias [3] and Outka and Foltz [2], who used lower quality gases with no additional in line purification.

5.7.5 Reaction rate data for H₂, D₂ and HD

COMSOL Multiphysics has been used to provide data on the instantaneous reaction rate of H₂, D₂, HD, Hₛ, Dₛ and Vₛ occurring in the Pd bed at specific times in exchange models. The resulting plots (discussed below) allow the reader to visualise the profiles of \( R_{H_2} \), \( R_{D_2} \), \( R_{HD} \), \( R_{H_s} \), \( R_{D_s} \) and \( R_{V_s} \) (Reactions R16, R17 and R18) along the axial distance \( z \) in the Pd bed. These plots arise from fitting kinetic parameters to experimental data. The fitted kinetic rate constants drive the reaction rate expressions (Reactions R16, R17 and R18) which are displayed on the following plots.

The following sections aim to give the reader an understanding of how the reaction progresses as a function of time within the Pd bed, in terms of the surface and gaseous species concentrations. The figures presented in the next section essentially plot the evolution of the hydrogen isotope exchange reaction based on the derived kinetics from earlier sections of the thesis. Because of the previously highlighted issues with regards to experimental artefacts and the need for additional experiments and subsequent model validation, the modelling results need to be treated with some caution. However, the main objective here is to provide the reader with additional, traditionally unobtainable, information regarding the surface reaction species. The following data show how, if the reaction kinetics can be thoroughly validated, the behaviour of the reaction front, consumption of gaseous/surface species and insights into reaction mechanisms can be derived from the kinetic COMSOL Multiphysics model. Furthermore, the data presented herein aim to show how the existence of additional influential areas (i.e.
subsurface regions, other surface sites and crystal structures) of the Pd bed could be elucidated using the kinetic model.

While there may be inaccuracies in the current work, due to insufficient time, regarding the kinetics, activation energies and lack of extensive model validation. The current model provides future researchers with a useful tool to investigate hydrogen isotope exchange. The data presented henceforth could be validated in tandem with the validation exercise proposed for the derived kinetics. Once the kinetics of the hydrogen isotope exchange process have been determined conclusively through experimentation and model fitting, the following reaction rate data would provide a valuable insight into the phenomena occurring within the Pd bed as a function of time. This would enable novel and valuable insights into the hydrogen isotope exchange process (and Pd-H-D system) not previously reported in the literature.

5.7.5.1 Low pressure PdD to PdH exchange reaction rate profiles (208 K):
Figure 5-19(a) – (c) and Figure 5-20(a) – (c) show the reaction rate profiles for the gaseous and surface species for the low pressure D-H exchange carried out at 208K, respectively. The profiles arise from fitting experimental data using the reaction rate constants \( k_1 \) and \( k_{-1} \) considered in the COMSOL Multiphysics model. Figure 5-19(a) shows the \( \text{H}_2 \) reaction rate profile at various times in the exchange reaction. What is immediately evident is the high initial rate of reaction of gaseous \( \text{H}_2 \) at the front of the Pd bed at 1 second (blue line). The peak is high and sharp representing a large consumption of \( \text{H}_2 \) within the first 0.002 m of the Pd bed. As time progresses the rate at the entrance is seen to drop. At 10 seconds (red line) the rate of consumption of \( \text{H}_2 \) drops by half at the front of the Pd bed. The rate profile begins to spread and \( \text{H}_2 \) reaction is occurring over a larger portion of the Pd bed. As more time passes the \( \text{H}_2 \) volumetric reaction rate profile stretches and \( \text{H}_2 \) is consumed over the majority of the Pd bed at smaller rate than observed initially. After 50 seconds (pink, yellow and black lines on Figure 5-19(a)) the rate is relatively constant and a stretched exchange front is observed to move through the Pd bed. This suggests that after the high initial rate at the entrance of the Pd bed there is significant \( \text{H}_2 \) still present in the Pd bed undergoing continued reaction.
Figure 5-19 Low pressure D-H exchange reaction rate profiles (208 K): (a) H₂; (b) D₂; (c) HD. The legend shows the different sample times used in the chart (seconds).
Figure 5-19(b) shows the volumetric reaction rate profile for D$_2$. As would be expected at the entrance to the Pd bed, a large formation of D$_2$ is recorded which coincides with the large H$_2$ consumption. As time progresses the rate of D$_2$ formation remains high and a consistent front moves through the Pd bed. From 5 – 20 seconds (green, red and aqua lines) the leading edge of the D$_2$ front is observed to drop below the x-axis. This represents D$_2$ consumption immediately ahead of the advancing D$_2$ front. This indicates that some of the D$_2$ gas that has been displaced is indeed adsorbing to the Pd surface ahead of the D$_2$ front.

Figure 5-19(c) shows the volumetric reaction rate profile of gaseous HD species. At 1 second (blue line) there is a high rate of HD formation (shown by the positive values on Figure 5-19(c)) at the entrance to the Pd bed as would be expected upon admission of H$_2$ gas. Within 0.1 cm this high rate of formation becomes a high rate of consumption of HD gas. As time progresses a similar trend is observed (see pink line). HD formation continues over larger portions of the initial parts of the Pd bed before the trend switches and HD is consumed. The switch occurs at the point (axial distance (z)) in the Pd bed where the D$_2$ formation and H$_2$ consumption fronts are. Looking at Figure 5-19(a) - Figure 5-19(c), whenever H$_2$ was consumed (and therefore reacting with the PdD surface) there was a front of D$_2$ being formed slightly ahead by HD reacting with the surface. The author notes that the formation rate of D$_2$ is significantly higher during the entire low pressure 208 K PdD to PdH exchange reaction.

Figure 5-20(a) – (c) present the volumetric reaction rate profiles of the surface species ($R_{H_s}$, $R_{D_s}$ and $R_{D_{2s}}$) at the same time intervals as Figure 5-19. Firstly, the reaction rate values for the surface species are significantly higher than those calculated for the gaseous species. This is because for every gas molecule that adsorbs to the Pd surface, two surface species are created. Figure 5-20(a) shows the profiles of H$_s$. At 1 second there was a high rate of Hs formation, coinciding with the high rate of H$_2$ consumption shown on Figure 5-19(a). As time progresses, like the H$_2$ profile but mirrored, the rate of formation of H$_s$ begins settle to a lower value (ca. 1500 mol m$^{-3}$ s$^{-1}$) and the profile is observed to stretch over a greater axial distance. The formation of H$_s$ species is mirrored by a similar rate of consumption of D$_s$ species, which coincides with the peaks observed on Figure 5-19(b) for D$_2$ formation (see pink lines). The previously discussed D$_2$ adsorption ahead of the front (Figure 5-19(b) at 5 – 20 seconds) can also be seen on
Figure 5-20(b) and (c) as a formation of D₅ species and consumption of vacant sites (V₅).

Another interesting feature present on the 1 second profiles on Figure 5-20(a) – (c) is the generation of V₅ immediately after the high initial consumption of D₅ (and V₅) and formation of H₅. This peak can be seen at ~0.025 m axial distance on Figure 5-20(c). The peak coincides with D₅ consumption and therefore represents D₂ desorption leaving vacant sites which are not filled by addition of H₅ species. Figure 5-20(b) shows that at 5 seconds (green line) displaced D₂ gas adsorbs to the Pd surface, generating D₅ species, which refill the vacant sites generated early in the exchange.
Figure 5-20 Low pressure D-H exchange surface species reaction rate profiles (208 K): (a) H\textsubscript{s}; (b) D\textsubscript{s}; (c) V\textsubscript{s}. The legend shows the different sample times used in the chart (seconds).
5.7.5.2 Low pressure PdD to PdH exchange reaction rate profiles (293 K):

Figure 5-21(a) – (c) and Figure 5-22(a) – (c) show the volumetric reaction rate profiles for the gaseous and surface species considered in the COMSOL Multiphysics kinetic model. One noticeable feature which was different to the data for the 208 K experiments was the size of the reaction rate of all species. The calculated rates from fitting the rate constants to experimental data were greater than those at 208 K, as would be expected. Figure 5-21(a) and (b) demonstrate the extremely high initial (at 1 second) rates of reaction at the beginning of the Pd bed (see blue lines). Here H$_2$ consumption is mirrored with D$_2$ generation almost exactly. Figure 5-21(c) shows that at 1 second (blue) HD was produced at the very beginning of the Pd bed, but immediately after it is consumed through displacement of additional D$_2$. As time progresses the HD profiles start to show continued generation over more of the Pd bed as incoming H$_2$ is reacting with residual D atoms in Pd.

Interestingly, after 50 seconds (pink) the rates associated with the exchange front settle to lower values than seen on the 208 K exchange experiments (Figure 5-19(a) – (c)), i.e. the height of the H$_2$, D$_2$ and HD peaks in the 208 K experiment are higher than those obtained at 293 K. The rate of H$_2$ consumption and D$_2$ generation in the 293 K data settle at ~700 mol m$^{-3}$ s$^{-1}$, while HD peaks at ~150 mol m$^{-3}$ s$^{-1}$ after 20 seconds. This explains the delayed appearance and smaller quantity of HD in the experimental data, as well as the longer period D$_2$ at the start of the experiment (Figure 5-11(b)). It is also likely that the suppressed peaks at 293 K are linked to the lower permeability (κ) found at this temperature. A lower permeability means less H$_2$ gas made its way into the Pd bed, and therefore lower reaction rates would be observed. This hypothesis is supported by comparing the location of the exchange front in the 208 K and 293 K data (Figure 5-19 and Figure 5-21). Looking at the 50 second data, it is clear to see that in the 208 K exchange the exchange front was at approximately 0.0125 m, whereas in the 293 K data the front was at an axial distance of z = 0.0075 m. This phenomenon was also evident in Figure 5-11(a) and (b). The appearance of HD takes approximately double the time in the 293 K exchange. Furthermore, the HD peak is significantly lower in the 293 K experimental data, corresponding to the lower reaction rates presented on Figure 5-21(a) – (c).

Figure 5-22(a) – (c) show the volumetric reaction rates for the surface species in the 293 K exchange. Figure 5-22(a) shows that there was a high initial rate of formation of H$_s$
which is accompanied by high rates of consumption of D₈ and V₈. After 20 seconds the rate of H₈ generation settles around 1000 mol m⁻³ s⁻¹ and forms a constant shape front that progresses through the Pd bed. Figure 5-22(b) shows the rate profile for D₈. After the initial high rate of consumption the rate profiles move above the x-axis signifying generation of D₈. This accompanies a reduction in V₈ (Figure 5-22(c)) which indicates that the displaced D₂ species was adsorbing to surface sites further down the Pd bed. This can be observed on Figure 5-21(b) where the D₂ species drops below the x-axis signifying consumption.
Figure 5-21 Low pressure D-H exchange reaction rate profiles (293 K): (a) $\text{H}_2$; (b) $\text{D}_2$; (c) HD. The legend shows the different sample times used in the chart (seconds)
Figure 5-22 Low pressure D-H exchange surface species reaction rate profiles (293 K): (a) H; (b) D; (c) V. The legend shows the different sample times used in the chart (seconds)
5.7.5.3 Low pressure PdD to PdH exchange reaction rate profiles (373 K):

Figure 5-23(a) – (c) present the volumetric reaction rate profiles for H$_2$, D$_2$ and HD for the low pressure 373 K D-H exchange. Similar trends are observed to the two previous temperature exchanges. There is a high initial rate of H$_2$ consumption accompanied by a high D$_2$ generation rate. Again, the HD rate profiles start in generation as would be expected with the incoming H$_2$ gas stream. The profiles then quickly fall into consumption as the displaced HD species progress further into the Pd bed and react to form additional D$_2$. Figure 5-23(b) shows the rate profiles of D$_2$. These can be seen to drop below the x-axis signifying consumption of D$_2$ species. For example, the red line on Figure 5-23(b) shows that at 10 seconds there is significant D$_2$ consumption approximately half way through the Pd bed. This consumption can also be seen on Figure 5-24(b) as significant generation of D$_3$ species and reduction in V$_s$.

Referring to Figure 5-24(c), it can be seen that the magnitude of the consumption of V$_s$ is lower than the other two exchanges carried out at 208 K and 293 K. This corresponds to a lower maximum possible total loading of isotopic species in Pd at 373 K. There are therefore less overall sites available for adsorption and consequently less vacant sites are consumed/occupied. A similar trend was observed in the H$_s$ and D$_s$ species.
Figure 5-23 Low pressure D-H exchange reaction rate profiles (373 K): (a) H₂; (b) D₂; (c) HD. The legend shows the different sample times used in the chart (seconds)
Figure 5-24 Low pressure D-H exchange surface species reaction rate profiles (373 K): (a) $H_s$; (b) $D_s$; (c) $V_s$. The legend shows the different sample times used in the chart (seconds).
5.7.5.4 Low pressure PdH to PdD exchange reaction rate profiles (208 K):

Figure 5-25(a) – (c) present the volumetric reaction rate profiles for H\textsubscript{2}, D\textsubscript{2} and HD, respectively, obtained from modelling the 208 K H-D exchange experimental data. Immediately there are significant differences to the data obtained for the favourable D-H exchanges. First of all the magnitude of the reaction rates is far less than observed in the D-H exchanges. Figure 5-25(a) shows the rate profiles for H\textsubscript{2}. The profiles show that at the start of the exchange (ca. 1 second (blue line)) there is a relatively high generation of H\textsubscript{2} at the beginning of the Pd bed. This high generation then tails off over the whole length of the Pd bed, rather than falling into sharp defined peaks as observed in the D-H exchanges. H\textsubscript{2} is therefore being generated throughout the Pd bed at the start (ca. 1 second) of the experiment, albeit in low quantities. This suggests that at the start of the experiment low amounts of H\textsubscript{2} are generated by desorption of H\textsubscript{s} species throughout the Pd bed and it is not only residual H\textsubscript{2} gas in the reactor that appears at the start of the experimental data (Figure 5-12(a)). This can also be seen on Figure 5-26(a) (blue line). The surface rate profile of H\textsubscript{s} shows that this species is consumed throughout the Pd bed at the start of the experiment.
Figure 5-25 Low pressure H-D exchange reaction rate profiles (208 K): (a) H\textsubscript{2}; (b) D\textsubscript{2}; (c) HD. The legend shows the different sample times used in the chart (seconds)
The general observation at all times on Figure 5-25(a) is that H₂ is generated throughout the Pd bed, suggesting that H₂ gas persists in the bed as the reaction proceeds. This would be expected considering hydrogen has a greater affinity for the Pd surface compared with deuterium [9, 15]. Figure 5-25(c) shows the rate profiles for HD. The profiles shown here are wide indicating that HD is reacting over large portions of the Pd bed. This coincides with what was observed for H₂.

Figure 5-25(b) shows the volumetric reaction rate profiles of D₂ at different times in the Pd bed. Interestingly, compared to the profiles of H₂ (and HD) the initial rate of reaction of D₂ is very high (see blue line). This represents a large consumption of D₂ species at the entrance to the Pd bed. However, looking at Figure 5-25(a) it is obvious that this consumption is not producing similar quantities of H₂. Figure 5-26(c) shows that the D₂ is in fact adsorbing onto vacant sites on the Pd surface (blue line). This explains the low production rates of H₂ and HD that are observed at 1 second into the exchange. After 1 second the rate profiles show that the rate of D₂ consumption falls over time as the D₂ front makes its way through the Pd bed. At 50 seconds (pink line on Figure 5-25(b)) the rate is almost constant throughout the majority of the bed. Past 50 seconds (yellow and black lines) there remains a low rate of D₂ consumption indicating that the exchange reaction continues for significantly longer than the more thermodynamically favourable D-H exchanges.

Figure 5-26(c) shows the rate profiles of Vs. What is clear from this figure is that in this exchange direction the vacant sites play a greater role in the exchange reaction compared to the D-H exchange. By comparing Figure 5-26(b) with Figure 5-26(c) one can see that the production of Dₛ sites is closely linked with the consumption of Vₛ indicating that adsorbing Dₛ species are occupying vacant sites rather than displacing Hₛ species (see the low consumption of Hₛ in Figure 5-26(a)).
Figure 5.26 Low pressure H-D exchange surface species reaction rate profiles (208 K): (a) $H_s$; (b) $D_s$; (c) $V_s$. The legend shows the different sample times used in the chart (seconds).
5.7.5.5 Low pressure PdH to PdD exchange reaction rate profiles (293 K):

Figure 5-27(a) – (c) show the volumetric reaction rate profiles for H₂, D₂ and HD for the 293 K H-D exchange. The general shape of the gaseous species rate profiles are similar to those observed at 208 K. The peak reaction rate values are slightly less than those at 293 K. The reason for this is similar to that explained for the low pressure 293 K D-H exchange. The fitted permeability value (κ) for this exchange direction was lower than both the 208 K and 373 K exchanges. This causes less gas to permeate into the Pd bed, and consequently less reaction can take place. A further consequence of this was the observed fronts (of H₂, D₂ and HD) occur at lower axial values than observed in the 208 K exchange. The low κ value could be due to the influence of additional physical phenomena not considered in the COMSOL Multiphysics model. For instance, diffusion in the bulk Pd lattice was not considered. This could have a significant influence on the gas speed of travel through the bed, and it is possible that at 293 K the effects of diffusion in the bulk were more pronounced than in the other temperatures investigated here. There remains a need for more experiments to determine confidently whether this hypothesis is correct.
Figure 5.27 Low pressure H-D exchange reaction rate profiles (293 K): (a) H$_2$; (b) D$_2$; (c) HD. The legend shows the different sample times used in the chart (seconds).
Figure 5-28 Low pressure H-D exchange surface species reaction rate profiles (293 K): (a) Hs; (b) Ds; (c) Vs. The legend shows the different sample times used in the chart (seconds).
Figure 5-28(a) – (c) shows the volumetric reaction rate profiles of the surface species (Hₜ, Dₜ and Vₛ). The general trends were again similar to those observed at 208 K. Figure 5-28(a) shows again the importance of the vacant sites (Vₛ) in this exchange direction. Adsorption of D₂ takes place almost entirely on vacant sites. Little consumption of Hₜ sites was observed compared to Dₜ generation and Vₛ consumption. Figure 5-28(a) shows that after 20 seconds there was a small amount of Hₜ generation corresponding to adsorption of HD. This furthers the hypothesis that H₂ and Hₜ species persist in this exchange direction far longer than in the D-H exchange. This was observed in reality as the increased length of time the H-D experiments take to compete (Figure 5-12).

Another evident feature of this exchange was that HD was a major source of Hₜ and Dₜ generation (see Figure 5-27(c) and Figure 5-28(a) and (b)).

5.7.5.6 Low pressure PdH to PdD exchange reaction rate profiles (373 K):

Figure 5-29(a) – (c) present the volumetric reaction rate profiles of H₂, D₂ and HD for the low pressure 373 K H-D exchange. The general shape of this plots are similar to those observed for the 208 K and 293 K exchanges. The overall peak reaction rates are higher than those of 208 K and 293 K, as would be expected for the highest temperature exchange. The peaks in the 373 K exchange are more defined indicating a sharper front moving through the Pd bed. Another difference occurs in the rate profiles for H₂ (Figure 5-29(a)). Here, after 10 seconds (red line), and approximately half way through the Pd bed, H₂ is consumed. This indicates H₂ undergoes further adsorption immediately ahead of the displaced H₂ front moving through the Pd bed. Figure 5-29(a) and (c) also demonstrate that the H₂ and HD fronts move through the bed roughly at the same speed, with the HD front just in front.

Figure 5-30(a) – (c) show the reaction rate profiles of Hₜ, Dₜ and Vₛ for the low pressure 373 K PdH to PdD exchange. Figure 5-30(a) presents the data for Hₜ. As was previously described, after 10 seconds the additional H₂ adsorption ahead of the displaced H₂ front can be seen in the generation of Hₜ species. Furthermore, the high initial rate of D₂ adsorption can be accounted for by the consumption of Hₜ species (desorption of H₂) and Vₛ species alike, rather than by Vₛ alone as was the case in the previous lower temperature exchanges. This suggests that at this temperature incoming D₂ gas has sufficient energy to displace Hₜ species, forming H₂. In general, the rates of
H₃ consumption stay higher in the 373 K exchange than any of the other low pressure H-D exchanges.

Figure 5-30(b) shows the D₃ reaction rate profile. After the initial high rate, the profiles are observed to drop dramatically to lower values as time progresses. At greater lengths of time (ca. 50 seconds) the generation of D₄ sites was mainly accounted for by the adsorption of HD species (see Figure 5-29(c) and Figure 5-30(b)). The leading edge of the front at 50 seconds (pink line) corresponds to the HD consumption peak. The tail edge of this front was produced by D₂ adsorption, which at this time was quite low in comparison to HD consumption. This indicated that at later times in this exchange HD is the main source of D₃ (and H₃) generation in the Pd bed.
Figure 5-29 Low pressure H-D exchange reaction rate profiles (373 K): (a) H₂; (b) D₂; (c) HD. The legend shows the different sample times used in the chart (seconds).
Figure 5-30 Low pressure H-D exchange surface species reaction rate profiles (373 K): (a) H; (b) D; (c) V. The legend shows the different sample times used in the chart (seconds).
5.7.5.7 1 L min⁻¹ PdD to PdH exchange reaction rate profiles (208 K):

Figure 5-31(a) – (c) present the volumetric reaction rate profiles of H₂, D₂ and HD for the 208 K 1 L min⁻¹ D-H exchange. Figure 5-32(a) – (c) show the surface reaction rate profiles for Hₜ, Dₜ and Vₜ, respectively. The figures have considerably less lines plotted on them because the exchange at this pressure (ca. 5.5 bar) occurs much more rapidly than those at low pressure. Another immediate observation is the magnitude of the reaction rate peaks in these figures. The reaction rates under these conditions are considerably higher than those at low pressure. This suggests that the reaction rates are dependent on the pressure of the exchange experiment. According to traditional theory this can be explained by the number of collisions with the Pd surface. At high pressure molecules collide with the surface more frequently, leading to an increased probability of interaction. Furthermore, at higher pressure the proportion of molecules possessing the required energy (activation energy Eₐ) for reaction increases.

Figure 5-31(a) shows the reaction rate profiles for H₂. At the start of the experiment (ca. 1 second (blue line)) the rate of reaction at the entrance to the Pd bed is very high with a peak value of ~8500 mol m⁻³ s⁻¹. This peak indicates that after 0.5 seconds the H₂ front has made its way through approximately half of the Pd bed. As time progresses the reaction rate profile spreads indicating H₂ was being generated over a large portion of the Pd bed. Figure 5-31(b) presents the profiles for D₂. Coinciding with the H₂ consumption peak at 0.5 seconds (blue), was a large generation of D₂, as would be expected. Immediately after this peak, was a zone where D₂ was consumed. This signifies that displaced D₂ species were moving through the Pd bed and undergoing further adsorption creating additional Dₜ sites (which can be seen in Figure 5-32(b)). At 1 second (green line) this adsorption zone was found to grow and the reaction rate increased, creating additional Dₜ species in place of vacant sites Vₜ (see Figure 5-32(c)) further down the Pd bed. This was an interesting finding because in the areas of the Pd bed where this additional D₂ adsorption was occuring the octahedral sites within the Pd lattice should have been occupied by D atoms from the start of the experiment. This raises the question as to where the additional D atoms were adsorbing. It is possible that the displaced D₂ was adsorbing to tetrahedral sites within the Pd bed. Evidence of tetrahedral site occupation by D atoms has been found previously [44, 54]. Another possibility is that the incoming/adsorbing D₂ species were causing D atoms to migrate onto available tetrahedral sites within the Pd lattice, freeing up octahedral sites for D₂ to
adsorb into. Tetrahedral sites are known to act as a transitional state in octahedral-octahedral site hopping within Pd [43, 52]. The exact explanation for this observation will require further investigation, both in terms of experiments and modelling. Some of the additional D₈ species generation downstream of the displaced D₂ can also be accredited to HD adsorption (see Figure 5-31(c)).

By 10 seconds into the exchange (pink) very little D₂ was being generated in the majority of the bed, despite there being H₂ consumption. The H₂ consumption observed in the later stages of the exchange was accounted for by the formation of new H₈ species and generation of HD with the residual D₈ surface species (see Figure 5-31(c) and Figure 5-32(a)).

Figure 5-32(c) shows the reaction rate profile for Vₛ. Interestingly it appears that the vacant sites only play a significant role in the exchange during the initial stages of the exchange at 208 K. This can be seen by the two large consumption peaks on the figure. After 1 second the rate of consumption of Vₛ drops significantly. Again, this consumption of vacant sites was driven by the additional adsorption of D₂ as it progresses down the axial distance of the Pd bed. To a lesser extent the drop was also accredited to adsorption of HD created during the initial H₂ interaction with D atoms on the Pd surface. This HD adsorption also aids in enhancing the progress of H₈ generation in the Pd bed. This can be observed on Figure 5-32(a) as the spreading of the green line across the axial distance in correspondence with the H₂ gas front (Figure 5-31(a)) and the HD gas front (Figure 5-31(c)). The two fronts combine to enhance the reach of the H₈ front.
Figure 5-31 1 L min$^{-1}$ D-H exchange reaction rate profiles (208 K): (a) H$_2$; (b) D$_2$; (c) HD. The legend shows the different sample times used in the chart (seconds).
Figure 5-32 1 L min⁻¹ D-H exchange surface species reaction rate profiles (208 K): (a) H⁺; (b) D⁺; (c) V⁺. The legend shows the different sample times used in the chart (seconds).
5.7.5.8 1 L min⁻¹ PdD to PdH exchange reaction rate profiles (293 K):

Figure 5-33(a) – (c) show the volumetric reaction rate profiles of H₂, D₂ and HD for the 293 K 1 L min⁻¹ D-H exchange. Figure 5-34(a) – (c) show the volumetric surface reaction rate profiles of Hₛ, Dₛ and Vₛ, respectively. One immediately obvious difference from the 208 K data is the sharpness of the reaction rate peaks. The peak values are also significantly higher than the 208 K exchange. Both H₂ consumption and D₂ generation reactions proceed through the Pd bed in very sharp fronts. Furthermore, there was far less HD produced by H₂ collisions with the PdD surface, which was evident from the low HD reaction rate peaks on Figure 5-33(c) (ca. 700 mol m⁻³ s⁻¹). This suggests that more H₂ collisions with the Pd surface were resulting in direct D₂ desorption. This hypothesis is supported by the large consumption peaks immediately after the displaced D₂ peaks on Figure 5-33(b). Here, D₂ was being adsorbed onto vacant sites on the Pd surface (see Figure 5-34(c)). What was also evident from the data for Vₛ was that any HD that was generated was adsorbed onto vacant sites, leaving little remaining in the free gas. This can be seen on the Vₛ consumption peak at 0.5 seconds nearest to the start of the axial distance. Further evidence of this can be seen on Figure 5-13(b). The experimental data shows almost no HD appearing in the first 10 seconds of the experiment. After 10 seconds, the HD peak arrives in a suppressed form. This all points to an increased likelihood of direct H₂ to D₂ exchange with reduced HD production as an intermediate at 293 K. The reason for this could again be the existence and influence of sub-surface sites within Pd [122-124]. Another possible explanation is the existence of additional surface reaction mechanisms, such as the Eley-Rideal mechanism, which were not considered in the COMSOL Multiphysics model.

The above findings agree with the low value of the equilibrium constant (Kₑ𝑞) found during experimentation for the 293 K exchange; Kₑ𝑞 = 0.25. This low value compared with the value obtained from static Sievert’s type experiments (Kₑ𝑞 = 3.25) indicates that little HD was produced and direct D₂ desorption may be favoured. The reason behind this cannot be fully elucidated currently; more experiments at temperatures in the vicinity of 293 K are needed alongside different formulations of the kinetic model allowing for the existence of sub-surface and bulk sites within Pd.

Another interesting feature of these plots is the increasing distance between the displaced D₂ front and the D₂ front that is undergoing additional adsorption further into
the Pd bed. This can be observed using the 2.5 second line (red) on Figure 5-33(b). The
D₂ generation (displaced) peak corresponding with H₂ adsorption and reaction occurs at
approximately 0.005 m, while the second D₂ consumption (adsorption) peak can be seen
at approximately 0.017 m. This demonstrates that D₂ gas moves faster through a
deuterided Pd bed (PdD) than H₂, which is slowed by large scale reaction. In reality it
appears that the additional D₂ adsorption (immediately after the displaced D₂ peak)
moves quickly through the Pd bed. Again, the influence of tetrahedral transition sites
could be an explanation for this finding. The additional D₂ adsorption was accounted for
by consumption of vacant sites entirely. However, as described in the 208 K paragraph,
the available ‘stable’ octahedral sites would be occupied due to initial loading of Pd into
the β-phase. Therefore, this additional D₂ adsorption could be occurring on tetrahedral
sites, or the D₂ adsorption was possibly causing D atoms residing in octahedral sites to
migrate into tetrahedral sites under the dynamic high pressure conditions occurring
during the exchange initially.
Figure 5-33 1 L min⁻¹ D-H exchange reaction rate profiles (293 K): (a) H₂; (b) D₂; (c) HD. The legend shows the different sample times used in the chart (seconds).
Figure 5-34 1 L min\(^{-1}\) D-H exchange surface species reaction rate profiles (293 K): (a) H\(_s\); (b) D\(_s\); (c) V\(_s\). The legend shows the different sample times used in the chart (seconds)
5.7.5.9 1 L min\(^{-1}\) PdD to PdH exchange reaction rate profiles (373 K):

Figure 5-35(a) – (c) presents the volumetric reaction rate profiles of H\(_2\), D\(_2\) and HD for the 373 K 1 L min\(^{-1}\) D-H exchange, respectively. Figure 5-36(a) – (c) shows the volumetric reaction rate of the surface species, H\(_s\), D\(_s\) and V\(_s\), respectively. Immediately it was clear that the rate profiles for this exchange are significantly different to those found for the 293 K and 208 K D-H exchanges. Figure 5-35(a) shows the rate profile for H\(_2\). Initially there is a large consumption of H\(_2\) gas species at a rate of \(~50,000\) mol m\(^{-3}\) s\(^{-1}\) at 0.5 seconds into the exchange (blue line). Referring to Figure 5-35(b) it is clear that this consumption of H\(_2\) is not accompanied by a similar high rate of D\(_2\) generation. The rate of D\(_2\) generation at 0.5 seconds was found to be \(~15,000\) mol m\(^{-3}\) s\(^{-1}\) which is only approximately 30 % of the reaction rate of H\(_2\). The deficit can be found in HD production (Figure 5-35(c)), which shows a large generation peak at 0.5 seconds that matches that of H\(_2\) consumption. Initially, therefore, HD was produced in large amounts in preference to D\(_2\).

Furthermore, Figure 5-36(b) shows that there is a large consumption of D\(_s\) accompanying the initial H\(_2\) adsorption seen in Figure 5-35(a). This loss of D\(_s\) species initially (blue line; 0.5 seconds) was due to HD desorption. The number of mols of H atoms created by this initial adsorption of H\(_2\) would be double the value presented on Figure 5-35(a), therefore \(~100,000\) mol m\(^{-3}\) s\(^{-1}\) H atoms should be added to the Pd surface at 0.5 seconds. The calculated value from the COMSOL Multiphysics model for H\(_s\) generation is approximately half this value, however. This suggests that upon adsorption one atom of H remains on the Pd surface while the other combines with a D atom and desorbs to form HD. Figure 5-36(c) shows that during the initial stages of the exchange the number of vacant sites changes very little since the reaction rate remains small. This supports the HD formation hypothesis. As time progresses the rate of HD formation remains consistently higher than rate of D\(_2\) formation, suggesting that HD production at 373 K was favoured throughout the exchange reaction.

While D\(_2\) production remains low throughout the exchange, the shape of the rate profiles is of interest. At 0.5 seconds the D\(_2\) rate profile resembles a flat peak over the first 0.006 m of the Pd bed. This indicates that the D\(_2\) formation rate was low (in comparison to the other two gas species) and occurring over a significantly larger portion of the Pd bed than the sharp peaks of H\(_2\) consumption and HD formation. This ‘spreading’ was likely to the higher pressure of the gas species at this temperature, and
therefore increased gas velocity through the Pd bed. Immediately after 0.006 m, a combination of upstream H₂ and HD adsorption cause the D₂ rate profile to move into consumption. H₂ and HD are consumed just prior to 0.006 m (Figure 5-35(a) and (c)) which causes D₈ species to be displaced as D₂, see the ‘shoulder’ on the blue line on Figure 5-36(b) in the region of 0.006 m. This displaced D₂ then appears to undergo additional adsorption onto the Pd surface in the available vacant sites (Vₛ), see Figure 5-36(c). Similarly to the 293 K exchange, these additional peaks of D₂ adsorption move faster through the Pd bed via the available vacant sites (see green and blue lines on Figure 5-35(b) and Figure 5-36(c)).

This finding could again be an indication of tetrahedral site occupancy as was outlined for the two previous exchanges at 208 K and 293 K. The model achieved the best fit by manipulating the kinetic rate constants for adsorption and the elucidated values predict that displaced D₂ goes onto adsorb onto vacant sites within the Pd. It is worth pointing out that the model deals with surface processes only, but the large scale consumption of vacant sites suggests that the ‘extra’ sites are available beyond what was programmed into the model initially for D₈ concentration. The author hypothesises that these ‘extra’ sites are becoming available due to tetrahedral occupancy during additional adsorption of D₂ displaced by incoming H₂ and HD. It is possible that the high pressure and concentrated front of displaced D₂ causes D₈ species to migrate to less stable tetrahedral sites usually assumed to be a transition state (or an intermediate stage in atom hopping between octahedral sites).

In summary, at high temperature, as is the case in this exchange, the collision potential of the incoming gas was significantly higher than in the other 1 L min⁻¹ D-H exchanges at 208 K and 293 K due to increased temperature, pressure and flowrate. The increased collisions with the surface appear to favour production of HD over formation of D₂. This also corresponds with the higher recorded Kₑ$q$ value for the 373 K exchange. Another likely contributing factor causing the preference towards HD formation was the lower loading and (consequently) fewer available sites for adsorption/absorption.
Figure 5-35 1 L min\(^{-1}\) D-H exchange reaction rate profiles (373 K): (a) \(\text{H}_2\); (b) \(\text{D}_2\); (c) HD. The legend shows the different sample times used in the chart (seconds).
Figure 5-36 1 L min⁻¹ D-H exchange surface species reaction rate profiles (373 K): (a) Hₛ; (b) Dₛ; (c) Vₛ. The legend shows the different sample times used in the chart (seconds).
5.7.5.10 1 L min\(^{-1}\) PdH to PdD exchange reaction rate profiles (208 K):

Figure 5-37(a) – (c) shows the volumetric rate profiles of H\(_2\), D\(_2\) and HD for the 208 K 1 L min\(^{-1}\) H-D exchange, respectively. Figure 5-38(a) – (c) presents the volumetric reaction rate profiles of the surface species, H\(_s\), D\(_s\), and V\(_s\), respectively. Here the Pd was initially loaded with H atoms and D\(_2\) gas was flowed through the Pd bed at \(\sim7.5\) bar. Figure 5-37(a) shows the rate profiles for H\(_2\) at different times in the exchange reaction. The first immediate difference to the previous PdD to PdH exchanges is the generation of H\(_2\) instead of initial consumption. At 0.5 seconds (blue line) into the exchange H\(_2\) is generated at a constant rate up to 0.004 m into the Pd bed. The rate of displacement of H\(_2\) species prior to 0.004 m is accounted for by the consumption of D\(_2\) since both have a rate value of \(\sim3,000\) mol m\(^{-3}\) s\(^{-1}\). Following this, the reaction rate was observed to fall into consumption of H\(_2\). A similar trend was observed at 1 and 2.5 seconds (green and red lines). At these points H\(_2\) was being adsorbed onto the Pd surface ahead of the advancing front of displaced H\(_2\).

After 0.004 m there is a large consumption peak of D\(_2\) (Figure 5-37(b)) and HD (Figure 5-37(c)) immediately before the H\(_2\) peak was observed to ‘dip’ into consumption. This signifies that the simultaneous adsorption of HD and D\(_2\) was displacing H\(_2\). The displaced H\(_2\) then diffused a short distance further along the Pd bed and was adsorbed onto vacant sites (Figure 5-38(c)). The adsorption reaction rate of displaced H\(_2\) was small in comparison to the levels of HD and D\(_2\) consumed in the advancing front, suggesting larger quantities of HD and D\(_2\) in the gas phase. This demonstrates that H atoms were persisting in Pd and the two adsorbing gas species was occupying vacant sites as opposed to directly displacing H atoms, forming H\(_2\). This can be observed by referring to the large consumption of V\(_s\) (Figure 5-38(c)) which coincides with the two D\(_2\) and HD consumption peaks at 0.5 seconds (Figure 5-37(b) and Figure 5-37(c)).

Figure 5-37(b) shows that initially (within the first 1 second; blue and green lines) the rate of D\(_2\) reaction moves through the Pd bed as a sharp front which drops in intensity as it progresses. By 2.5 seconds (red line) the rate has settled to approximately that observed for H\(_2\) (Figure 5-37(a)). Interestingly, the rate of H\(_2\) generation remains roughly the same for the duration of the exchange. This again suggests that H atoms persist in Pd and the probability of H\(_2\) desorption remains low. This was seen on Figure 5-14(a) as a low quantity of H\(_2\) displaced initially in the exchange. Furthermore, the length of time HD is observed to be produced in the experiment suggests that exchange
is taking place through HD production and that one of the two D atoms (D₃), created by adsorbing D₂, soon recombine with Hₛ and desorb. This observation also explains the increased time necessary to complete the exchange when compared to the D-H exchange at 208 K (Figure 5-14(a) and Figure 5-13(a)).
Figure 5-37 1 L min$^{-1}$ H-D exchange reaction rate profiles (208 K): (a) $\text{H}_2$; (b) $\text{D}_2$; (c) HD. The legend shows the different sample times used in the chart (seconds)
Figure 5-38 1 L min⁻¹ H-D exchange surface species reaction rate profiles (208 K): (a) H⁺; (b) D⁺; (c) V⁺. The legend shows the different sample times used in the chart (seconds).
5.7.5.11 1 L min\(^{-1}\) PdH to PdD exchange reaction rate profiles (293 K):

Figure 5-39(a) – (c) show the volumetric reaction rate profiles of \(\text{H}_2\), \(\text{D}_2\) and HD obtained from modelling the 293 K 1 L min\(^{-1}\) H-D exchange. Figure 5-40(a) – (c) presents the volumetric reaction rate profiles of the surface species, \(\text{H}_s\), \(\text{D}_s\) and \(\text{V}_s\), respectively. The general shape of the plots were similar to those of the 208 K H-D exchange. Figure 5-39(a) shows that the initial generation of \(\text{H}_2\) exhibits the same behaviour, albeit at an increased rate to that found in the 208 K exchange. At 0.5 seconds into the exchange \(\text{H}_2\) was found to be generated at the entry to the Pd bed. Again, the profile was seen to dip into \(\text{H}_2\) consumption following this generation peak, signalling adsorption of the displaced \(\text{H}_2\) species. Comparing the \(\text{H}_2\) reaction fronts of the 208 K and 293 K exchange it is clear that in the 293 K exchange the front moves slower through the Pd bed (see red line on Figure 5-37(a) and Figure 5-39(a)). This can be explained by the higher reaction rates found in the 293 K exchange.

At 0.5 seconds the order of the most advanced species is \(\text{H}_2\), HD, followed by \(\text{D}_2\). This indicates that a band of \(\text{H}_2\) was advancing and adsorbing to vacant sites in the Pd. Following this there was a sharp zone of large scale HD consumption, meaning large quantities of HD were produced during the initial interactions at the entry of the Pd bed. Finally, the \(\text{D}_2\) gas stream was consumed over the initial 0.004 m of the Pd bed. The ‘dip’ in Figure 5-39(a) again shows that displaced \(\text{H}_2\) was adsorbed immediately ahead of the advancing \(\text{D}_2\) and HD reaction front. The size of the ‘dip’ is greater than observed at 208 K suggesting more \(\text{H}_2\) had been displaced into the gas phase. This would be expected considering the increased temperature of this exchange direction.

Over time, the rate profiles for \(\text{H}_2\), \(\text{D}_2\) and HD reduce and begin to spread across axial distance indicating that \(\text{H}_2\) generation and \(\text{D}_2/\text{HD}\) consumption was occurring over the majority of the Pd bed. This shows that in the 293 K PdH to PdD exchange the reaction does not proceed via a sharp front moving through the bed, as was found in the more thermodynamically favourable PdD to PdH exchange at 293 K.
Figure 5-39: 1 L min⁻¹ H-D exchange reaction rate profiles (293 K): (a) H₂; (b) D₂; (c) HD. The legend shows the different sample times used in the chart (seconds).
Figure 5-40 1 L min⁻¹ H-D exchange surface species reaction rate profiles (293 K): (a) H; (b) D; (c) V. The legend shows the different sample times used in the chart (seconds).
5.7.5.12 1 L min\(^{-1}\) PdH to PdD exchange reaction rate profiles (373 K):

Figure 5-41(a) – (c) show the volumetric reaction rate profiles of H\(_2\), D\(_2\) and HD obtained from modelling the 373 K 1 L min\(^{-1}\) exchange data obtained on the IsoEx apparatus. Figure 5-42(a) – (c) present the volumetric reaction rate profiles of H\(_s\), D\(_s\) and V\(_s\), respectively. The overall shape of all the plots are very similar to those found at 293 K. Figure 5-41(a) features the H\(_2\) consumption ‘dip’ immediately ahead of the D\(_2\) and HD reaction fronts. The magnitude of the consumption rate was greater than that found at 293 K. As was discussed in the previous section, this indicates a larger quantity of H\(_2\) in the gas phase due to displacement of H\(_s\) species by adsorbing D\(_2\) and HD. Physically this means that the concentration of D\(_s\) increased, causing H\(_2\) to desorb.
Figure 5-41 1 L min$^{-1}$ H-D exchange reaction rate profiles (373 K): (a) H$_2$; (b) D$_2$; (c) HD. The legend shows the different sample times used in the chart (seconds)
Figure 5-42 1 L min$^{-1}$ H-D exchange surface species reaction rate profiles (373 K): (a) H$_s$; (b) D$_s$; (c) V$_s$. The legend shows the different sample times used in the chart (seconds).
5.8 Analysis and discussion

5.8.1 Introduction

This section will discuss the findings presented in this chapter after the equilibrium model (from Section 5.6 onwards). The COMSOL Multiphysics kinetic model is discussed alongside its ability to fit experimental data, including the areas where the model is particularly successful and those where it could be improved. Permeability values derived from the model are also analysed and compared to those derived from experimental measurement. In addition to these the kinetic rate constants are discussed and evaluated against previous findings in the literature. The activation energies presented earlier in this chapter will also be discussed briefly and compared to literature. Finally, the general observations discovered from the reaction rate profiles are discussed.

At the end of this section future modelling recommendations are presented. These recommendations relate to ways in which the author believes the COMSOL Mulitphysics model can be improved to provide better fits to experimental data, and elucidate additional information about the physical phenomena occurring during isotope exchange reactions.

5.8.2 Discussion

Figure 5-11 - Figure 5-14 show the COMSOL Multiphysics kinetic modelling results alongside the experimental data for both exchange directions carried out at low pressure and 1 L min\(^{-1}\). Figure 5-11 and Figure 5-12 show the modelling results for the low pressure D-H and H-D exchanges. The model fits for all the experimental data obtained in this work are remarkable good. The fits were achieved by manipulating the six kinetic rate constants, the \(K_{eq}\) values and the Pd bed permeability. The magnitude and significance of the elucidated rate constant and \(K_{eq}\) values are discussed later in this section. The fitted permeability values offer some interesting discussion. As would be expected, the fitted permeability values for low pressure exchanges were higher than those found for the higher pressure 1 L min\(^{-1}\) exchanges. This was because the recorded pressure drop across the Pd bed for the low pressure exchanges was lower, and subsequently the permeability values were less. This finding agrees with Darcy’s law.
The magnitude of the permeability for the low pressure exchanges was in the region of $10^{-13}$, while the values for the 1 L min$^{-1}$ exchanges were in the region $10^{-14}$.

These values were deemed realistic when compared to the Pd particle size. The exact size of the Pd particles was deemed sensitive and fell under MoD non-disclosure policy. As such the permeability values were manually fitted around sensible $\kappa$ values derived from knowledge that the Pd particle size is in the range $500 \text{ nm} < d_p < 1.5 \mu \text{m}$. Using a value in the middle of this range in the following equation reveals a $\kappa$ value of the order $10^{-14}$.

$$\kappa = \frac{\varepsilon^2}{c(1-\varepsilon)^2s_0^2} \tag{5-115}$$

Figure 5-43 and Figure 5-44 show the fitted $\kappa$ values for the low pressure and 1 L min$^{-1}$ exchanges, respectively. $\kappa$ was plotted against pressure drop over the Pd bed ($\Delta P$). The three increasing $\Delta P$ values correspond to the three temperatures investigated in both types of exchange experiment. For the low pressure exchange the $\kappa$ plots were observed to not follow an increasing linear relationship. Both the D-H and H-D $\kappa$ values exhibit a drop in the expected trend at 293 K ($\Delta P = 0.6$ bar). This corresponds to a decrease in permeability at 293 K. The exact cause of this observation is unknown at present and more investigation would be needed to identify if this was a real finding or the consequence of damage to the Pd bed or increased compaction during bed loading. Alternatively, if this observation does indeed represent a real finding it could be explained by an increased likelihood of exchange at this temperature. It is known that the bulk and subsurface can play a significant role in the exchange under certain conditions and it may be the case that at 293 K these areas within the Pd bed were more accessible. This would cause the apparent permeability of the Pd bed to be less because more gas would be adsorbed/absorbed into the Pd structure, slowing the progress of the advancing gas front through the bed. In modelling isotope exchange reactions in Pd the $\kappa$ values in the COMSOL Multiphysics model were found to be the main driver in fitting the timescale of the exchange profile, i.e. the time at which the features were observed experimentally.
Figure 5-43 Low pressure Pd bed permeability values from COMSOL Multiphysics kinetic model. Straight line plots have been included as a guide to the reader.

Figure 5-44 shows the permeability data for the 1 L min\(^{-1}\) exchanges. Both the D-H and H-D exchanges exhibit linear relationships with increasing pressure drop over the Pd bed. The \(\kappa\) values for the D-H exchange were found to be higher than the values for the H-D exchange. This can be explained by the knowledge that D atoms diffuse through Pd faster than H atoms. The displaced D atoms therefore appeared at the exit of the Pd bed as D\(_2\) quickly, which reduced the fitted \(\kappa\) value for this exchange direction. Furthermore, the porosity of the initially deuterided Pd bed (PdD\(_y\)) was higher than an initially hydride Pd bed (PdH\(_x\)) because the magnitude of swelling of the Pd lattice is greater under hydride conditions. This effectively opens up the available space for the gas stream to move through the Pd bed, and consequently a higher permeability was found while fitting the model to experimental data.

The 1 L min\(^{-1}\) permeability values for the D-H and H-D exchanges do not appear to exhibit the shift at 293 K as was found for the low pressure exchanges. While there is slight shift away from a linear trend at 293 K it was by no means as large as observed in the low pressure exchanges. Again, this could be an indication that the Pd bed used in the 293 K low pressure experiments was overly compacted during the bed loading procedure. If this was not the case, however, it could be an indication that the hypothesised processes involving the bulk and subsurface were less significant at increased pressure. The author recommends that further investigation should be carried out into permeability of Pd beds using well characterised Pd with known particle size.
and morphology. In the current study, due to MoD sensitivity, insufficient powder characterisation was performed.

The reason for the lower observed $\Delta P$ values for the D-H compared to the H-D exchanges was the reduced viscosity of the incoming $H_2$ species compared to $D_2$. This was also the case for the low pressure $\kappa$ values.

![Figure 5-44](image)

Figure 5-44 1 L min$^{-1}$ Pd bed permeability values from COMSOL Multiphysics kinetic model. Straight line plots have been included as a guide to the reader.

As identified earlier in Section 5.6.4, there are some features of the experimental data that could not be reproduced using the kinetic model. Most notably in the 1 L min$^{-1}$ 208 K H-D exchange. The ‘crossover’ point of the $H_2$ and $D_2$ signals found during experimentation occurred earlier than the model predicted. The model predicted the ‘crossover’ to occur at the same point as the peak in the HD curve, as was found in the rest of the isotope exchanges carried out at low and high pressure. As discussed earlier, the reason for this is unclear at present and could be due to a damaged Pd bed or the action of additional physical/chemical phenomenon not considered in the COMSOL Multiphysics kinetic model. The author tends to support the second hypothesis because the results obtained for different temperature exchanges using that particular Pd bed were consistent and exhibited expected behaviour. Furthermore, a number of experimental repeats were completed for each temperature H-D exchange and similar behaviour was observed in all 208 K experiments.
This exchange direction is unfavourable thermodynamically because H atom adsorption/absorption is ‘preferred’ by the Pd-H(D) system. Thermodynamically the hydride phase of Pd (PdH) is more stable than the deuteride (PdD) phase, having a lower Gibbs free energy. The entropy of the system is higher when H atoms reside in Pd because there are more sites available for H atoms than for D atoms. At 208 K in the H-D exchange the initial H loading on Pd was at a maximum of ～PdH_{0.8} and there was therefore little scope to increase the entropy of the system further. Furthermore, the probability of exchanging a D atom for an H atom bound to the surface was significantly reduced due to the lower pressure energy of the incoming gas stream. For these reasons, the D₂ species would arrive sooner through the Pd bed because of fewer surface reactions consuming the advancing gas front. In real terms the exchange profile (in this case) would show a dropping H₂ signal corresponding to the free gas overpressure being driven out of the reactor by the incoming D₂ gas. Following this, the D₂ gas would appear promptly, and in all likelihood, before the HD signal. The shape of the HD curve shown on Figure 5-14(a) would suggest that it was produced as a result of prolonged exposure to pure D₂ gas in the free space within the Pd bed. This hypothesis was supported by the low and elongated HD curve, which suggests that HD was generated at a slow rate for prolonged lengths of time. Additionally, the fitted value of the equilibrium constant was K_{eq} = 0.7. This was significantly lower than the value predicted by empirical relationships derived from measurements carried out in static conditions (K_{eq} = 2.91; Sievert’s apparatus) [9, 120]. The gas phase was therefore not in equilibrium with Pd and less HD was produced, resulting in a depressed HD peak height.

With regards to the other low pressure and 1 L min⁻¹ exchanges, the K_{eq} values obtained from model fits make for interesting discussion.

Table 5-15 K_{eq} values derived from fitting experimental data from both low pressure exchange directions

<table>
<thead>
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<th>Temperature (K)</th>
<th>K_{eq}</th>
<th>K_{eq} (empirical)</th>
<th>Temperature (K)</th>
<th>K_{eq}</th>
<th>K_{eq} (empirical)</th>
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</tbody>
</table>
Table 5-15 shows the $K_{eq}$ values for both low pressure exchange directions. Alongside each of the fitted $K_{eq}$ values are the $K_{eq}$ values derived from the empirical relationship outlined in the literature for the Pd-H(D) system. The low pressure exchanges were carried out with an upstream gas pressure of 1.5 – 1.7 bar, depending on the temperature. The $K_{eq}$ values for the low pressure D-H exchange show significant departure from the values published in the literature. In particular, the $K_{eq}$ value for the 293 K exchange was substantially lower than the empirical value. The values for the 208 K and 373 K exchanges are approximately half those found from static measurements. The $K_{eq}$ values used for fitting model data are equivalent to the concentration ratio $K$ (or apparent equilibrium constant) found by analysing the effluent concentration of $H_2$, $D_2$ and HD leaving the reactor as a function of time. Conclusively this means that the gas phase equilibrium of $H_2$, $D_2$ and HD in the presence of Pd was not complete during the low pressure D-H exchange.

This finding was not repeated during the low pressure H-D exchanges. The fitted $K_{eq}$ values indicate that the gas phase did indeed equilibrate with the Pd bed. This can be seen by referring to the matching values of $K_{eq}$ from modelling and calculated from empirical data. The exact reason for the difference between D-H and H-D exchanges was unclear but is probably due to a number of factors. Firstly, for a low $K_{eq}$ value to arise the concentration of HD in the gas phase must be less and the concentration of $H_2$ and $D_2$ must be higher according to the following equation:

$$K_{eq} = \frac{[HD]^2}{[H_2][D_2]}$$

Consequently, in the D-H exchanges the quantity of HD gas being produced by the equilibration reaction ($H_2 + D_2 \leftrightarrow 2HD$) must be less than in the H-D exchange. The dynamic nature of the exchanges carried out in this work would have had a significant impact on the equilibration reaction, however, why this should be observed for the D-H exchange and not H-D exchange raises questions. One possible explanation was the occurrence of ‘direct’ exchange events during the D-H exchange, whereby the incoming $H_2$ species directly displaces $D_2$ in preference to the production of HD. Certainly, the magnitude of the kinetic rate constants for the $D_2$ and $H_2$ surface processes are generally larger in comparison to those involving HD for the low pressure D-H exchanges. The calculated $E_a$ values for the low pressure D-H exchange also appear to support the
above hypothesis. Both $E_a$ values for the adsorption and desorption reactions associated with HD were negative. This suggests that other surface processes were dominant in this exchange direction and that there was a negative relationship with temperature, i.e. the rate of the two HD surface processes decreases with increasing temperature or moreover, the scale of the rate increase with temperature does not ‘keep up’ with the increase in rate of the other surface processes involving H$_2$ and D$_2$.

Furthermore, the overall rate constant values for the D-H exchange were significantly higher than those obtained for the low pressure H-D exchanges. The surface processes in the D-H exchanges were therefore occurring at enhanced rates. The significance being the gas phase species were consumed faster in the D-H exchanges. Coupling this with Pd’s increased affinity for H atoms would result in less HD and H$_2$ remaining in the gas phase. This would lower the values of $K_{eq}$ found during the D-H exchanges. The author highlights that the low pressure exchanges were performed at higher pressures than the majority of other investigations in the literature and used a unique Pd powder which due to MoD sensitivity could not be characterised fully. It is therefore difficult to make firm conclusions on the exact cause of these observations.

The $K_{eq}$ values for the low pressure H-D exchanges match those predicted from empirical relationships derived by Wicke and Nernst [9, 120]. This demonstrates that the gas phase equilibrates fully with the Pd during the exchange reaction. The reason why the H-D exchanges equilibrate and the D-H exchanges do not is debateable. The rate constant values obtained from fitting the low pressure H-D exchanges are considerably less than those found for the D-H exchanges. Firstly, this explains the increased time required to complete the exchange in the H-D experiments. Secondly, the rates of the surface processes were less than in the D-H exchange and changes to the gas phase composition occurred less quickly. Consequently, more D$_2$ remained in the gas phase, with some passing through the Pd bed with little interaction with the Pd surface. Furthermore, during exchange events, modelling suggests that any D$_2$ that was adsorbed to the Pd surface displaced only one surface H atom in the form of HD. This can be attributed to Pd’s higher affinity for H atoms, and consequently it seeks to ‘keep’ H atoms within its lattice. Surface D atoms created through D$_2$ adsorption were therefore more likely to desorb as HD in the H-D exchanges. Consequently, more HD was produced in these experiments (see Figure 5-12). This explains the higher $K_{eq}$ values.
found and suggests that during the H-D exchanges the intermediate molecule HD was formed preferentially over H\textsubscript{2} desorption, and there was fewer ‘direct’ exchange events occurring as was hypothesised for the D-H exchanges earlier.

The calculated $E_a$ values for the low pressure H-D exchanges support this. Table 5-13 shows that the energy barrier for H\textsubscript{2} desorption was higher than that for HD. The value for D\textsubscript{2} desorption was similar to that of HD. However, when referring to the value of $k_{-3}$ it was clear that the rate of D\textsubscript{2} desorption was less than H\textsubscript{2} and HD in the low pressure H-D exchanges. The significance of this was that D\textsubscript{2} desorption was less favoured at higher temperatures and the rates of HD and H\textsubscript{2} desorption were significantly higher. At 373 K the adsorption rate constant for D\textsubscript{2} was significantly higher than at 208 K and 293 K. This means that D\textsubscript{2} was adsorbed to the Pd surface at a faster rate compared to H\textsubscript{2}. Combining this with a larger H\textsubscript{2} desorption rate constant meant that H\textsubscript{2} did not persist in the solid phase for as long as was observed in the lower temperature exchanges. Furthermore, the adsorption rate constant for HD at 373 K was found to be significantly larger than H\textsubscript{2}, meaning HD was also adsorbed at a faster rate. The effect of these findings was a longer period of ‘pure’ H\textsubscript{2} recorded at the start of the 373 K exchange, a sharper overall shape of the HD curve and shorter exchange completion time (see Figure 5-12(c)).

Table 5-16 $K_{eq}$ values derived from fitting experimental data from both 1 L min\textsuperscript{-1} exchange directions

<table>
<thead>
<tr>
<th>PdD to PdH exchange</th>
<th>Temperature (K)</th>
<th>$K_{eq}$</th>
<th>$K_{eq}$ (empirical)</th>
</tr>
</thead>
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<tr>
<td></td>
<td>208</td>
<td>1.65</td>
<td>2.91</td>
</tr>
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<td>293</td>
<td>0.25</td>
<td>3.25</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>1.8</td>
<td>3.44</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PdH to PdD exchange</th>
<th>Temperature (K)</th>
<th>$K_{eq}$</th>
<th>$K_{eq}$ (empirical)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>208</td>
<td>0.7</td>
<td>2.91</td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>3.2</td>
<td>3.25</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>2.9</td>
<td>3.44</td>
</tr>
</tbody>
</table>

Table 5-16 presents the $K_{eq}$ values found from fitting the 1 L min\textsuperscript{-1} isotope exchange experimental data. The values obtained for the D-H exchange show significant departure from the empirical data. The 208 K D-H exchange was found to have a $K_{eq} = 1.65$. This indicates that HD production was not what would be expected from static, Sievert’s type measurements, and the gas phase was therefore not in equilibrium with Pd. Figure 5-13(a) does, however, demonstrates that significant HD was produced during this exchange, albeit at a reduced rate. The length of time HD was produced was due to the slow rates and the initial loading of the Pd. At 208 K the stoichiometry was
There was therefore a greater quantity of D atoms to be removed during the exchange. HD was therefore produced for longer while the exchange was completed. The initial D$_2$ signal detected here was due to the gaseous D$_2$ overpressure in the IsoEx reactor at the start of the exchange (5.5 bar). There may have also been a small quantity of D$_2$ arriving as a consequence of H$_2$ adsorption at the entry to the Pd bed.

The exchange carried out at 293 K was found to have a very low $K_{eq}$ value. This low value corresponds to the depressed HD peak observed in the experimental data (Figure 5-13(b)). The gas species leaving the reactor were not in equilibrium with Pd. What was also clear from Figure 5-13(b) was the increased length of time that near pure D$_2$ was detected. Similarly to the low pressure 293 K D-H exchange, this indicates that large scale D$_2$ desorption occurs during the initial stages of the exchange and any HD that was produced goes on to displace additional D$_2$ rather than continue through the Pd bed. This large quantity of D$_2$ desorption again suggests (similar to the low pressure D-H exchanges) that ‘direct’ exchange events may have been occurring, i.e. incoming H$_2$ gas was adsorbing and promoting immediate desorption of D$_2$, rather than formation of HD. This hypothesis was further supported by the similar scale of the kinetic rate constants for the H$_2$ and D$_2$ adsorption and desorption processes, and the smaller rate constant values for the HD adsorption and desorption processes.

Table 5-11 shows the rate constants obtained from fitting experimental data for the various reactions considered in the exchange. The data for the D-H 293 K exchange shows that, in comparison to HD, the values of the rate constants for the H$_2$ and D$_2$ adsorption and desorption processes were significantly larger. The D$_2$ desorption rate constant was large which explains the large amount of pure D$_2$ observed at the start of the exchange. The rate constants for H$_2$ adsorption and desorption were also significant and mirrored the D$_2$ adsorption and desorption values. The high adsorption rate of H$_2$ was to be expected due to the high affinity Pd has for H atoms, however, the desorption rate constant was more surprising. This suggests that, according to the modelling findings, the rates of H$_2$ desorption are high in this particular exchange. One explanation could be that incoming H$_2$ gas could be displacing H atoms bound to the surface from previous interactions with the D loaded Pd surface. These ‘secondary’ H$_2$ species (arising from the Pd surface) could then contribute to additional D$_2$ desorption.
Consequently, the value of the $D_2$ desorption rate constant would be even higher, as was the case here.

The activation energies also support this theory. The calculated activation energy for $D_2$ desorption was significantly lower than the other surface processes indicating that there was a lower energy barrier to surmount and accordingly more $D_2$ desorption was found. Referring to Table 5-11 it is clear that the value of $k_{-3}$ for the D-H exchange at 293 K was significant in comparison to the HD desorption value ($k_{-2}$). The role of the Pd surface and subsurface could be the cause. The subsurface region within Pd has been found to facilitate desorption of surface species under certain conditions and even change the reaction mechanism away from Langmuir-Hinshelwood as was used here [122]. At 293 K and the pressures investigated here the subsurface region may be causing enhanced $D_2$ desorption by lowering the activation energy. There is also the possibility that the reaction mechanism may involve subsurface and bulk sites, which was not considered here.

It is clear that further investigation would be needed (see Chapter 7) to draw firm conclusions on whether either of these explanations is correct because the previous studies investigating the subsurface were carried out under vacuum using ion beams, and those involving changing reaction mechanisms were carried out using different Pd morphology and pressures [122, 123]. The current COMSOL Multiphysics model could be modified to include descriptions of the subsurface, bulk and surface regions within Pd. Furthermore, the rates of transfer between the three could also be included and investigated to elucidate the effect of each in exchange experiments.

Figure 5-13(c) shows the D-H exchange carried out at 373 K. The equilibrium constant value for this exchange was found to be $K_{eq}=1.8$. This again demonstrates that the gas phase was not in equilibrium according to static measurements. The inlet pressure (8 bar) and the high porosity of the Pd bed ($\varepsilon = 0.77$) were likely contributors to this model finding. The dynamic setup of the experiments also brings into question the validity of applying empirical relationships found from static Sievert’s type measurements in a flowing exchange system.

Figure 5-13(c) exhibits an initial period of pure $D_2$ detected in the effluent. This was in no doubt made up of a quantity of gas arising from the initial $D_2$ overpressure in the
reactor (which is also a feature of the COMSOL Multiphysics model), however it
appears there was also a significant quantity of detected D\textsubscript{2} arising from surface
reaction. The incoming H\textsubscript{2} gas was therefore efficiently displacing the surface D atoms.
Furthermore, the amount of HD detected was significantly higher than the 293 K D-H
exchange. The rate constants for the surface processes involving HD (\(k_2\) and \(k_{-2}\)) for
the 373 K exchange were found to be two orders of magnitude larger than the 293 K
exchange. The \(k_i\) values for the H\textsubscript{2} surface processes were also significantly higher.
Accordingly, the amount of HD produced during this exchange was greater than at 293
K. The fitted rate constant values for the D\textsubscript{2} surface processes (\(k_3\) and \(k_{-3}\)) were larger
than the values found at 293 K, but did not increase in magnitude as much as the
adsorption/desorption rate constant values for H\textsubscript{2} and HD did with increasing the
temperature to 373 K. This meant that there was large amounts of H\textsubscript{2} adsorption (and
desorption) alongside HD adsorption (and desorption), while the kinetics for D\textsubscript{2} were
small in comparison. The effect of this is the initial pure period of the D\textsubscript{2} curve was
shorter than that recorded at 293 K, but slightly longer than that at 208 K. Because of
the large kinetic values for HD adsorption and desorption, the HD curve features a high
peak and sharp appearance. This indicates a sharp mixed gas front containing mostly
HD moved through the Pd bed ahead of the incoming H\textsubscript{2} front. The detected D\textsubscript{2} at the
start of the exchange was made up of the gaseous D\textsubscript{2} overpressure in the IsoEx reactor
at the start of the experiment (8 bar) followed by a ‘slug’ of D\textsubscript{2} which was displaced by
incoming H\textsubscript{2}. The author believes therefore that the majority of the D atoms contained
within the Pd bed were removed by production of intermediate HD. Another
contributing factor to the sharp appearance of all the gas curves was the initial loading
of D atoms on Pd. At 373 K the stoichiometry is \(~\text{PdD}_{0.5}\). The quantity of D atoms to be
exchanged for H atoms was therefore significantly less than in the low temperature
exchanges. The overall time for the exchange reaction would therefore be reduced at
373 K, as was found during experimentation.

Figure 5-14 shows the exchange profiles for the 1 L min\textsuperscript{-1} H-D exchanges carried out at
208 K, 293 K and 373 K. Similarly to the low pressure H-D exchanges the overall
timescale of these exchanges were longer than the D-H exchanges. Furthermore, the
amount of HD produced during each exchange was significantly more than the D-H
exchanges. This caused the calculated \(K_{eq}\) values for the H-D exchanges to be larger
and closer to the value reported in the literature from static measurements (see Table 5-
16). The 1 L min\(^{-1}\) H-D 208 K exchange (Figure 5-14(a)) exhibits the largest departure from empirical \(K_{eq}\). The equilibrium constant found from fitting experimental data was \(K_{eq} = 0.7\). The amount of HD produced was therefore less than would be expected. This indicates the gas phase did not equilibrate with the Pd. The inlet gas pressure being the lowest value for all the H-D exchanges (7.5 bar), but not appreciably lower than the higher temperature exchanges. The gas viscosity was also the lowest due to the temperature of the exchange. These two factors would create a comparatively high gas velocity compared to the higher temperature exchanges at 293 K and 373 K. The mixed gas was therefore in the vicinity of the Pd surface for shorted periods of time, reducing the probability of an exchange event and gas residence time in the vicinity of the Pd surface. This would reduce the likelihood of the gas phase equilibrating with the Pd. Furthermore, Pd’s preferential affinity for H atoms and the low temperature would also act to hinder gas phase equilibration.

The initial pure H\(_2\) detected can be accredited to the gaseous H\(_2\) overpressure in the reactor at the start of the experiment. Following this period of pure H\(_2\) the experimental signal was observed to drop rapidly in conjunction with a sharply rising D\(_2\) signal before the appearance of HD. This demonstrates that some D\(_2\) was arriving through the Pd bed with little or no interaction with the H loaded Pd surface. The HD curve was found to appear shortly after the signals for H\(_2\) and D\(_2\) were observed to ‘crossover’. HD was then produced for long periods, albeit at a lower rate than would constitute the gas species being in equilibrium. These features could not be reproduced using the COMSOL Multiphysics kinetic model despite significant manipulation of the model variables and parameters. The ‘crossover’ point of the H\(_2\) and D\(_2\) curves was always found to occur at the same time as the peak in the HD curve. However, the general shape of the HD curve was matched satisfactorily suggesting that the derived kinetic values for HD are valid. The HD adsorption kinetic rate constant was found to be significantly larger than the corresponding desorption constant. This indicates that any HD produced during D\(_2\) adsorption events was preferentially re-adsorbed to form surface H\(_s\) and D\(_s\) species. The effect of this can be observed by referring to the depressed HD curve on Figure 5-14(a).

The kinetics elucidated from the model for H\(_2\) surface processes show that adsorption and desorption rates were slow. This means that H atoms were persisting in the solid
phase for increased lengths of time. HD was consequently detected for longer periods as D₂ ‘struggles’ to remove all the H atoms from the Pd, and HD was preferentially formed over direct H₂ desorption. This finding was not surprising considering the greater affinity Pd has for H atoms over D atoms. The longer timescales of HD production can also be attributed to the higher initial loading of H atoms in Pd at 208 K. The stoichiometry at 208 K is ~PdH₀.₈. The H atom loading was at a maximum for the Pd-H(D) system and therefore any incoming D₂ species required longer periods of time to exchange all the H atom species.

Figure 5-14(b) shows the exchange profile and kinetic model data for the 1 L min⁻¹ 293 K H-D exchange. The fitted $K_{eq}$ value from the model was $K_{eq} = 3.2$. This was very close to the value from empirical data, indicating that the gas phase in the vicinity of the exchange front was in equilibrium with the Pd surface. This can be observed on Figure 5-14(b) by the large symmetrical HD peak. The H₂ kinetics indicate that far more H₂ and HD desorption occurred during this exchange (see Table 5-12) compared with that found for the 208 K exchange. The consequence of this was that there was more HD and H₂ in the gas phase which contributed to the larger $K_{eq}$ value. It therefore appears that the increased temperature and higher inlet pressure associated with this particular exchange encourage desorption of H₂ and HD whilst also promoting lasting D₂ adsorption. This can be seen by referring to the higher rate constant for D₂ adsorption compared to that for D₂ desorption. This suggests that D₂ was adsorbing and remaining on the Pd surface. Another supporting argument for this observation was the low $E_a$ value recorded for the D₂ adsorption process ($E_a = 3.6$ kJ mol⁻¹). This was far lower than other activation energies recorded for the surface adsorption processes for H₂ and HD and indicates that there was a low energy barrier to overcome for D₂ to adsorb forming D₃ species. As temperature was increased the proportion of the gas molecules with the required interaction energy increased and consequently more D₂ was adsorbed as temperature increased. Interestingly, the $E_a$ value for the D₂ desorption process was less than that calculated for adsorption ($E_a = 2.7$ kJ mol⁻¹).

The cause of this appears complex but one possible explanation is that the activation energy has pressure dependence [136], or the dynamic nature of the experiments and high partial pressure influx of D₂ encourage additional D atom desorption, resulting in a lower calculated activation energy ($E_a$). Another possibility could be additional surface
reaction mechanisms not considered in the COMSOL Multiphysics model of hydrogen isotope exchange, for instance the Eley-Rideal mechanism which would allow for additional D₂ production by direct interaction of gaseous D₂ with surface bound D atoms. Furthermore, the existence and influence of subsurface regions in Pd’s structure have been postulated to cause changes to the activation energy of surface processes [122, 124]. It is certainly possible that was what was found here. This observation also coincides with the other non-Arrhenius behaviour observed at 293 K in the low pressure D-H and H-D and 1 L min⁻¹ D-H exchanges. Many of the Arrhenius plots exhibit an anomalous point at 293 K (or slight kink around 293 K), suggesting some more complex phenomena may have been occurring. More investigation is needed to conclusively explain these findings.

Figure 5-14(c) shows the exchange profile and kinetic model data for the 1 L min⁻¹ 373 K H-D exchange. The fitted $K_{eq}$ value from the model was $K_{eq} = 2.9$. This was lower than the empirical value of $K_{eq} = 3.44$. This indicates that HD production at the exchange front was not as high as would be expected from static dosing type measurements. The cause of this is possibly the high inlet pressure of this exchange (8 bar) and the high porosity of the Pd bed under the lower Pd loading conditions associated with 373 K. These two factors would cause increased gas velocity through the pores of the Pd bed, allowing less time for gaseous interaction with the Pd surface compared to the 1 L min⁻¹ H-D exchange at 293 K. The kinetics of all the surface processes involving H₂, D₂ and HD were significantly greater in magnitude compared to the other two temperatures investigated. This explains why the $K_{eq}$ value was still relatively large. While the gas velocity was higher at 373 K, the kinetics were also greater which would help to compensate the reduced time for gaseous interaction, and thus HD was still produced in significant quantities, warranting a $K_{eq}$ value close to the empirical value.

Figure 5-14(c) demonstrates that at 373 K the general profile of the exchange was sharper. The initial period of H₂ was somewhat less than observed at 293 K. This could be due to the lower initial loading of H atoms on Pd. At 373 K the stoichiometry was ~PdH₀.₆. The effect of this would be less H₂ gas displaced from the Pd by incoming D₂. Furthermore, the quantity of detected HD would be less because there were fewer H atoms available to form HD molecules. The overall shape of the HD curve was also
sharper compared to the 293 K exchange. This indicates that the exchange front was confined to a smaller volume of the Pd bed and the majority of surface interactions took place within it. Referring to the kinetics (Table 5-12) it was clear that the rates of all surface processes were higher at 373 K. This explains the sharpened front. Surface species were exchanged at increased rates and there was therefore less ‘spreading’ observed in the exchange profiles. This observation can be seen by comparing the exchange profiles for the 293 K and 373 K H-D exchanges (Figure 5-14(b) and Figure 5-14(c)). The fitted kinetic rate constant values for the 293 K exchange were smaller in magnitude and the exchange front was therefore more spread out and less defined. The HD curve for the 293 K H-D exchanges was broader, indicating HD was produced over a larger proportion of the Pd bed.

At 373 K the amount of D₂ adsorption was higher than at the other lower temperatures. This can be observed by referring to the $k_3$ values in Table 5-12. The increased D₂ adsorption causes more H₂ and HD to be displaced in a short period of time which sharpens the observed exchange front. This can be seen by referring to the kinetics for H₂ and HD desorption in Table 5-12. They are at their highest in the 373 K exchange.

5.8.2.1 Summary

Due to the quantity of data discussed in the above section a succinct summary will now be presented.

Overall the quality of the COMSOL Multiphysics kinetic model fit to experimental data was very good. By varying the six kinetic rate constants involved in the surface reactions considered in the model all the exchange data has been modelled effectively. Useful kinetic data, activation energies and information relating to the reaction mechanisms have been elucidated. The Langmuir-Hinshelwood reaction mechanism has been found to be very satisfactory in describing the majority of exchanges carried out here, both at high (1 L min⁻¹ flowrate experiments) and low pressure (ca 1.5 bar). In some cases, most notably the 1 L min⁻¹ H-D exchange carried out at 208 K, the exchange profile could not be matched entirely. The reason for this is not fully apparent at present, however the author believes the fit could be improved by investigating alternate reaction mechanisms (such as the Eley-Rideal or Bonhoeffer-Farcus) and including the bulk and subsurface regions of Pd alongside the description of the surface processes.
The elucidated kinetic values mostly agree with traditional understanding of reaction rates, although some of the exchanges investigated exhibit anomalous behaviour with respect to temperature. This is particularly evident at 293 K. All the exchanges carried out at this temperature exhibited trends akin to slightly non-Arrhenius behaviour, suggesting there are other factors at work. Some of the subsequent activation energy values for the surface reactions have been found to be negative (i.e. $E_a$ values for HD adsorption/desorption during the low pressure D-H exchange) which suggests either temperature dependent activation energies, other surface processes are dominant or spontaneous reactions. Negative activation energies have been found in reactions involving molecules (or atoms) being captured into a potential wells (as is the case in hydrogen isotope exchange). As the temperature is increased the probability of a molecule being caught in a potential well reduces. As such the observed reaction rate for these processes decreases with increasing temperature, and hence negative activation energies can be elucidated from linear Arrhenius type analysis. The author notes that far more investigation is needed to explain these findings. It may be necessary to examine the isotope exchange reactions using transition state theory and other quantum mechanical methodologies which are outside the scope of this work.

Another major finding of this work was the low $K_{eq}$ values associated with the D-H exchanges both at low and high pressure. These indicated that the gas phase was not fully equilibrating in these exchanges. The cause of this was postulated to be the greater affinity Pd has for H atoms over D atoms, or described another way, a more negative Gibbs free energy value for H atom absorption into the Pd lattice. This causes large kinetic rate constants for the D-H exchanges in comparison to those found for the H-D exchanges. Subsequently, the rates of reaction of the gas phase species were large and therefore the gas phase composition changes rapidly, preventing the gas phase from reaching equilibrium with Pd. Another finding from the kinetic modelling of the D-H exchange was the apparent ability for the incoming H$_2$ species to cause ‘direct’ exchange events, whereby D$_2$ gas was directly displaced by incoming H$_2$ gas adsorption. This finding was hypothesised after examining the size of the H$_2$ and D$_2$ surface kinetic rate constant in comparison to HD. The HD rate constants in the D-H exchanges were smaller, meaning less HD was produced during these exchanges in comparison to the H-D experiments. These ‘direct’ exchange events would lower the apparent equilibrium constant values ($K_{app}$) (found during analysis of the effluent data)
because less HD would be produced during an exchange. These ‘direct’ exchange events were examined by Foltz and Melius during their seminal investigation into hydrogen isotope exchange in Pd [1, 2]. They stated that HD was ‘chronically under-produced’. While this finding did not match their experimental data obtained at lower pressure and in a larger Pd bed of reduced porosity, it is quite probable that under the conditions investigated here (i.e. high porosity and higher pressure) that these ‘direct’ exchange events do occur. The COMSOL Multiphysics model certainly appears to support this theory and the data obtained for the 1 L min\(^{-1}\) 293 K D-H exchange shows significant evidence for ‘direct’ exchange of H\(_2\) for D\(_2\). However, the author again highlights that more investigation is required to draw firm conclusions on these hypotheses. This would include trialling different reaction mechanisms within the COMSOL Multiphysics kinetic model. These trials could also shed light on the poor fits to some of the other experimental data, for example the Eley-Rideal or Bonhoeffer-Farcus reaction mechanisms may be more appropriate under certain conditions and may be applicable to the challenging results observed at 293 K.

With regards to the H-D exchanges, both the 1 L min\(^{-1}\) and low pressure experimental data was fitted remarkably well by the COMSOL Multiphysics kinetic model developed as part of this work. The model was capable of reproducing the changing exchange profiles with increased pressure and temperature. The author admits there can be some minor improvement on the model fits, but these slight mismatches would be easy to remedy through continued manipulation of the kinetic rate constants, \(K_{eq}\) values and Pd bed permeability. Overall in the H-D exchanges the gas phase was found to achieve equilibrium with the Pd bed within the advancing exchange fronts. The reasoning behind this has been postulated to be caused by the different absorption characteristics of H and D atoms in Pd. H atoms persist on the Pd surface and subsequently more HD was produced rather than ‘direct’ desorption of H\(_2\) species. However, in the 373 K H-D exchanges, both at 1 L min\(^{-1}\) and low pressure, the adsorption rate constant for D\(_2\) was found to increase significantly in comparison to the other temperature exchanges. This suggested that at high temperature D\(_2\) adsorption increased and there was an increased likelihood that H\(_2\) would desorb from the Pd surface instead of HD.

Finally, the author wants to highlight that the data presented here needs further validation against additional experimental data. This can be done by using the kinetic
COMSOL model to predict the outcome of an experiment at a temperature not yet investigated. Further validation can be done by carrying out a significant number of additional experimental repeats at the existing temperatures. Experimental validity could be confirmed by analysing the experimental uncertainty of a number of experimental repeats under a constant pressure/temperature regime. This would remove the uncertainty and inaccuracies arising from the IsoEx experimental setup and inherent artefacts. The recommended rig changes are highlighted in the Future Work section.
Chapter Six

Thermodynamics of hydrogen isotope exchange
Chapter 6. Thermodynamics of hydrogen isotope exchange

6.1 Introduction

The Heat Transfer in Porous Media COMSOL Multiphysics interface has been used to examine the heat effects occurring during both exchange directions. This section presents and analyses the findings of the heat transfer modelling. Two means of analysis have been used: 3D temperature profiles of the Pd bed at a specific time (5 seconds) during each exchange; and 1D plots displaying the temperature profile (in the axial (z) direction) at a number of timesteps in the model.

It is known that there are significant heat effects during hydrogen isotope exchange reactions with Pd [15, 47, 65]. The D-H exchange is known to be exothermic, while the reverse H-D exchange is endothermic. The results of these analyses are presented and discussed in the following sections.

Note: these heat effects are directly driven by the derived kinetics presented in the Modelling Chapter. They’re therefore affected by the possibility of inherent inaccuracies until the kinetic model can be validated against additional experiments. This was not possible during the current thesis due to time and economic constraints (i.e. cost of additional D$_2$ gas).

The results presented herein demonstrate the ability of the kinetic COMSOL model to elucidate the heat effects occurring in the Pd bed, without the need for temperature probes located within the Pd bed which are especially difficult to install and maintain bed integrity. With validated kinetics the model could be used to predict the heat evolution from the Pd bed during an exchange reaction, enabling process using this phenomena to be designed more efficiently.

6.2 Heat transfer model formulation

The Heat Transfer in Porous Media interface has been used to describe heat transfer in the porous Pd bed. The interface uses the following form of the heat equation:
\[
(\rho C_p)_{eq} \frac{dT}{dt} + \rho_G C_{p,G} \mathbf{u} \cdot \nabla T = \nabla \cdot (k_{eq} \nabla T) + Q
\]  

where:

- \( \rho_G \) is the fluid density (kg m\(^{-3}\)).
- \( C_{p,G} \) is the fluid heat capacity at constant pressure (J K\(^{-1}\) mol\(^{-1}\)).
- \( (\rho C_p)_{eq} \) is the equivalent volumetric heat capacity at constant pressure.
- \( k_{eq} \) is the equivalent thermal conductivity (W m\(^{-1}\) K\(^{-1}\)).
- \( \mathbf{u} \) is the fluid velocity field (m s\(^{-1}\)). \( \mathbf{u} \) is the Darcy velocity (described by the Darcy’s Law and Free and Porous Media Flow interfaces) and is the volume flow rate per unit cross sectional area. The average linear velocity (the velocity in the pores) can be calculated as \( \mathbf{u}_L = \frac{\mathbf{u}}{\varepsilon} \), where \( \varepsilon \) is the fluid’s volume fraction (the porosity of the porous Pd).
- \( Q \) is the heat source (or sink) (W m\(^{-3}\)).

The equivalent conductivity of the solid-fluid system, \( k_{eq} \) relates the conductivity of the solid \( k_p \) and the conductivity of the fluid, \( k_G \) by:

\[
k_{eq} = \varepsilon_p k_p + \varepsilon_G k_G
\]  

The equivalent volumetric heat capacity of the solid-fluid system is calculated by:

\[
(\rho C_p)_{eq} = \varepsilon_p \rho_p C_{p,Pd} + \varepsilon_G \rho_G C_{p,G}
\]  

where \( \varepsilon_p \) is the solid material’s (Pd) volume fraction, which is related to the volume fraction of the fluid \( \varepsilon_G \) (porosity) by:

\[
\varepsilon_p + \varepsilon_G = 1
\]

The following table presents the known parameters used while modelling the heat transfer processes occurring in the Pd bed as a function of time:
### Table 6-1 Heat transfer modelling parameters

<table>
<thead>
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<th>Parameter</th>
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</thead>
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</tr>
<tr>
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<tr>
<td>Enthalpy of H$<em>2$ absorption ($dH</em>{H_2}$)</td>
<td>-37</td>
<td>kJ mol$^{-1}$</td>
</tr>
<tr>
<td>Enthalpy of D$<em>2$ absorption ($dH</em>{D_2}$)</td>
<td>-33.6</td>
<td>kJ mol$^{-1}$</td>
</tr>
<tr>
<td>Enthalpy of HD absorption ($dH_{HD}$)</td>
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<td>kJ mol$^{-1}$</td>
</tr>
<tr>
<td>Enthalpy of equilibrium co-proportionation reaction ($dH_{eq}$)</td>
<td>-0.65</td>
<td>kJ mol$^{-1}$</td>
</tr>
<tr>
<td>Molar heat capacity of Pd ($C_{Pd}$)</td>
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<td>J mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>Specific heat capacity of Pd ($C_{Pd,spec}$)</td>
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<td>J kg$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>Reactor heat transfer coefficient ($h_{reactor}$)</td>
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<td>W m$^{-2}$ K$^{-1}$</td>
</tr>
<tr>
<td>Solid material volume fraction ($\theta_p$)</td>
<td>0.227</td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity of Pd bed ($k_p$)</td>
<td>0.185</td>
<td>W m$^{-1}$ K$^{-1}$</td>
</tr>
</tbody>
</table>

One heat source and one heat sink were included in the heat transfer modelling. The heat source arose from the evolution of heat due to the chemical reactions occurring within the Pd bed. The heat sink represented heat losses to the surroundings through the reactor wall in the vicinity of the Pd bed. The heat source ($Q_{Heat}$) was described as follows:

$$Q_{Heat} = -(R_{eq}dH_{eq} - R_{H_2}dH_{H_2} - R_{D_2}dH_{D_2} - R_{HD}dH_{HD})$$  \[6-5\]

where: $R_{eq}$ is the reaction rate of the equilibrium co-proportionation reaction ($H_2 + D_2 \rightleftharpoons 2HD$) (mol m$^{-3}$ s$^{-1}$). $R_{H_2}$, $R_{D_2}$ and $R_{HD}$ were the volumetric reaction rate of H$_2$, D$_2$ and HD, respectively (mol m$^{-3}$ s$^{-1}$). The other terms are as described in Table 6-1. The units of $Q_{Heat}$ are W m$^{-3}$. The heat sink ($Q_{Loss}$) (i.e. heat loss to environment) was described as follows:

$$Q_{Loss} = A_s h_{reactor}(T_{amb} - T)$$  \[6-6\]

where: $A_s$ is the specific area of the reactor surrounding the compacted Pd bed (m$^{-1}$). $T_{amb}$ was the ambient temperature in the environment chamber for each exchange; and $T$ was the temperature variable calculated by the COMSOL Multiphysics model. The units of $Q_{Loss}$ were W m$^{-3}$. 
The adsorption enthalpies for H\textsubscript{2} and D\textsubscript{2} are widely available from the literature \[15, 65\]. The adsorption enthalpy for HD was taken to be an average of the values for H\textsubscript{2} and D\textsubscript{2}.

### 6.3 Pd bed temperature profiles

The temperature profiles calculated during the COMSOL Multiphysics simulations are now presented and discussed. The plots show data from various time steps in the simulation, for example 1 second, 5 seconds and 100 seconds.

#### 6.3.1 Low pressure PdD to PdH exchange (208 K):

Figure 6-1(a) shows the temperature profiles arising in the Pd bed during the low pressure D-H exchange carried out at 208 K. Figure 6-1(b) presents a 3D temperature profile occurring in the Pd bed at 5 seconds into the exchange. Figure 6-1(a) clearly shows that at 1 second (blue line) into the exchange there was a high temperature spike, peaking at 310 K, at the entry to the Pd bed. This spike represents a 100 K temperature increase in the vicinity of the region of initial reaction of H\textsubscript{2} with the deuterided Pd bed. As time progresses the temperature spike was found to decrease as the exchange front progresses through the bed. By 5 seconds (green line) the temperature at the exchange front reduced to 270 K, indicating a +60 K increase over the starting temperature of the Pd bed. This temperature increase was the same as reported by Charton \[65\]. As time progresses further the temperature profiles were found to decrease in peak height and begin to spread across the Pd bed, indicating that the exchange reaction was taking place over a larger portion of the bed, albeit at a lower rate because the heat evolution was less. Towards the end of the exchange, at 100 seconds (yellow line), a wide low profile was observed with a peak temperature value of 225 K. This demonstrates that after the initial stages the exchange reaction rate settled to a lower value and subsequently less heat was generated. By these later stages of the exchange a significant portion of the surface D atoms would have been displaced by H\textsubscript{2} resulting in fewer surface reactions taking place.

Interestingly, the COMSOL Multiphysics model shows that after admission of H\textsubscript{2} gas to the front of the Pd bed there was a decrease in temperature of \(~20\) K occurring immediately after the initial high temperature spike (blue line). This feature coincides with the generation of vacant sites (V\textsubscript{s}) observed on Figure 5-20(c) and the consumption
of D₂ on Figure 5-20(b). This indicates that D₂ desorption was occurring ahead of the advancing H₂/HD reaction front. The D₃ species bound to the surface were spontaneously desorbing by consuming energy from the surroundings, thereby causing a decrease in the calculated temperature. A similar cooling ‘zone’ was found at 5 seconds (green line) approximately 0.01 m into the Pd bed. The cooling in this case only amounted to ~5 K. After 5 second this feature was observed to disappear indicating that this localised cooling ahead of the initial reaction front only occurs in the early stages of the exchange. The reason for this phenomenon is unknown at present. More investigation is needed to determine whether this is a real effect or consequence of anomalies/inaccuracies in the heat transfer model.

Figure 6-1 Temperature profiles in Pd bed during low pressure D-H exchange carried out at 208 K: (a) Pd bed temperature profiles at various timesteps; (b) 3D bed temperature profile taken at 5 seconds into the exchange. The legend in (a) shows the different sample times used in the chart (seconds). The legend in (b) shows the temperature scale.
6.3.2 Low pressure PdD to PdH exchange (293 K):

Figure 6-2(a) shows the temperature profiles arising in the Pd bed during the low pressure D-H exchange carried out at 293 K. Figure 6-2(b) presents a 3D temperature profile occurring in the Pd bed at 5 seconds into the exchange. Figure 6-2(a) shows that the exchange was exothermic and, similarly to the 208 K data, there was a large temperature spike at 1 second into the exchange reaction. The peak of this spike was 316 K, indicating a temperature rise of 23 K. This was significantly lower than was found for the low pressure D-H 208 K exchange, however. Another difference found in the 293 K temperature profiles was broader temperature peaks. This indicates that the reaction front was spread over a larger portion of the Pd bed. This can be further visualised by referring to Figure 6-2(b). The 3D temperature profile shows that heat evolution from reaction was spread across a larger area of the Pd bed compared to the narrow band of heat generation in the 208 K exchange.

Furthermore, the 293 K data exhibits no areas of cooling as was found in the 208 K exchange. All the temperature profiles remain positive for the duration of the exchange. However, referring to the 5, 10 and 20 second temperature profiles on Figure 6-2(a) (green, red and aqua lines) it can be seen that the temperature profiles exhibit two distinct regions of high temperature, indicating two areas where reaction was occurring. One reaction zone remained at the entrance to the Pd bed and progressed slowly, while the other moved through the bed quicker. Referring to Figure 5-22(b) and (c) it can be concluded this ‘quicker’ front was displaced D$_2$ re-adsorbing to vacant sites on the Pd surface further along the axial distance of the bed. This adsorption of D$_2$ species caused an increase in D$_s$ species and a reduction in V$_s$ species. Accompanying these reactions was heat generation which resulted in the appearance of dual peaks on the temperature profiles.
6.3.3 **Low pressure PdD to PdH exchange (373 K):**

Figure 6-3(a) shows the temperature profiles arising in the Pd bed during the low pressure D-H exchange carried out at 373 K. Figure 6-3(b) presents a 3D temperature profile occurring in the Pd bed at 5 seconds into the exchange. Figure 6-3(a) shows that the exchange at 373 K was exothermic and significant heat was generated in the exchange reaction front. Again there was a high initial temperature spike upon admission of H\(_2\) gas to the Pd bed entry. The temperature was found to be ~450 K at 1 second into the exchange (blue line on Figure 6-3(a)). This indicates that there was a temperature rise of ~80 K associated with the exchange reaction initially. After 5 seconds...
seconds the temperature of the exchange front had reduced to 385 - 400 K. As the exchange proceeded, the temperature of the reaction front reduced further until it settled at ~385 K whereby the profiles began to broaden indicating surface reactions were occurring over larger portions of the Pd bed. After 50 seconds (pink and yellow profiles) the profile resembled a wide symmetrical peak. This coincides with the beginning of HD detection in Figure 5-11(c). At 100 seconds (yellow) the front edge of the peak began to exit the Pd bed at axial distance $z = 0.03175$. It can therefore be surmised that the lower level heat generation was linked to H atom adsorption/absorption into the surface sites remaining after the initial high rate of H$_2$ adsorption had displaced the majority of the D atoms from the surface. Consequently, during this period, more HD was produced from the residual D atom content in Pd by reaction with the incoming H$_2$ species. At this point the temperature profile settled at a lower value.

Similarly to the 373 K exchange, the emergence of dual peaks in the temperature profiles was found. This can be observed by referring to the temperature profiles between 10 – 20 seconds (red and aqua lines on Figure 6-3(a)). The cause of these dual peaks was two separate zones of reaction progressing through the Pd bed, one closer to the Pd bed entrance and one moving through the bed at a greater rate. Like the 293 K data this can be accredited to additional adsorption of D$_2$ further along the Pd bed.
6.3.4 Low pressure PdH to PdD exchange (208 K):

Figure 6-4(a) shows the temperature profiles arising in the Pd bed during the low pressure H-D exchange carried out at 208 K. Figure 6-4(b) presents a 3D temperature profile occurring in the Pd bed at 5 seconds into the exchange. The first immediate difference compared to the low pressure D-H exchanges was the reaction was endothermic. This can be observed in both Figure 6-4(a) and Figure 6-4(b). The temperature during the exchange was found to decrease well below the starting temperature (208 K). Figure 6-4(a) shows that, similarly to the D-H exchanges, the most dramatic temperature effects occur immediately after the incoming gas (D$_2$) was
admitted to the reactor. The temperature at 1 second into the low pressure H-D exchange was found to drop to 120 K, a reduction of 88 K below the initial temperature. H-D exchanges are known to be endothermic due to the difference in quantum states occupied by H and D atoms [15, 17, 37, 38]. Because of this difference in energy levels within Pd, energy is required to exchange H atoms with D atoms, hence the reaction was found to be endothermic. The size of the cooling, however, was surprising.

All of the profiles on Figure 6-4(a) up to 20 seconds exhibit areas of exothermic release (heating). This can be observed by referring to the profiles that exceed the 208 K starting temperature. The cause of this feature was the creation of H₈ species by H₂ adsorption into vacant sites (V₈) on the Pd surface (see Figure 5-26(c)). Therefore, displaced H₂ gas created by the adsorption of incoming D₂ was re-adsorbing to Pd creating heat. The magnitude of the temperature increase associated with this adsorption was found to be ~5 K.
6.3.5 Low pressure PdH to PdD exchange (293 K):

Figure 6-5(a) shows the temperature profiles arising in the Pd bed during the low pressure H-D exchange carried out at 293 K. Figure 6-5(b) presents a 3D temperature profile occurring in the Pd bed at 5 seconds into the exchange. Figure 6-5(a) shows that the H-D exchange carried out at 293 K was endothermic. At 1 second into the exchange the endothermic heat profile was found to peak at a value of ~243 K. This represents a reduction in temperature of 50 K compared to the starting temperature. The magnitude was therefore not as large as was calculated in the 208 K H-D exchange. The overall shape of the temperature profiles in Figure 6-5(a) were very similar to those obtained at
208 K. The profiles again exhibit areas of heating downstream of the main reaction endothermic front. The magnitude of the temperature rise in these regions was found to be similar (if not slightly larger) to what was recorded during the 208 K exchange.

The progress of the temperature front into the Pd bed after 5 seconds was less when compared to what was calculated for the 208 K exchange (Figure 6-5(b)). This corresponds to the lower permeability value found during model fitting to the 293 K experimental data (compared to the other two temperatures).
Figure 6-5 Temperature profiles in Pd bed during low pressure H-D exchange carried out at 293 K: (a) Pd bed temperature profiles at various timesteps; (b) 3D bed temperature profile taken at 5 seconds into the exchange. The legend in (a) shows the different sample times used in the chart (seconds). The legend in (b) shows the temperature scale.

6.3.6 Low pressure PdH to PdD exchange (373 K):

Figure 6-6(a) shows the temperature profiles arising in the Pd bed during the low pressure H-D exchange carried out at 373 K. Figure 6-6 (b) presents a 3D temperature profile occurring in the Pd bed at 5 seconds into the exchange. Figure 6-6(a) shows the endothermic nature of the 373 K exchange. The peak temperature drop at 1 second into the exchange (blue line) was 53 K. Again the general shape of the profiles was similar to the other two exchanges. However, one noticeable difference was the rate at which the heat front (reaction front) was moving through the Pd bed compared to the other two temperatures. This can be observed by referring to the distance between the profile...
peaks at the different temperatures. In the 373 K the peaks are more ‘spread out’ indicating the reaction front, and therefore heat evolution front, was moving through the Pd bed quicker than at the two other temperatures. This was to be expected considering the higher pressure of the inlet gas at 373 K and the increased reaction kinetic rate constants. These two factors would have caused the reaction front to progress through the Pd bed at a higher velocity. This effect can also be observed on Figure 6-6(b).

Figure 6-6 Temperature profiles in Pd bed during low pressure H-D exchange carried out at 373 K: (a) Pd bed temperature profiles at various timesteps; (b) 3D bed temperature profile taken at 5 seconds into the exchange. The legend in (a) shows the different sample times used in the chart (seconds). The legend in (b) shows the temperature scale.
6.3.7 1 L min⁻¹ PdD to PdH exchange (208 K):

Figure 6-7(a) shows the temperature profiles arising in the Pd bed during the 1 L min⁻¹ D-H exchange carried out at 208 K. Figure 6-7(b) presents a 3D temperature profile occurring in the Pd bed at 5 seconds into the exchange. The temperature profile was exothermic because the D-H exchanges are more thermodynamically favourable; there was a greater Gibbs free energy for the exchange of D atoms for H atoms compared with the reverse exchange. The biggest difference between the low pressure and 1 L min⁻¹ D-H exchanges was the magnitude of temperature increase. The high pressure 1 L min⁻¹ exchanges exhibit dramatic temperature rises initially at the entrance to the Pd bed. At 0.5 seconds into the exchange a ~825 K temperature peak was found at 0.004 m into the bed. This was a ~615 K increase over the initial 208 K starting temperature in the localised area of the reaction front. After 1 second (green line on Figure 6-7(a)) the temperature profile widens indicating heat evolution (and therefore reaction) over a large portion of the Pd bed. The peak of this profile was 650 K which demonstrates the overall reaction rate has slowed by 1 second into the exchange, compared to what was observed at 0.5 seconds. However, the level of heat evolution was still significant. The higher pressure of the 1 L min⁻¹ exchanges caused increased H₂ adsorption kinetics. This resulted in a higher reaction rate and therefore increased heat evolution calculated by the model. The magnitude of the temperature increase was, however, surprising.

The width of the 1 second temperature profile (green line) was due to a number of combined effects. Referring to Figure 5-32(b) and (c) it appears that displaced D₂ species moved through the Pd bed (as D₂) and re-adsorbed to vacant sites within the Pd bed, generating heat. This combined with the HD adsorption front (immediately behind the D₂ adsorption front) and the adsorption of H₂ (immediately behind the HD front) caused the wide peak observed at 1 second. The adsorption of the advancing D₂ front onto vacant sites (V₅) suggests that D₂ was adsorbed onto large amounts of vacant sites that did not exist at the start of the model. The physical explanation of this was challenging. However, it could indicate that D₂ was adsorbing onto vacant tetrahedral sites, unoccupied whilst the system was static at the start of the exchange. If the tetrahedral sites were considered in the model the available ‘total sites’ would have increased significantly. This is because in the β-phase D atoms would be occupying all the available octahedral sites, which are understood to be the most stable sites for H or D atoms to reside in, and not the adjacent (and plentiful) tetrahedral sites. Evidence of
tetrahedral site occupation has been found in the literature previously [44, 54]. Adsorption of D$_2$ onto ‘additional’ tetrahedral sites would increase the temperature in the Pd bed, as was found here. Because the model does not differentiate between the two different site types within Pd it was difficult to draw firm conclusions on this hypothesis. The model treats both octahedral and tetrahedral sites as ‘sites’ available for reaction.

After 2.5 seconds the temperature dropped to ~250 K and heat was evolved over the entire Pd bed. Furthermore, by 2.5 seconds the initial high temperature peak has passed through the bed and the observed temperature was associated with the ‘shoulder’ observed on the 1 second profile (green line). As time progressed further the temperature profiles were found to drop towards the starting temperature (208 K) indicating the exchange reaction was complete and negligible amounts of adsorption/absorption was occurring.

The 5 second 3D temperature profile (Figure 6-7(b)) demonstrates that the exchange front had progressed to the exit of the bed and a temperature peak of 250 K was found. Moreover, by 5 seconds the temperature at the entrance of the Pd bed had returned to 208 K.
Figure 6-7 Temperature profiles in Pd bed during 1 L min$^{-1}$ D-H exchange carried out at 208 K: (a) Pd bed temperature profiles at various timesteps; (b) 3D bed temperature profile taken at 5 seconds into the exchange. The legend in (a) shows the different sample times used in the chart (seconds). The legend in (b) shows the temperature scale.

6.3.8 1 L min$^{-1}$ PdD to PdH exchange (293 K):

Figure 6-8(a) shows the temperature profiles arising in the Pd bed during the 1 L min$^{-1}$ D-H exchange carried out at 293 K. Figure 6-8(b) presents a 3D temperature profile occurring in the Pd bed at 5 seconds into the exchange. The 0.5 second and 1 second temperature profiles (blue and green lines, respectively) demonstrate that there was a very high initial heat evolution associated with H$_2$ adsorption, similar to the 208 K. The peak temperature was 875 K. This was a ~580 K increase in the initial 0.004 m of the Pd bed. After 1 second the temperature profiles were observed to split into two peaks. This indicates that the initial high temperature peak moved through the Pd bed quickly.
The cause of this appeared to be displaced $\text{D}_2$ gas progressing through the Pd bed at a fast rate and adsorbing to the Pd, consuming vacant sites ($V_v$). The incoming $\text{H}_2$ gas was adsorbed earlier in the Pd bed (see Figure 5-33 and Figure 5-34(b) - (c)) coinciding with the lower temperature peak at 2.5 seconds (red line). The $\text{H}_2$ reaction front therefore moved through the Pd bed at a slower rate while displaced $\text{D}_2$ gas progressed quickly through a series of adsorption events with the deuterided Pd. These adsorption events involving $\text{D}_2$ were with vacant sites. As with the 208 K D-H exchange, this could be accredited to $\text{D}_2$ adsorbing onto tetrahedral sites within Pd [44, 54].

Figure 6-8(b) shows the 5 second temperature profile in 3D. It represents the $\text{H}_2$ reaction front occurring earlier in the Pd bed. The high temperature peak had already passed through the bed. The temperature of the $\text{H}_2$ reaction front was found to be ~380 K which was lower than the temperature found initially at 0.5 seconds. At this point the reaction rates had reduced compared to those found at the Pd bed entrance when $\text{H}_2$ gas was admitted to the reactor. Initially the $\text{H}_2$ gas was colliding at high pressure with the PdD surface, causing high reaction rates and heat evolution. As the reaction front progresses further into the Pd bed the effective pressure in the Pd bed was reduced (compared to the inlet pressure). This reduced the overall reaction rate and therefore the energy released due to adsorption/absorption. The $\text{H}_2$ exchange front after 1 second had a lower temperature peak than at the initial seconds of the exchange. It was also likely that the displaced $\text{D}_2$ gas carries away a large portion of the initial heat with it as it moves through the Pd bed.

The cause of the fast $\text{D}_2$ progression through the bed could be accredited to the higher inlet pressure of the $\text{D}_2$ gas species and the known increased diffusion rate of D atoms in Pd [59]. Both these effects would be magnified by the high temperature associated with the initial exchange of $\text{H}_2$ for $\text{D}_2$. 
Figure 6-8 Temperature profiles in Pd bed during 1 L min\(^{-1}\) D-H exchange carried out at 293 K: (a) Pd bed temperature profiles at various timesteps; (b) 3D bed temperature profile taken at 5 seconds into the exchange. The legend in (a) shows the different sample times used in the chart (seconds). The legend in (b) shows the temperature scale.

6.3.9 1 L min\(^{-1}\) PdD to PdH exchange (373 K):

Figure 6-9(a) shows the temperature profiles arising in the Pd bed during the 1 L min\(^{-1}\) D-H exchange carried out at 373 K. Figure 6-9 (b) presents a 3D temperature profile occurring in the Pd bed at 5 seconds into the exchange. Figure 6-9(a) demonstrates the exchange at this temperature exhibited a very high initial temperature associated with the H\(_2\) reaction front. The maximum temperature achieved at the entrance to the Pd bed was ~950 K (blue line). This was higher than was found for the 1 L min\(^{-1}\) 293 K exchange. Furthermore, the temperature profiles were found to ‘settle’ at slightly higher values than was found in the 293 K. The reason there was not a more notable increase
was hypothesised to be the available surface sites at 373 K. The initial stoichiometry of the Pd bed was PdD_{0.5} and the final hydride stoichiometry was PdH_{0.6}. There was therefore less initial adsorption of H_2/HD compared to the 293 K exchange because less surface sites were available for adsorption at 373 K. This caused the peak recorded temperature in the Pd bed to be close to that observed at 293 K because less (in comparison) energy was evolved in the form of heat. The author also highlights the potential alternate mechanisms and influence of subsurface region in the 293 K exchange which could have had additional effects on the heat evolution.

The two high temperature peaks at 0.5 and 1 second were found to be quite wide. This was due to the combined heat generation by adsorbing H_2, HD and additional D_2 adsorption onto vacant sites. The 5 second 3D temperature profile indicates that the reaction front was in the middle of the Pd bed and spread over a significant portion of the Pd bed. Heat was therefore evolved over a large portion of the Pd bed compared to that found for the 1 L min^{-1} 293 K exchange. Consequently, there was a greater amount of HD formed during the exchange.
6.3.10 1 L min⁻¹ PdH to PdD exchange (208 K):

Figure 6-10(a) shows the temperature profiles arising in the Pd bed during the 1 L min⁻¹ H-D exchange carried out at 208 K. Figure 6-10(b) shows the temperature profiles for later times in the exchange reaction in order to clarify certain features not visible when all time profiles were plotted on a single chart. Figure 6-10(c) presents a 3D temperature profile occurring in the Pd bed at 5 seconds into the exchange. Figure 6-10(a) demonstrates that at the initial stages of the exchange (between 0.5 seconds and 2.5 seconds) there was significant heat generated in the Pd bed. The temperature at 0.5 seconds (blue line) was found to spike at ~850 K. The temperature increase associated
with this peak was +640 K. This behaviour was similar to what was found for the 1 L min⁻¹ D-H exchanges. In both exchange directions there was a large initial spike in temperature related to high levels of reaction as gas was introduced into the front of the bed. The magnitude of heat generation was caused by large scale adsorption of D₂ and HD onto the Pd surface (see Figure 5-37(b) and (c)). These species were adsorbing onto vacant sites (Vₛ) (which can be seen on Figure 5-38(a), (b) and (c)) rather than displacing Hₛ species. This can be seen by the increase in Hₛ on Figure 5-38(b). This suggests that during the initial few seconds of the exchange, where the system was at its most dynamic in terms of pressure changes, there was occupation of additional surface sites. The explanation of this observation could lie in the existence of two sites within the Pd lattice; octahedral and tetrahedral. Traditionally the octahedral sites are assumed to host H or D atoms in Pd. However, some studies have highlighted the possibility of tetrahedral site occupation under certain experimental conditions [44, 54]. Tetrahedral sites are also hypothesised to take part in the transition of atoms from octahedral sites to other octahedral sites, i.e. they are a hopping site [15]. It could therefore be hypothesised that during the initial highly transient period of the exchange there was adsorption and occupation of tetrahedral sites.

In the D-H exchanges the temperature was found to fall to a positive value above the initial temperature of the Pd bed after 2.5 seconds, indicating heat generation. After 2.5 seconds into the 208 K H-D exchange the temperature profiles drop below the initial temperature, indicating the reaction at this point had become endothermic and was consuming energy from the surroundings in order for the exchange reaction to proceed. At this point (around 5 seconds into the exchange) the consumption of Hₛ and Dₛ were found to be approximately equal and the influence of vacant sites was significantly reduced (see Figure 5-38). This suggests that by this point there was a shift in the apparent adsorption. Incoming D₂ gas molecules were displacing Hₛ species to form H₂, rather than the incoming D₂ occupying vacant sites. This caused the system temperature profiles to drop below the initial temperature because this process was endothermic and therefore consumed energy. The enthalpy of adsorption/absorption (the empirical determined values include the dissociation and surface to bulk transfer steps into Pd) for H₂ is higher than for D₂. Subsequently, the enthalpy associated with desorption of H₂ was higher than the value for adsorption of D₂ and consequently the system consumes energy when exchanging H₂ for D₂.
Figure 6-10(b) demonstrates that after 4 seconds the 208 K H-D exchange was endothermic. The temperature profiles show that during the exchange the temperature in the bed dropped to 194 K; a 14 K decrease over the initial temperature. Figure 6-10(c) shows the 3D temperature profile at 5 seconds. From this it was clear that at 5 seconds the temperature at the entrance of the Pd bed was low and at the exit it was above the initial temperature. The higher temperature at the exit of the bed is due to the upstream tailing of the high temperature peaks created during the initial stages of the exchange. This can also be seen on Figure 6-10(b) (blue).
Figure 6-10 Temperature profiles in Pd bed during 1 L min\(^{-1}\) H-D exchange carried out at 208 K: (a) Pd bed temperature profiles at various early timesteps; (b) Pd bed temperature profiles at various early timesteps (c) 3D bed temperature profile taken at 5 seconds into the exchange. The legend in (a) shows the different sample times used in the chart (seconds). The legend in (b) and (c) shows the temperature scale.
6.3.11 1 L min$^{-1}$ PdH to PdD exchange (293 K):

Figure 6-11(a) shows the temperature profiles arising in the Pd bed during the 1 L min$^{-1}$ H-D exchange carried out at 293 K. Figure 6-11(b) shows the temperature profiles for later times in the exchange reaction in order to clarify certain features not visible when all time profiles were plotted on a single chart. Figure 6-11(c) presents a 3D temperature profile occurring in the Pd bed at 5 seconds into the exchange. Similarly to the 208 K 1 L min$^{-1}$ H-D exchange, Figure 6-11(a) shows that there was again high temperature peaks found. At 0.5 seconds (blue line) into the 293 K exchange the temperature was found to peak at 750 K, representing a temperature rise of 457 K. At 1 second (green line) the temperature peak had moved further through the Pd bed and the temperature had decreased to ~700 K. By 2.5 seconds (red line) this high temperature front had left the Pd bed with a peak temperature found to be ~325 K.

Referring to Figure 5-40(c) it is clear that these heat evolution peaks are associated with adsorption of D$_2$ and HD onto vacant sites on the Pd surface. This again suggests D atom occupation of tetrahedral sites because at the conditions investigated here (i.e. initial reactor pressure and incoming pressure $P_m$) the Pd was in the $\beta$-phase and, within reason, all available octahedral sites are occupied by H atoms. The adsorption and subsequent absorption of incoming D atoms into the tetrahedral sites would release a significant amount of energy as was found here. Alternatively, the incoming high pressure gas was triggering large amounts of octahedral sites to become available for adsorption. However, the only way in which this could happen would be for H$_s$ species to be displaced forming H$_2$, which was not found in the reaction rate data for H$_2$ (Figure 5-39(a)).

As was found for the 208 K exchange, as time progresses the exchange moves to an endothermic process with a temperature decrease peaking at ~20 K.
Figure 6-11 Temperature profiles in Pd bed during 1 L min⁻¹ H-D exchange carried out at 293 K: (a) Pd bed temperature profiles at various early timesteps; (b) Pd bed temperature profiles at various early timesteps (c) 3D bed temperature profile taken at 5 seconds. The legend in (a) shows the different sample times used in the chart (seconds).

The legend in (b) and (c) shows the temperature scale.
6.3.12 1 L min\(^{-1}\) PdH to PdD exchange (373 K):

Figure 6-12(a) shows the temperature profiles arising in the Pd bed during the 1 L min\(^{-1}\) H-D exchange carried out at 373 K. Figure 6-12(b) shows the temperature profiles for later times in the exchange reaction in order to clarify certain features not visible when all time profiles were plotted on a single chart. Figure 6-12(c) presents a 3D temperature profile occurring in the Pd bed at 5 seconds into the exchange. Figure 6-12(a) demonstrates the high temperature peaks which were again found. The peak temperature at 0.5 seconds into the exchange (blue line) was 850 K. The general shapes of the exothermic profiles were similar to those found at 208 K and 293 K, albeit with higher peaks. The temperature increase at 0.5 seconds was 477 K which was lower than the value of the temperature rise found during the 293 K and 208 K exchange simulations. The explanation of this finding was the lower ‘total sites’ in the model. At 373 K the stoichiometry was PdH\(_{0.6}\), compared to PdH\(_{0.7}\) and PdH\(_{0.8}\) for the 293 K and 208 K exchanges, respectively. This meant there were fewer vacant sites available for D\(_2\) adsorption. Fewer available vacant sites caused a lower heat accumulation than was observed at 293 K and 208 K.

The high temperature peaks show clear evidence of the adsorption of D\(_2\) into vacant sites (see Figure 5-41(b) and Figure 5-42(b) and (c)). As stated earlier, the author believes this to be due to the influence of tetrahedral sites in Pd. This hypothesis would need to be investigated further by including a description of the two different available sites (octahedral and tetrahedral) within Pd in the COMSOL Multiphysics model. This modification would also need to include a description of the different energies associated with adsorption/absorption onto the different sites in order to draw firm conclusions on the influence of tetrahedral sites.

Figure 6-12(b) demonstrates that after 4 – 5 seconds the exchange the temperature profiles were endothermic. As discussed before, after these times the exchange takes place via displacement of surface H\(_8\) species by incoming D\(_2\) and there was little change in the consumption of vacant sites (Figure 5-42(c)). This process was therefore endothermic.
Figure 6-12 Temperature profiles in Pd bed during 1 L min\(^{-1}\) H-D exchange carried out at 373 K: (a) Pd bed temperature profiles at various early timesteps; (b) Pd bed temperature profiles at various early timesteps (c) 3D bed temperature profile taken at 5 seconds. The legend in (a) shows the different sample times used in the chart (seconds).

The legend in (b) and (c) shows the temperature scale.
6.4 Discussion

Analysis of the thermodynamics and heat effects occurring in the Pd beds during hydrogen isotope exchanges has revealed some interesting, and sometimes surprising, findings. While there was no experimental ‘in bed’ temperature data to compare the heat transfer model findings to, the good fits to experimental data of the COMSOL Multiphysics kinetic model allow significant insights into the heat effects occurring within Pd beds during both D-H and H-D exchanges. Modelling the heat effects occurring during exchanges in Pd produced results in line with previous studies in the literature [65]. The D-H exchanges have been shown, as expected, to be exothermic processes generating significant heat during the simulations. The H-D exchanges were found to be endothermic processes, as expected. The low pressure (ca. 1.5 bar) D-H exchanges showed more modest temperature rises than the 1 L min\(^{-1}\) exchanges. They were found to be close in magnitude to those found by Charton [65] during their modelling of the heat transfer processes occurring during isotope exchanges at low pressure.

Charton [65] modelled Foltz and Melius’ [1] results for their exchange carried out at ~1.5 bar and thus only investigated the D-H process at 298 K. They found a temperature rise of ~60 K. The simulated (herein) temperature rises during the 208 K and 373 K were found to be 60 K and 80 K, respectively. These appear to match closely to Charton’s values, however, the temperature rise during the 293 K D-H exchange was found to peak at 313 K, representing a 20 K increase over the initial temperature in the reactor. The explanation could reside in the hypothesis of ‘direct’ exchange events occurring at this temperature and the resultant variation in activation energies of the adsorbing/desorbing species.

The author highlights that the experimental results for the 293 K D-H exchange show significant departure from those found by Foltz and Melius [1] (and further investigated by Charton [65]). The production of HD was markedly lower than Foltz and Melius found and the length of ‘pure’ D\(_2\) evolution at the start of the exchange was significantly longer. These findings were found over a number of repeats on the same Pd bed and during exchanges with replacement ‘fresh’ beds. The author therefore believes the findings at 293 K represent real effects. Furthermore, analysis of the experimental method used by Foltz and Melius raises some concerns based on the experience found
herein with Pd bed preparation. Foltz and Melius exposed their Pd bed to a number of cycles of hydrogen (deuterium) loading and removal via vacuum. In the authors experience these processes cause irrevocable damage to the Pd bed, causing large cracks and even disintegration of the bed. The author believes that Foltz and Melius’ Pd bed may have suffered from significant cracking which would have opened the structure of the bed, exposing incoming gas to increased Pd surface area. This would have had the effect of increasing the amount of HD production and reduced the appearance time for this species. It would have also reduced the length of the ‘pure’ D$_2$ at the start of the experiment. Both features are found in Foltz and Melius’ results.

Moreover, the Pd particle size used in the current study was smaller than that used by Foltz and Melius and the Pd bed was compressed to a lower bulk density (3 g cm$^{-3}$). This created a far higher overall bed porosity in the experiments herein. The effect of this was faster gas velocity through the bed and reduced exposure to the Pd surface for reaction to occur. This combined with the shorter Pd bed length used in this work would significantly affect the observed physical processes, and therefore the heat effects are not entirely comparable. The findings discussed in previous sections of this work suggest that there may be evidence of additional Pd surface process occurring, a ‘direct’ exchange of incoming H$_2$ species for D$_2$, and a significant departure from gas phase equilibrium at 293 K. These findings significantly affect the COMSOL Multiphysics model of the heat transfer processes, particularly the finding that the HD adsorption and desorption rate constants were relatively unaffected by increasing temperature. In fact, the rate constants for both surface process were found to decrease to a plateau after 208 K (i.e. increasing the temperature beyond 293 K did not increase the fitted rate constants as would be expected in an Arrhenius type relationship). This could point to additional surface/subsurface/bulk processes involving H$_2$ and D$_2$ which could generate heat in an unexpected/unaccounted for manner, or indeed lower the activation energy required for desorption. The negative activation energies found for the HD surface processes certainly appear to support this hypothesis. To draw firm conclusions on whether this hypothesis is indeed the correct, further model development will be required to modify the current model to include a description of bulk and subsurface processes. In tandem with this a modification to the IsoEx will be required to include a temperature sensor within (or in close proximity to) the Pd bed to record real temperature effects.
The 1 L min\(^{-1}\) D-H exchanges simulations showed rather dramatic temperature rises during the initial periods of the exchange reactions. The D-H exchanges at 208 K, 293 K and 373 K were found to have temperature rises of 615 K, 580 K and 577 K, respectively, within the first 0.5 seconds of the simulation. These large temperature increases arise from the larger reaction rates found in the 1 L min\(^{-1}\) exchanges compared to the low pressure runs. The adsorption kinetics were found to be significantly higher for the 1 L min\(^{-1}\) exchanges during fitting, largely due to the increased pressure driving force at the entrance to the Pd bed in these exchanges. Additionally, immediately after the simulation commences a large dynamic pressure change was introduced into the system (as was the case in actual experiments). Incoming gas was therefore entering the system at high velocity and colliding with the front of the Pd bed. These factors combine to increase the number of gas-solid interactions occurring and this resulted in considerably more heat being generated initially. Evidence of this link to the initial admission of high pressure gas can be found by referring to the heat profiles for the 1 L min\(^{-1}\) D-H exchanges (Figure 6-7, Figure 6-8 and Figure 6-9). The temperature ‘spike’ at the start of the experiment was found to dissipate after ~2.5 seconds in each of the three temperatures. This indicates that after the initial highly dynamic period the exchange reaction ‘settles’ and heat generation was more modest for the remainder of the exchange reaction. The ‘settled’ temperatures were ~260 K, ~385 K and ~425 K for the 208 K, 293 K and 373 K exchanges, respectively.

The low pressure H-D exchange simulation showed the process was endothermic. The temperature decrease during the 208 K, 293 K and 373 K were found to be 88 K, 50 K and 53 K, respectively. The 293 K H-D exchange exhibits a similar trend to that found for the D-H exchanges, that is, its value was out of sequence with the two other values. In this case the 293 K exchange was found to have a smaller temperature decrease than the 208 K and 373 K. The cause of this was again postulated to be due to the surface processes involving D\(_2\). In the 293 K H-D exchange the value of the D\(_2\) adsorption rate constant was found to be three times larger than the adsorption kinetic of HD and 15 times larger than the H\(_2\) adsorption kinetic. The desorption kinetics were found to be comparable for each of the three gas species (H\(_2\), HD and D\(_2\)). The higher adsorption kinetic rate constant for D\(_2\) drives the reaction rates of D\(_2\) with the Pd surface. Since adsorption is an exothermic process, large amounts of heat were released, causing the lower simulated endothermic temperature drop at this temperature. Furthermore, this
effect was magnified by the dynamic nature of the initial period of the exchange and large subsequent pressure changes of D$_2$ in the system. Essentially there was a greater quantity of D$_2$ adsorbing compared to any of the other surface processes involving HD or H$_2$.

The simulated heat effects in the 1 L min$^{-1}$ H-D exchanges make for interesting discussion. While the overall profiles of the H-D exchanges were endothermic, initially they were not. In the 1 L min$^{-1}$ H-D simulations an initial period of heat generation was found. These early periods of high heat generation were only found before 2.5 seconds in each of the three exchanges carried out at 208 K, 293 K and 373 K. After this the profiles became endothermic. These high temperature peaks were found to be linked to D$_2$ (and HD) adsorption onto vacant sites. The significance of this was hypothesised to be D atom occupation of (or transition through) tetrahedral sites within Pd ‘freeing up’ vacant sites for D$_2$ adsorption. The reasoning behind this was that at the start of an experiment the Pd was in the β-phase and the majority of available octahedral sites would be occupied. The reaction of D$_2$ with large amounts of vacant sites in the model simulation suggests that additional sites were involved in the exchange. The only other sites available for atoms to reside in an fcc metal, such as Pd, are the tetrahedral sites. As pointed out in earlier sections, tetrahedral occupancy has been observed previously [44, 54]. However, another explanation is the higher heat of absorption of H. At the start of the experiment displaced H$_2$ and HD could be readsorbing causing additional H atoms to be absorbed into vacant octahedral sites within the Pd lattice, resulting in a higher calculated temperature peak.

Overall the heat transfer modelling efforts for both exchange directions have been successful. They have provided useful insights into the potential heat effects occurring during isotope exchange reactions with Pd. Certainly, more investigations are needed to come to firm conclusions as to whether the above hypotheses are indeed correct. As was identified previously, thorough continuations to the experimental plan as well as modifications to the IsoEx rig and COMSOL Multiphysics kinetic model are needed to investigate the heat effects and thermodynamics of the system conclusively. These modifications and recommendations are discussed in detail in the Future Work section of this thesis.
Chapter Seven

Conclusions and Future Work
Chapter 7. Conclusions and Future Work

7.1 Conclusions

The aim of this thesis was to develop a thorough parametric model that could simulate the effluent gas composition leaving a flow reactor as a function of time, for both hydrogen isotope exchange directions, D-H and H-D. The aim of this being, to develop an understanding of the underlying kinetics and mechanisms of the hydrogen isotope exchange process and to trial at least one existing surface reaction mechanism, such as the Langmuir-Hinshelwood mechanism. Furthermore, an additional aim was to investigate how such a model relates to what is already known and reported about the kinetics of the interactions of hydrogen (and deuterium) with solid palladium.

A thorough experimental plan was developed and executed in order to provide the experimental data sets needed to validate the models developed in this work. Hydrogen isotope exchange in packed powder palladium beds has been investigated under two pressure regimes and at a number of temperatures which give an insights to the exchange process under normal (ambient) and extreme conditions. The following conclusions can be drawn from this work:

1. The IsoEx apparatus was installed, de-snagged and commissioned successfully during this work. A successful experimental procedure was developed which can be used by future investigators to complete exchange experiments in a reduced time, therefore reducing the amount of time spent setting up a flow apparatus to examine hydrogen isotope exchange. Significant understanding of Pd beds was also developed. The experimental procedure for maintaining Pd beds in the β-phase allowed numerous experiments to be performed on one bed, reducing the amount of Pd waste created during the project. A high resolution mass spectrometer was commissioned and optimised for the study of the low molar mass gas species used in this work. This involved developing calibration methodology for all three gas species (H₂, D₂ and HD) and adhering to a strict calibration schedule to ensure the results from the spectrometer were accurate and trustworthy. HD gas was particularly troublesome in calibrating since the
gas is not freely available. The apparatus was modified to allow calibration using costly pure HD gas. Another modification which ensured gas quality was the installation of in line purifiers to remove impurities to sub ppb levels from the gas streams. This was deemed necessary after experiencing first-hand the effects of surface poisoning by adsorption of impurities.

2. The hydrogen isotope exchange process involves a number of complex phenomena which are influenced significantly by the conditions of the exchange process. The experimental results demonstrate that the exchange profiles vary greatly depending on the pressure regime and the temperature of the reaction. Furthermore, significant differences were observed between the D-H and H-D exchange reaction processes. Again both exchange directions were affected by pressure and temperature in differing ways. The D-H process was consistently more efficient and completed in less time than the H-D exchange in all pressure regimes and temperatures. For example, under the low pressure regime (1.3 – 1.7 bar upstream pressure) the timescale of the D-H exchanges was of the order of ~500 seconds, while the H-D exchanges required ~1200 seconds to complete. Under the high pressure regime (5 – 8 bar upstream pressure) the D-H exchange were found to complete in ~25 seconds, while the H-D exchanges required 80 seconds. This demonstrated that the exchange process could be significantly altered by controlling the upstream pressure of the isotopic species flowed into the reactor.

3. The extent of equilibration between the gas and solid phases in the exchange front was analysed using the application of the apparent equilibrium constant, or concentration ratio ($K_{app}$). This demonstrated that in almost all of the exchanges, whether carried out under high pressure or low pressure regimes, the reaction front was not in equilibrium as would be expected from previous studies involving Sievert’s type dosing apparatus.

4. The seminal hydrogen isotope exchange model developed by Foltz and Melius [1] was found to be capable of only simulating their results obtained at 298 K and ca. 1 bar inlet gas pressure. The Foltz and Melius model was recreated in
MATLAB and used to simulate their experimental results. Upon applying the MATLAB based model to the experimental results obtained in this work it was found to be incapable of reproducing any of the experimental data satisfactorily. This was due to limitations in the formulation of the model. Despite the solution being equated using explicit and implicit methods, the model description was found to be flawed and numerical shocks consistently arose in the solutions causing them MATLAB code to crash. The model formulation was modified extensively to attempt to remove these problems but no acceptable solution was found that allowed the higher pressure exchange data from this work to be modelled.

5. More success was found when recreating the Foltz and Melius model in COMSOL Multiphysics. COMSOL Multiphysics, with the Chemical Reaction Engineering module, was purchased alongside a very powerful workstation with 128 GB RAM and dual processors to nullify any previous problems encountered through lack of RAM or processing power. The formulation of the Foltz and Melius model was coded into COMSOL Multiphysics, a far more powerful programme with built in physics equations describing fluid flow and reactions, to attempt to model the IsoEx exchange data. The model was found to be partially satisfactory in simulating the experimental results, with some exchanges being modelled quite well. However, a fundamental assumption of the Foltz and Melius model was found to be incorrect: the assumption of equilibrium in all spatial points in the Pd bed and at all points in time. The equilibrium constant values used in the COMSOL Multiphysics version of Foltz and Melius’ model were shown to be a main driver for poor simulation results. Furthermore, the isotope exchange probability was a major constraint on the modelling process. Outside of a certain range of probability values ($1 \times 10^8 < p > 3 \times 10^7$) the model failed to resolve and no simulation results were obtained. This significantly constrained the model.

6. A full kinetic model of the process successfully simulated all the experimental data obtained on the IsoEx apparatus at a number of pressures and temperatures in one-dimension, two-dimensions and three-dimensional geometry. COMSOL Multiphysics was used to create a model of the hydrogen isotope exchange
process which considered the reaction kinetics of the surface processes deemed most relevant to the Pd powder used in the experiments. The Langmuir-Hinshelwood surface reaction mechanism proved highly capable describing the exchange reaction on Pd powder; all of the isotope exchange experiments were fitted satisfactorily using this mechanism. Since the Pd particles were small the rate limiting step was assumed to be the surface processes because bulk diffusion in the particles was considered fast in comparison. This assumption aligned with a number of previous studies in the literature that identified the surface processes at the slowest step in the reaction mechanism, involving the highest activation energies. The comprehensive kinetic model developed in this thesis considered the adsorption and desorption mechanisms of the three gas species (H₂, D₂ and HD). The built in physics descriptions within COMSOL Multiphysics were used to provide comprehensive descriptions of the fluid flow and surface reactions. The software computed the mass and energy balances based on conservation or mass and energy principles. The free fluid flow was described by the Navier-Stokes equations in all geometries. Darcy’s law was applied for the porous media flow in the one and two dimensional models, but in three dimensions an extended form of the Navier-Stokes equations were used to simulate the flow of gases through the porous Pd bed. The forward (adsorption) and reverse (desorption) kinetic rate constants describing the rates of the surface reactions were arbitrarily manipulated to fit the IsoEx experimental data. A description of the known equilibration reaction was also included into the model to provide consistent initial conditions for the model to start from. This reaction was driven by the specification of the equilibrium constant (K_{eq}). To maintain thermodynamic consistency, the reverse rate constant for HD desorption was constrained by the known K_{eq} values for the equilibration reaction between mixed isotope (H₂ and D₂) gas species and Pd. In some cases, when experimental data proved troublesome to simulate, this reverse rate constant was also arbitrarily manipulated to provide an improved fit to experimental data. This technique was very successful in bringing the model simulations in line with experimental data. This provided more evidence that the equilibrium assumption outlined by Foltz and Melius was not entirely correct in dynamic flowing systems, as was the case in this thesis. Moreover, the experimentally
determined $K_{app}$ values for the each specific exchange reaction were applied to the COMSOL Multiphysics kinetic model. It was found the addition of these values in place of the traditional $K_{eq}$ value significantly enhanced the model fits. This again provided more evidence that the equilibrium assumption was not correct in a dynamic system. Finally, some of exchanges could not be fitted to a high accuracy with the Langmuir-Hinshelwood surface reaction mechanism. It was postulated that under the specific experimental conditions where this was the case, another surface reaction mechanism may be more appropriate, such as the Eley-Rideal or Bonhoeffer-Farcus mechanisms. Implementing these mechanisms into the COMSOL Multiphysics kinetic model could provide a higher level of fit to experimental data under specific conditions.

7. COMSOL Multiphysics was used to plot the reaction rate profiles occurring through the bed at different times throughout the exchanges. Large reaction rates were found during the initial dynamic conditions (< 5 seconds) before the rates settled to lower values as more of the hydrogen capacity of the Pd beds was consumed. Furthermore, during the D-H exchange the dynamic conditions appeared to suggest the admission of high pressure hydrogen triggered large scale D$_2$ migration through the porous bed. Dual reaction peaks were therefore calculated as D$_2$ (and D atoms) moved through the bed causing additional desorption in the downstream portions of the bed. The role of vacant sites was shown to be very important in both exchange processes. Some of the unexplained phenomena and large involvement of vacant sites in the exchange reactions was accredited to the existence and influence of additional regions or reaction mechanisms in the Pd structure affecting the exchange process. Subsurface sites have been shown to low activation energies for desorption processes. These were postulated to be affecting the exchange process in both directions.

8. The activation energies of all the surface processes was analysed using Arrhenius plots. The magnitude of the low pressure hydrogen isotope exchange surface process activation energies was found to be lower than those found at the higher pressure (1 L min$^{-1}$) exchanges. The low pressure activation energies
were found to be of the same magnitude as those found by Luo et al [60], who investigated exchange in a Sievert’s apparatus using ultra-pure gases and low pressures. The conclusion was made that because the IsoEx rig featured ultra-purification of the gas species that these results were comparable and that the higher activation energies found by Carsten and Encinias [3] and Outka and Foltz were affected by the inclusions of impurities in their gas streams. Larger activation energies were calculated for the 1 L min$^{-1}$ exchanges. This was accredited to the larger quantities of impurities (even with ultra-purification) adsorbing to the Pd surface under conditions between 5.5 – 8.3 bar. The 1 L min$^{-1}$ activation energies were therefore of the order of those found by Outka and Foltz [2] and Carstens and Encinias [3] who used lower purity gases but lower inlet gas pressures. Some of the activation energies for the specific surface processes were found to be negative, suggesting that the processes had no real temperature dependence or that other processes in the overall reaction mechanism were dominating the process. It was also hypothesised that these negative activation energies could suggest the processes were spontaneous and therefore not rate limiting. However, acknowledgement was made to the fact that additional experimentation is required to validate the kinetic model and the subsequent derived activation energies. Moreover, thorough model testing is required through predictive methods (i.e. the kinetic COMSOL model should be used to predict the experimental outcome of experiments not yet carried out).

9. The thermodynamics of the hydrogen isotope exchange process in both directions have been examined using COMSOL Multiphysics. Heat transfer was coupled to the fluid flow and reaction descriptions to provide insights into the heat effects occurring in each of the exchange reactions. The D-H exchanges were found, as has previously been shown by Charton et al [65], to be exothermic. In particular, the temperature rise in the Pd bed was found to be of the order found by Charton et al [65], approximately 60 – 80 K. However, during the very early stages of the exchanges (< 2 seconds) very large temperature spikes were found which corresponded to large scale H$_2$ adsorption associated with the dynamic conditions. The unfavourable H-D processes exhibited endothermic behaviour. The temperature was found to decrease in magnitude by roughly the same amount as found by Charton et al, approximately
60 – 80 K. However, in the initial dynamic period of the H-D exchanges the temperature was found to rise in accordance with adsorption of D₂ onto vacant sites. After the initial few seconds of the exchanges, the temperature was calculated to fall below the starting temperature, indicating dominance of the endothermic reactions.

Overall this thesis has achieved its original aims as described in Chapter 1. Additional understanding of the Pd-H(D) isotope exchange system has been elucidated alongside individual rate constants for the three surface processes involving H₂, D₂ and HD. Furthermore, novel hydrogen isotope exchange data is in the process of being published which examines the exchange under new experimental conditions using a unique apparatus specially designed for the thesis. Finally, the work presented here provides an excellent starting point from which future investigators can continue the study into hydrogen isotope exchange over Pd powder. All the findings can be built upon to provide a thorough multiphysics understanding of the exchange process.

7.2 Future work

Whilst the work carried out during this project has been extensive, there are still a number of areas which require additional investigation to validate not only the hypotheses made herein but those already existing in the literature. The Pd-H(D) system has been one of the most widely studied systems since Thomas Graham began his investigations in the 19th century [5]. Despite this, there still remains significant uncertainty around the physical and chemical processes occurring during hydrogen absorption by Pd. The hydrogen isotope exchange project at the University of Bath has the potential to elucidate substantial additional understanding of the Pd-H(D) system and its behaviour under dynamic and steady state conditions. It is imperative that the IsoEx rig be used to its full potential in the future because the apparatus is unique in the world and has significant capabilities in terms of operating conditions that others do not. Furthermore, the rig was the result of significant investment both in terms of design and capital expenditure. This section will introduce the proposed work that, in the author’s belief, would make best use of the equipment. These improvements/modifications to both the IsoEx rig and COMSOL Multiphysics kinetic model are now discussed in detail.
There are three main areas in which any future work should focus: experiments, modelling and rig modifications. Firstly, the experimental plan should be extended to investigate both exchange directions at additional temperatures and pressures. The temperatures investigated so far involved examining relative extremes of the available temperature range. There needs to be additional experiments performed in between these existing studies. For instance, the author recommends that experiments should be carried out at: 230 K, 260 K, 280 K, 300 K, 350 K, 450 K and 500 K. All these temperatures are well within the capability of the IsoEx rig since the reactor coil heater can achieve a temperature of 573 K. While this may appear to involve a large number of experiments, it is deemed entirely possible to carry these out, for example, in another PhD studentship. There will be no need for experimental setup trials as was necessary during this work because a successful and efficient methodology exists. Furthermore, investigating a wide range of temperatures as has been highlighted above would allow a detailed picture of the temperature effects to be elucidated and kinetic model validation to be carried out. The author particularly recommends focussing on temperatures around 293 K. This temperature has raised significant questions about the physical and chemical processes occurring within Pd, as can be seen by referring to the unexpected $K_{eq}$, permeability and $k_i$ values found during this work. It will be important for these varied temperature experiments to be carried out under strict pressure control so any effects arising from pressure are negated.

Another focus of the future work should be on investigating the effects of pressure on both exchange directions. In the current work the maximum pressure achieved was 8 bar. The IsoEx rig has the ability to investigate hydrogen isotope exchanges using upstream pressures up to 200 bar. The author would recommend beginning investigating exchanges at pressures up to 50 bar initially due to the high cost of 200 bar D$_2$ cylinders. Similarly to the proposed temperature experiments, the temperature control during these experiments will be imperative in extracting useful information about the effects of pressure on the exchange.

Further interesting experiments would involve investigating the exchange reactions under steady state conditions. The IsoEx rig is capable of flowing mixed gas streams into the reactor (i.e. 50:50 H$_2$:D$_2$; 25:75 H$_2$:D$_2$; 75:25 H$_2$:D$_2$). During these runs the production would reach a steady state value. It would be interesting to compare the
effluent apparent equilibrium constant (or concentration ratio) from these experiments to existing empirical relationships for $K_{eq}$ in the literature to see if the reaction was indeed at equilibrium and matched data from static Sievert’s type measurements. Moreover, experiments in this format would allow for elucidation of the steady state rate laws and kinetics. These may not be applicable to dynamic experiments as was the subject here, however, they could still reveal information about the surface reaction mechanisms occurring at steady state.

Another important addition to the experimental plan going forward is the need to investigate commercially available Pd powder. In the current work a special Pd powder has been used that is subject to MoD non-disclosure policy. As such, the powder could not be characterised in any detail. This made it difficult to determine whether the isotope exchange features observed herein were a function of the experimental conditions or the morphology/structure/topology of the Pd powder. It is recommended that any future work be performed on commercial Pd powder (including perhaps Pd alloy systems) that is well characterised in terms of surface topology, particle size, morphology and composition. Using a commercial powder would also allow additional techniques to be employed to investigate the isotope exchange reaction in Pd. This could be either inelastic neutron scattering, or indeed neutron diffraction techniques.

The second major area of future work should focus on continued model development. The current COMSOL Multiphysics kinetic model (including heat transfer) was very capable of describing both exchange directions via the Langmuir-Hinshelwood surface reaction mechanism. However, in treating the process as involving only (or being rate limited by) the surface causes some of the more intricate details to be overlooked. For example, some of the fitted kinetic values lump a number of processes together (i.e. dissociation, surface diffusion, surface-to-bulk transfer steps (or dissolution) and bulk diffusion). In future these individual processes will need to be included if a thorough kinetic model is to be developed that allows the user to elucidate the true rate determining physical/chemical process. The model should almost certainly be extended to include descriptions of the bulk and subsurface regions of the Pd particles. The influence of the subsurface has been shown to have a significant effect on desorption activation energies [122, 124, 138-140]. Including the population of these regions, and how they changes with pressure and temperature, into the model would be a significant
achievement in any future studies and would allow the influence of these regions to be elucidated. Furthermore, the kinetic model should be modified to include descriptions of the surface diffusion and differences in bulk diffusion coefficients for H₂, D₂ and HD. This may not affect the outcome of the model greatly, but for completeness it is deemed necessary. The model as it exists is, however, a very good starting point for future investigations.

Another avenue to explore will be different surface reaction mechanisms (e.g. Eley-Rideal and Bonhoeffer-Farcus etc). These may offer additional insights into the exchanges that could not be fit perfectly during this work, despite significant variation in the model parameters. This may suggest the existence of different reaction mechanisms under certain experimental conditions. Furthermore, the heat effects of the exchange process need to be directly coupled to the kinetics of the model through the activation energies. This will require further experimentation and modelling to conclusively determine accurate activation energies which can be implemented into Arrhenius type equations describing the kinetic rate constants.

There are a number of modifications to the IsoEx rig that would aid future hydrogen isotope exchange experiments. Firstly, a very useful addition to the rig would be a bypass line in which gases can be flowed directly to the mass spectrometer (see Figure 6-13). This would aid in gas characterisation prior to experiments. For example, to record the background levels of impurities in the incoming gases to a hydride (deuterided) Pd bed. Having the ability to bypass the reactor would allow Pd beds to remain in their hydrided (deuterided) state whilst using the mass spectrometer. This would prevent Pd beds from having to be removed/replaced in order to perform characterisation tests on inlet gas streams, reducing the cost associated with Pd usage.
Another recommended modification would be the addition of faster switching valves in the inlet control section of the rig. Currently, the switching valves are satisfactory when performing non pre-flow type experiments, whereby either H₂ (or D₂) is allowed to flow into a deuterided Pd bed (or hydrided) under static conditions in a deuterium (or hydrogen) atmosphere. These type of experiments have been the focus of the current work, however, the IsoEx rig can also perform ‘flow switching’ experiments. These involve starting the experiment with a flow of the corresponding gas to what is initially loaded on the Pd bed. For instance, if the Pd bed is initially deuterided (PdDᵧ) then the initial flowing gas will be deuterium. After a stable flow of gas has been established the switching valves on the inlet are operated to introduce the opposite isotope to enact an isotope exchange reaction within the Pd. These switching type experiments were trialled during the first few months of this project, however, the switchover between inlet gases was found to be not satisfactory. Rather than there being a sharp front between the two gas species, there was a period of tailing between the gases. New faster switching valves would help to remove this.

Furthermore, these experimental effects were also found during the non pre-flow type experiments in some cases. However, this was due to the MFCs installed on each inlet gas line. In some isotope exchange experiments the MFCs struggled to reach a flow setpoint in a smooth manner, and quite often they overshot the setpoint causing a period where the flow would be reduced in order to drop to the required setpoint. While the
effect of this was deemed minimal there was still a short period at the start of the experiments where the flows, and therefore upstream pressures, were not stable. This was despite regular calibration of the MFCs. To remove this effect the author recommends investigating alternative MFCs. This may involve purchasing some new lower flow rated MFCs to install on the rig when performing experiments using flowrates below 5 L min\(^{-1}\).

Finally, another important aspect of any future work will be collaborations between the different research groups investigating hydrogen isotope exchange in the UK. Currently, there are studies being performed (sponsored by AWE) at Salford University and Imperial College London. Each research group is undertaking research into different aspects of hydrogen isotope exchange. For instance, at the University of Bath high pressure exchanges have been performed, while at Salford the quantum effects occurring within Pd during an exchange are being investigated. The author believes it necessary for AWE sponsored projects investigating isotope exchange to collaborate in future, bringing the findings of the various groups together into one coherent picture of the isotope exchange process. The insights, for example, into the quantum states of hydrogen isotopes in Pd could be of particular use to the IsoEx project considering the evidence for the existence and influence of bulk and subsurface regions within Pd.
References


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Supplementary Information

A. Mass spectrometer scan parameters

Scan Parameters:

Acquisition Range  This allows the user to select the range of the scan in terms of number of counts performed by the instrument. The acquisition range starts in the 10-13 and rises to 10-5. The instrument is usually set to start at 10-7, meaning the instrument will perform 107 counts.

Auto Range  When selected, this allows the analyser to automatically change the range and follow change in input signal.

Dwell Time  Defines the time used to acquire a single point in the scan. A value may be typed directly into text boxes within the software, in milliseconds. Alternatively, a percentage value can be selected, instructing the machine to search for a single point for a specified percentage of the default dwell time programmed into the software.

Settle Time  Define the time to allow the electronics to settle before the scan is started. Like the dwell time, either a time in milliseconds or a percentage of the default settle time can be selected.

Auto Zero  When selected, this forces the analyser to perform an automatic zeroing function at the start of each scan. This corrects any errors due to amplifier offsets and leakage currents.

Instrument Environmental Parameters:

Detector:

Multiplier  Part of the SEM detector. Here voltage is applied to produce electrons within the detector. Voltage is changed to match the signal from the Faraday detector.

Filter:

Focus  The focus parameter is changed to alter the voltage applied to the triple ion filter. It is a plate that extracts the ions from the source and repels the electrons back into the source. It needs to be more negative than the electron energy. Increasing it may
increase the sensitivity of the instrument slightly. It can be increased if electron energy is decreased.

**Quad:**

*Delta-m* Allows greater resolution in the lower ranges. A positive delta-m increases resolution but reduces sensitivity (and vice versa). Default resolution is 1 amu wide.

*Resolution* Same effect as delta-m but for the higher ranges.

**Source:**

*Cage* The voltage supplied to the cage is selected using this parameter. Its default voltage is 3V. During initial commissioning this has increased to 3.7V.

*Electron-emission* This parameter controls the electron emission from the source (filament). Increasing voltage increase the electrical pressure of the bombarding electrons colliding with the gases entering the mass spectrometer. It is a useful parameter to increase instrument sensitivity.

*Electron Energy* Electron energy is the energy required to ionise the atoms and molecules within the source

*Emission* Increasing the emission increases the number of electrons being emitted from the filament. Like electron-emission, it is useful for increasing sensitivity.

**B. MATLAB model derivation**

The MATLAB code used in the equilibrium Foltz and Melius based modelling are shown below. The code shown below is an example code for a 300 K D-H exchange. Three files are used, the script (`IsoExscript`) and two function files, one for the calculation of the gaseous mole fractions and another for calculation of the isotope exchange rate:

**IsoEX SCRIPT FILE**
% ISOEX MATLAB SCRIPT - AUTHOR: SIMON OWENS

%---------------------------------------------------------------------

global temp R mave surf_0 alpha salpha k_ex K_eq

pd_rho = 12023;                % Palladium density (kg/m^3)
pd_am  = 0.10642;              % Palladium atomic mass (kg/mol)
pd_mrho = pd_rho/pd_am;        % Palladium molar density (mol/m^3)

sd0 = pd_mrho*0.65;            % Initial number of deuterium atoms in bed
                                % (mol/m^3)

m = 20;                        % Number of timesteps

n = 100;                       % Number of spatial steps

tend = 40;                      % Total time for calculation (s)

dt = 1e-6;                     % Step size
                                % [can also be dt=20/(m+1) or dt=tend/(m+1)]

L = 1.7e-2;                    % Length of Pd bed (m)

dx = L/(n+1);                  % Spatial step size

dp = 5e-7;                     % Pd particle diameter (m)

Kozeny = 5;                    % Kozeny constant (-)

logKeq = -(155/(4.57*temp))+0.6276; % Equilibrium constant equation

K_eq = 10^(logKeq);            % Equilibrium constant [i.e. 3.267 @ 299K]

K_eq = 3.267;

atm = 101325;                  % Atmospheric pressure (Pa)

R = 8.3145;                    % Universal gas constant (J/K.mol)

temp = 300;                    % Temperature of reactor (K)
mave = 0.003; % Average molecular mass of species (kg/mol)
surf_0 = 6/dp; % Specific surface area of spherical Pd particles (1/m)
alpha = 2.4; % Separation factor (-)
salpha = sqrt(alpha); % Square root of separation factor
k_ex = 2.6e-7/sd0; % Isotope exchange coefficient
pore = 0.75; % Porosity of bed (-)
kbed = (1/Kozeny)*((pore^3)/((surf_0^2)*((1-pore)^2))); % Permeability coefficient
mu = 8.76e-6; % Gas viscosity (Pa.s)

% Setup Solution Matrices
sd_sol = zeros(n+1,m+1);
sh_sol = sd_sol;
gh_sol = sd_sol;
gd_sol = sd_sol;
rate = zeros(n+1,m*4+1);

sd_sol(:,1) = sd0/(n+1);
gh_sol(1,1) = (6*atm)/(R*temp);
rate(:,1) = fn_rate(sd_sol(:,1),sh_sol(:,1),gd_sol(:,1),gh_sol(:,1));
rt = rate(:,1);

% Simple first order updates
for j=2:m+1;

% Deuterium solid first (sd)
sd_sol(:,j)=sd_sol(:,j-1)-dt*rt;


%Update rate
rate(:,(j-2)*4+2)=fn_rate(sd_sol(:,j),sh_sol(:,j-1),gd_sol(:,j-1),gh_sol(:,j-1));
rt=rate(:,(j-2)*4+1);

%Hydrogen solid next (sh)
sh_sol(:,j)=sh_sol(:,j-1)+dt*rt;

%Update rate
rate(:,(j-2)*4+3)=fn_rate(sd_sol(:,j),sh_sol(:,j),gd_sol(:,j-1),gh_sol(:,j-1));
rt=rate(:,(j-2)*4+2);

%Calculate pore velocity
vf=((kbed*R*temp)/(mu*pore))*deriv_first((gd_sol(:,j)+gh_sol(:,j-1)),dx)';

%Deuterium gas next (gd)
gd_sol(:,j)=gd_sol(:,j-1)+dt*((1-pore)/pore)*rt+deriv_first(gd_sol(:,j-1).*vf,dx)';

%Update rate
rate(:,(j-2)*4+4)=fn_rate(sd_sol(:,j),sh_sol(:,j),gd_sol(:,j),gh_sol(:,j-1));
rt=rate(:,(j-2)*4+3);

%Update pore velocity
vf=((kbed*R*temp)/(mu*pore))*deriv_first((gd_sol(:,j)+gh_sol(:,j)),dx)';

%Hydrogen gas next (gh)
gh_sol(:,j)=gh_sol(:,j-1)-dt*((1-pore)/pore)*rt+deriv_first(gh_sol(:,j-1).*vf,dx)';

%Update rate
rate(:,(j-2)*4+5)=fn_rate(sd_sol(:,j),sh_sol(:,j),gd_sol(:,j),gh_sol(:,j));

[fghd,fgh2,fgd2]=fn_fg(gd_sol(:,j),gh_sol(:,j));

end
**Mole fraction FUNCTION FILE:**

function [fghd,fgh2,fgd2] = fn_fg(gd,gh)

```matlab
global temp R mave surf_0 alpha salpha k_ex K_eq

fgh = gh./(gh+gd);  \%Atomic mole fraction of H atoms in gas phase
fgd = gd./(gh+gd);  \%Atomic mole fraction of D atoms in gas phase

%Introduce simple variable prior to calculation of HD mole fraction

c1 = -(K_eq/(4-K_eq));
c2 = 2/(4-K_eq);
c3 = (K_eq^2)/4;
c4 = 4*K_eq*(1-(K_eq/4)).*fgh.*fgd;

%Calculate HD/H2/D2 mole fractions [**see F&M paper for description**]

fghd = c1+c2*sqrt(c3+c4);
fgh2 = fgh-0.5*fghd;
fgd2 = fgd-0.5*fghd;

end
```

**Rate FUNCTION FILE:**

function rate = fn_rate(sd,sh,gd,gh)

```matlab
global temp R mave surf_0 k_ex K_eq alpha salpha

%Define rate expression used in F&M paper

c1=0.25*k_ex*sqrt((8*R*temp*alpha)/(pi*mave));
c2=gh.*sd-((gd.*sh)/alpha);

%Calculate rate

rate=c1*c2;
```
C. COMSOL kinetic model inlet conditions derivation

In order to specify the inlet conditions to the kinetic COMSOL model the following proofs have been used to define the HD and D₂ mole fractions at the inlet based on a known H₂ mole fraction:

\[ \text{H}_2(g) + \text{D}_2(g) \rightleftharpoons 2\text{HD}(g) \tag{C-1} \]

\[ K_{\text{eq}} = \frac{x_{\text{HD}}^2}{x_{\text{D}_2}x_{\text{H}_2}} \quad \text{or} \quad K_{\text{eq}} = \frac{c_{\text{HD}}^2}{c_{\text{D}_2}c_{\text{H}_2}} \tag{C-2} \]

It is known that the sum of all gaseous mole fractions (H₂, D₂ and HD) must equal 1:

\[ x_{\text{H}_2} + x_{\text{D}_2} + x_{\text{HD}} = 1 \tag{C-3} \]

Therefore,

\[ x_{\text{D}_2} + x_{\text{HD}} + x_{\text{H}_2} - 1 = 0 \tag{C-4} \]

And so,

\[ x_{\text{D}_2} + \sqrt{K_{\text{eq}}^{x_{\text{D}_2}}x_{\text{D}_2}} + (x_{\text{H}_2} - 1) = 0 \tag{C-5} \]

Hence,

\[ \sqrt{x_{\text{D}_2}} = \frac{-\sqrt{K_{\text{eq}}^{x_{\text{H}_2}}x_{\text{H}_2} + \sqrt{K_{\text{eq}}^{x_{\text{H}_2}}x_{\text{H}_2} - 4(x_{\text{H}_2} - 1)}}}{2} \tag{C-6} \]

\[ = -\sqrt{\frac{K_{\text{eq}}^{x_{\text{H}_2}}x_{\text{H}_2}}{4}} \pm \sqrt{\frac{K_{\text{eq}}^{x_{\text{H}_2}}x_{\text{H}_2}}{4} + (1 - x_{\text{H}_2})} \tag{C-7} \]

Taking all square roots are strictly positive, and \((1 - x_{\text{H}_2}) > 0\)

\[ \sqrt{x_{\text{D}_2}} = \sqrt{\frac{K_{\text{eq}}^{x_{\text{H}_2}}x_{\text{H}_2}}{4} + (1 - x_{\text{H}_2})} - \sqrt{\frac{K_{\text{eq}}^{x_{\text{H}_2}}x_{\text{H}_2}}{4}} \tag{C-8} \]

\[ = \sqrt{\frac{K_{\text{eq}}^{x_{\text{H}_2}}x_{\text{H}_2}}{4} \left( 1 + \frac{4(1-x_{\text{H}_2})}{K_{\text{eq}}^{x_{\text{H}_2}}} - 1 \right)} \tag{C-9} \]

The above equation (C-9) is equally valid on substitution of \(x_{\text{D}_2}\) for \(x_{\text{H}_2}\) and vice versa.

Squaring equation C-9 gives:
\[ x_{D_2} = \frac{K_{eq}X_{H_2}}{4} \left( \sqrt{1 + \frac{4(1-x_{H_2})}{K_{eq}X_{H_2}}} - 1 \right)^2 \]  

\[ = \frac{K_{eq}X_{H_2}}{4} \left( 1 + 4\frac{1-x_{H_2}}{K_{eq}X_{H_2}} + 1 - 2 \sqrt{1 + \frac{4(1-x_{H_2})}{K_{eq}X_{H_2}}} \right) \]  

\[ = \frac{K_{eq}X_{H_2}}{2} \left( 1 + 2\frac{1-x_{H_2}}{K_{eq}X_{H_2}} - \sqrt{1 + \frac{4(1-x_{H_2})}{K_{eq}X_{H_2}}} \right) \]  

\[ x_{D_2} = \frac{K_{eq}X_{H_2}}{2} + \left( 1 - x_{H_2} \right) - \frac{K_{eq}X_{H_2}}{2} \sqrt{1 + \frac{4(1-x_{H_2})}{K_{eq}X_{H_2}}} \]  

Hence,

\[ 1 - x_{H_2} - x_{D_2} = x_{HD} = \frac{K_{eq}X_{H_2}}{2} \sqrt{1 + \frac{4(1-x_{H_2})}{K_{eq}X_{H_2}}} - \frac{K_{eq}X_{H_2}}{2} \]  

\[ = \alpha \left[ \frac{1+2(1-x_{H_2})}{\alpha} - 1 \right] \]  

Therefore the separation factor is:

\[ \alpha = \frac{K_{eq}X_{H_2}}{2} \]