KINETICS OF HYDROGEN AND ZIRCONIUM INTERACTIONS

by

Juan Andrés LLUGER-BARCELO


A thesis submitted for the degree

of

DOCTOR OF PHILOSOPHY

in the Faculty of Engineering

of the

UNIVERSITY OF LONDON

June 1979

Department of Chemical Engineering and Chemical Technology

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY

LONDON S.W.7.
The belief in the inner harmony of our world is and always will remain the fundamental motive for all scientific creation.

ALBERT EINSTEIN and LEOPOLD INFELD
The Evolution of Physics, Cambridge Univ. Press, 1971, p. 296

I call before me, above all, those who in office, laboratory and factory, through their vision of truth or despite their error, truly believe on the progress of earthly reality and who today will take up again their impassioned pursuit of the light.

PIERRE TEILHARD DE CHARDIN
The kinetics of the absorption and emission of hydrogen from zirconium foil shows that two activation energies are involved. These energies are attributed to the dissolution of hydrogen into zirconium metal on the one hand, and to the decomposition of precipitated zirconium hydride and emission of hydrogen on the other. Their difference is found to correspond well with the heat of solution of hydrogen in α-zirconium.

The studies of neutron inelastic scattering further suggest that two forms of hydrogen coexist in zirconium during the process of partially hydriding the metal foil. One of these forms of hydrogen clearly responds to the neutron diffraction, whereas the other does not appear to be bound to the metal lattice. In zirconium hydride powder only the bound form of hydrogen appears to be present.

Photomicrographic analysis also shows the presence of two phases in hydried zirconium metal.
PREFACE

In order to keep the text to a reasonable length, all references and some definitions are included in the Notes at the end of the text. These Notes are essential to the complete understanding of the text.

A small part of the text, namely the classification of filtered neutron fluxes (Section 3.2.2.3), has already been published in my report "Neutron inelastic scattering from hydrogen in zirconium hydride" presented in 1974 for the degree of M.Sc. in Engineering at the University of London and for the D.I.C.

When British units are used in design specifications they have been converted to S.I. units.

***

I should like to thank:-

Prof. G.N. Walton, who gave continuous advice and guidance throughout the work;

J.G. Williams and E.A.Y. Caesar, who made available the U.L.R. spectrometer for the neutron scattering;

M. Albarsanz, who provided the facilities for doing the metallographic analysis;

I.B. Drummond, who suggested the way of purifying the TSG gas;

V. Cañada-Blanch, who generously provided a grant, which was administered under the auspices of the British Council.

Finally, I must thank Mrs J.R. Slade-Pluck, Miss E.R. Anderson and B. Holt for typing and presentation of the work.
TABLE OF CONTENTS

ABSTRACT

PREFACE

TABLE OF CONTENTS

LIST OF FIGURES AND PLATES

LIST OF TABLES AND APPENDICES

CHAPTER 1  GENERAL INTRODUCTION

1.1  PREAMBLE

1.1.1  Metallurgy of Zirconium

1.1.2  Nuclear Technology: Corrosion

1.1.3  Neutron Diffraction

1.1.4  Storage of Hydrogen

1.2  BIBLIOGRAPHICAL REVIEW

1.2.1  General Reviews

1.2.2  Absorption of Hydrogen

1.2.2.1  Oxide Film

1.2.2.2  Mechanism of Absorption

1.2.3  Emission of Hydrogen

1.2.4  Neutron Inelastic Scattering

CHAPTER 2  THEORETICAL CONSIDERATIONS

2.1  THE ABSORPTION OF HYDROGEN

2.1.1  The Arrhenius equation

2.1.2  The rate-limiting step of absorption of H by Zr

2.1.3  Hydridic model proposed for Zr-H system

2.1.4  Diffusion of Hydrogen and precipitation of hydride
2.2 NEUTRON DIFFRACTION
2.2.1 Proton vibrations in a crystal lattice
2.2.2 Principles of neutron diffraction
2.3 THE EVOLUTION OF HYDROGEN

CHAPTER 3 EXPERIMENTAL METHODS AND DESCRIPTION OF APPARATUS
3.1 ABSORPTION
3.2 NEUTRON DIFFRACTION
3.2.1 Double axis arrangement
3.2.1.1 The neutron source
3.2.1.2 The spectrometer and the monochromator crystal
3.2.1.3 The filter as analyser and the detector
3.2.2 Modifications to the downscattering apparatus to achieve optimal efficiency
3.2.2.1 The detector
3.2.2.2 The sample holder
3.2.2.3 The filter
3.3 THERMOGRAVIMETRIC ANALYSIS
3.3.1 Description of the Components
3.3.1.1 The TSG-1 Furnace
3.3.1.2 Gas connections
3.3.2 Calibration and operation procedures

CHAPTER 4 EXPERIMENTAL RESULTS
4.1 ABSORPTION RESULTS
4.2 NEUTRON DIFFRACTION RESULTS
4.3 EVOLUTION RESULTS
4.4 MICROGRAPHIC ANALYSIS RESULTS
4.4.1 Grain boundary precipitates
4.4.2 The habit plane of intragranular hydride
4.4.3 Origin of crack formation

CHAPTER 5 ANALYSIS AND INTERPRETATION OF RESULTS

5.1 ANALYSIS OF ABSORPTION

5.1.1 Diffusion of Hydrogen in Zirconium

5.1.2 Dissolution of Hydrogen atoms in Zirconium

5.2 ANALYSIS OF NEUTRON DIFFRACTION

5.2.1 The Count-rate at the Peak

5.2.2 The Area Parameter

5.3 ANALYSIS OF MICROGRAPHIC RESULTS

5.4 ANALYSIS OF DESORPTION

5.4.1 Fractional rate of emission and Plateau-time

5.4.2 Rate of emission and Hydrogen content

5.4.3 Low and High temperature stepping emission experiments

5.5 CORRELATION BETWEEN ABSORPTION AND DESORPTION OF HYDROGEN

CHAPTER 6 CONCLUSIONS

NOTES

FIGURES AND PLATES

TABLES

APPENDICES

REFERENCES
LIST OF FIGURES

1 Transmission cross-section
2 Doppler effect
3 Cross-section plan view of the neutron diffraction experiment
4 Elevation and plan of the detector
5 Cross-section of beryllium
6 Aluminium sample holder
7 Classification of filtered fluxes
8 Thermobalance apparatus (TSG-1)
9 Deviation of measured magnetic transition temperatures
10 Pressure against time
11 Exposure time against temperature
12 Arrhenius plot
13 Count-rate spectrum
14 Isotherms giving the weight loss of H in the low temperature stepping experiment No. 127
15 Isotherms giving the maximum relative weight loss of H
16 Effect of the initial pressure on the rate of absorption of H
17 Fraction of H absorbed against initial pressure
18 Peak count-rate as a function of weight of H
19 Power generated by U.L.R.C. between 14th July 1977 and 28th April 1978
20 Neutron diffraction response in non-standard samples
21 Area parameter as a function of weight of H
22 Area parameter as a function of bound hydrogen density
23 Area parameter as a function of the total weight of H
24 Progression of ϒ-Zr with H concentration
25 Unbound hydrogen in α-Zr
26 Slope of time against plateau-time
LIST OF FIGURES (cont'd)

27  Time taken to evolve the first 40% of H for each isotherm against H content at time zero

28  Isotherms giving the rate of emission in the low temperature stepping experiment No. 126

29  Isotherms giving the rate of emission in the high temperature stepping experiments

30  Arrhenius plot

LIST OF PLATES

1  Orientated precipitates (H/Zr = 0.723)

2  Orientated precipitates (H/Zr = 0.975)

3  Progression of β-Zr (H/Zr = 0.723)

4  Progression of β-Zr (H/Zr = 0.975)

5  Orthogonal crack (H/Zr = 1.225)

6  Parallel crack (H/Zr = 1.225)
LIST OF TABLES

1 Relative partial molal enthalpy for the solution of hydrogen in α-zirconium
2 Energies of the first vibrational level for zirconium hydride
3 Data for the classification of filtered fluxes
4 Data for count-rate spectrum
5 Relative weight loss of hydrogen with temperature
6 Fraction of hydrogen absorbed with pressure
7 Data for homogeneous standard and non-standard experiments
8 Data for non-homogeneous standard experiments
9 Data for neutron diffraction response in non-standard samples
10 Bound hydrogen density in standard and non-standard samples
11 Data from micrographic analysis of non-standard samples
12 Data of atomic radii and sizes of interstices in zirconium

LIST OF APPENDICES

1 Analysis of zirconium foil specimens
2 The definition of the algorithm to find the average maximum rate of absorption of hydrogen in zirconium foil
3 Delft Algol version 1/9/75 program
4 Relation of heat of solution to activation energies
1.1 PREAMBLE

1.1.1 METALLURGY OF ZIRCONIUM

Cladding and pressure tubing materials are used in nuclear reactors to protect the nuclear fuel from corrosion, to provide heat transfer surfaces and to furnish structural support. Zirconium has a combination of mechanical, chemical and nuclear properties which particularly suit it for such a use in water nuclear reactors (1). In effect, zirconium has a low thermal neutron cross-section (0.182 barns), an inherently good corrosion resistance in water and liquid metals, a high melting temperature (1855 ± 5°C) and a high change of phase temperature (862 ± 5°C) from hexagonal close-packed α to body-centred cubic β structure.

In spite of its hexagonal structure zirconium is not highly anisotropic in its thermal expansion properties. The thermal expansion coefficient parallel to the c-axis (6.32 x 10^{-6} ± 0.01 °C^{-1}) is higher than the perpendicular to the c-axis (5.64 x 10^{-6} ± 0.01 °C^{-1}). The thermal conductivity of zirconium at room temperature is approximately 0.211 watts cm^{-1} °C^{-1}. This thermal conductivity decreases slightly with increasing temperature, so that at the critical temperature of 300°C it has a value of 0.187 watts cm^{-1} °C^{-1}. Since the thermal stress is proportional to Young's modulus (2) multiplied by the thermal expansion coefficient, divided by the thermal conductivity, in zirconium it would be limited accordingly. This thermal stress in zirconium is approximately one sixth of that generated in stainless-steel for an identical temperature rise.
The corrosion behaviour of zirconium is characterized by a transition from an initial low quasi-cubic rate law to a more rapid linear rate law. The exposure time when this transition occurs is dependent upon temperature and is affected by impurities and alloying elements. Additions of small amounts of iron, nickel or chromium, in conjunction with tin, are shown to improve the corrosion resistance.

The main alloy, which is Zircaloy-2, was developed by Westinghouse Electric Corp. This alloy contains in weight 1.5% of tin, 0.12% of iron, 0.10% of chromium and 0.053% of nickel additions.

Other important alloys are:

a) Zircaloy-4 with 1.45% of tin, 0.21% of iron, 0.11% of chromium and 0.004% of nickel additions.

b) Zirconium-Niobium with 2.5% of niobium.

c) Ozhennite-0.5 which contains 0.2% of tin, 0.1% of iron, 0.1% of nickel and 0.1% of niobium additions.

1.1.2 NUCLEAR TECHNOLOGY: CORROSION

Many limitations exist in the use of zirconium alloys in a nuclear reactor. Of these the most important one is corrosion to which the irradiation effect is contributory. As a result of this corrosion, an impoverishment occurs in the mechanical properties limiting the time during which these alloys can be used:

i) In water reactors (P.W.R. and B.W.R.) these alloys, used as cladding of the fuel element, must withstand three years of corrosion and irradiation at a temperature of about 300°C.
ii) In CANDU and S.G.H.W.R., where the zirconium alloys are used for pressure tubes, they must withstand corrosion and irradiation for 20 to 30 years at the same or slightly higher temperatures.

Zirconium in the presence of hot water or steam is corroded according to these partial and total reactions:

\[
2 \text{H}_2\text{O} \rightarrow 2 \text{O}^- + 4 \text{H}^+ \\
\text{Zr} \rightarrow \text{Zr}^{4+} + 4 \text{e}^- \\
4 \text{H}^+ + 4 \text{e}^- \rightarrow 2 \text{H}_2
\]

This total reaction can be represented in its molecular form:

\[
\text{Zr} + 2 \text{H}_2\text{O} \rightarrow 2 \text{O}^- + \text{Zr}^{4+} + 2 \text{H}_2
\]

Some of the hydrogen released by the corrosion reaction dissolves in zirconium. Zircaloy-2 picks up about 10 - 20% of the hydrogen produced by this reaction at 400 °C in steam and about 5 - 15% at 360°C in water. By contrast, unalloyed zirconium picks up about 30% of the hydrogen released under the same conditions (3).

When the solubility limit of hydrogen in zirconium is reached, zirconium hydride is formed as thin platelets. When this zirconium hydride is formed, the hydrogen becomes bound in the metal lattice and can cause embrittlement. This is regarded as the greatest limiting factor on the working life of zirconium alloys.
1.1.3 NEUTRON DIFFRACTION

Chemical analysis of hydrogen in zirconium hydride is incapable of distinguishing between hydrogen dissolved in zirconium and that which is bound in a characteristic lattice. One of the aims of this project was to measure the quantity of hydrogen that becomes bound in the lattice and which can cause embrittlement. With this aim in view, the result of my research project completed in 1974 in the University of London Reactor Centre (U.L.R.C.), entitled "A technique for measuring bound hydrogen in zirconium hydride by neutron inelastic scattering" has been applied to the present work. An experiment was designed to study the intensity, as a function of energy, of neutrons scattered from interstitial atoms in zirconium hydride. Partially hydried metal was studied in order to trace the kinetics of the hydride formation and the activation energy of absorption-desorption cycle was calculated at every step of the process.

1.1.4 STORAGE OF HYDROGEN

The overall project is of value in the field of storage of hydrogen for power generation purposes. Zirconium as a gas reservoir for hydrogen and as a source of pure hydrogen previously stored in the metal, presents a unique challenge to industrial research programmes. This application requires the production of thermodynamic information on the zirconium-hydrogen system some of which is provided here along with kinetic information of the transfer rates of hydrogen during the absorption-desorption cycle. The combined effects of lattice dilation and thermal stress, occurring during the absorption-desorption cycle, are also of importance in evaluating the potential lifetime of zirconium as a solid storage medium.
1.2 BIBLIOGRAPHICAL REVIEW

1.2.1 GENERAL REVIEWS

The bibliography has been kept to a manageable size largely because reviews of literature on the subject, over the past few years, have been published elsewhere. Occlusion of hydrogen by metals has been the matter of exhaustive scientific studies. Smith (4) in 1948, Libowitz (5) in 1960, Gibb (6) in 1962 and Goldschmidt (7) in 1967 are among the more important researchers in the field. The best reviews referring in particular to the occlusion of hydrogen in zirconium and zirconium alloys are those of Cox (8) and Ellis (9) both in 1968.

1.2.2 ABSORPTION OF HYDROGEN

De Boer and Fast (10) found that hydrogen absorption by zirconium was rapid at a temperature range 300 - 400°C. Hall et al. (11), at the same time as they confirmed the results of de Boer and Fast, found that absorption of hydrogen was already taking place at room temperature. Hayes et al. (12) found that the hydride embrittles the zirconium, but to restore the ductility of the metal it was sufficient to heat the hydride specimen to 700°C in vacuum. The rate of absorption was determined by Belle et al. (13) for the temperature range 250 - 425°C at 1 atm pressure. They found that the reaction follows a parabolic law with an activation energy of 17200 ± 200 cal/g-atom. Libowitz (14) reported that zirconium absorbs hydrogen up to the composition Zr H_{1.98}. The phase diagram was first established by Sieverts and Roell (15) from equilibrium pressure data.
1.2.2.1 OXIDE FILM

During the uptake of hydrogen by zirconium, the observation of an exposure time (16) induced some investigators to attribute it to the oxide film being dissolved into the metal and to relate it to the annealing time. Gulbransen and Andrew (17), after describing in detail and presenting the limitations of Smith's theory (18) - in which an expanding and contracting series of rifts are used to explain active and passive states of the metal - interpret the occlusion of hydrogen in the metal in terms of a stable oxide film formed readily on the surface and limiting the rate of the metal to hydrogen reaction. These authors reported that after preheating for one hour at temperature of 300, 500 and 700°C, the induction period is nil, but heating for an hour at 150°C needs an exposure time of 5 to 10 minutes. In both of these experiments hydrogen was preheated at a pressure equal to or lower than 10⁻⁶ mm Hg. Belle and co-workers (19) reported that the exposure time was generally less than 5 minutes, though it was independent of the annealing time, provided that the pressure was equal to or less than 10⁻⁴ mm Hg. Only recently Shaltiel et al. (20) reported that annealing at temperatures of about 1000°C for a period of a week or so, some zirconium pseudobinary compounds absorb hydrogen at room temperature and a 1 atm without any exposure time. However, they reported the peculiar behaviour of the Zr (V₀.₃ Fe₀.₇)₂ compound which need about two hours before hydrogen is absorbed at or above a temperature of 150°C.

1.2.2.2 MECHANISM OF ABSORPTION

Gulbransen and Andrew (21) explain the mechanism controlling
the hydrogen absorption as twofold (i) an activated diffusion and (ii) a dissociation of hydrogen into atoms. According to them the hydrogen diffuses into the metal without forming a hydride film. The rate of the reaction deviates from a linear law, to be directly proportional to the square root of the hydrogen pressure following Sievert's parabolic rate law. Among the investigators supporting a diffusion controlled reaction, Belle et al. (22) suggest the formation of several layers of ZrH$_2$ and ZrH during the metal to hydrogen reaction. However, they say in conclusion that the effect of these hydride phases on the kinetics of the reaction is not known. The interstitial solution model was proposed by Martin and Rees (23). Marino (24) presents a model of supersaturation and concomitant hydride growth in the matrix of α-phase of Zircaloy, in order to explain the mechanism by which the hydrogen is absorbed and the hydride film formation inhibited. The steady-state distribution of hydrogen in the α-phase of zirconium is given, according to Marino, by a hyperbolic cosine law. Recently, Une (25) suggested that the mechanism controlling the absorption of hydrogen in Zircaloy-2 is a phase boundary reaction with an activation energy of 16300 cal/g-atom. He noted the omission of the geometrical consideration of the sample when Belle et al. (26) interpreted the absorption mechanism as a diffusion controlled process.

1.2.3 EMISSION OF HYDROGEN

Gulbransen and Andrew (27) found that the dissolution of the δ-phase of zirconium was the mechanism controlling the evolution of hydrogen. Mallett and Albrecht (28) considered it possible that surface effects determine the degassing rates. They also mention that the evolution of hydrogen from iron pellets is size dependent and that
this could also be the case with zirconium preparations.

1.2.4 NEUTRON INELASTIC SCATTERING

Fermi (29) first predicted that the total scattering cross-section will indicate the manner in which hydrogen is bound in a crystal lattice as an harmonic oscillator. McReynolds et al. (30) measured the total cross-sections of hydrogen in zirconium hydride following the Fermi predictions. Pelah et al. (31) and Andresen et al. (32) used a cold neutron beam and beryllium filter to measure an optical peak around 0.13 eV for hydrogen in zirconium hydride. Whittemore (33) located the peaks due to excitation of the acoustic and optical energy levels in zirconium hydride.
CHAPTER 2

THEORETICAL CONSIDERATIONS

2.1 ABSORPTION OF HYDROGEN

2.1.1 THE ARRHENIUS EQUATION

The rate at which molecules or atoms undergo chemical transformation is proportional to the number of molecules or atoms in an approximately activated condition. This number is an exponential function of the temperature and of the activation energy in the following form:

\[ k = A \exp\left( -\frac{E}{RT} \right) \]  

where

- \( k \) = the reaction rate constant (sec\(^{-1}\))
- \( A \) = a numerical constant which represents the frequency of vibration of the particles per second
- \( E \) = the activation energy (cal/g-atom)
- \( R \) = the thermodynamic gas constant at a value of 1.987 cal per degree per g-atom
- \( T \) = the temperature reaction in degrees Kelvin

If two or more value-pairs \((k,T)\) have been empirically determined, from \(|1|\) is obtained:

\[ E = R \frac{T_2 T_1}{T_2 - T_1} \ln \frac{k_2}{k_1} \]  

2.1.2 THE RATE-LIMITING STEP OF THE ABSORPTION OF HYDROGEN BY ZIRCONIUM

If the Arrhenius equation represents, for any one process, the relation between the rate at which a chemical change proceeds...
and the temperature, it can also throw light on the actual mechanisms of the chemical change.

In order to determine those mechanisms, a kinetic analysis of the rate of absorption of hydrogen in zirconium is required. A number of separate processes are isolated in this analysis (34):

1) A preliminary process on the surface:
   i) chemisorption of the molecule
   ii) splitting apart the molecule into atoms or ions

2) Diffusion of hydrogen atoms, ions or molecules through the oxide or other surface film.

3) Transfer of the hydrogen molecules, atoms or ions through the interface oxide-metal.

4) Diffusion of hydrogen along the grain-boundaries or through the metal lattice.

5) Formation and growth of one or more hydride phases.

With each of these processes a characteristic reaction energy is associated. A mean value for each has been calculated from published data as follows:
- the average reaction energy for surface absorption is
  - 16750 cal/g-atom (35)
- the dissociation energy of hydrogen (36) associated with this equilibrium reaction \( \frac{1}{2} \text{H}_2 \rightarrow \text{H} \) is
  - 52100 cal/g-atom (37)
- The average reaction energy for diffusion is
  - 8135 cal/g-atom (38)
- the average dissolution energy is
  - 13094 cal/g-atom (see Table 1)
- the heat of formation of the hydrides from zirconium metal and molecular hydrogen gas
  i) for the f.c.c. \( \varepsilon \)-phase, with \( \text{H/Zr} = 1.59 \) to \( 1.66 \) (50) is
    - 33700 cal/g-atom (51)
  ii) for the f.c.t. \( \varepsilon \)-phase, with \( \text{H/Zr} = 1.66 \) to \( 1.92 \) (52) is
    - 38900 cal/g-atom (53)

In a hypothetical multistage reaction, the highest reaction energy corresponds to the transition energy of the rate-limiting step of the reaction, that is, the slowest step governing the overall rate of the reaction (54). Thus, the question is to determine which one of all these steps controls the rate of the overall process of taking-up hydrogen.

2.1.3 HYDRIDIC MODEL PROPOSED FOR ZIRCONIUM-HYDROGEN SYSTEM

From the models of hydride transition metals proposed by Wiberg and Amberger (55) the hydridic model is the one which is more widely applied to the zirconium-hydrogen system. In this hydridic model the \( 1s^2 \) electrons surround the proton \( \text{H}^+ \), and the \( \text{H}^- \) lattice site
so obtained is embedded in an electron gas of comparatively low density. In this model the covalent bond of the hydrogen exists simultaneously with a covalent delocalised bond of metal to metal atoms, with these characteristics:

1) the stoichiometry is low: \[ \text{Zr}^{2+} + \text{H}^{2-} \]
   \[1.76-1.98\]

2) this model suffers no loss of metallic properties. The metallic state is then certain

3) on the contrary, the state of the hydrogen is uncertain and can be: \[\text{H}^0, \text{H}^{\delta-}, \text{H}^{\delta+}, \text{H}_2^0\] or \[\text{H}_2^+\]

4) in consequence of the foregoing the system receives different names:
   a) occlusion or inclusion hydride (56)
   b) semi-metallic hydride (57)
   c) interstitial or insertion compound (58)
   d) alloy (59)
   e) solid solution of hydrogen (60)
   f) non-stoichiometric compound (61)

The physical model proposed by Wiberg and Amberger, requires, according to Rees (62), some assumptions to be accepted for the solution of hydrogen in zirconium:

1) The hydrogen atoms occupy interstitial sites only, mainly tetrahedral sites.

2) In the model there are no defects of either of these types:
   a) Sochtky type - when zirconium sites are vacant
   b) Frenkel type - when zirconium atoms occupy interstices in the zirconium lattice, mainly octahedral sites.

3) The interphase energy of hydrogen atoms between gas and interstitial sites is not dependent on lattice symmetry or
temperature. And the same assumption applies to the interaction energy between hydrogen atoms placed interstitially.

2.1.4 DIFFUSION OF HYDROGEN AND PRECIPITATION OF HYDRIDE

The model of supercharging of hydrogen proposed by Marino (63) to explain the absorption of hydrogen in Zircaloy, is based on the assumption that the physical absorption of hydrogen occurs with simultaneous growth of the hydride phase and precipitation of hydride in the matrix.

Considering a thin foil of metal with a thickness of 2L and x = 0 at the centre of the sample, a balance flux of hydrogen can be expressed by the following second-order differential equation:

\[
D \frac{\partial^2 C_m}{\partial x^2} = \frac{\partial C_m}{\partial t} + R_p
\]

where

- \( D \) = the diffusion coefficient of hydrogen in the \( \alpha \)-phase
- \( C_m \) = the hydrogen concentration in the \( \alpha \)-phase
- \( x \) = the positional coordinate
- \( R_p \) = the rate of growth of the hydride phase
- \( t \) = time

The initial condition is:

\[ C_m = C_{eq} \text{ at } t = 0 \text{ for } -L < x < L \]

where \( C_{eq} \) = the equilibrium concentration of hydrogen in the \( \alpha \)-phase.

The boundary condition is:

\[
\left[ \frac{\partial C_m}{\partial x} \right] = -\frac{J_\circ}{D} \quad \text{for } t > 0
\]

\[
\frac{\partial C_m}{\partial x} \bigg|_{x = \pm L} = \frac{J_\circ}{D}
\]

where \( J_\circ \) = the interphase flux
The diffusion coefficient, $D$, controls the balance flux, in which

$$Rp = K (Cm - Ceq) \bar{A}p$$

where $K (Cm - Ceq)$ = the number of solute atoms per unit area of precipitate deposited per unit time

$\bar{A}p$ = the relation between the area offered by the hydride particles and the volume of the matrix, with units of cm$^{-1}$

Defining $K \bar{A}p = \alpha^2$

where $\alpha$ = the precipitation parameter

the balance flux may be written as follows:

$$\frac{\partial^2 (Cm - Ceq)}{\partial x^2} - \frac{\partial (Cm - Ceq)}{\partial t} - \frac{\alpha^2}{D} (Cm - Ceq) = 0$$

When the steady-state (ss) is reached, then $\frac{\partial Cm}{\partial t} = 0$ and the balance flux becomes:

$$(Cm - Ceq)_{ss} = \frac{J_0}{\alpha D^{1/2}} \cos h \left[ \frac{\alpha x}{D^{1/2}} \right]$$

$$\sin h \left[ -\frac{\alpha L}{D^{1/2}} \right]$$

Then, the distribution of hydrogen in the $\alpha$-phase, at a constant temperature, is given by this hyperbolic cosine law.

If the concentration of hydrogen on the surface is constant, then $Cm = Cs$ at $x = \pm L$ and for $t > 0$

where $Cs$ = the concentration on the surface.

When the supersaturation on the surface is obtained, after a sufficiently long time, then the balance flux is given by:

$$(Cs - Ceq) = \frac{J_0}{\alpha D^{1/2}} \cot h \left[ -\frac{\alpha L}{D^{1/2}} \right] \text{ at } x = \pm L$$
If a uniform supercharging occurs, the final balance is:

\[(Cs - C_{eq}) = \frac{J_0}{\alpha^2 L} \text{ for } \frac{\alpha L}{D^{1/2}} \ll 1\]

Then, the growth of the hydride phase is not controlled by the diffusion rate but the diffusion rate does effect the supersaturation process.

2.2 NEUTRON DIFFRACTION

2.2.1 PROTON VIBRATIONS IN A CRYSTAL LATTICE

According to Fermi's theory (64) the effect of neutron scattering from a proton (hydrogen nucleus) of zirconium hydride, is such that the proton may be considered as an isotropic harmonic oscillator. This occurs when the proton is part of the lattice structure and vibrates within the constraints imposed by it. Fermi showed that the interaction between the neutron and the bound nucleus can be described by a pseudo-potential defined as follows:

\[V = \frac{2\pi \hbar^2}{\mu} \delta(r_n - r_N)\]

where

- \(r_n\) and \(r_N\) are the position vectors for the neutron and the nucleus respectively
- \(a = \text{'free scattering length'}\) of the nucleus
- \(\hbar = \frac{h}{2\pi}, \text{ where } h \text{ is the Planck's constant of a value of } 6.625 \times 10^{-27} \text{ erg sec}\)
- \(\mu = \text{ the reduce mass of the neutron-nucleus system given by the following relation}\)
\[ u = \frac{m M}{m + M} \]

where \( m \) = the mass of the neutron
\( M \) = the mass of the nucleus

When the energy of the incident neutron is greater or equal to the quantum of oscillation, an energy equal to \( \hbar v \) may be transferred from the neutron to the system. This energy corresponds to the transition energy of the oscillator from its ground state to the first excited state. The neutron is scattered with an energy reduced by \( \hbar v \). If both initial and final energies are known and the scattered neutrons detected the transition can be measured. This process, known as downscattering, introduced by Woods et al. (65) to study zirconium hydride, has been used in the present work.

To study this oscillator, it is necessary to define the relation between the energy of the incoming neutron and the total scattering cross-section of the protons. By plotting on Figure 1 the theoretical cross-section of hydrogen against the energy of the incident neutrons, the free proton is found to have a total cross-section value of \( \sigma \) free which is about 20 barns, then a proton bound to an infinite mass has a total cross-section four times the value of \( \sigma \) free.

Experimental measurements listed in Table 2 give the value of about 0.140 eV for the quantum of oscillation of hydrogen in zirconium hydride. This quantum is normally associated with the narrow range of optical frequencies. In this optical mode of vibration the hydrogen atoms vibrate out of phase with the metal atoms, but because the metal atoms are much heavier than the hydrogen atoms (91:1),
the proton is considered to be bound to an infinite mass.

Fermi theorised that the proton and the zirconium are optically vibrating in opposition to each other with the frequencies ranging

\[
\frac{1}{2\pi} \sqrt{\frac{2k'}{M}} \quad \text{to} \quad \frac{1}{2\pi} \sqrt{\frac{2k' (M+M')}{MM'}}
\]

Where \( M \) = the mass of the proton

\( M' \) = the mass of zirconium

\( k' \) = the restoring force per unit displacement from the equilibrium point

Figure 1 shows that the curves between two consecutive integer values of \( E/\hbar \omega \), become lower with increasing neutron energy. There is some broadening of these curves by Doppler effect. This effect is caused by the thermal motion of the environment of the proton. It was assumed that the proton was bound to an infinite mass. A correction can, however, be made on Fermi's theory taking into account the Doppler effect as illustrated in Figure 2.

2.2.2 PRINCIPLES OF NEUTRON DIFFRACTION

When the de Broglie equation

\[
\lambda = \frac{h}{mV}
\]

is applied to a thermal neutrons having a velocity equal to 2000 m sec\(^{-1}\), it is found that the neutrons have a wave-length of about 1.9 A. This value is of the same order of magnitude as the wavelength of X-rays. On this basis neutrons were first successfully diffracted by Mitchell and Powers, who used a radium-beryllium neutron source and a magnesium
oxide single-crystal.

Neutron wavelengths are of the same order of magnitude as the internuclear distances in the crystal. When these wavelengths are scattered from a regular crystal lattice, they can interfere with each other. This is based on the principle that the neutrons reflected from successive planes are in phase when the path difference is an integral multiple of $\lambda$.

In the spectrum of energy obtained from the neutron diffraction, the position of neutron peaks are given, as with X-rays, by the Bragg law:

$$n\lambda = 2d \sin \theta$$

where $n = a$ positive integer denoting the order of reflection

$\lambda = the$ neutron wave-length

$d = the$ interplanar spacing of the crystal

$\theta = the$ angle between crystal planes and the direction of the incoming neutron beam

The Bragg angle $\theta$ is chosen such that the diffracted wave length is near to the peak of the Maxwellian velocity distribution of the thermal neutrons coming from the reactor, the contribution of neutrons in the scattered beam from the sample, with values of $n$ greater than 1, is small. Calculations of the second order contamination, at the range of interest in this experiment, gives about 5% of the count-rate value (78). In consequence, the second order contamination and the successive higher orders are relatively small and can be ignored. The total count-rate may be taken to be the first order term.
2.3 THE EVOLUTION OF HYDROGEN

The form of evolution of hydrogen from zirconium which has been charged with hydrogen beyond the solubility limit is different from what might be expected upon heating a supersaturated solution.

Assuming that the extra hydrogen, above that corresponding with the solubility, is contained in supersaturated solid solution, it would be expected that the supersaturation would be completely ended when any thermal or other disturbance transforms the metastable condition into an unstable one. Then, the reversible system would return, by a single uninterrupted process, to the condition of equilibrium, the saturated state.

In the zirconium-hydrogen system this would mean a quick and almost total expulsion of hydrogen at a temperature at which the rate of emission became noticeable. Such behaviour would be analogous not only to that of liquid supersaturated solution but to that of supersaturated crystals where separation into the stable phases occurs steadily toward equilibrium condition, if a sufficiently elevated temperature is maintained.

The behaviour of zirconium-hydrogen system, however, will be shown to be completely different.

The typical differential equation for a supersaturated system is:

\[ \frac{dF}{dt} = -p (F - F_0) \]
where \( F_0 = \) the saturation concentration
\( F = \) the supersaturation concentration
\( \frac{dF}{dt} = \) the rate of increase of concentration
\( p = \) the fractional emission per second (or absorption)

Integrating this equation
\[
Fe^{pt} = F_0 e^{pt} + C
\]

Solving this equation given the initial condition:
when \( t = 0 \), \( F = F_i \) and \( C = (F_i - F_0) \)

where \( F_i = \) the initial concentration

gives:
\[
\frac{F - F_0}{F_i - F_0} = e^{-pt}
\]

If \( F_0 \) is small the equation becomes:
\[
\ln \frac{F}{F_i} = -pt
\]

Plotting now the logarithm of fractional hydrogen left against \( t \), the slope will give the value of \( p \).
CHAPTER 3

EXPERIMENTAL METHODS AND DESCRIPTION OF APPARATUS

3.1 ABSORPTION OF HYDROGEN

Zirconium was supplied as 0.100 and 1.180 mm thick foil by Goodfellow Metals Limited. The zirconium contained less than 900 ppm by weight of impurities (Appendix 1). Specimens 40 mm x 20 mm in size were abraded with 240, 300, 420, 500 and 600 grade silicon carbide paper and rapidly washed in distilled water before operation.

The zirconium specimens were contained in a silica boat within a detachable silica reactor tube. In the temperature range 25 - 660°C the specimens could be maintained at any given temperature to an accuracy of ± 1°C. The all-glass apparatus could be evacuated to a pressure of < 10⁻⁵ mm Hg.

Hydrogen was absorbed in a constant volume in the temperature range 400 - 550°C, and the change of pressure was recorded throughout the process every minute.

The procedure for hydrogenation was as follows. First the sealed silica tube was evacuated. The zirconium was annealed under vacuum at 660°C for 1, 2 or 3 hours. Purified hydrogen was then introduced into the known volume of the apparatus to a pressure sufficient to produce the required zirconium hydride composition.
A temperature control was introduced since the zirconium-hydrogen reaction is exothermic. The response time of the temperature to the rate of cooling was faster than the rate of hydriding. During the highest rate of reaction a control of ± 8°C was achieved.

The gas purification system consists of:

i) A 'de-oxo' unit, based on the palladium catalyst, for the conversion of oxygen present in the hydrogen to water vapour. At ambient temperature oxygen was reduced to less than 1 vpm.

ii) A pure zirconium plate placed at 450°C in a first silica tube before the hydrogen was introduced into the final silica reactor, removed most of the remaining oxygen and other impurities.

Thus the hydrogen gas reaching the sample can be considered highly purified.
3.2 NEUTRON DIFFRACTION

The technique used in this work was to choose initial neutron energies using a standard single crystal spectrometer and detect scattered neutrons of a known energy by filtering the scattered beam through a polycrystalline filter (79).

3.2.1 DOUBLE AXIS ARRANGEMENT

Neutron energy selection by diffraction was performed with a double axis arrangement, each axis located where a neutron beam changed direction. The first axis was perpendicular to the floor and passed through the single crystal which scattered the monoenergetic beam from the crystal to the sample (Fig. 3). The second axis was parallel to the floor and passed through the zirconium hydride sample which scattered neutrons into the detector, situated vertically beneath the sample (Fig. 4).

3.2.1.1 THE NEUTRON SOURCE

The neutron source used for the study was a polyethylene scattering block in a tangential collimator tube of the University of London Reactor Centre (U.L.R.C.): This reactor is a 100 kW light water moderated swimming pool type with a thermal flux at the centre of $10^{12}$ neutrons cm$^{-2}$ sec$^{-1}$ and at the scattering block of approximately $6.3 \times 10^{10}$ neutrons cm$^{-2}$ sec$^{-1}$.

The collimator tube passes through the graphite of a thermal column, terminating at the scattering block, at a distance of about 50 cm from the centre of the core. The collimator is made from low
carbon mild steel cylinders, consisting of 8 sections with internal diameters ranging from 8.9 cm at the internal end to 4.5 cm at the external end. The outside diameter of the mild steel collimator is 13.3 cm, and the total length of the tube is 255 cm.

3.2.1.2 THE SPECTROMETER AND THE MONOCHROMATOR CRYSTAL

The equipment used for the experiment was situated in front of the collimated beam hole at the face of the reactor.

When the shutter of the tube was opened (see the cross-sectional plan view of the experiment in Fig. 3), the neutron beam fell onto a single monochromator crystal placed on the spectrometer. As a consequence of this, a monoenergetic beam was extracted from the crystal.

The spectrometer, designed by Alston and Jones (80) at the U.L.R.C., is accurate to within 1 minute of arc in its arm. A similarly fine accuracy is achieved in the movement of a goniometer placed in the centre of the spectrometer and holding the single crystal. The goniometer permits the crystal movement to be independent of the movement of the arm.

A mechanism giving a 2 : 1 angular relationship between the crystal table and the arm of the spectrometer was used. This guarantees that an equality between incident and reflected angles was maintained when the arm position was changed. The arm held the sample and the
detector equipment.

The monochromator placed in the spectrometer was a beryllium single crystal. This crystal, 7.1 cm x 4.5 cm x 0.55 cm in size, is cut in such a manner that the 0002 planes are at 4° from the largest face.

Knowing the crystallographic dimensions of the beryllium, \( a = 2.28561 \, \text{Å} \) and \( c = 3.5843 \, \text{Å} \), the value of the spacing between the planes of the atoms, \( d \), is found to be \( 3.5843/2 \, \text{Å} \).

The value of \( 2d \) and the Bragg angle \( \theta \) being known, it is possible to find the value of the energies of the neutron beam extracted from the monochromator crystal, using the de Broglie equation. The relation is given by:

\[
\lambda (\text{Å}) = \frac{0.2865}{\sqrt{E(\text{eV})}}
\]

Beyond the beryllium crystal, the residual beam was allowed to pass into a remote beam-stop. This beam-stop has a cylindrical cadmium-lined re-entrant hole of 15.2 cm internal diameter, sufficient to contain all the width of the incoming beam. The hole is 30.5 cm deep to avoid the reflection of radiation into the counter. The overall beam-stop is a parallelepiped of a solid borated resin 25.4 cm square at the end and 35.6 cm long. The parallelepiped itself is surrounded by lead, 10.2 cm thick.

The neutron beam reflected by the beryllium crystal, with an angle twice the Bragg angle \( \theta \), fell onto the sample holder.
3.2.1.3 THE FILTER AS ANALYSER AND THE DETECTOR

When a neutron beam falls onto the sample, neutrons are scattered in all directions. The detector was placed vertically below the sample, as can be seen in Figure 4, so that only those neutrons which are scattered through an angle of 90° to the vertical were detected.

Before detection, the neutron beam intersected a polycrystalline filter containing many crystal grains oriented at random. A neutron scatters when it meets a crystal with such an angle that the Bragg law (see Eq. 3) is satisfied. Not all the neutrons are reflected because a maximum value of the interplanar distance, \( d_m \), exists for each crystal lattice. The longest wavelength that can be reflected is given by \( \sin \theta = 1 \) when the crystal plane is perpendicular to the neutron direction. This wavelength is given by the relation:

\[
\lambda_m = 2d_m
\]

A neutron with wavelength greater than \( \lambda_m \) is not reflected and passes through the crystal since the cross-sections for absorption and for other scattering are very small.

A polycrystal of beryllium offers suitable filter properties and is used in this study. The longest possible neutron wavelength that can result in Bragg scattering is about 3.6 Å and corresponds to an energy called the Bragg cut-off. This energy is thus related to a sudden transition between low and high transmission properties of the material. The neutron transmission, \( T \), is defined as the ratio between the transmitted intensity, \( I \), and the incident intensity,
I₀, and shows that the Bragg cut-off for beryllium crystal is about 0.0056 eV (Fig. 5). Neutrons below this energy can be referred to as cold neutrons.

The filter was constructed from 2.5 cm thick and 10.2 cm diameter discs of polycrystalline beryllium separated by 0.5 mm thick cadmium annular discs with a centre hole of 5.1 cm diameter. The pieces of beryllium were placed in a closed cadmium can 0.5 mm thick with a 5.1 cm diameter hole at each end. The beryllium discs were covered with aluminium foil 0.05 mm thick, to contain and protect the beryllium.

The cadmium can containing the filter was shielded with pieces of polyethylene and supported above the detector, which was shielded with borated polyester resin.

3.2.2 MODIFICATIONS TO THE DOWNSCATTING APPARATUS TO ACHIEVE OPTIMAL EFFICIENCY

In order to perform the downscattering technique, three pieces of equipment were carefully selected to optimise the detection of neutrons inelastically scattered from zirconium hydride:

1. A convenient detector which provides a sufficient number of counts from the scattered cold neutrons

2. A sample holder which permits observation of different thicknesses of the powder sample as well as foil specimens.
3. An appropriate thickness of filter to eliminate the thermal neutrons while allowing cold neutrons to reach the detector.

3.2.2.1 THE DETECTOR

A boron trifluoride proportional counter is an appropriate detector for cold neutrons. A Twentieth Century BF$_3$ - 15 EB 20/ 50 G (81) was chosen. In all the proportional counters, produced by Twentieth Century, with a 50 mm diameter, the inactive length is 3.5 cm.

![Diagram](image)

dimensions $a = 3.5$ cm; $b =$ active length + $a = 18.5$ cm
inside pressure. $p = 20$ cm Hg

The real efficiency of the detector can be estimated by these equations:

$$\epsilon = \frac{I_0 - I(x)}{I_0}$$

$$\epsilon = 1 - \exp\left(-1.7 \times 10^{-2} \cdot p \cdot L \cdot E^{1/4}\right)$$

where $\epsilon =$ the efficiency
$p =$ the gas pressure in atm
$L =$ the active length in cm
$E =$ the energy in eV
Relating Equations (5) and (6) the final efficiency is given by:

$$\varepsilon_{a,b} = e^{-ca} - e^{-cb}$$

where \(a\) and \(b\) are the dimensions of the counter

$$c = 1.7 \times 10^{-2} \rho E^{-1/4}$$

This detector has a small active length and low gas pressure resulting from the Equation (7) in:

a) a relatively high efficiency for the cold neutrons

$$\varepsilon (E = 0.0056 \text{ eV}) = 0.480$$

b) a relatively low efficiency for the thermal neutrons

$$\varepsilon (E = 0.025 \text{ eV}) = 0.313$$

3.2.2.2 THE SAMPLE HOLDER

An aluminium sample holder was constructed which could permit the use of samples containing different quantities of zirconium hydride powder or foil. The samples were held between two windows separated by aluminium frames of 20 mm x 40 mm (Fig. 6) ranging from 1.59 mm to 8.50 mm thick. The sample was oriented in a plane at an angle of 45° from the horizontal, after finding by experiment that this gave the greatest intensity of scattered cold neutrons to the detector.

3.2.2.3 THE FILTER

A thickness of polycrystalline beryllium was chosen to suppress the thermal neutron component of the scattered beam while allowing transmission of much of the cold neutron component. Because
of the Bragg cut-off, neutrons with an energy higher than the energy cut-off suffer a larger attenuation by a beryllium filter than do neutrons with an energy lower than the energy cut-off. The relative degree of removal of neutrons below or above the cut-off is a function of the filter thickness. In addition, because the number of neutrons scattered towards the detector is inversely proportional to the square of the distance to the detector, an excessively thick filter could reduce the available neutrons by requiring the detector to be placed to a greater distance.

A choice of filter thickness was made using a cylindrical sample of zirconium hydride with a diameter of 2.67 cm as a scatterer. The intensity of the neutron beam was measured using a different number of beryllium pieces (2, 4, 6, 8) and also without beryllium at all. The experimental count-rates obtained, with statistical errors, were plotted in Figure 7. In this figure, a theoretical line for cold neutrons was calculated by choosing a line asymptotic to the data for large $x$ with a slope predicted by a cross-section of 0.5 barns using the expression

$$I = I_o \exp (-\Sigma x)$$

By means of this line, the theoretical contribution of cold neutrons detected without using a filter, $I_o^{\text{cold}}$, was found, at the left end of this theoretical line, when the thickness of the filter becomes zero.

Knowing the experimental count-rate ($I_o^{\exp} = 5.15$ counts sec$^{-1}$) and the value of $I_o$ for cold neutrons ($I_o^{\text{cold}} = 0.32$ neutrons sec$^{-1}$),
it was possible to calculate the value of $I_0$ for thermal neutrons ($I_{0,\text{th}} = 4.83$ neutrons sec$^{-1}$). The theoretical contribution to the total intensity of thermal neutrons, for any thickness of beryllium, was estimated using a cross-section of 7 barns. With these values, the corresponding theoretical solid line for thermal neutrons was drawn (Fig. 7).

In fact, if a comparison is made between the experimental count-rate and the sum of thermal and cold theoretical contributions (Table 3) a difference is observed: the value of the sum is lower than the experimental count-rate. This difference is due to the supplementary radiation that reaches the counter. The radiation is partly caused by the multiple scattering effect and partly by the background. In the case of the multiple scattering effect, neutrons are returned in the direction of the detector by additional scatters. The background is caused by other unwanted radiation, which usually consists of fast neutrons and gamma-radiation.

It is convenient to plot a dotted line in Figure 7 related to the estimated thermal neutron contribution made up of unscattered, multiple scattered and background radiation. This estimated contribution was obtained by subtracting the cold neutron contribution from the experimental count-rate and may be considered as an overall background to the cold neutrons.

In conclusion, after these comparative studies, five pieces of beryllium were chosen to perform the experiment. This choice of five pieces of beryllium gave the minimum thickness needed to cause the cold neutrons to predominate. In this case, about 0.07 counts per second is the value of estimated thermal neutrons while the experimental
count-rate is 0.22 counts per second. In consequence, 68% of the count-rate (0.15 counts sec\(^{-1}\)) is due to the contribution of the relevant cold neutrons. The remaining 32% of the count-rate is considered to be transmission of unscattered thermal neutrons, thermal multiple scattering and background radiation.

### 3.3 THERMOGRAVIMETRIC ANALYSIS

The thermogravimetric analysis registers the change in weight of the sample on an X-Y recorder as the temperature is programmed. The Perkin-Elmer TSG - 1 model of thermobalance records very small changes in weight due to its extreme sensitivity (20 µg full scale). Thus this balance was used in all experiments where the evolution of hydrogen was measured.

### 3.3.1 DESCRIPTION OF THE COMPONENTS

The components of the model TGS - 1 (Fig. 8) include:

i) A Cahn RG electrobalance, which is mounted in a vacuum chamber permitting control of the atmosphere around the sample suspended in a platinum pan inside the furnace from the balance beam above it.

ii) A furnace for heating the sample in accordance with the temperature selected.

### 3.3.1.1 THE TSG - 1 FURNACE

The hollow cylindrical furnace is supported from below inside a hangdown tube on the vacuum bottle. The furnace consists of a 152 µm
platinum wire wound on a 0.95 cm diameter aluminium oxide mandrel joined to a 0.16 cm alumina tube through which the heating wire passes to the external lead wires. The base of the furnace holds a gas inlet tube for atmosphere control. The furnace acts as both heater and temperature sensor.

3.3.1.2 GAS CONNECTIONS

When the thermobalance was in use, oxygen purified argon flowed around the sample to carry away hydrogen and to ensure a constant atmosphere.

The argon zero grade used was 5N purity with three impurities (CO$_2$, H$_2$O and hydrocarbons) reduced and analysed.

The removal of oxygen from argon by absorption was done by BASF R3 - 11 catalyst. This catalyst has the form of 5 x 3 mm pellets with a composition of approximately 30% copper in highly dispersed form stabilised on a carrier. In the reduced state, oxygen is removed without having to add hydrogen or carbon monoxide at the same time, until the copper is finally oxidized

$$\text{Cu} + \frac{1}{2}\text{O}_2 \rightarrow \text{CuO} \quad \Delta H = -37.1 \text{ kcal/g-atom}$$

When supplied, the active components of the catalyst were in the oxidized state and were reduced with hydrogen at a temperature range 160 - 300°C to form condensed water. Using the catalyst in silica and stainless-steel apparatus it was possible to achieve a purity of approximately 0.1 ppm of oxygen (83).
3.3.2. CALIBRATION AND OPERATION PROCEDURES

The temperature calibration of the TSG - 1 was established by heating ferromagnetic standards (alumel, nickel, perkaloy, iron and hisat-50), held in a magnetic field through their Curie temperatures. The resulting change in the magnetic force appears as a loss of weight in the recorder trace at the corresponding point in the temperature scan. The deviation of the measured temperature from the standard value was plotted in Figure 9 as a function of temperature in the range 150 - 1000 °C. In this figure the curve was used to rectify temperature values measured with the selected control settings.

Cold-pressed compact pellets of zirconium hydride were compacted at 0.75 tons in normal conditions. The pellets were approximately 0.16 cm thick, with surface areas of about 0.26 cm² and an average weight of 48 mg. Maintaining the cross-section of the pellets constant and changing their thickness, experiments were performed to investigate if the rate of emission was dependent on the size of the sample. The results indicate that in the range of thickness 0.64 - 3.08 mm there is no dependence. This means that the material is porous and that the emission is dependent only on the internal structure.

The sensitivity of the balance was one division (0.25 cm) 0.2 µg. The weight change was estimated at one tenth of a division ($0.2 \times 10^{-7}$ g).

The argon was purified with the catalyst at about 135°C and it flowed into the vacuum chamber at a rate of 150 cc/min.
The heating scan rate was 80°C/min. In typical experiments, the sample was first heated to 400°C and then the temperature increased by steps of 50°C until 900°C was reached. The temperature was held at each step until the observed rate of emission of hydrogen was zero.
4.1 ABSORPTION RESULTS

One of the aims of this project was to study the rate with which hydrogen is taken up by zirconium metal. Figure 10, where pressure is plotted against time, shows the characteristic shape of the curve of this process.

The first section of the graph indicates that an exposure time is required for the hydrogen to be absorbed. This exposure time depends on the thickness of the metal and its preparation, mainly the time and temperature of annealing. One of these variables, the annealing time, was studied. The result of this study shows (Fig. 11) that the exposure time is reduced with an increase in the temperature of hydriding. But when the time of annealing is increased the exposure time is always smaller.

The second section of the graph (Fig. 10) represents the optimal absorption of the hydrogen, before the metal became saturated. This takes a relatively short time and the process depends mainly on the temperature of hydriding. A Delf Algol program was used to estimate the central linear portion of each graph representing the average maximum rate of absorption of hydrogen (see Appendix 2 for a definition of the algorithm and Appendix 3 for a program listing).
Knowing the maximum rate of absorption a plot was made of the fractional rate against the inverse of the absolute temperature (Fig. 12). The activation energy for absorption of hydrogen by zirconium, as deduced from the figure, was found to be 13412 cal/g-atom, in the temperature range 400 - 550°C.

The standard deviation for the points plotted on the absorption of hydrogen graph was found by grouping the data. However, because only nine readings were available, the statistical accuracy of the standard deviation cannot be guaranteed. The same procedure was adopted when analysing the data for the emission graph.

The theoretical values are taken from the diffusion coefficients given by Kearns (84) for absorption of hydrogen in α-zirconium, in the temperature range 275 - 700°C. This graph is plotted in Figure 12 by a dotted line.
4.2 NEUTRON DIFFRACTION RESULTS

Neutrons scattered from the sample which pass through the beryllium filter were recorded after a period of 24000 seconds. This count-rate corresponding to the peak of the first vibrational level of energy was recorded at a Bragg angle equal to 12°20'. Subtracted from this count-rate is a general background detected in two 12000 second measurements at equidistant sides of the peak. These latter measurements were recorded at 11° and 13°40' Bragg angles. The experimental setting of these backgrounds is in agreement with the resolution, that is, the full width at half height of the peak, given by both Whittemore (85) and Pan (86). The average resolution for the first level of vibration of zirconium hydride given by these two authors is 0.030 eV.

According to Eqs. 3 and 4 the energies corresponding to the peak and to the background measurements are 0.140, 0.175 and 0.114 eV, the wavelengths being 0.766, 0.684 and 0.847 Å respectively.

In non-standard samples (87) different densities of hydrogen were prepared from low partially hydrided metal to saturated hydride. Thus the relation of H/Zr in the non-standard samples varied from 0.723 to 1.981.

For standard samples, in order to simulate a different density of hydrogen, varying thickness of zirconium hydride were used. Thicknesses from 1.3 to 7.8 mm were studied (see Table 4).
The results of both non-standard and standard samples were plotted in Fig. 13 showing a very noticeable peak, which depends on the quantity of hydrogen. For the standard samples the count-rate at the peak varied from 0.74 counts per second for the thickest sample containing 344 mg of hydrogen, to 0.42 counts per second for the thinnest sample containing 61 mg of hydrogen. For the non-standard samples the count-rate of the peak ranged from 0.48 to 0.35 counts per second when the weight of hydrogen varied from 122 to 39 mg. In the case of samples containing less than 39 mg of hydrogen a peak was barely distinguishable from the base line and the experiment run under similar conditions was no longer sensitive to the hydrogen in the sample.
4.3 EVOLUTION RESULTS

In typical experiments (88) the temperature was increased by steps of 50 ± 5 degrees starting at room temperature (89). At a moderate temperature, the system began by evolving hydrogen quickly, but the rate of evolution diminished rapidly becoming practically zero. Only then the temperature was increased to the next step. In Fig. 14, where the hydrogen weight loss is plotted against time, there appears a plateau for every isotherm. In this typical experiment every increment of temperature produces a plateau, even though the rate of emission increases with increasing temperature.

The maximum value of relative weight loss of hydrogen, i.e. weight loss of hydrogen at a given temperature over the initial weight of hydrogen at the beginning of this step, according to the following diagram:

\[
\text{Relative weight loss} = \frac{W_o - W_f}{W_o}
\]

corresponds to the temperature range 680 - 735 °C with a value of 63% (see Fig. 15 and Table 5). At that temperature range only a small
amount of hydrogen, about 10%, is left in the sample.

4.4 RESULTS OF MICROGRAPHIC ANALYSIS

Several zirconium hydride specimens with a H/Zr relation ranging from 0.72 to 1.98 were prepared (90) using a reactive dissolvent with a composition of 5% volume of HF and 3% volume of HNO₃. Diamond and magnesium oxide were used for the last two stages of polishing the materials. The samples were mounted to be viewed with bright field illumination.

4.4.1 GRAIN BOUNDARY PRECIPITATES

Grain structure is found in α-zirconium as well as in β-zirconium (91). In the present samples the size of the grains is about 37 ± 3 μ (see micrographs Nos. 2 and 4). This agrees well with the size of 40 μ reported by Hardie (92) annealing zirconium under similar conditions as the ones used in these experiments. He annealed for 90 minutes at 750 °C under 10⁻³ mm Hg of pressure.

4.4.2 THE HABIT PLANE OF INTRAGRANULAR HYDRIDE

Westlake (93) was able to establish beyond reasonable doubt that the needles observed along the grain boundaries were zirconium hydride. With increasing hydrogen concentration, these hydride needles became platelets parallel to the {10 10} planes of the matrix (94).
In micrograph No. 1 it can be seen the nucleus of \( \alpha \)-zirconium sample with the formation of platelets of hydrides (95) with a preferential tendency to be orientated in a certain direction, parallel to the surface of the sample (96). This orientation varies by an angle of \( \pm 13 \) degrees (97).

Micrograph No. 2 shows a transition zone between \( \alpha \) and \( \beta \) phase of zirconium. Most of the hydride is precipitated in the \( \beta \)-phase of zirconium. The hydride is mainly on the grain boundaries and as intragranular platelets orientated in an angle of \( \pm 9.5 \) degrees.

In Micrograph No. 5, where the ratio \( H/Zr \) is 1.22, the precipitates are orientated in all directions.

4.4.3 ORIGIN OF CRACK FORMATION

Micrograph No. 5 shows a total cross-section with a crack orthogonal to the surface. The origin of this crack could be mechanical or even due to the surface configuration in which an inflection point can be observed.

Micrograph No. 6 shows another part of the former specimen with a crack parallel to the surface. This particular crack could very well be caused by the hydrogen, in which case it is called a primary crack. This is caused by the concentration gradient of hydrogen, high enough as to form a concentration barrier. This layer of hydride prevents further hydriding and could be the main cause of embrittlement in the specimen (98).
CHAPTER 5

ANALYSIS AND INTERPRETATION OF RESULTS

5.1 ANALYSIS OF ABSORPTION

5.1.1 DIFFUSION OF HYDROGEN IN ZIRCONIUM

Through the analysis of the relation between gas pressure and dissolution rate of hydrogen it should be possible to determine if the diffusion of hydrogen takes place in the molecular or in the atomic form. The equilibrium reaction and the constant of reaction are defined as follows:

\[
\begin{align*}
\text{H}_2 + 2\text{H} & \rightarrow K = \frac{k_1}{k_2} = \frac{[\text{H}]}{[\text{H}_2]} \\
\text{k}_1 & \text{rate of absorption of hydrogen}
\end{align*}
\]

If the rate of absorption of hydrogen appears to be proportional to \([\text{H}_2]\), then the hydrogen diffuses as molecules. But if it is proportional to \([\text{H}_2]^\frac{1}{2}\) then what diffuses are hydrogen atoms.

The lines represented in Fig. 16, where relative hydrogen pressure is plotted against time for several initial pressures, show that the slope of the lines increases with rising initial pressure.

Figure 17 shows a plot of the fraction of hydrogen absorbed per second against the initial pressure, the data being taken from Figure 16. The lower scale shows the initial pressure, \(p_0\), the upper scale shows the square root of the initial pressure (see Table 6). The square root relation gives a linear plot through the origin.
This means that hydrogen diffuses into zirconium in an ionized or atomic condition, thus explaining the high penetrability of zirconium by hydrogen (99).

From the slope of the linear relation of Figure 17 the value of the rate constant is estimated to be $2 \times 10^{-10}$ for concentrations of hydrogen in zirconium ranging from 5150 to 9400 ppm.

5.1.2 DISSOLUTION OF HYDROGEN ATOMS IN ZIRCONIUM

If hydrogen diffuses into zirconium in an ionized or atomic condition, the enthalpy levels involved in the solution of gaseous hydrogen in zirconium at constant pressure can be, then, represented according to the following diagram

\[
\begin{align*}
H \text{(gas)} & \quad \Delta H' \quad \Delta H'' \quad \Delta H_{\text{sol}} \\
\frac{1}{2}H_2 \text{(gas)} & \quad [H]_\alpha
\end{align*}
\]

where $[H]_\alpha$ represents the concentration of hydrogen dissolved in the $\alpha$-phase of zirconium.

The overall reaction is the sum of two partial reactions in two steps:

i) the molecule of hydrogen is split into atoms at the surface of the metal

ii) the atoms are introduced into the interstices of the metal
where \( \Delta H_{\text{sol}} = \left[ \bar{H}^0 \left[ H \right]_\alpha - \frac{1}{2} H^0 H_2(\text{gas}) \right] \)

i.e., the relative partial molal enthalpy for the solution of molecular hydrogen gas in \( \alpha \)-zirconium

The value of the heat of solution is negative indicating that the process takes place exothermally.

5.2 ANALYSIS OF NEUTRON DIFFRACTION

5.2.1 THE COUNT-RATE AT THE PEAK

To analyse the count-rate corresponding to the energy of the optical peak of vibration of bound hydrogen in both standard and non-standard samples (100), a graph was plotted (Fig. 18) with the experimental data given in Table 7.

Figure 18 shows an increase of neutron scattering with an increasing weight of hydrogen. The upper continuous line of this figure corresponds to the observed standard values obtained when the reactor was operating at full power. And the lower continuous line corresponds to the samples studied when the reactor was generating 92% of its total capacity.
A U-235 fission chamber, placed at the beam-stop and recording the intensity of the neutron beam during operating time, was used as a reference. After performing experiments at a lower power for 240 hours and at a higher power for 123 hours, it was possible to deduce, for the latter values, a ratio equal to 0.919 as the deviation of the neutron intensity (Fig. 19). As a result, the count-rates obtained during the lower power period were normalized when divided by this ratio. When the results were plotted in Figure 18 they fitted well with the upper continuous line (see points 3, 4 and 8).

However, when a similar treatment was applied to the non-standard samples (101), the upper dotted line of Figure 18, obtained when the values of the lower dotted line were divided by the ratio 0.919, deviates from the standard line by a factor which increases with the decreasing density of hydrogen.

It was possible that this deviation factor could be attributed to the non-homogeneous distribution of hydrogen in the sample. To test this eventuality, some non-homogeneous standard samples were prepared such that the hydride was placed in one half of the sample holder, while the other half was occupied by pure zirconium. Table 8 shows that this arrangement provided relations between the weight of zirconium and hydride ranging from 0.49 to 1.38. The resulting count-rates of these samples fitted well with the upper continuous line of Figure 18 (see points 7 and 8). This indicates that a non-homogeneous distribution of hydrogen is not responsible for the deviation of the non-standard line.
The falling of the previously mentioned non-standard line cannot be attributed to a change of the hydrogen vibration energy because McReynolds et al. (102) in their experiments find no significant change in the energy of the optical vibration level of hydrogen in zirconium hydride. They used samples in the composition range $\text{ZrH}_{1.2} - \text{ZrH}_{1.9}$.

Representing the ratio between the observed and the expected count-rates against the H/Zr ratio, a graph was plotted (see Fig. 20 and Table 9) in which the dotted line represents the maximum fraction of hydrogen that responds to the neutron diffraction under constant experimental conditions.

5.2.2 THE AREA PARAMETER

The same treatment, as that used to analyse the count-rate, was applied to the area parameter associated with each peak (103).

This area parameter was defined by means of the equation:

$$A = C_2 - \frac{1}{2} (C_1 + C_3)$$

where $C_2$ = the experimental count-rate corresponding to the optical peak of vibration energy, including all background counts. This count-rate was measured over 24000 seconds.

$C_1$ and $C_3$ are the experimental count-rates symmetrically placed at each side of the peak and considered as measures of the overall background. The background is, primarily, thermal neutrons multiple scattered in the filter. The counting time for each background was 12000 seconds.
Similarly, the standard deviation of A for each of the area parameter was calculated:

\[ \sigma_A = \pm \sqrt[4]{\frac{2C_2 + C_1 + C_3}{t}} \]

where \( t = 12000 \) seconds.

When the area parameter over the weight of hydrogen was plotted against the weight of hydrogen (Fig. 21), a different result was obtained for the standard and for the non-standard samples. The slope of the fitted lines is negative for those values which are standard and positive for those values which are non-standard (104).

The negative slope of the standard fitted line, however, was not unexpected. Pan (105) had already observed, in inelastic downscattering experiments, a diminution in neutron transmission with an increasing thickness of the sample.

For the non-standard samples, although there are large uncertainties, the best fitted line appears to be as shown in Figure 21. It is possible that the positive slope of this line is due to an increase of the amount of unbound hydrogen at low hydrogen densities.

Figure 20, where the ratio between the observed and the expected area parameters is plotted against the H/Zr ratio, was based on this last assumption. The continuous line of that figure
represents the maximum fraction of hydrogen that can be bound under constant experimental conditions. Comparing columns 4 and 5 of Table 9 it can be seen that the area parameter fractions are lower than the fractions obtained with the count-rates of the peak. The standard deviation of each of these two fractions is the same, but the background increases with the increasing weight of hydrogen. Therefore, the area parameter fraction can be considered to represent better the fraction of unbound hydrogen for any composition of the zirconium-hydrogen system.

On the same assumption, values for the area parameter for each sample were plotted in Fig. 22 against the number of bound hydrogen atoms per cm² (see Table 10). In the case of the non-standard samples, the fraction of unbound hydrogen has been subtracted according to the values given in Table 9.

The resultant solid line of Figure 22 tends to a straight line as the thickness of the sample tends to zero. The line passes through the origin, implying that all hydrogen atoms of the standard samples contribute to the peak (106). With reduced hydrogen densities, a significant fraction of the hydrogen in the non-standard samples appears to be dissolved (unbound) and seemingly does not contribute to the area parameter. This is shown in Figure 23 where the area parameter is plotted as a function of the total weight of hydrogen for equal weights of sample. This plot shows that the standard samples respond better to the neutron diffraction than do the non-standard ones with similar weight.
These experimental results, for neutron diffraction, can be interpreted on the assumption that two forms of hydrogen were present in the partially hydrided material (non-standard samples). However, because the neutron intensities available from the U.L.R. were low, the uncertainties in measuring the neutron scattering were found to be large. Thus, it was not possible to establish conclusively that two forms of hydrogen co-exist, by means of neutron diffraction alone.
Figure 20 is consistent with the assumption that hydrogen was present in non-standard samples in at least two states: 'dissolved' (unbound) hydrogen, which is mobile and 'precipitated' hydrogen, which is interstitially fixed in the lattice structure. The hydrogen in the first state will not contribute to the neutron diffraction. The second type of hydrogen, present in the form of the stable γ-phase (107), does respond to the neutron diffraction.

Micrographic analysis of some non-standard samples also suggests that the hydrogen was present in these two states.

By measuring in the micrographs Nos. 3, 4 and 6 the variation of depth of δ-zirconium with hydrogen content, a plot was made of the fraction of depth of δ-zirconium over the total thickness of the sample against the atom ratio H/Zr, \( P_\beta \) (see Fig. 24 and Table 11). Hydrogen was absorbed in only one surface of the sample because of the way it rested in the silica boat. This can be seen clearly in the micrographs.

If, as Figure 24 suggests, the depth of penetration of hydrogen implies a more favourable transition of the solid α-phase of zirconium, then most of the γ-hydride will remain in the δ-phase of zirconium (108). This agrees with the observation of Fast that hydrogen precipitates better in the δ than in the α-phase of zirconium and he attributes this to the electronic interactions:
'As opposed to nitrogen and oxygen, the solubility of hydrogen in the b.c.c. form of zirconium is much greater than in the h.c.p. form of the metal. The electronic interaction is apparently more favourable when the hydrogen occupies the small interstices (109) of the b.c.c. metal than when it is in the larger interstices of the h.c.p. form' (110).

When the fraction of unbound hydrogen was plotted against the fraction of depth of α-zirconium over the total thickness of the sample, it is seen that the amount of unbound hydrogen increases with the increasing depth of α-zirconium (see Fig. 25 and Table 11).

According to Figure 25 most of the unbound hydrogen appears to be in the α-phase of zirconium. At the same time, the area in cross-section of the α-phase depends, according to Figure 24, on the concentration of hydrogen. Accepting this evidence, the fact that the hydrogen is unbound could explain quantitatively why in one of the non-standard samples with the same composition as the standard one, a minimum of 13.5% of the hydrogen does not respond to the neutron diffraction (111). This value of unbound hydrogen increases with decreasing density of hydrogen, until for the smaller H/Zr ratio, equal to 0.72, 19.3% of the total hydrogen appears to be unbound.
5.4 ANALYSIS OF DESORPTION

5.4.1 FRACTIONAL RATE OF EMISSION AND PLATEAU-TIME

Figure 14 shows a clear plateau at the end of each isotherm when no hydrogen loss occurs. Defining plateau-time as the time during which a plateau was maintained at a constant temperature, several experiments were performed to determine if the length of this plateau-time was influencing the rate of emission when the temperature was increased by 50°C. Plateau-times were recorded ranging from several seconds to fifteen minutes.

Plotting the fractional rate of emission, obtained from three experiments, against the plateau-time, a value of \( p \) equal to \( 7.74 \pm 0.03 \times 10^{-4} \text{ sec}^{-1} \) was measured with plateau-times ranging from 30 to 150 seconds (Fig. 26). The values for the fractional rate of emission were obtained at 735°C and the plateau-times measured at 680°C.

The constant result obtained, in Figure 26, for the fractional rate of emission suggests that the plateau-time is not a time in which precipitated hydrogen dissolves into the metal and that no hydrogen atoms are able to jump over the thermal barrier \( kT \) without a temperature rise.

5.4.2 RATE OF EMISSION AND HYDROGEN CONTENT

In order to determine if the rate of evolution of hydrogen is a function of the hydrogen present in the sample, a graph was plotted of the time of losing the first 40% of hydrogen at each
isotherm against the amount of hydrogen present in the sample at
the beginning of this time, according to the following diagram:

\[ \text{H weight loss} \]
\[ A = \text{the hydrogen weight loss at T temperature} \]
\[ t = \text{time to evolve the first 40\% of A} \]

Figure 27 shows that there is no linear relationship
between the four points plotted for each of the three temperatures
(680, 735 and 790°C). Thus indicating that, for a given temperature,
there is no linear dependence between the rate of emission and the
quantity of hydrogen present in the sample.

5.4.3 LOW AND HIGH TEMPERATURE STEPPING EMISSION EXPERIMENTS

To determine if there is any relation between the rate of
emission and the way in which the sample is heated, a second set of
experiments, defined as high temperature stepping emission experiments
(see note 88 above), was undertaken. These high temperature stepping
experiments were performed heating the sample without previous steps
up to 680°C (Exp. No. 125), 735°C (Exp. No. 123) and 790°C (Exp. No. 124).
The logarithm of the remaining fractional weight of hydrogen, i.e., the amount of remaining hydrogen at any given time over the initial weight of hydrogen at the same temperature, was plotted against time, according to the following diagram:

\[
\text{Fractional weight of } H = \frac{W_t}{W_0}
\]

The slope of the lines (see Figs. 28 and 29) gave the value of \( p \), in this equation, when \( W_f \approx 0 \):

\[
\frac{F_t}{F_i} = e^{-pt} \quad \text{(see Section 2.3)}
\]

where
- \( F_t \) = the fractional weight of \( H \) at time \( t \)
- \( F_i \) = the fractional weight of \( H \) at \( t \) equal zero
- \( p \) = the fractional emission per second

When the logarithm of \( p \) was plotted against the inverse of the absolute temperature, two different slopes for low and high temperature stepping experiments were obtained (Fig. 30). The corresponding lines give the value of the activation energy, \( E \), for each process according to this equation:

\[
p = p' \exp (-E/RT)
\]
The results of $E$ obtained are tabulated below:

<table>
<thead>
<tr>
<th>Types of emission experiment</th>
<th>Range of Temperature, $^\circ$C</th>
<th>Activation Energy, $E$, cal/g-atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>High temperature stepping</td>
<td>680-790</td>
<td>23497</td>
</tr>
<tr>
<td>low temperature stepping</td>
<td>625-735</td>
<td>25953</td>
</tr>
</tbody>
</table>

The small difference between the slopes of these two lines suggests that the large quantities of hydrogen held in supercharged zirconium is not contained interstitially in supersaturated solid solution. This suggestion implies that the solubility of hydrogen is concomitant with the solubility of $\delta$ hydride in the metal. It is possible to describe the solution as taking place in two steps:

1) the $\delta$ hydride is converted into $\alpha$-phase and hydrogen
2) the hydrogen gas in dissolved in $\alpha$-zirconium

\[
\delta \text{Zr H}_{1.5}^+ + \frac{3}{4} \text{H}_2 \rightarrow \alpha \text{Zr} + \frac{3}{4} \text{H}_2 \tag{8}\]
\[
\alpha \text{Zr} + \frac{3}{2} [\text{H}]\alpha \tag{10}\]
\[
\delta \text{Zr H}_{1.5}^+ \rightarrow \alpha \text{Zr} + \frac{3}{2} [\text{H}]\alpha \tag{10}\]
where \([\text{H}]_\alpha\) represents the hydrogen dissolved in the \(\alpha\)-phase.

According to Gulbransen and Andrew (112), for the experimental ranges 10\(^{-4}\) - 10\(^{-1}\) mm Hg and 425 - 460°C, the heat of reactions of [8] and [9] are:

\[
\left[ \bar{H}^0 [\text{H}]_\delta \right. - 1/2 \left. \bar{H}^0 [\text{H}2(\text{gas})] \right] = -22875 \text{ cal/g-atom of H}
\]

\[
\left[ \bar{H}^0 [\text{H}]_\alpha \right. - 1/2 \left. \bar{H}^0 [\text{H}2(\text{gas})] \right] = -14250 \text{ cal/g-atom of H}
\]

where \([\text{H}]_\delta\) represents the hydrogen in the \(\delta\) hydride

As a consequence, the heat of reaction of [10] is given by

\[
\left[ \bar{H}^0 [\text{H}]_\alpha \right. - \left. \bar{H}^0 [\text{H}]_\delta \right] = 22875 - 14250 = 8625 \text{ cal/g-atom of H}
\]

5.5 CORRELATION BETWEEN ABSORPTION AND DESORPTION OF HYDROGEN

The activation energies (\(E\)) and the enthalpy levels (\(\Delta H\)) involved in the absorption-desorption cycle of hydrogen from zirconium could be represented according to the following diagram:
The difference between the activation energy for absorption of hydrogen gas per gram atom (see Section 4.1) and the activation energy of emission of hydrogen gas per gram atom, by low stepping experiments (see Section 5.4.3) is:

\[ E_{\text{absorption}} - E_{\text{emission}} = 13412 - 25953 = -12541 \text{ cal/g-atom} \]

This difference appears to correspond to the heat of solution of hydrogen in \( \alpha \)-zirconium. The value

\[ \Delta H_{\text{solution}} = -13094 \text{ cal/g-atom}, \]

averaged over ten investigators (see Table 1), corresponds well with the above. The standard deviation of the results of the ten investigators, 1426 cal/g-atom, is about three times greater than the difference between the average and the present experimental result. The correspondence between the difference of activation energies and the heat of solution of hydrogen in \( \alpha \)-zirconium, can be shown from thermodynamic considerations (see Appendix 4).

According to the hypothesis represented in this diagram the total activation energy for emission of hydrogen from \( \delta \text{ZrH}_{1.5} \) would be

\[ 8625 + 25953 = 34578 \text{ cal/g-atom} \]

This high value is not observed and it is concluded that the rate-controlling step of the emission of hydrogen is not the decomposition of solid hydride, but the removal of dissolved hydrogen from \( \alpha \)-zirconium.

The difference between low and high temperature stepping experiments, shown in Figure 30, is attributed to the differences in the concentration of \([H]_\alpha\) in the metal phase.
CHAPTER 6

CONCLUSIONS

The difference between the activation energy for absorption of hydrogen gas and the activation energy for emission of hydrogen gas has been found to correspond to the heat of solution of hydrogen in α-zirconium.

The experimental results, for neutron diffraction, could be interpreted on the assumption that two forms of hydrogen were present in the partially hydrided zirconium (non-standard samples). However, because the neutron intensities available from the U.L.R. were low, the uncertainties in measuring the neutron scattering were found to be large. Thus it was not possible to establish conclusively that two forms of hydrogen co-exist, by means of neutron diffraction alone.

Micrographic analysis further suggested that these two forms of hydrogen co-exist in partially hydrided metal. The amount of dissolved hydrogen increases with a decreasing H/Zr ratio. The maximum percentage of dissolved hydrogen was found to be 19.3% when the Zr/H ratio was at a minimum, 0.72.

According to the hypothesis represented in the diagram shown in Section 5.5, the growth of the hydride phase is not controlled by the diffusion rate but by the dissolution of hydrogen. No activation energy has been found to be involved in the transition from the dissolved hydrogen in α-zirconium to the hydride phase. The activation
energy required to evolve the unbound hydrogen from the sample is about twice the heat of solution of hydrogen in α-zirconium. However, this activation energy is not as great as might be expected from the diagram. The smaller activation energy required, principally in high stepping experiments, further suggests that at higher temperatures only the α phase is stable. Thus the removal of dissolved hydrogen from α-zirconium is the rate-controlling step of the emission of hydrogen.
NOTES

(1) The significance of the application of zirconium in water nuclear reactors is demonstrated by the number of this type of reactor throughout the world. At the beginning of 1979 there were 236 nuclear reactors under construction, able to produce electric power of 213000 MW. Of these reactors 198, representing a capacity of 180000 MW, are light water reactors. In all of these reactors, 1/4 are Boiling Water Reactors (B.W.R.) and the rest are Pressurized Water Reactors (p.W.R.), zirconium is used as the cladding material for the nuclear fuel (data taken from Le Monde, Paris, 9 May 1979). On the other hand zirconium is also used for pressure tubing in natural uranium heavy water Canadian system reactors (CANDU) and in steam heavy water reactors (S.G.H.W.R.).

(2) The Young's modulus of elasticity for zirconium is $94.5 \times 10^9$ N m$^{-2}$.


(8) B. Cox, J. Nucl. Mat. 28(1968) 1-47.

(9) C. E. Ells, J. Nucl. Mat. 28(1968) 129-151.


(17) E. A. Gulbransen and K. F. Andrew, ibid, p.349.
(18) D. P. Smith, ibid, p.5-6

(19) J. Belle et al., ibid, p.212.

(20) D. Shaltiel, I. Jacob and D. Davidov, J. Less Common Met. 53(1977) 117.


(22) J. Belle et al., ibid., p.213.


(25) K. Une, ibid., p.93.

(26) J. Belle et al., ibid., p.211.

(27) E. A. Gulbransen and K. F. Andrew, J. Met. 7(1955) 136.


(35) J. Belle et al., ibid., p.211; K. Une, ibid., p.93.


This value has been estimated from published graphs by D. G. Westlake, J. Nucl. Mat. 7(1962) 346.

(48) E. A. Gulbransen and K. F. Andrew, J. Met. ibid., p.143.

(49) The value reported by M. W. Mallett and M. W. Albrecht, ibid., p.145, is $-7830 \pm 400$ cal/g-atom at range of $10^{-5} - 10^{-3}$ mm Hg and 700 - 800 °C. 'It is seen' - remark the authors in p.144 - 'that the heat of solution increases with increasing oxygen content. For each increase of 0.1 w/o in the oxygen content of $\alpha$-zirconium the heat of solution of hydrogen increases by
about 500 cal/g-atom. This indicates that there is some interaction between the oxygen and hydrogen atoms within the zirconium lattice in the concentration range of this work. This is the reason why this value was not taken into consideration here.


(52) K. G. Barraclough and C. J. Beevers, ibid., p.127.


(54) The energy changes involved in phase change are small relative to the energy values mentioned earlier and therefore they are not considered here. For instance, the heat of transition of the solid α-phase of zirconium is 920 cal/g-atom. Cf. A. L. G. Rees, Trans. Faraday Soc. 50(1954) 335.


(56) A. Sieverts and E. Roell, ibid., p.289.

(57) A. Sieverts and A. Gotta, Z. anorg. allgem. Chem. 172(1928)1.
(58) G. Hägg, Z. Physik Chem. (B) 11(1931)433; ibid., 12(1931)33.

(59) A. R. Ubbelohde, ibid., p.295.


(63) G. P. Marino, ibid., p.335. This model excludes two other possibilities: i) there is no supersaturation in the \( \alpha \)-phase of zirconium, ii) the supersaturation in the \( \alpha \)-phase is indefinite.


and G. C. Pomraning, the M.I.T. Press, Massachusetts, Mass., 1966, p. 27.


(74) A. D. B. Woods et al., ibid., p. 494.

(75) W. L. Whittemore and A. W. McReynolds, Phys. Rev. 113 (1959) 806.

(76) I. Pelah et al., ibid., p. 1092.

(77) A. Andresen et al., ibid., p. 1093.

(79) A. D. B. Woods et al., ibid, p.489.


(81) A counter of 15 cm active length, 3.5 cm inactive length, enriched in boron-10, filled with gas at a pressure of 20 cm Hg, 50 mm diameter and with copper end window 0.071 mm thick.


(83) Cf., Badishe Anilin and Soda Fabrik AG, Technical leaflet No. M5076e.

(84) J. J. Kearns, J. Nucl. Mat. 43(1972) 330.

(85) W. L. Whittemore, ibid., GA-4490.

(86) S. S. Pan and F. J. Webb, ibid., p.195.

(87) Standard sample is the reference powder preparation with a composition equal to Zr H1.458 manufactured by K. and K. Laboratories Inc., Plainview, N.Y. and Hollywood, Calif. The powder was analysed by Henry Wiggin and Company Ltd., Hereford, England. Non-standard samples are those zirconium foil preparations supplied by Goodfellow Metals Ltd., Cambridge, England, and hydrided in the course of the present work.
These typical experiments will be called low temperature stepping emission experiments. They are named thus because the temperature steps start at room temperature. They must be distinguished from later experiments (see Section 5.4.3), where the sample will be heated without previous steps up to a high temperature at a rate of 80°C/min, and then the isothermal emission of hydrogen studied. The latter will be called high temperature stepping emission experiments.

The temperatures have been corrected according to the calibration curve of Figure 9.

Specimens prepared and analysed in the Geotecnia y Cimientos S.A. Laboratories, Madrid.


D. Hardie, J. Nucl. Mat. 45(1972) 265.


Sailer and Dickenson have identified this platelets precipitated along crystallographic planes of the zirconium matrix as a hydride. Cf. H. Sailer and R. F. Dickenson, Metallographic Identification of Non-metallic Inclusions in Zirconium, Batelle Memorial Institute, Columbus, Ohio, BMI-74, July 1951.

Ells reported that the colony of platelets are aligned within $12^\circ$ of the principal hydride direction. Cf. C. E. Ells, ibid., p.132.

J. E. Bailey, ibid., p.279.

D. P. Smith, ibid., p.232.

Some of the published data related to the centre of the single phonon optical peak are listed in Table 2 and compared with the equivalent result of the present work, which agrees well with the literature.

All the experiments with non-standard samples were performed during lower reactor power.

A. W. McReynolds et al., ibid., p.297.

This area parameter, which is proportional to the area under the peak, gives the counts per second at the peak, after subtracting the background.

The equation of the best straight line through the points of Figure 21 was determined by the method of least squares.

(106) To date this is the best evidence about the state in which hydrogen is present in the standard zirconium hydride.


(108) The transition temperature of the solid α-phase of zirconium was first found by Vogel and Tonn to be $862 \pm 5^\circ C$. Cf. R. Vogel and W. Tonn, *Z. anorg. allgem. Chem.* 202(1931)292. But if hydrogen is present, then this temperature can be lowered some $200^\circ C$ according to an early observation of de Boer and Fast. Cf. J. H. De Boer and J. D. Fast, *ibid.*, p.353.


(111) This value of 13.5% has been calculated by interpolating the fraction of unbound hydrogen, the data given in column 5 of Table 11.

(112) E. A. Gulbransen and K. F. Andrew, J. Met., ibid., p.140.
Figure 1  TRANSMISSION CROSS-SECTION

Relative hydrogen cross-section \( \sigma / \sigma_{\text{free}} \)

Energy of incident neutron \( (E/E_0) \)
Figure 2  DOPPLER EFFECT

\[
\begin{align*}
&\text{MH (M is of infinite mass)} \\
&\text{ZrH}
\end{align*}
\]

Relative hydrogen cross-section \( \left( \sigma / \sigma_{\text{free}} \right) \)

Energy of incident neutron \( (E/\hbar) \)
Figure 3  CROSS-SECTION PLAN VIEW OF THE NEUTRON DIFFRACTION EXPERIMENT

KEY:
1 shutter
2 monocrystal-Be
3 sample holder
4 beam-stop

scale: 1m

- concrete
- borated resin
- lead
Figure 4  ELEVATION AND PLAN OF THE DETECTOR
Figure 5  CROSS-SECTION OF Be

Energy (eV)

$\sigma_T$ (barns)
Figure 6  ALUMINIUM SAMPLE HOLDER

WINDOWS

8 off .030cm

FRAMES

4 off .030cm
8 off .127cm
2 off .260cm
Figure 7  CLASSIFICATION OF FILTERED FLUXES

Rate, counts/sec

-1.0
-1.0
-0.1
-0.1
-0.01
-0.01
-0.001
-0.001
-0.0001
-0.0001

0 2 4 6 8

number of Be pieces

\( I_{0,\text{th}} \)

\( I_{0,\text{cold}} \)

\( \text{theoretical cold neutrons} \)

\( \text{theoretical thermal neutrons} \)

\( \text{estimated overall background} \)

\( \text{overall background} \)

\( \times \text{experimental values} \)

\( \text{choice of experimental conditions} \)
Figure 8  THERMOBALANCE APPARATUS (TSG-1)

KEY:
1. Vacuum Bottle
2. Hangdown Tube
3. Furnace
4. Pt Stirrup and Pan
5. Baffle assembly
6. Phototube
7. Coarse Zero

Dimensions:
- INLET: 7.6 cm
- OUTLET: 10.2 cm
- 30.5 cm
- 14 cm
- 16 cm
Figure 9 DEVIATION OF MEASURED MAGNETIC TRANSITION TEMPERATURES

- Alumel
- Nickel
- Permalloy
- Iron
- Hisat-50
Figure 10  PRESSURE VS TIME

![Pressure vs Time Graph]

- Time, min
- Pressure (mm Hg)
Figure 11

EXPOSURE TIME AGAINST TEMPERATURE

Annealed in vacuum at 660°C

- 180 min
- 120 min

1/Exposure time, min⁻¹

1/Temperature, 10³ K⁻¹
High Temperature Stepping Emission Experiments

Figure 12 ARRHENIUS PLOT

Temperature (°C)

800 750 700 650 600 550 500 450 400

10^{-2} 10^{-3} 10^{-4} 10^{-5}

LITERATURE VALUES (84)
Absorption Experiments
Low Temperature Stepping Emission Experiments
High Temperature Stepping Emission Experiments

p sec^{-1}

1/Temperature (K^{-1} \times 10^{3})
Figure 13  COUNT-RATE SPECTRUM

- Standard samples
- Non-standard samples

Rate, counts x sec\(^{-1}\)

Angle θ:

11°  12°20'  13°40'

Samples:
- 1
- 2
- 3
- 4
- 5
- 6
- 9-10
- 11
- 12
- 13-14
Figure 14. ISOTHERMS GIVING THE WEIGHT LOSS OF H IN THE LOW TEMPERATURE STEPPING EXPERIMENT No. 127

Initial Weight of ZrH$_{1.458}$ = 32.1mg
Figure 15  ISOTHERMS GIVING THE MAXIMUM RELATIVE WEIGHT LOSS OF H
Figure 16  EFFECT OF THE INITIAL PRESSURE ON THE RATE OF ABSORPTION OF H

Temperature = 450°C

<table>
<thead>
<tr>
<th>Exp.No.</th>
<th>Initial Pressure (mm Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>442</td>
<td>162</td>
</tr>
<tr>
<td>432</td>
<td>594</td>
</tr>
<tr>
<td>412</td>
<td>668</td>
</tr>
</tbody>
</table>
temperature = 450°C

Figure 17  FRACTION OF H ABSORBED VERSUS INITIAL PRESSURE
Overall count-rate of the peak (counts s⁻¹)

PEAK COUNT-RATE AS A FUNCTION OF WEIGHT OF HYDROGEN

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Higher power corrected points</th>
<th>Lower power uncorrected points</th>
<th>Lower power corrected points</th>
<th>Fitted lines</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
<td>□</td>
<td>△</td>
<td>○</td>
<td>-----</td>
</tr>
<tr>
<td>Non-standard</td>
<td>X</td>
<td></td>
<td>+</td>
<td>----</td>
</tr>
</tbody>
</table>

Total weight of H (g)
Figure 19  POWER GENERATED BY ULRC BETWEEN 14th JULY 1977 AND 28th APRIL 1978

- Average = 4.275 counts sec\(^{-1}\)
- Average = 3.929 counts sec\(^{-1}\)

DATE (day, month)
Figure 20 NEUTRON DIFFRACTION RESPONSE IN NON-STANDARD SAMPLES

- PEAK fraction
- AREA fraction
Figure 21  AREA PARAMETER AS A FUNCTION OF WEIGHT OF HYDROGEN

[Graph showing the area parameter as a function of total weight of H (g). The graph includes fitted lines and data points representing standard and non-standard values, along with standard deviations.]
Figure 22: AREA PARAMETER AS A FUNCTION OF BOUND HYDROGEN DENSITY

Area Parameter, $A$ (counts sec$^{-1}$)

Density of bound hydrogen (atoms x cm$^{-2}$ x $10^{-21}$)

- STANDARD VALUES
- NON-STANDARD VALUES
- STANDARD DEVIATION
Figure 23  AREA PARAMETER AS A FUNCTION OF THE TOTAL WEIGHT OF HYDROGEN
Figure 24  PROGRESSION OF $\beta$-$Zr$ WITH HYDROGEN CONCENTRATION
Figure 25  UNBOUND HYDROGEN IN $\alpha$-Zr
Figure 26  SLOPE OF TIME VERSUS PLATEAU-TIME

Standard deviation = ± 0.03 × 10^{-4} \text{ sec}^{-1}
Figure 27

TIME TO EVOLVE THE FIRST 40% OF H FOR EACH ISOTHERM AGAINST H CONTENT AT TIME ZERO

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>△</td>
<td>680</td>
</tr>
<tr>
<td>□</td>
<td>735</td>
</tr>
<tr>
<td>○</td>
<td>790</td>
</tr>
</tbody>
</table>

WT of remaining H, μg
Figure 28  ISOTHERMS GIVING THE RATE OF EMISSION IN THE LOW TEMPERATURE STEPPING EXPERIMENT No. 126

Initial WT of ZrH$_{1.458}$ = 78.0mg
Figure 29  ISOTHERMS GIVING THE RATE OF EMISSION IN THE HIGH TEMPERATURE STEPPING EXPERIMENTS
Figure 30 ARRHENIUS PLOT

- High Temperature Stepping Emission Experiments
- Low Temperature Stepping Emission Exp. No. 126
MICROGRAPH No. 1

BATCH No. 044 \[ \frac{H}{Z} \approx 0.723 \] (x 500)

MICROGRAPH No. 2

BATCH No. 043 \[ \frac{H}{Z} \approx 0.975 \] (x 500)
MICROGRAPH No. 1

BATCH No. 044  \( \frac{H}{Zr} = 723 \)  (x 500)

MICROGRAPH No. 2

BATCH No. 043  \( \frac{H}{Zr} = 975 \)  (x 500)
MICROGRAPH No. 3

Batch No. 044 \[ \frac{H}{Zr} = 0.723 \] (x125)

MICROGRAPH No. 4

Batch No. 043 \[ \frac{H}{Zr} = 0.975 \] (x125)
MICROGRAPH No. 3

Batch No. 044

$\alpha$-Zr

$\beta$-Zr

$H/Z_r = 0.723$ (x125)

MICROGRAPH No. 4

Batch No. 043

$\alpha$-Zr

$\beta$-Zr

$H/Z_r = 0.975$ (x125)
MICROGRAPH No. 5

Batch No. 041  \(H/Zr = 1.225\)  (\(x125\))

ORTHOGONAL CRACK

MICROGRAPH No. 6

Batch No. 041  \(H/Zr = 1.225\)  (\(x125\))

PARALLEL CRACK
MICROGRAPH No. 5

Batch No. 041

$H/Zr = 1.225$

ORTHOGONAL CRACK

MICROGRAPH No. 6

Batch No. 041

$H/Zr = 1.225$

PARALLEL CRACK
### Table 1

Relative Partial Molal Enthalpy for the solution of Hydrogen in α-Zirconium

<table>
<thead>
<tr>
<th>Source</th>
<th>Year</th>
<th>Reference</th>
<th>Experimental range</th>
<th>ΔH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nagasaka, Yamashina</td>
<td>1976</td>
<td>(39)</td>
<td>$10^{-4}$-$10^{-2}$</td>
<td>500-800</td>
</tr>
<tr>
<td>Tada, Huang</td>
<td>1971</td>
<td>(40)</td>
<td>$10^{-3}$-760</td>
<td>400-900</td>
</tr>
<tr>
<td>Ricca, Giorgi</td>
<td>1967</td>
<td>(41)</td>
<td>$10^{-7}$-$10^{-3}$</td>
<td>450-750</td>
</tr>
<tr>
<td>Erickson</td>
<td>1966</td>
<td>(42)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hardie</td>
<td>1965</td>
<td>(43)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Someno</td>
<td>1960</td>
<td>(44)</td>
<td>$10^{-3}$-30</td>
<td>500-900</td>
</tr>
<tr>
<td>La Grange et al.</td>
<td>1959</td>
<td>(45)</td>
<td>600-800</td>
<td></td>
</tr>
<tr>
<td>Douglas</td>
<td>1958</td>
<td>(46)</td>
<td>0-900</td>
<td></td>
</tr>
<tr>
<td>Ellis, McQuillan</td>
<td>1956/7</td>
<td>(47)</td>
<td>$10^{-1}$-760</td>
<td>480-950</td>
</tr>
<tr>
<td>Gulbransen, Andrew</td>
<td>1955</td>
<td>(48)</td>
<td>$10^{-4}$-$10^{-1}$</td>
<td>425-600</td>
</tr>
</tbody>
</table>

Average of 10 values (49) - 13094±1426
### TABLE 2

Energies of the first vibrational level for Zirconium Hydride

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Year</th>
<th>Reference</th>
<th>Sample</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beg and Ross</td>
<td>1967</td>
<td>(66)</td>
<td></td>
<td>0.137 ± 0.002</td>
</tr>
<tr>
<td>Koppel</td>
<td>1966</td>
<td>(67)</td>
<td></td>
<td>0.137</td>
</tr>
<tr>
<td>Harling and Leonard</td>
<td>1965</td>
<td>(68)</td>
<td></td>
<td>0.141 ± 0.003</td>
</tr>
<tr>
<td>Janik and Kowalska</td>
<td>1965</td>
<td>(69)</td>
<td></td>
<td>0.134</td>
</tr>
<tr>
<td>Pan and Webb</td>
<td>1965</td>
<td>(70)</td>
<td>ZrH₂</td>
<td>0.137 ± 0.006</td>
</tr>
<tr>
<td>Whittemore</td>
<td>1965</td>
<td>(71)</td>
<td></td>
<td>0.14</td>
</tr>
<tr>
<td>Flotow and Osborne</td>
<td>1962</td>
<td>(72)</td>
<td>ZrH₂</td>
<td>0.146</td>
</tr>
<tr>
<td>Tomasch</td>
<td>1961</td>
<td>(73)</td>
<td>ZrH₁.58</td>
<td>0.130</td>
</tr>
<tr>
<td>Woods et al.</td>
<td>1961</td>
<td>(74)</td>
<td>ZrH₁.8</td>
<td>0.140</td>
</tr>
<tr>
<td>Whittemore et al.</td>
<td>1959</td>
<td>(75)</td>
<td>ZrH₁.5</td>
<td>0.137</td>
</tr>
<tr>
<td>Pelah et al.</td>
<td>1957</td>
<td>(76)</td>
<td>ZrH₁.5</td>
<td>0.134 ± 0.015</td>
</tr>
<tr>
<td>Andresen et al.</td>
<td>1957</td>
<td>(77)</td>
<td>ZrH₁.5</td>
<td>0.130 ± 0.005</td>
</tr>
<tr>
<td>Present work</td>
<td></td>
<td></td>
<td>ZrH₁.46</td>
<td>0.140</td>
</tr>
<tr>
<td>Number of Be pieces</td>
<td>Experimental count-rate (counts sec$^{-1}$)</td>
<td>Theoretical cold contribution (neutrons sec$^{-1}$)</td>
<td>Theoretical thermal contribution (neutrons sec$^{-1}$)</td>
<td>Total Theoretical intensity (neutrons sec$^{-1}$)</td>
</tr>
<tr>
<td>---------------------</td>
<td>------------------------------------------</td>
<td>------------------------------------------</td>
<td>------------------------------------------</td>
<td>------------------------------------------</td>
</tr>
<tr>
<td>0</td>
<td>5.152 ± 0.11</td>
<td>.3200</td>
<td>4.8320</td>
<td>5.1520</td>
</tr>
<tr>
<td>2</td>
<td>.880 ± 0.05</td>
<td>.2338</td>
<td>.0599</td>
<td>.2937</td>
</tr>
<tr>
<td>4</td>
<td>.282 ± 0.03</td>
<td>.1709</td>
<td>7.43x10$^{-4}$</td>
<td>.1716</td>
</tr>
<tr>
<td>6</td>
<td>.160 ± 0.026</td>
<td>.1249</td>
<td>9.11x10$^{-6}$</td>
<td>.1249</td>
</tr>
<tr>
<td>8</td>
<td>.100 ± 0.024</td>
<td>.0912</td>
<td>1.14x10$^{-7}$</td>
<td>.0912</td>
</tr>
</tbody>
</table>

Cross-sections 
( cold = $\sigma_{\text{cold}} = 0.5$ barns, 
E$_{\text{cold}} = 0.0617$ cm$^{-1}$ 
(see Reference §2) 
( thermal = $\sigma_{\text{th}} = 7.0$ barns, 
E$_{\text{th}} = 0.8641$ cm$^{-1}$

### TABLE 4

**Data for count-rate spectrum (Fig. 13)**

<table>
<thead>
<tr>
<th>Sample Batch No.</th>
<th>H/Zr (g)</th>
<th>Sample wt. (g)</th>
<th>Total wt. of H (g)</th>
<th>Total wt. of H Sample wt.</th>
<th>Count-rate of the peak (counts sec⁻¹)</th>
<th>Count-rate E=0.175eV (counts sec⁻¹)</th>
<th>Count-rate E=0.114eV (counts sec⁻¹)</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>STD</td>
<td>1.458</td>
<td>3.8451</td>
<td>0.0610</td>
<td>0.0159</td>
<td>0.423</td>
<td>0.342</td>
<td>0.361</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>1.458</td>
<td>6.8753</td>
<td>0.1093</td>
<td>0.0159</td>
<td>0.482</td>
<td></td>
<td>2.87</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>1.458</td>
<td>9.1735</td>
<td>0.1456</td>
<td>0.0159</td>
<td>0.542</td>
<td>0.375</td>
<td>0.384</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>1.458</td>
<td>9.3806</td>
<td>0.1490</td>
<td>0.0159</td>
<td>0.527</td>
<td>0.362</td>
<td>0.370</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>1.458</td>
<td>15.4587</td>
<td>0.2455</td>
<td>0.0159</td>
<td>0.643</td>
<td>0.389</td>
<td>0.388</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>1.458</td>
<td>21.6330</td>
<td>0.3435</td>
<td>0.0159</td>
<td>0.742</td>
<td>0.438</td>
<td>0.434</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>1.458</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.59</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>1.458</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8.50</td>
</tr>
<tr>
<td>9</td>
<td>044</td>
<td>0.723</td>
<td>4.8659</td>
<td>0.0386</td>
<td>0.0079</td>
<td>0.349</td>
<td>0.296</td>
<td>0.317</td>
</tr>
<tr>
<td>10</td>
<td>044</td>
<td>0.723</td>
<td>5.1511</td>
<td>0.0408</td>
<td>0.0079</td>
<td>0.346</td>
<td>0.295</td>
<td>0.316</td>
</tr>
<tr>
<td>11</td>
<td>043</td>
<td>0.975</td>
<td>5.1084</td>
<td>0.0545</td>
<td>0.0107</td>
<td>0.363</td>
<td>0.307</td>
<td>0.323</td>
</tr>
<tr>
<td>12</td>
<td>041</td>
<td>1.225</td>
<td>6.0473</td>
<td>0.0808</td>
<td>0.0134</td>
<td>0.417</td>
<td>0.329</td>
<td>0.341</td>
</tr>
<tr>
<td>13</td>
<td>039</td>
<td>1.921</td>
<td>5.8647</td>
<td>0.1219</td>
<td>0.0208</td>
<td>0.477</td>
<td>0.341</td>
<td>0.363</td>
</tr>
<tr>
<td>14</td>
<td>042</td>
<td>1.956</td>
<td>5.7726</td>
<td>0.1221</td>
<td>0.0212</td>
<td>0.467</td>
<td>0.334</td>
<td>0.356</td>
</tr>
</tbody>
</table>
TABLE 5

Relative weight loss of H with temperature (Fig. 15)

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Total wt loss of H (%)</th>
<th>Relative weight loss of H (%) *</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>572-625 °C</td>
<td>625-680 °C</td>
</tr>
<tr>
<td>127</td>
<td>53.5</td>
<td>2.5</td>
</tr>
<tr>
<td>126</td>
<td>62.5</td>
<td>3.7</td>
</tr>
<tr>
<td>125†</td>
<td>72.1</td>
<td>-</td>
</tr>
<tr>
<td>157</td>
<td>84.5</td>
<td>6.6</td>
</tr>
<tr>
<td>110</td>
<td>99.0</td>
<td>5.8</td>
</tr>
</tbody>
</table>

* Relative weight loss of H = \( \frac{\text{wt loss of H at a given temperature}}{\text{initial wt of H at that temperature}} \)

† High temperature stepping emission experiment
### TABLE 6

**Fraction of hydrogen absorbed with pressure (Fig. 17).**

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Fraction of H absorbed per second x 10^6 *</th>
<th>Initial pressure $P_0$ (mmHg)</th>
<th>$\sqrt[10]{P_0}$ (mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>412</td>
<td>4.33</td>
<td>668</td>
<td>25.85</td>
</tr>
<tr>
<td>432</td>
<td>3.75</td>
<td>594</td>
<td>24.4</td>
</tr>
<tr>
<td>442</td>
<td>2.00</td>
<td>162</td>
<td>12.7</td>
</tr>
</tbody>
</table>

*Values taken from Figure 16.*
### TABLE 7

Data for homogeneous standard and non-standard experiments (Figs. 18, 21, 23)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Observed overall count of the peak (counts sec(^{-1}))</th>
<th>Corrected overall count-rate of the peak E=0.175eV</th>
<th>Observed overall count of the peak E=0.114eV</th>
<th>Corrected overall count-rate of the peak E=0.114eV</th>
<th>Area Parameter Total wt. of H (counts sec(^{-1}) g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10145</td>
<td>0.423</td>
<td>4109</td>
<td>4332</td>
<td>0.0710±0.0057</td>
</tr>
<tr>
<td>2</td>
<td>11565</td>
<td>0.482</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>11951</td>
<td>0.498</td>
<td>13004</td>
<td>0.542</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>11624</td>
<td>0.484</td>
<td>12649</td>
<td>0.527</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>15443</td>
<td>0.643</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>17800</td>
<td>0.742</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>15950</td>
<td>0.427</td>
<td>13921</td>
<td>0.517</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>16243</td>
<td>0.481</td>
<td>13269</td>
<td>0.512</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>16536</td>
<td>0.498</td>
<td>13812</td>
<td>0.538</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>16824</td>
<td>0.483</td>
<td>14270</td>
<td>0.547</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>17369</td>
<td>0.643</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>17801</td>
<td>0.742</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>18199</td>
<td>0.438</td>
<td>15522</td>
<td>0.477</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>19531</td>
<td>0.429</td>
<td>16111</td>
<td>0.467</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 7

Notes:-

* Energy of the peak = 0.140 eV. Counting time = 24000 seconds

** The overall counts obtained during lower reactor power were normalized when divided by the ratio 0.919

† Counting time = 12000 seconds
## TABLE 8

Data for non-homogeneous standard experiments (Fig. 18)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>ZrH$_{1.458}$ H wt (g)</th>
<th>Pure Zr wt (g)</th>
<th>Pure Zr wt</th>
<th>Overall count observed</th>
<th>Peak (E = 0.140 eV)</th>
<th>Overall observed count-rate Peak (counts sec$^{-1}$)</th>
<th>Overall count corrected Peak</th>
<th>Overall corrected count-rate Peak (counts sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>3.7519</td>
<td>0.0597</td>
<td>5.1908</td>
<td>1.38</td>
<td>10563</td>
<td>0.440</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>14.3039</td>
<td>0.2271</td>
<td>7.0447</td>
<td>0.49</td>
<td>13307</td>
<td>0.554</td>
<td>14480</td>
<td>0.603</td>
</tr>
</tbody>
</table>


### TABLE 9

Data of neutron diffraction response in non-standard samples (Fig. 20)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Batch No.</th>
<th>H/Zr</th>
<th>Observed count-rate at Peak* (Expected count-rate at Peak)</th>
<th>Observed Area Parameter† (Expected Area Parameter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>044</td>
<td>0.723</td>
<td>$\frac{0.350}{0.415} = 0.843 \text{ (15.7%)}$</td>
<td>$\frac{0.967}{1.198} = 0.807 \text{ (19.3%)}$</td>
</tr>
<tr>
<td>11</td>
<td>043</td>
<td>0.975</td>
<td>$\frac{0.371}{0.430} = 0.863 \text{ (13.7%)}$</td>
<td>$\frac{0.973}{1.184} = 0.822 \text{ (17.8%)}$</td>
</tr>
<tr>
<td>12</td>
<td>041</td>
<td>1.225</td>
<td>$\frac{0.410}{0.459} = 0.893 \text{ (10.7%)}$</td>
<td>$\frac{0.985}{1.160} = 0.849 \text{ (15.1%)}$</td>
</tr>
<tr>
<td>13</td>
<td>039</td>
<td>1.921</td>
<td>$\frac{0.475}{0.503} = 0.944 \text{ (5.6%)}$</td>
<td>$\frac{1.008}{1.125} = 0.896 \text{ (10.4%)}$</td>
</tr>
<tr>
<td>14</td>
<td>042</td>
<td>1.956</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* These data are taken from Figure 18

† These data are taken from Figure 21

Note: The figures in brackets represent the percentage of unbound hydrogen.
**TABLE 10**

Bound hydrogen density in standard and non-standard samples (Fig. 22)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Batch No.</th>
<th>H/Zr</th>
<th>Total density of H (atoms cm(^{-2}) x 10(^{-21}))</th>
<th>Density of bound H (atoms cm(^{-2}) x 10(^{-21}))</th>
<th>Experimental Area Parameter (counts sec(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>STD</td>
<td>1.458</td>
<td>4.554</td>
<td>4.554</td>
<td>0.0710 ± 0.0057</td>
</tr>
<tr>
<td>3</td>
<td>STD</td>
<td>1.458</td>
<td>10.866</td>
<td>10.866</td>
<td>0.1624 ± 0.0062</td>
</tr>
<tr>
<td>4</td>
<td>STD</td>
<td>1.458</td>
<td>11.111</td>
<td>11.111</td>
<td>0.1613 ± 0.0061</td>
</tr>
<tr>
<td>5</td>
<td>STD</td>
<td>1.458</td>
<td>18.310</td>
<td>18.310</td>
<td>0.2551 ± 0.0066</td>
</tr>
<tr>
<td>6</td>
<td>STD</td>
<td>1.458</td>
<td>25.623</td>
<td>25.623</td>
<td>0.3058 ± 0.0070</td>
</tr>
<tr>
<td>9</td>
<td>044</td>
<td>0.723</td>
<td>2.881</td>
<td>2.334</td>
<td>0.0430 ± 0.0052</td>
</tr>
<tr>
<td>10</td>
<td>044</td>
<td>0.723</td>
<td>3.050</td>
<td>2.470</td>
<td>0.0402 ± 0.0052</td>
</tr>
<tr>
<td>11</td>
<td>043</td>
<td>0.975</td>
<td>4.068</td>
<td>3.376</td>
<td>0.0483 ± 0.0053</td>
</tr>
<tr>
<td>12</td>
<td>041</td>
<td>1.225</td>
<td>6.033</td>
<td>5.188</td>
<td>0.0847 ± 0.0056</td>
</tr>
<tr>
<td>13</td>
<td>039</td>
<td>1.921</td>
<td>9.107</td>
<td>8.378</td>
<td>0.1252 ± 0.0059</td>
</tr>
<tr>
<td>14</td>
<td>042</td>
<td>1.956</td>
<td>9.123</td>
<td>8.393</td>
<td>0.1221 ± 0.0058</td>
</tr>
</tbody>
</table>
**TABLE 11**

Data from Micrographic analysis of non-standard samples (Figs. 24 and 25)

<table>
<thead>
<tr>
<th>Micrograph No.</th>
<th>Batch No.</th>
<th>H/Zr</th>
<th>F_β = depth of β-Zr (μ)</th>
<th>Fraction of unbound H, F_u*</th>
<th>F_α = depth of α-Zr (μ)</th>
<th>Overall thickness (μ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>044</td>
<td>0.723</td>
<td>320/1206 = 0.265</td>
<td>0.19</td>
<td>886/1206 = 0.735</td>
<td>1206/1206 = 1</td>
</tr>
<tr>
<td>4</td>
<td>043</td>
<td>0.975</td>
<td>603/1206 = 0.500</td>
<td>0.18</td>
<td>603/1206 = 0.500</td>
<td>1206/1206 = 1</td>
</tr>
<tr>
<td>6</td>
<td>041</td>
<td>1.225</td>
<td>856/1206 = 0.710</td>
<td>0.15</td>
<td>350/1206 = 0.290</td>
<td>1206/1206 = 1</td>
</tr>
<tr>
<td>-</td>
<td>039</td>
<td>1.921</td>
<td>1206/1206 = 1</td>
<td>0.10</td>
<td>0/1206 = 0</td>
<td>1206/1206 = 1</td>
</tr>
</tbody>
</table>

* The ratio of observed area over expected area (see Table 9).
**TABLE 12**

Data of atomic radii and sizes of interstices in Zirconium (values in nm)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Zr radius, R</th>
<th>Octahedral interstice, $r_6^*$</th>
<th>Tetrahedral interstice, $r_4^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-Zr (h.c.p.)</td>
<td>0.160</td>
<td>0.066</td>
<td>0.036</td>
</tr>
<tr>
<td>$\beta$-Zr (b.c.c.)</td>
<td>0.157</td>
<td>0.024</td>
<td>0.046</td>
</tr>
</tbody>
</table>

$^*$ Radii of the largest sphere that can be accommodated in the octahedral interstices without distorting the zirconium lattice structure.

$^+$ Radii of the largest sphere that can be accommodated in the tetrahedral interstices without distorting the zirconium lattice structure.

$r_n^*, n = \text{the number of spheres surrounding an interstice.}$
APPENDIX 1

ANALYSIS OF ZIRCONIUM FOIL SPECIMENS

(values in ppm by weight)

<table>
<thead>
<tr>
<th>Element</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>700 - 720</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>18 - 24</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>3 - 4</td>
</tr>
<tr>
<td>Copper</td>
<td>1 - 2</td>
</tr>
<tr>
<td>Indium</td>
<td>possible</td>
</tr>
<tr>
<td>Iron</td>
<td>5</td>
</tr>
<tr>
<td>Magnesium</td>
<td>2 - 5</td>
</tr>
<tr>
<td>Silicon</td>
<td>5</td>
</tr>
<tr>
<td>Silver</td>
<td>1</td>
</tr>
<tr>
<td>Zinc</td>
<td>50</td>
</tr>
</tbody>
</table>
The central linear portion of the graph is found as follows: readings are examined until the two consecutive readings with the greatest difference are found. These two readings are always assumed to be part of the line segment. Readings either side of these two are examined and added to the set in order of the magnitude of the differences from the set. The process continues until readings are found, on both sides, which differ by more than the subtraction of the average difference from the maximum difference. This may be illustrated as thus:

<table>
<thead>
<tr>
<th>readings</th>
<th>differences</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_0$</td>
<td>$d_1$</td>
</tr>
<tr>
<td>$x_1$</td>
<td>$d_2$</td>
</tr>
<tr>
<td>$\cdots$</td>
<td>$\cdots$</td>
</tr>
<tr>
<td>$x_i$</td>
<td>$d_{i-1}$</td>
</tr>
<tr>
<td>$\cdots$</td>
<td>$\cdots$</td>
</tr>
<tr>
<td>$x_k$</td>
<td>$d_k$</td>
</tr>
<tr>
<td>$x_{k+1}$</td>
<td>$d_{j-1}$</td>
</tr>
<tr>
<td>$\cdots$</td>
<td>$\cdots$</td>
</tr>
<tr>
<td>$x_j$</td>
<td>$d_j$</td>
</tr>
<tr>
<td>$\cdots$</td>
<td>$\cdots$</td>
</tr>
<tr>
<td>$x_n$</td>
<td>$d_{n-1}$</td>
</tr>
</tbody>
</table>
\[ d_k = \text{the maximum difference} \]
\[ a = \text{average \{ } d_i \dot{\ldots} \dot{\ldots} d_k \dot{\ldots} \dot{\ldots} d_{j-1} \text{\}} \]

The set is delimited when

\[ (a - d_{i-1}) > (d_k - a) \]

and

\[ (a - d_j) > (d_k - a) \]
0 'BEGIN'
1 'INTEGER'J,N,NO;
2 J:=O;
3 AGAIN: J:=J+1;
4 'INTEGER'(O,NO);
5 IF NO=O THEN 'GOTO'FIN;
6 'INTEGER'(O+N);
7 N:=N-1;
8 'BEGIN'
9 'INTEGER'A,B,I,X;
10 'REAL'ARRAY'D,DD,S,SD(/0..N/);
11 'REAL'DMAX,T,G,GD;
12 'REAL'PROCEDURE AV(C,E,F);
13 'REAL'ARRAY'C; 'INTEGER'E,F;
14 'BEGIN'
15 X:=O;
16 'FOR'I:=E'STEP'1'UNTIL'F'DO'
17 X:=X+C(/I/);
18 AV:=X/(F-E+1);
19 'END';
20 'PROCEDURE'SEARCH(C,P,Q);
21 'REAL'ARRAY'C;'INTEGER'P,O;
22 'BEGIN'
23 DMAX:=P;
24 'FOR'I:=P+1'STEP'1'UNTIL'O'DO'
25 DMAX:=I;
26 'END';
27 'PROCEDURE'SEARCH(C,P,Q);
28 'REAL'ARRAY'C; 'INTEGER'P,Q';
29 T:=AV(C,A,B-1);  
30 T:=T-0.1;
31 T:=T-0.1;
32 T:=T-0.1;
33 T:=T-0.1;
34 T:=T-0.1;
35 T:=T-0.1;
36 T:=T-0.1;
37 'END';
38 'ELSE''GOTO'K;
39 'END';
40 'ELSE''BEGIN'
41 'BEGIN'
42 A:=A-1''GOTO'L;
43 'END';
44 'ELSE''GOTO'K;
45 'END';
46 'ELSE''BEGIN'
47 'BEGIN'
48 'ELSE''BEGIN'
49 'BEGIN'
50 T:=AV(C,A+1+B);
51 T:=T-0.1;
52 T:=T-0.1;
53 'END';
54 'END';
55 'ELSE''GOTO'K;
56 'END';
57 'ELSE''GOTO'K;
58 'END';
59 'END';
60 'END';
61 'END';
62 'END';
63 'FOR'I:=O'STEP'1'UNTIL'N'DO'
64 INREAL(0'O(I/));
65 'FOR'I:=O'STEP'1'UNTIL'N-1'DO'
\[
\begin{align*}
S(I) &= \frac{(D(I-1) + 2N(I) + D(I+1))}{4}; \\
\text{FOR} I &= 1 \text{STEP} 1 \text{UNTIL} N \text{DO} \\
DD(I) &= D(I-1) - D(I); \\
\text{FOR} I &= 2 \text{STEP} 1 \text{UNTIL} N-1 \text{DO} \\
SD(I) &= S(I-1) - S(I); \\
\text{OUTSTRING}(1, \text{PROCESS NO} \}\); \\
\text{OUTINTEGER}(1, j); \\
\text{LINE}(1, 1); \\
\text{OUTSTRING}(1, \text{SAMPLE NO} \}); \\
\text{OUTINTEGER}(1, n0); \\
\text{LINE}(1, 1); \\
\text{OUTSTRING}(1, \text{NO OF VALUES} \}); \\
\text{OUTINTEGER}(1, 4); \\
\text{LINE}(1, 1); \\
\text{OUTSTRING}(1, \text{VALUES DIFFERENCES} \}); \\
\text{OUTSTRING}(1, \text{SMOOTHED VALUES DIFFERENCES} \}); \\
\text{FOR} I &= 0 \text{STEP} 1 \text{UNTIL} N \text{DO} \ \begin{align*}
\text{BEGIN} & \\
\text{FIX}(1, 3, 5, D(I)); \\
\text{BLANK}(1, 25); \\
\text{IF} I > 0 \text{AND} I < N \text{THEN} \begin{align*}
\text{FIX}(1, 3, 5, D(I+1)); \\
\text{BLANK}(1, 25); \\
\text{IF} I > 0 \text{AND} I < N-1 \text{THEN} \begin{align*}
\text{SEARCH}(DD, 2, N-1); \\
\text{OUTSTRING}(1, \text{A=} \}); \\
\text{OUTINTEGER}(1, A); \\
\text{OUTSTRING}(1, \text{B=} \}); \\
\text{OUTINTEGER}(1, B); \\
\text{LINE}(1, 1); \\
\text{BLANK}(1, 38); \\
G &= \frac{(D(B) - D(A))}{(B-A)}; \\
\text{SEARCH}(SD, 3, N-2); \\
\text{OUTSTRING}(1, \text{A=} \}); \\
\text{OUTINTEGER}(1, A); \\
\text{OUTSTRING}(1, \text{B=} \}); \\
\text{OUTINTEGER}(1, B); \\
\text{LINE}(1, 1); \\
\text{GD} &= \frac{(S(B) - S(A))}{(B-A)}; \\
\text{OUTSTRING}(1, \text{GRAD=} \}); \\
\text{FIX}(1, 3, 5, GD); \\
\text{BLANK}(1, 20); \\
\text{OUTSTRING}(1, \text{GRAD=} \}); \\
\text{FIX}(1, 3, 5, GD); \\
\text{LINE}(1, 10); \\
\text{END} \}; \\
\text{GOTO} \text{AGAIN}; \\
\text{FIN} \}; \text{END} \\
\end{align*}
\end{align*}
\end{align*}
\]
RELATION OF HEAT OF SOLUTION TO ACTIVATION ENERGIES

The correspondence between the difference of activation energies and the heat of solution of hydrogen in α-zirconium, can be shown from thermodynamic considerations.

The absorption-desorption reactions and the reaction constants are defined as follows:

\[ \text{Zr} + \frac{1}{2} \text{H}_2 \xrightarrow{\text{k}_1} \text{ZrH}_{1.5} \]

\[ \text{k}_1 = k_1' \ e^{-E_1/RT} \]

\[ \text{k}_2 = k_2' \ e^{-E_2/RT} \]

The rate of absorption is equal to \( k_1 [\text{Zr}] [\text{H}_2]^\frac{1}{2} \)

The rate of desorption is equal to \( k_2 [\text{ZrH}_{1.5}] \)

At equilibrium, the rates of the two reactions are equal, thus

\[ k_1 [\text{Zr}] [\text{H}_2]^\frac{1}{2} = k_2 [\text{ZrH}_{1.5}] \]

Consequently, the equilibrium constant, K, is

\[ K = \frac{[\text{ZrH}_{1.5}]}{[\text{Zr}] [\text{H}_2]^\frac{1}{2}} = \frac{k_1}{k_2} = \frac{k_1' \ e^{-E_1/RT}}{k_2' \ e^{-E_2/RT}} = \frac{k_1'}{k_2'} \ e^{-(E_1-E_2)/RT} \]
\[ \frac{k_1'}{k_2'} = e^p \quad \text{then} \quad K = e^{\left[ p - \frac{E_1-E_2}{RT} \right]} \quad [11] \]

On the other hand, the free energy change, as a function of \( K \), is also given by

\[ \Delta F_o = -RT \ln K \quad \text{which implies} \quad K = e^{-\Delta F_o/RT} \quad [12] \]

where \( \Delta F_o \) is the difference of free energies of standard states, \( \Delta F_o \), as a function of the difference in entropy, can also be expressed

\[ \Delta F_o = \Delta H_o - T \Delta S \quad [13] \]

From Eqs. [11] and [12]

\[ -\frac{\Delta F_o}{RT} = p - \frac{(E_1-E_2)}{RT} \quad \text{implying} \quad -\Delta F_o = RTp - (E_1-E_2) \]

Then, Eq. [13] can be rewritten as follows

\[ -\Delta H_o + T \Delta S = RTp - (E_1-E_2) \quad \text{for all values of} \ T \]

Finally, by equating coefficients of \( T \)

\[ p = \frac{\Delta S}{R} \quad \text{and} \quad \Delta H_o = E_1-E_2 \]

Hence, the heat of solution of hydrogen is found to be equal to the difference of the activation energies.
REFERENCES

(The last figures, in brackets, refer to the addendum)

ALSTON, W.C.H.,


ALSTON, W.C.H. and JONES, T.C.,


ANDRESEN, A., McREYNOLDS, A.W., NELKIN, M.S., ROSENBLUTH, M.N. and
WHITTEMORE, W.L.,


BAILEY, J.E.,


BAIN, A.S., ALLISON, G.M., HOWE, L.M. and RIDAL, A.,

Clalk River Nuclear Laboratories, Clalk River, Ontario,


BARRACLOUGH, K.G. and BEEVERS, C.J.,

J. Nucl. Mat. 34 (1970) 125. (50, 52)

BEG, M.M. and ROSS, D.K.,

Proc. Symp. Neutron Inelastic Scattering, IAEA, Vienna,

vol. 2, 1968, p.299. (66)
BELLE, J., CLELAND, B.B. and MALLET, M.W.,
J. Electrochem. Soc. 101 (1954) 211. (13, 16, 19, 22, 26, 35)

BRADBROOK, J.S., LORIMER, G.W. and RIDLEY, N.,
J. Nucl. Mat. 42 (1972) 142. (107)

CARPENTER, G.J.C.,
J. Nucl. Mat. 48 (1973) 264. (107)

COX, B.,
J. Nucl. Mat. 28 (1968) 1. (8)

DE BOER, J.H. and FAST, J.D.,

DOUGLAS, T.B.,
J. Am. Chem. Soc. 80 (1958) 5040. (46)

ELLS, C.E.,
J. Nucl. Mat. 28 (1968) 129. (9, 97)

ELLS, C.E. and MCQUILLAN, A.D.,
J. Inst. Met. 85 (1956-7) 89. (47)

ERICKSON, W.H.,

FAST, J.D.,
Interaction of Metals and Gases, vol. 2: Kinetics and Mechanisms,
FERMI, E.,
Ric. Sci. 7 (1936) 13. (29)

FERMI, E.,
Nuclear Physics - Notes on Quantum Mechanics, University Chicago Press, Chicago, 1950. (64)

FLOTOW, H.E. and OSBORNE, D.W.,

GIBB, T.R.P., Jr.,
Progr. Inorg. Chem. 3(1962) 315. (6, 36, 37)

GOLDSCHMIDT, H.J.,

GULBRANSEN, E.A. and ANDREW, K.F.,
Trans. Met. Soc. AIME 185 (1949) 515. (21)

GULBRANSEN, E.A. and ANDREW, K.F.,

GULBRANSEN, E.A. and ANDREW, K.F.,

GULBRANSEN, E.A. and ANDREW, K.F.,
J. Met. 7 (1955) 136. (27, 48, 112)
HÄGG, G.,
Z. Physik Chem. (8) 11 (1931) 433. (58)

HÄGG, G.,
Z. Physik Chem. (8) 12 (1931) 33. (58)

HALL, M.N.A., MARTIN, S.L.H. and REES, A.L.C.,
Trans. Faraday Soc. 41 (1945) 306. (11, 60)

HARDIE, D.,
J. Nucl. Mat. 17 (1965) 88. (43)

HARDIE, D.,
J. Nucl. Mat. 45 (1972) 265. (92)

HARLING, O.K. and LEONARD, B.R., Jr.,
Symp. Inelastic Scattering of Neutrons by Condensed Systems,
Brookhaven National Laboratory, Upton, N.Y., BNL 940 (C-45), 1966,
p. 96. (68)

HAYES, E.T., ROBERSON, A.H. and ROBERTSON, R.H.,
J. Electrochem. Soc. 97 (1950) 316. (12)

HUGHES, D.J. and SCHWARTZ, R.B.,
Neutron Cross Sections, Brookhaven National Laboratory, Upton, N.Y.,
BNL 325, 2nd ed., 1958. (82)

JANIK, J.A. and KOWALSKA, A.,
in Thermal Neutron Scattering, ed. by ECELSTAFF, P.A., Academic
KASS, S.,
Proc. Meeting on Zirconium-Technology and Economics, Atomic

KAUFMAN, P.D., DANIELSON, P. and BAROCH, E.F.,
Symp. Zirconium in Nuclear Applications, ASTM, STP-551, 1974,
p. 52. (91)

KEARNS, J.J.,
J. Nucl. Mat. 43 (1972) 330. (84)

KOPPEL, J.U.,
in Reactor Physics in the Resonance and Thermal Regions, vol. 1:
Neutron Thermalization, ed. by GOODJOHN, A.J. and POMRANING, G.C.,
The M.I.T. Press, Massachusetts, Mass., 1966, p. 27. (67)

LA GRANGE, L.D., DYKSTRA, L.J., DIXON, J.M. and MERTEN, U.,
J. Phys. Chem. 63 (1959) 2035. (45)

LAVES, F.,

LIBOWITZ, G.G.,
J. Nucl. Mat. 2 (1960) 1. (5)

LIBOWITZ, G.G.,
J. Nucl. Mat. 5 (1962) 228. (14)

LIBOWITZ, G.G.,
LIBOWITZ, G.G.,
The solid-state chemistry of binary metal hydrides, Benjamin Inc., New York, 1965, p. 66. (51, 53)

MCREYNOLDS, A.W., NELKIN, M.S., ROSENBLUTH, M.N. and WHITTEMORE, W.L.,
Proc. 2nd UN Int. Conf. PUAE, U.N. Geneve, 16 (1958) 297. (30, 102)

MALLETT, M.W. and ALBRECHT, W.M.,
J. Electrochem. Soc. 104 (1957) 142. (28, 38, 49)

MARINO, G.P.,
Mater. Sci. Eng. 7 (1971) 335. (24, 63)

MARTIN, S.L.H. and REES, A.L.G.,
Trans. Faraday Soc. 50 (1954) 343. (23)

NAGASAKA, M. and YAMASHINA, T.,
J. Less Common Met. 45 (1976) 53. (39)

NATH, B., LORIMER, G.W. and RIDLEY, N.,
J. Nucl. Mat. 49 (1973-4) 262. (107)

PAN, S.S. and WEBB, F.J.,
Nucl. Sci. Eng. 23 (1965) 194. (70, 86, 105)

PELAH, I., EISENHAUER, C.M., HUGHES, D.J. and PALEVSKY, H.,
Phys. Rev. 108 (1957) 1091. (31, 76)

REES, A.L.G.,
RENTSCHLER, H.C. and HENRY, D.E.,
Trans. Electrochem. Soc. 87 (1945) 289. (60)

RICCA, F. and GIORGI, T.A.,
J. Phys. Chem. 71 (1967) 3627. (41)

RIDLEY, N., CAULKIN, K.C. and LORIMER, G.W.,
Congr. Int. L'Hydrogène dans les Metaux, Ed. Science et Industrie,
1972, p. 484. (107)

SALLER, H. and DICKENSON, R.F.,
Metallographic Identification of Non-metallic Inclusions in
Zirconium, Battelle Memorial Institute, Columbus, Ohio, BMI-74,
July 1951. (95)

SAWATZKY, A.,
J. Nucl. Mat. 2 (1960) 62. (38)

SCHWARTZ, C.M. and MALLET, M.W.,

SHALTIEL, D., JACOB, I. and DAVIDOV, D.,
J. Less Common Met. 53 (1977) 117. (20)

SIEVERTS, A. and GOTTA, A.,
Z. anorg. allgem. Chem. 172 (1928) 1. (57)

SIEVERTS, A. and GOTTA, A.,
Z. anorg. allgem. Chem. 187 (1930) 155. (53)
SIEVERTS, A. and ROELL, E.,
Z. anorg. allgem. Chem. 153 (1926) 289. (15, 56)

SMITH, D.P.,
(4, 18, 99)

SOMENO, M.,
Nippon Kinzoku Gakkaishi 24 (1960) 249. (44)

TADA, M. and HUANG, Y.C.,
Titanium - Zirconium 19 (1971) 260. (40)

TOMASCH, W.J.,

UBBELOHDE, A.R.,

UNE, K.,

VOGEL, R. and TONN, W.,
Z. anorg. allgem. Chem. 202 (1931) 292. (108)

WESTLAKE, D.G.,
J. Nucl. Mat. 7 (1962) 346. (47)
WESTLAKE, D.G.,

J. Nucl. Mat. 16 (1965) 215. (93)

WHITTEMORE, W.L.,


WHITTEMORE, W.L.,


WHITTEMORE, W.L. and MCREYNOLDS, A.W.,

Phys. Rev. 113 (1959) 806. (75)

WIBERG, E. and ANBERGER, E.,


WOODS, A.D.B., BROCKHOUSE, B.N., SAKAMOTO, M. and SINCLAIR, R.N.,