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ORTHOHYDROGEN, PARAHYDROGEN AND HEAVY HYDROGEN

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ORTHOHYDROGEN, PARAHYDROGEN AND HEAVY HYDROGEN

by

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CONTENTS

Preface *page* xiii

Part I

ORTHOHYDROGEN AND PARAHYDROGEN

Chap. I. The Discovery of Orthohydrogen and Parahydrogen 1

II. Theory 3

1. Theoretical foundations 3

2. The calculation of the equilibrium concentration, specific heat and rotational energy of orthohydrogen and parahydrogen 13

III. The Properties of the Hydrogen Modifications 20

1. The analysis of ortho-parahydrogen mixtures 20

2. Preparation of parahydrogen 28

3. Specific heat 33

4. Heat of conversion 37

5. Vapour pressure and melting point 39

6. Spectra 43

7. Chemical properties 47

8. Cross-sectional area, viscosity and crystal structure 48

9. Magnetic properties 49

10. Entropy, free energy and chemical constant 51

(*a*) Entropy 51

(*b*) Free energy 55

(*c*) Chemical constant 56

Chap. IV. THE KINETICS OF THE ORTHO-PARAHYDROGEN CONVERSION *page* 60

1. The homogeneous conversion 60
   (*a*) The thermal reaction 60
   (*b*) The interaction of parahydrogen with hydrogen atoms 66
   (*c*) Theoretical treatment of the reaction $H + p\text{-}H_2 \rightleftarrows o\text{-}H_2 + H$ 70
   (*d*) The conversion in the liquid and the solid phase 76
   (*e*) Homogeneous catalysis by paramagnetic substances 79
2. The heterogeneous conversion 89
   (*a*) Low temperature mechanism 92
   (*b*) High temperature mechanism 96

V. APPLICATIONS 102

1. Determination of the H atom concentration in chemical reactions 103
2. Energy exchange between hydrogen and metals 105
3. Self-diffusion of hydrogen 108

VI. ORTHO AND PARA SYSTEMS IN OTHER MOLECULES 110

Part II

HEAVY HYDROGEN

Chap. I. The Discovery of Heavy Hydrogen *page* 115

II. The Preparation and Determination of Heavy Hydrogen 118

1. Nomenclature 118

2. The preparation of heavy hydrogen 118

(*a*) Fractional distillation of liquid hydrogen 118
(*b*) Diffusion methods 119
(*c*) Electrolysis of water 123
(*d*) Other methods 131

3. The estimation of heavy hydrogen 131

(*a*) Spectroscopic method 132
(*b*) Mass spectroscopic method 133
(*c*) Thermoconductivity method 134
(*d*) Specific-gravity method 136
(*e*) Refractometric method 138
(*f*) Other methods 139

4. Abundance of heavy hydrogen in natural sources 139

III. The Properties of Heavy Hydrogen 142

1. Mass, spin and magnetic moment 142

2. Transmutations produced by deutons 144

3. Kinetic properties 147

4. Spectrum of D, HD, D_2 and other D-compounds 148

(*a*) The atomic spectrum 148
(*b*) Molecular spectra of HD and D_2 151
(*c*) Spectra of other D-compounds 155

5. Ortho-para equilibrium 157

6. Rotational energy and specific heat 161

7. Entropy and free energy 165

Chap. III. THE PROPERTIES OF HEAVY HYDROGEN (*contd.*)

8. The chemical constants and the dissociation of heavy hydrogen *page* 167
9. Vapour pressure 168
10. Properties of heavy water 171
11. Properties of some D-compounds 173

IV. THE CHEMISTRY OF HEAVY HYDROGEN 176

1. Equilibria 176
   (*a*) The equilibrium $H_2+D_2 \rightleftharpoons 2HD$ 176
   (*b*) The equilibria $H_2+DCl \rightleftharpoons HD+HCl$ and $H_2+DI \rightleftharpoons HD+HI$ 179
   (*c*) The equilibria $H_2O+HD \rightleftharpoons HDO+H_2$ and $H_2O+D_2O \rightleftharpoons 2HDO$ 180
2. Kinetics 186
   (*a*) The interaction of light and heavy hydrogen 187
   (*b*) The hydrogen-water reaction 189
   (*c*) The hydrogen-chlorine and the hydrogen-bromine reactions 191
   (*d*) The hydrogen-ethylene reaction 193
   (*e*) The hydrogen-oxygen and the hydrogen-nitrous oxide reactions 195
   (*f*) The dissolution of metals in water or acids 197
   (*g*) Exchange reactions with heavy water 199
   (*h*) Some reactions in aqueous solution 201
   (*i*) Biological experiments with heavy water 202

Bibliography 205

ILLUSTRATIONS

Fig. 1. The Rotational Specific Heat of Hydrogen . *page* 19
2. Thermal Conductivity Cell of Bonhoeffer and Harteck 22
3. Thermal Conductivity Cell 22
4. Arrangement for the Analysis of Ortho-Para-hydrogen Mixtures 23
5. Calibration Curve for the Determination of the Ortho-Parahydrogen Concentration . 24
6. Arrangement of Geib and Harteck for Concentration Measurements at low Pressures . 25
7. The Principle of Farkas' Method for very low Pressures 26
8. The Arrangement for Concentration Measurements at very low Pressures . . . 27
9. Apparatus for the Production of Pure Para-hydrogen 30
10. The Preparation of 42–48 per cent Para-hydrogen 31
11. Demonstration of the Ortho-Parahydrogen Interconversion 32
12. The Rotational Specific Heat of Hydrogen . 34
13. The Specific Heat of Liquid and Solid Hydrogen 36
14. The Specific Heat of Solid Hydrogen at very low Temperatures 36
15. Levels of the Lyman bands 43
16. Levels of the Werner bands 45
17. The Spectrum of Parahydrogen 46
18. The Homogeneous Re-conversion of Para-hydrogen 62
19. The Re-conversion of p-H_2 at 650° C. . . . 63
20. The Energy Mountain of the Reaction $H+H_2 \rightleftharpoons H_2+H$ 72

Fig. 21. Plastic Model of the Energy Mountain of the Reaction $H + H_2$ . . . . . *page* 73
22. The Energy Mountain of the Reaction $H + H_2$ 74
23. The Re-conversion of Parahydrogen Catalyzed by O_2 80
24. The Re-conversion of Parahydrogen Catalyzed by O_2 81
25. The Re-conversion of Parahydrogen Catalyzed by O_2 81
26. The Ortho-Parahydrogen Conversion on Charcoal 90
27. Experimental Arrangement for the Investigation of the Catalytic Ortho-Parahydrogen Conversion according to the Stationary Method 92
28. The Activity of Different Specimens of Charcoal 93
29. The Heat Consumption of Active and Poisoned Wires 106
30. The Accommodation Coefficient of Parahydrogen on Pt 107
31. Hertz' Diffusion Apparatus for the Separation of Isotopes 120
32. The Diffusion of the Hydrogen Isotopes through Palladium 121
33. The Energy Levels in the Adsorption of the Hydrogens 122
34. Experimental Arrangement for the Concentration of Heavy Water by Electrolysis . 125
35. The Enrichment of the Heavy Hydrogen in the Electrolysis 128
36. The Principle of the Micro-thermal Conductivity Method for the Estimation of Heavy Hydrogen 135
37. Calibration Curve. 135
38. Micro-Float of Gilfillan and Polanyi . . 137
39. The Disintegration of Lithium by Protons according to $Li^7 + H^1 = 2He^4$ . . . 145

Fig. 40. The Disintegration of Lithium by Deutons *page* 145
41. The Tracks of H^3 and H^1 flying in Opposite Directions formed in the Reaction $D^2+D^2=H^3+H^1$ 146
42. $H\alpha$, $H\beta$ and $H\gamma$ lines of Light and Heavy Hydrogen 150
43. The $H\alpha$ Lines of Light and Heavy Hydrogen 150
44. The Spectra of the Hydrogen Molecules . 155
45. The Spectrum of AlD 156
46. The Formation of Orthodeuterium and Parahydrogen 160
47. The Specific Heat Curves for the Molecules H_2, D_2 and HD 164

PREFACE

THE investigations of the last few years have revealed that hydrogen is not such a simple gas as was originally assumed. It was shown in 1929 by Bonhoeffer and Harteck that ordinary hydrogen is a mixture of two gases, ortho- and parahydrogen, having distinctly different properties. In 1931 Urey, Brickwedde and Murphy discovered the existence of a third sort of hydrogen, heavy hydrogen.

The purpose of this book is to describe the preparation, properties and chemical behaviour of these different kinds of the same element and to illustrate how the investigations connected with this subject have contributed to the solution of some chemical and physical problems.

The first part of this book deals with the modifications of ordinary hydrogen and the second with its heavier isotope. This strict separation, which may seem somewhat artificial to the reader, is due to the circumstance that the first part was written at a time when very little was known about heavy hydrogen, the original purpose of the book being to cover the subject of orthohydrogen and parahydrogen only. In the last two years, however, more and more information has been obtained about the hydrogen isotope, and it seemed desirable to add a second part describing the behaviour and properties of this new substance.

I have to thank Prof. G. Hertz, Prof. E. Hulthén, Dr P. I. Dee and Mr F. C. Goodeve for providing original photographs, also the Akademische Verlagsgesellschaft m.b.H., Verlag Springer, *Physical Review*, *Nature*, the Faraday Society, and *Sitzungsberichte der Preussischen Akademie der Wissenschaften* for their kind permission to reproduce figures.

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A. F.

Laboratory of Colloid Science,
University of Cambridge.
November, 1934.

PART I

ORTHOHYDROGEN AND PARAHYDROGEN

CHAPTER I

THE DISCOVERY OF ORTHOHYDROGEN AND PARAHYDROGEN

THE new quantum theory led in 1927 to the assertion that normal hydrogen is a mixture of two gases containing two different sets of molecules and having different optical and thermal properties.

It was a real triumph for theory when in 1929 Bonhoeffer and Harteck succeeded in bringing forward experimental evidence for the existence of the two different modifications of hydrogen. These experiments were not only a valuable support for the quantum theory but at the same time they opened up a new field in physical chemistry by the application of the results obtained in this investigation.

The historical development leading to the theoretical prediction of the existence of two modifications of hydrogen and to the experimental confirmation was as follows.

In 1926 Heisenberg [6] explained the existence of orthohelium and parahelium on the basis of quantum mechanics by his helium theory. From analogous considerations Heisenberg and Hund [6a, 9] postulated the existence of the two kinds of hydrogen. By their theory it was possible to explain the alternating intensity in the molecular spectra discovered by Mecke [11] in 1924. Dennison [3] applied their considerations to the falling off of the rotational specific heat of hydrogen, thus finding a final explanation for this phenomenon, observed in 1912 by Eucken [27]. According to Dennison's theory hydrogen cooled to low temperatures is not in thermodynamical equilibrium with respect to the proportions of the

two kinds of hydrogen, rather the equilibrium corresponding to high temperatures is "frozen". This was confirmed by the experiments of McLennan and McLeod [43] on the Raman effect of liquid hydrogen. Following E. U. Condon's suggestion in 1928 Giauque and Johnston [35] kept a sample of hydrogen for six months at a low temperature to induce the attainment of equilibrium, but as the observed effect (change of vapour pressure) was very small they failed to draw any conclusions from their experiments.

Finally in 1929 Bonhoeffer and Harteck [15, 16] were able to publish experiments in which they successfully catalyzed the attainment of equilibrium, isolated one of the hydrogen modifications and described a great many of its properties. About the same time Eucken and Hiller [28, 30] also obtained positive results in approaching the equilibrium by observing a change in the specific heat of samples of hydrogen cooled down to low temperatures for some time.

CHAPTER II

THEORY

1. Theoretical foundations

The hydrogen molecule is composed of two atoms and each of these atoms consists of a nucleus, i.e. a proton, and an electron. Besides the translational motion of the whole molecule the two nuclei perform a vibrational motion in the direction of the line joining the nuclei and a rotational motion around a direction perpendicular to the molecular axis. While every translational velocity and direction is possible the other two motions are quantized, i.e. only certain motions are allowed which can be characterized by definite integral quantum numbers. Similarly the motions of the electrons are also quantized.

According to the quantum theory neither the electron nor the proton is to be regarded as a point charge, for they possess a mechanical momentum, a so-called spin (corresponding to a model "spinning" around its axis), equal to $\frac{1}{2}$ if measured in units of $h/2\pi$, h being Planck's constant. In general a mechanical momentum i can have $2i+1$ different positions with respect to the direction of an external field, therefore the spins both of the electrons and of the protons can have two different relative (antiparallel and parallel) orientations.

Heitler and London [7] showed, however, that in the ground state of the hydrogen molecule the electron spins have always antiparallel orientation, as two hydrogen atoms with parallel electron spins repel each other and no molecule can be formed.

On the other hand, both antiparallel and parallel orientation of the nuclear spin can occur in the molecule, and these different orientations combined with certain values of the rotational quantum number distinguish the two hydrogen modifications from each other.

The parahydrogen molecules have antiparallel nuclear spins and even rotational quantum numbers, while the ortho-

hydrogen* molecules possess parallel nuclear spins and odd rotational quantum numbers.

There is justification for giving different names to the two modifications of hydrogen, since spontaneous conversion of these two different sets of molecules practically does not take place either by radiation† or in collision processes and the ortho- and paramolecules can actually be considered as molecules of two gases differing from each other in certain optical and thermal properties.

In order to obtain the energy states for the hydrogen molecule according to quantum mechanics, it is simplest to start from the analogous problem in classical mechanics.‡

In our case we have a system of four particles, two protons and two electrons, with repulsion and attraction according to Coulomb's law. In classical mechanics such a system can be described by a Hamiltonian function in which the kinetic energy is given as a function of the impulses p_k and the potential energy as a function of the positional co-ordinates q_k. In a system not subject to external forces the energy is constant:

$$H(p_k, q_k) = E \qquad \ldots\ldots(1).$$

In quantum mechanics we have to replace the impulses and the energy E by operators and to apply these to the wave function ψ. Using Cartesian co-ordinates p_k is to be replaced by $\frac{h}{2\pi i}\cdot\frac{\partial}{\partial x_k}$ (h = Planck's constant, $i = \sqrt{-1}$), and in this case we obtain the differential equation

$$H\left(\frac{h}{2\pi i}\cdot\frac{\partial}{\partial x_k}, x_k\right)\psi = E\psi \qquad \ldots\ldots(2),$$

representing the so-called Schroedinger equation.

* The names orthohydrogen and parahydrogen were chosen by Bonhoeffer and Harteck[15] on analogy with the nomenclature for the helium atom (orthohelium and parahelium), but it must be emphasized that the distinction between the hydrogen modifications is based on the different orientation of the nuclear spins, while in the case of helium it depends on the orientation of the electron spins.

† The absence of the interconversion ortho-para, i.e. the non-occurrence of a transition changing the rotational quantum number by ± 1, is contrary to the behaviour of unsymmetrical molecules such as HCl.

‡ Cf. Ruark-Urey, *Atoms, Molecules and Quanta*, Chapters XV, XIX, McGraw-Hill Book Co., Inc., New York.

In general this equation is not soluble for every value of E, at least not if the function ψ is submitted to some plausible physical conditions such as being single valued and finite. There are only solutions if E is equal to certain discrete eigenvalues E_n. The functions corresponding to these eigenvalues are the eigenfunctions ψ_n, they are orthogonal to each other, i.e.

$$\int \psi_n^* \psi_m d\tau = 0 \quad \text{if} \quad n \neq m \qquad \ldots\ldots(3),$$

where ψ^* is the conjugated complex value to ψ, and the integration is to be expanded over the whole space.

To obtain the classical energy equation for the hydrogen molecule we shall replace the molecule by a schematic model, the exact mathematical treatment being rather difficult.

The vibration of the nuclei can be neglected, as its amplitude is very small compared with molecular dimensions. As we are interested chiefly in the rotational motion of the nuclei, the motion of the electrons can also be neglected because of their small mass. Thus our model is the so-called rigid rotator with a free axis which is represented by two mass points moving at a constant distance from each other.

The classical energy equation for this rotator has the following form in the polar co-ordinates θ and ϕ:

$$\frac{1}{2I}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\phi}\right) - E = 0 \qquad \ldots\ldots(4),$$

I designating the moment of inertia. In this case the potential energy is zero. Replacing the impulses and E by the corresponding operators,* we obtain the Schroedinger equation

$$\frac{1}{\sin\theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\cdot\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2 I}{h^2}E\psi = 0 \ldots\ldots(5).$$

This is the well-known differential equation of Legendre. The coefficient of ψ has to be the product of two consecutive integers to make ψ single valued† and finite. This gives as a result

$$\frac{8\pi^2 I E_J}{h^2} = J(J+1) \quad \text{or} \quad E_J = \frac{h^2}{8\pi^2 I}J(J+1) \ldots(6).$$

* The impulses expressed in polar co-ordinates are not to be replaced in the same way as the impulses expressed in Cartesian co-ordinates.

† The single-valued character requires that the function ψ should have its

This eigenvalue E_J is the energy of the rotational level with the quantum number J and the angular momentum

$$\sqrt{J(J+1)}\,h/2\pi,$$

and is equal except for an additional term to the expression with the "half-integer" quantum numbers resulting from the study of band spectra:

$$E_J' = \frac{h^2}{8\pi^2 I}(J+\tfrac{1}{2})^2 \qquad \ldots\ldots(6a).$$

The eigenfunctions belonging to the eigenvalues E_J are the spherical surface functions

$$\psi_{J,m} = e^{im\phi}\sin^{|m|}\theta \,.\, P_J^{|m|}(\cos\theta) \qquad \ldots\ldots(7),$$

m having the values $-J, -J+1, \ldots, 0, \ldots, J-1, J$, and $P_J^{|m|}$ being defined by the following equations ($x = \cos\theta$):

$$P_J^{|m|}(x) = \frac{d^m P_J(x)}{dx^m}, \quad P_J(x) = \frac{1}{2^J J!}\cdot\frac{d^J(x^2-1)^J}{dx^J} \qquad \ldots\ldots(8).$$

The $P_J^{|m|}$ functions have the following form:

$P_0^0(x) = 1,$

$P_1^0(x) = x, \qquad P_1^1(x) = 1,$

$P_2^0(x) = \tfrac{3}{2}x^2 - \tfrac{1}{2}, \quad P_2^1(x) = 3x, \qquad P_2^2(x) = 3,$

$P_3^0(x) = \tfrac{5}{2}x^3 - \tfrac{3}{2}x, \quad P_3^1(x) = \tfrac{15}{2}x^2 - \tfrac{3}{2}, \quad P_3^2(x) = 15x, \quad P_3^3(x) = 15,$

etc. $\qquad \ldots\ldots(8a).$

It is evident that E_J itself does not depend on m and that there are $2J+1$ different eigenfunctions ψ belonging to the same eigenvalue E_J. This $2J+1$-fold "degeneracy" means that the statistical weight g_J* of the rotational level with the energy E_J is $2J+1$. In Bohr's quantum theory this degeneracy has been described by the vector diagram, according to which a vector of the length J representing the angular momentum in the state J† (measured in units of $h/2\pi$) can have $2J+1$

original value after a period of 2π. For the plane rotator $\psi = \begin{cases}\sin m\phi \\ \cos m\phi\end{cases}$, so in this case it is evident that m can only have integral values.

* The statistical weight of a degenerated state is given by the number of states into which it splits in a suitable external field.

† In quantum mechanics the angular momentum is $\sqrt{J(J+1)}\,h/2\pi$ (see above).

different integral (or half integral) projections on a given direction. On account of this positional quantization in a magnetic field m is called the magnetic quantum number.

The solution of the Schroedinger equation, considering also the motion of the electrons (cf. de Kronig[10]), can be written approximately as

$$\psi = \chi_n (q_{1,2}, q_{\mathrm{I,II}}) \psi_{Jm} (\phi, \theta) \qquad \ldots\ldots(9),$$

where χ_n represents a wave function depending on the mutual position of the electrons and protons in the molecule and $q_{1,2}$ and $q_{\mathrm{I,II}}$ are spatial co-ordinates of the electrons and nuclei, respectively.

The explanation of the connection between spin orientation and rotational quantum number is based on a fundamental theory first introduced by Heisenberg[6, 6a] and applied to electrons.

The fact that equal electrons (or protons) are in principle indistinguishable causes the wave functions to have certain properties of symmetry according to the symmetry of the Schroedinger equation for the particles. As $|\psi|^2$ represents the probability of the presence of the electron at a certain point in space, $|\psi|^2$ must remain unchanged if the spatial co-ordinates of two electrons are interchanged. With this postulate two forms of wave functions are compatible: one of them is symmetrical in the spatial co-ordinates of the electrons, i.e. remains unchanged by the interchange of the spatial co-ordinates of the electrons, the other is antisymmetrical in the spatial co-ordinates, i.e. changes sign when these co-ordinates are interchanged. The spin functions $\Sigma(s_1, s_2, \ldots)$ depending on the spin co-ordinates* s_1, s_2, ... have the same properties of symmetry, i.e. they do or do not change their sign if the spin co-ordinates of two electrons are interchanged. The total wave function is the product of the spatial wave function and the spin function $\psi . \Sigma$. In atomic spectra only those forms of the spatial wave function and of the spin functions occur whose product, i.e. the total wave function, changes sign if the

* The spin co-ordinates indicate the direction of the electronic spin.

spatial and spin co-ordinates of two electrons are interchanged, i.e. when

$$\psi(q_1, q_2, \dots q_k, q_l, \dots q_n)\,\Sigma(s_1, s_2 \dots s_k, s_l, \dots s_n) = -\psi(q_1, q_2, \dots q_l, q_k, \dots q_n)\,\Sigma(s_1, s_2 \dots s_l, s_k, \dots s_n) \quad \dots\dots(10).$$

This symmetry postulate in respect to the total wave function is a consequence of Pauli's principle, according to which all states containing two electrons in the same quantum level are forbidden, as by this postulate all functions containing the same spatial and spin co-ordinates for two electrons actually vanish. The antisymmetry postulate is fulfilled both by the functions $\psi_{\text{antisymm.}} \cdot \Sigma_{\text{symm.}}$ and by the functions $\psi_{\text{symm.}} \cdot \Sigma_{\text{antisymm.}}$

The same holds for the symmetry properties of the spatial wave functions $\chi_n \cdot \psi_J$ of diatomic molecules: interchanging the spatial co-ordinates of the nuclei, the wave functions may or may not change their sign.

In the case of the hydrogen molecule we know the symmetry properties both of ψ_J and χ_n, and thus it is possible to decide which rotational states are symmetrical or antisymmetrical in the spatial co-ordinates.

The interchange of the nuclei can be carried out by giving at first the molecular axis an opposite direction and then by reflecting the electrons at the centre of the molecule. The χ function is naturally not altered by the first transformation, which does not involve a change of the inner molecular configuration, and it remains unaltered by the second transformation.* The rotational wave function is converted by the first transformation from

$$\psi_J(\phi, \theta) \quad \text{to} \quad \psi_J(\phi + \pi, \pi - \theta),$$

changing by the factor $(-1)^J$, but remains unaltered on the second transformation. Thus the spatial wave function $\chi_n \cdot \psi_J$ is symmetrical in the spatial co-ordinates for even rotational

* The electronic level corresponding to a χ function of this symmetry property is called "even" and designated by g (gerade). Cf. Jevons, *Report on Band-spectra of Diatomic Molecules*. Cambridge University Press (1932). The first excited electronic level of hydrogen is on the other hand "odd". Cf. Chapter III, § 6, p. 44.

quantum numbers and antisymmetrical for odd quantum numbers.

Similarly to the spin functions of the electrons the spin functions of the protons [$\Sigma(s_{\text{nucl.}})$] may be symmetrical in the spin co-ordinates if the two nuclear spins are parallel, or antisymmetrical if the nuclear spins have antiparallel orientation. As the total nuclear spin of the hydrogen molecule is $T=1$ if the spins are parallel, and zero if the spins are antiparallel, the statistical weight of the levels with parallel nuclear spins is three times as great as that of the levels with antiparallel spins (corresponding to $2T+1$ possible orientations in an external field).

In advance it cannot be decided whether Pauli's principle, i.e. the antisymmetry postulate with regard to the total wave function

$$\chi_n(q).\psi_J(\phi,\ \theta)\,\Sigma(s_{\text{nucl.}}),$$

is valid for nuclei.

The analysis of band spectra has shown that in the normal electronic state of hydrogen every rotational level is existent only in connection with one of the two orientations of the nuclear spin. If the parallel orientation of the nuclear spins is connected with the odd rotational numbers and the antiparallel orientation with the even quantum numbers we obtain the statistical weight of the level J:

$$p_J=\begin{cases} g_J.3=(2J+1).3, & \text{if } J \text{ is odd,} \\ g_J\ \ =(2J+1), & \text{if } J \text{ is even;} \end{cases}$$

in the contrary case, however,

$$p_J=\begin{cases} g_J\ \ =(2J+1), & \text{if } J \text{ is odd,} \\ g_J.3=(2J+1).3, & \text{if } J \text{ is even.} \end{cases}$$

Dennison [3] proved that of these two possibilities the former is in accordance with experiment, as only with this combination of nuclear spin orientation and quantum number was it possible to explain completely the decrease of the rotational specific heat of hydrogen. This means that the antisymmetry postulate concerning the total wave function is valid for the hydrogen nuclei too, i.e. the total wave function changes its

sign if the spatial and spin co-ordinates of the nuclei are interchanged.*

As the states with the higher statistical weight are called ortho states and those with the lower para states, the unexcited hydrogen molecules rotate with odd quantum numbers in the ortho states and with even quantum numbers in the para states.†

We have now to show that there are practically no transitions between ortho and para states. The transition may happen by spontaneous radiation or by collision with other hydrogen molecules. The ortho-parahydrogen conversion by radiation was treated by Wigner[17]. According to quantum mechanics the probability of spontaneous emission A_J^{J+1} corresponding to the transition between the rotational levels $J+1$ and J is expressed by the formula

$$A_J^{J+1} = \frac{64\pi^4 \nu_{J+1,J}^3 e^2}{3hc^3} |M_{J+1,J}|^2 \quad \ldots\ldots(11),$$

where $\nu_{J+1,J}$ is the frequency of the radiation emitted, $h = 6{\cdot}55 . 10^{-27}$ erg/sec., $c =$ (velocity of light) $3 . 10^{10}$ cm./sec., and $M_{J+1,J}$ is the so-called matrix element of the dipole moment of the molecule given by

$$M_{J+1,J} = \int \psi^*_{0,J+1} . P . \psi_{0,J} d\tau = \int \psi^*_{0,J+1} (r_1 + r_2 - R_I - R_{II}) \psi_{0,J} d\tau \quad \ldots\ldots(12),$$

r and R denoting the radius vector of the electrons and protons, respectively. The index 0 shows that the wave function refers to the unexcited state.

If the proton did not have a spin the corresponding wave functions would be exactly symmetrical or antisymmetrical, respectively, and in this case the probability of the transition would be exactly zero. For if we interchange the nuclei, the inner configuration is not changed, and therefore the dipole

* It must be added, however, that Pauli's principle, although generally valid for the electrons, cannot be applied in all cases to nuclei. Cf. Chapter VI, p. 111.

† For ortho and para states in the excited levels see Chapter III, § 6.

moment should not change. But as the antisymmetrical wave function changes its sign if the nuclei are interchanged, the relation

$$\int \psi^{\star +}_{0,J+1}(\mathrm{I},\mathrm{II})(r_1+r_2-R_\mathrm{I}-R_\mathrm{II})\psi^{-}_{0,J}(\mathrm{I},\mathrm{II})\,d\tau$$
$$= -\int \psi^{\star +}_{0,J+1}(\mathrm{II},\mathrm{I})(r_1+r_2-R_\mathrm{II}-R_\mathrm{I})\psi^{-}_{0,J}(\mathrm{II},\mathrm{I})\,d\tau \qquad \ldots\ldots(13)$$

($\psi^{+}_{0,J+1}$ and $\psi^{-}_{0,J}$ denoting the exactly symmetrical and antisymmetrical wave functions, respectively) must be satisfied, which is possible only if the integrals are zero.

In fact there is a perturbation as a consequence of the interaction of the nuclear spins and small supplementary terms are formed destroying the exact antisymmetry and symmetry of the wave functions. According to the perturbation theory the perturbed wave functions can be developed in a series of unperturbed wave functions of the excited electronic levels (designated by the index 1)

$$\psi_{0,J+1} = \psi^{+}_{0,J+1} + \sum_L A^{\pm}_{J+1,L}\psi^{\pm}_{1,L} \qquad \ldots\ldots(14),$$

and

$$\psi_{0,J} = \psi^{-}_{0,J} + \sum_K B^{\pm}_{J,K}\psi^{\pm}_{1,K} \qquad \ldots\ldots(14a).$$

The coefficients A and B are given by the formulae

$$A^{\pm}_{J+1,L} = \frac{1}{E_{1,L}-E_{0,J+1}}\int \psi^{\star +}_{0,J+1}.S.\psi^{\pm}_{1,L},$$

$$B^{\pm}_{J,K} = \frac{1}{E_{1,K}-E_{0,J}}\int \psi^{\star -}_{0,J}.S.\psi^{\pm}_{1,K} \qquad \ldots\ldots(15),$$

S designating the perturbation potential caused by the nuclear spin and $E_{1,L}-E_{0,J}=\Delta E$ the energy difference between the normal and the excited electronic level. Taking into consideration that of the terms resulting from formulae (13), (14) and (15) all terms having the form $\int \psi^{\star +}.P.\psi^{-}d\tau$ vanish (because of the non-combination of symmetrical and anti-

symmetrical levels), and that all terms containing the factor AB can be neglected, we obtain

$$M_{J+1,J} = \int \psi^{*+}_{0,J+1} \cdot P \left(\sum_K B^{+}_{J,K} \psi^{+}_{1,K}\right) d\tau + \int \sum_L A^{*-}_{J+1,L} \psi^{*-}_{1,L} \cdot P \cdot \psi^{-}_{0,J} \, d\tau \quad \ldots\ldots(16).$$

With the aid of formula (15) and other quantum mechanical relations we can find the order of magnitude of $M_{J+1,J}$:

$$M_{J+1,J} \simeq \frac{1}{\Delta E} \left(\int P\psi^{*+}_{0,J+1} \cdot P\psi^{+}_{0,J+1} \cdot \int S\psi^{*-}_{0,J} \cdot S\psi^{-}_{0,J} \right)^{\frac{1}{2}} \quad \ldots\ldots(17).$$

The first integral is about 10^{-15} cm.^{2} and the second approximately the square of the perturbation energy caused by the nuclear spin. As the perturbation may be estimated to be one-thousandth part of the multiplet separation in the spectrum of helium, i.e. $3 \cdot 10^{-6}$ volt (the magnetic moment of the proton being one-thousandth of that of the electron, cf. p. 50), and $\Delta E \simeq 10$ volts, $M_{J+1,J}$ has the order of magnitude of 10^{-14} cm. and thus the transition probability

$$A^{J+1}_{J} \simeq 10^{-10} \text{sec.}^{-1}$$

This figure corresponds to one transition in three hundred years.

Following the same principles of the quantum mechanical perturbation theory the probability of the ortho-para transition in collision processes was treated by Hall and Oppenheimer [4]. In this case the conversion is induced by the very small interaction of the nuclear magnetic moment with the magnetic moment of the rotating molecule.* Another possibility of the conversion of two parahydrogen molecules into orthohydrogen (or vice versa) may occur by the interchange of their nuclei. The relative probability of this effect in a gas kinetic collision is of the order

$$e^{-(M/m)^{\frac{1}{2}}},$$

m and M designating the mass of the electron and proton, respectively. At atmospheric pressure both effects give to-

* If the colliding molecules are paramagnetic this effect is increased considerably. Cf. Chapter IV § 1 (*e*).

gether 10^8 sec. = 3 years as the half lifetime of the ortho-para transition.

Thus we may conclude that in pure hydrogen gas under normal experimental conditions neither radiation nor collision can bring about ortho-parahydrogen conversion.

2. The calculation of the equilibrium concentration, specific heat and rotational energy of orthohydrogen and parahydrogen

The thermodynamical equilibrium between ortho- and parahydrogen is governed by Boltzmann's distribution law. According to this law the fraction of the molecules (N_J) of the total number (N_0) in the rotational state J is given by the equation

$$N_J = N_0 p_J . e^{-E_J/kT} \qquad \text{.....(18),}$$

where p_J and E_J denote the statistical weight and the energy of the state J respectively and k Boltzmann's constant. (N_0 may be taken as 1.) As all para molecules have even, all ortho molecules odd rotational quantum numbers, the relation of the concentration of the two modifications (β) is expressed by the formula

$$\beta = \frac{[\text{p-H}_2]}{[\text{o-H}_2]} = \frac{\sum_{J=\text{even}} p_J . e^{-E_J/kT}}{\sum_{J=\text{odd}} p_J . e^{-E_J/kT}} = \frac{Q_e}{Q_o} \qquad \text{.....(19),}$$

or if we consider that

$$E_J = J(J+1)\frac{h^2}{8\pi^2 I} = J(J+1)B \qquad \text{.....(20)}$$

and

$$p_J = g_{\text{nucl.}} g_J = \begin{cases} 2J+1 & \text{for } J = \text{even} \\ 3(2J+1) & \text{for } J = \text{odd} \end{cases} \qquad \text{.....(21),}$$

we find

$$\beta = \frac{\sum_{J=\text{even}} (2J+1) e^{-J(J+1)B/kT}}{\sum_{J=\text{odd}} 3(2J+1) e^{-J(J+1)B/kT}}$$

$$= \frac{1 + 5e^{-6B/kT} + 9e^{-20B/kT} + 13e^{-42B/kT} + \ldots}{3(3e^{-2B/kT} + 7e^{-12B/kT} + 11e^{-30B/kT} + \ldots)} \qquad \text{.....(22),}$$

where $B/k = 84{\cdot}837$;

since $h = 6{\cdot}55 . 10^{-27}$ erg/sec.,

$I = 4{\cdot}67 . 10^{-41}$ g.cm.^{2} (T. Hori [8]),

$k = 1{\cdot}373 . 10^{-16}$ erg/degree.

At high temperatures ($B \ll kT$), $\beta = \frac{1}{3}$, corresponding to the statistical weights due to the nuclear spin. This value of β is practically attained at room temperatures and thus normal

Table 1

Temperature ° K.	Ratio para:ortho	Percentage para-hydrogen	Temperature ° K.	Ratio para:ortho	Percentage para-hydrogen
20	544·8	99·82	85	0·8307	45·37
21	363·5	99·73	86	0·8123	44·82
22	251·6	99·60	87	0·7981	44·39
23	179·8	99·45	88	0·7781	43·76
24	132·2	99·25	89	0·7621	43·25
25	99·57	99·01	90	0·7469	42·75
30	32·07	96·98	91	0·7323	42·27
35	14·28	93·45	95	0·6801	40·48
40	7·780	88·61	100	0·6262	38·51
45	4·853	82·91	105	0·5829	36·82
50	3·327	76·89	110	0·5456	35·30
55	2·443	70·96	115	0·5152	34·00
60	1·890	65·39	120	0·4897	32·87
65	1·521	60·33	130	0·4498	31·03
70	1·264	55·83	140	0·4208	29·62
75	1·077	51·86	150	0·3994	28·54
76	1·046	51·13	160	0·3835	27·72
77	1·017	50·41	170	0·3715	27·09
78	0·9894	49·73	190	0·3555	26·23
79	0·9626	49·05	210	0·3463	25·72
80	0·9377	48·39	230	0·3409	25·42
81	0·9140	47·75	250	0·3377	25·24
82	0·8916	47·13	273	0·3357	25·13
83	0·8702	46·53	∞	0·3333	25·00
84	0·8500	45·95			

hydrogen (denoted henceforth by n-H_2) is composed of $\frac{1}{4}$ parahydrogen (p-H_2) and $\frac{3}{4}$ orthohydrogen (o-H_2). At low temperatures ($B \gg kT$), $\beta = \infty$, i.e. in equilibrium there is only pure parahydrogen. This corresponds to the anticipation that as the temperature is lowered all molecules gradually pass into the lowest state having the quantum number 0 which is a para state. Table 1 contains the ratio of para- to orthohydrogen and

the equilibrium concentration of p-H_2 expressed as a percentage $\left(=\frac{100\beta}{1+\beta}\right)$ for temperatures 20–273° K., computed* by Harkness and Deming [5].†

It must be emphasized that in general the equilibrium conditions relating to the o-H_2, p-H_2 concentrations are not set up because of the absence of intercombination. If, for example, n-H_2 is cooled to a low temperature all para molecules fall to

Table 2

Temperature ° K.	Hydrogen	$J=0$	$J=1$	$J=2$	$J=3$	$J=4$	$J=5$
50	Equilibrium	76·88	23·11	0·01	—	—	·
	Para	99·98	—	0·02	·	·	·
	Ortho	—	100·00	—	—	·	·
	Normal	24·995	75·00	0·005	—	—	—
100	Equilibrium	37·36	61·46	1·15	0·02	—	—
	Para	97·02		2·98	—	—	
	Ortho	—	99·95	·	0·05	—	
	Normal	24·25	74·97	0·74	0·03	·	
200	Equilibrium	18·65	71·67	7·27	2·38	0·03	0·002
	Para	71·82	—	28·05	—	0·13	—
	Ortho	—	96·78	—	3·21	—	0·003
	Normal	17·95	72·59	7·01	2·41	0·03	0·002
300	Equilibrium	12·89	65·78	11·78	9·07	0·40	0·08
	Para	51·40	—	47·0	—	1·59	—
	Ortho	—	87·80	—	12·10	—	0·10
	Normal	12·85	65·84	11·75	9·08	0·40	0·08

their lowest rotational level zero, and all ortho molecules to the lowest ortho level, i.e. to the rotational level 1. Dennison [3] succeeded in explaining the decrease of the rotational specific heat of hydrogen by making the assumption that the relative concentration of ortho and para molecules, 3:1 at ordinary temperatures, is not changed when the hydrogen is cooled down. On the other hand parahydrogen (or orthohydrogen), if once prepared, does not change to normal hydrogen but

* It is sufficient to consider the terms up to $J=5$ or 6.

† Although these concentrations had been computed by Giauque before the table of Harkness and Deming was published, we use these figures, as they are calculated especially for those temperatures used in the majority of the experiments.

represents a gas in which odd (or in o-H_2 even) rotational levels are not occupied. Table 2 shows the approximate percentages of the molecules present in the four different hydrogen mixtures, i.e. in the equilibrium mixture (e-H_2), parahydrogen (p-H_2), orthohydrogen (o-H_2) and normal hydrogen (n-H_2) in the different rotational levels.

The mean rotational energy of a mole of hydrogen is

$$E_{\text{rot.}} = \frac{N \Sigma N_J E_J}{\Sigma N_J}, \quad N = 6{\cdot}06 \,.\, 10^{23} \qquad \ldots\ldots(23).$$

Depending on whether the summation is extended over all values of J, over even J or odd J, we obtain the mean rotational energy of equilibrium hydrogen, parahydrogen or orthohydrogen respectively:

$$E_{\text{rot.}}^{\text{e-H}_2} = N \frac{\left(\sum_{J=\text{even}} (2J+1) J(J+1) B \,.\, e^{-J(J+1)B/kT} + 3 \sum_{J=\text{odd}}^{J} (2J+1) J(J+1) B \,.\, e^{-J(J+1)B/kT} \right)}{\sum_{J=\text{even}} (2J+1) e^{-J(J+1)B/kT} + 3 \sum_{J=\text{odd}} (2J+1) e^{-J(J+1)B/kT}}$$

$$= -R \frac{d \ln Q}{d\, 1/T} \qquad \ldots\ldots(24),$$

the numerator being the differential coefficient of the denominator with respect to $1/T$, R the gas constant and

$$Q = Q_o + Q_e.$$

Or introducing

$$\frac{B}{kT} = \sigma, \qquad \ldots\ldots(25),$$

$$E_{\text{rot.}}^{\text{e-H}_2} = -BN \frac{d \ln Q}{d\sigma} \qquad \ldots\ldots(24a),$$

$$E_{\text{rot.}}^{\text{p-H}_2} = -R \frac{d \ln Q_e}{d\, 1/T} = -BN \frac{d \ln Q_e}{d\sigma} \qquad \ldots\ldots(24b),$$

$$E_{\text{rot.}}^{\text{o-H}_2} = -R \frac{d \ln Q_o}{d\, 1/T} = -BN \frac{d \ln Q_o}{d\sigma} \qquad \ldots\ldots(24c).$$

The rotational energy of the normal hydrogen may be found

from that of its components, since the simple additive law is obeyed and

$$E_{\text{rot.}}^{\text{n-H}_2} = \tfrac{1}{4} E_{\text{rot.}}^{\text{p-H}_2} + \tfrac{3}{4} E_{\text{rot.}}^{\text{o-H}_2} \qquad \ldots\ldots(24d).$$

These rotational energies as computed by Giauque[31]* are given in Table 3.

Table 3. *Rotational energy of hydrogen gas in calories per mole*

Temperature ° K.	Pure para-hydrogen	Pure ortho-hydrogen	Equilibrium mixture	Normal hydrogen
0	0·00	337·17	0·00	252·88
15	0·00	337·17	0·04	252·88
20	0·00	337·17	0·63	252·88
25	0·00	337·17	3·39	252·88
30	0·00	337·17	10·28	252·88
40	0·05	337·17	38·63	252·89
50	0·20	337·18	78·38	252·94
75	5·77	337·22	165·61	254·36
100	30·56	338·59	219·78	262·17
125	80·09	341·83	258·41	276·39
150	146·61	351·40	292·94	300·20
175	219·09	368·54	328·44	331·17
200	290·22	393·59	366·76	367·75
225	357·04	425·69	408·19	408·53
250	419·27	463·46	452·30	452·41
273·1	473·34	502·16	494·84	494·91
298·1	529·12	546·92	542·46	542·47

At the absolute zero of temperature the rotational energy of p-H_2 and e-H_2 is zero, since all molecules occupy the rotational level 0, while o-H_2 molecules possess a rotational energy equal to 337 cal., that is, the energy of the first rotational level. With increasing temperature the rotational energies of the four different H_2 mixtures rise and at 400° K. all have the same value. (For the experimental measurement of rotational energy see Chapter III, § 4.)

As the specific heat is given in general by $C = dE/dT$, we

* In this calculation instead of the formula $E_J = (J+1).JB$ the following, given by Hyman, Birge and Jeppesen (*Nature*, **123**, 277, **125**, 462; *Phys. Rev.* **36**, 187 (1930)) was employed:

$$E_J = Bm^2 + Dm^4 + Fm^6,$$

with $m = J + \frac{1}{2}$, $D = -0{\cdot}0458$ cm.$^{-1}$, $F = 5{\cdot}18.10^{-5}$ cm.$^{-1}$, and B having practically the same value as above. This formula takes into account the minute stretching of the molecules by the rotation, and the consequent change in the moment of inertia.

find for the rotational specific heat of the different hydrogen mixtures:*

$$C_{\text{rot.}}^{\text{e-H}_2} = \frac{dE_{\text{rot.}}^{\text{e-H}_2}}{dT} \qquad \text{.....(26),}$$

$$C_{\text{rot.}}^{\text{p-H}_2} = \frac{dE_{\text{rot.}}^{\text{p-H}_2}}{dT} \qquad \text{.....(26}a\text{),}$$

$$C_{\text{rot.}}^{\text{o-H}_2} = \frac{dE_{\text{rot.}}^{\text{o-H}_2}}{dT} \qquad \text{.....(26}b\text{),}$$

$$C_{\text{rot.}}^{\text{n-H}_2} = \tfrac{1}{4} C_{\text{rot.}}^{\text{p-H}_2} + \tfrac{3}{4} C_{\text{rot.}}^{\text{o-H}_2} \qquad \text{.....(26}c\text{),}$$

or using formula (25)

$$C_{\text{rot.}}^{\text{e-H}_2} = R\sigma^2 \frac{d^2 \ln Q}{d\sigma^2} = R\sigma^2 \frac{d^2 \ln (Q_e + Q_o)}{d\sigma^2} \qquad \text{.....(27),}$$

$$C_{\text{rot.}}^{\text{p-H}_2} = R\sigma^2 \frac{d^2 \ln Q_e}{d\sigma^2} \qquad \text{.....(27}a\text{),}$$

$$C_{\text{rot.}}^{\text{o-H}_2} = R\sigma^2 \frac{d^2 \ln Q_o}{d\sigma^2} \qquad \text{.....(27}b\text{),}$$

$$C_{\text{rot.}}^{\text{n-H}_2} = R\sigma^2 \left(\frac{1}{4} \frac{d^2 \ln Q_e}{d\sigma^2} + \frac{3}{4} \frac{d^2 \ln Q_o}{d\sigma^2} \right) \qquad \text{.....(27}c\text{).}$$

This calculation was first carried out by Dennison [3]. He pointed out the fundamental difference between the formulae (27) and (27c): one of them representing the rotational specific heat of a gas in which ortho-parahydrogen equilibrium is momentarily established and the other the specific heat with unchanged ortho-para ratio as is the case in normal measurements.

Table 4 shows the different rotational specific heats computed by Giauque. Fig. 1 gives the same values graphically (Beutler [1].†)

At low temperatures all hydrogen mixtures behave as monatomic gases, and their rotational specific heat is zero. There are two remarkable maxima appearing in the $C_{\text{rot.}}^{\text{e-H}_2}$ and $C_{\text{rot.}}^{\text{p-H}_2}$ curves at 50° and 175° K. respectively, at which temperatures the curves show a rotational specific heat con-

* The total specific heat of gaseous hydrogen is $\frac{3}{2}R + C_{\text{rot.}}$

† A small correction of his values given by Däumichen [2] is considered.

siderably greater than R, the classical value of a rotator. With rising temperature (above 300° K.) all four curves approach this value asymptotically.

In Chapter III, § 3, we shall see that all experimental results are in perfect agreement with these values.

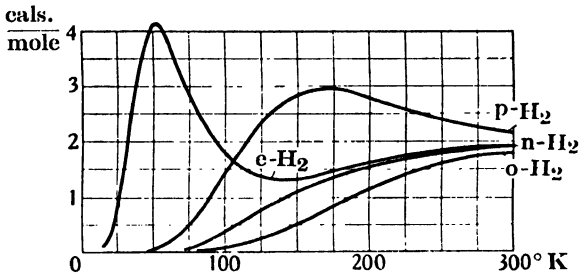


Fig. 1. The rotational specific heat of hydrogen.

Table 4. *Rotational specific heat of hydrogen gas in calories per degree per mole*

Temperature ° K.	Pure para-hydrogen	Pure ortho-hydrogen	Equilibrium mixture	Normal hydrogen
0	0·0000	0·0000	0·0000	0·0000
15	0·0000	0·0000	0·0028	0·0000
20	0·0000	0·0000	0·2649	0·0000
25	0·0000	0·0000	0·9196	0·0000
30	0·0001	0·0000	1·8795	0·0000
40	0·0049	0·0000	3·4465	0·0012
50	0·0399	0·0000	4·1042	0·0100
75	0·5177	0·0079	2·7263	0·1353
100	1·5041	0·0731	1·7498	0·4309
125	2·3981	0·2501	1·4138	0·7871
150	2·8451	0·5271	1·3801	1·1066
175	2·9046	0·8464	1·4708	1·3610
200	2·7674	1·1512	1·5965	1·5553
225	2·5777	1·4076	1·7148	1·7001
250	2·4056	1·6049	1·8101	1·8051
273·1	2·2819	1·7378	1·8756	1·8738
298·1	2·1862	1·8377	1·9254	1·9248

CHAPTER III

THE PROPERTIES OF THE HYDROGEN MODIFICATIONS

1. The analysis of ortho-parahydrogen mixtures

It is apparent that the difference in the specific heat of the two modifications of hydrogen can be used to prove that an ortho-parahydrogen conversion has taken place or to measure the concentration of their mixtures. This method, actually used by Eucken and Hiller[30], is, however, neither simple nor precise enough to detect minute changes in the concentration. Bonhoeffer and Harteck[17], therefore, worked out a method, based on the different thermal conductivities of the hydrogen modifications, which needs only small amounts of gas for each measurement.

The heat conductivity (λ) of a gas is expressed in terms of its specific heat at constant volume (C_v), coefficient of viscosity (η) and molecular weight (M) by

$$\lambda = k\eta C_v/M \qquad \ldots\ldots(1),$$

where the factor k allows for the fact that the mean energy of the molecules appears larger as the molecules possessing large amounts of kinetic energy travel faster and thus transfer their energy more rapidly. k is equal to 2·5 when the molecules possess only kinetic energy (i.e. in the case of H_2 at temperatures less than 50° K.) and to 1·9 if the rotational energy is completely available (i.e. with H_2 above 300° K.). In general k is approximately given by

$$k = \frac{2{\cdot}25R + C_r}{C_v} \qquad \ldots\ldots(2).$$

Thus the heat conductivity of normal and parahydrogen is

$$\lambda_{\text{n-H}_2} = (2{\cdot}25R + C_v^{\text{n-H}_2})\,\eta_{\text{n-H}_2}/M \qquad \ldots\ldots(3),$$

$$\lambda_{\text{p-H}_2} = (2{\cdot}25R + C_r^{\text{p-H}_2})\,\eta_{\text{p-H}_2}/M \qquad \ldots\ldots(3a).$$

Or assuming $\eta_{n\text{-}H_2} = \eta_{p\text{-}H_2}$ (compare p. 48),

$$\lambda_{p\text{-}H_2} = \lambda_{n\text{-}H_2} \frac{C_v^{p\text{-}H_2} + 2{\cdot}25R}{C_v^{n\text{-}H_2} + 2{\cdot}25R} \qquad \ldots\ldots(4).$$

For the determination of the heat conductivity Schleiermacher's method* was used, according to which the heat given up by an electrically heated wire stretched in a cylindrical cell containing the gas in question is measured.

If the cell is first filled with normal hydrogen and then with parahydrogen, and if the wire is heated with the same current, it reaches a higher temperature in the former case than in the latter, owing to the higher thermal conductivity of parahydrogen. It was shown by Bonhoeffer and Harteck that it is not necessary to compute the thermal conductivity, but the temperatures of the wire reached under certain conditions (pressure, heating current, wall temperature of the vessel) may serve as a measure of the o-p-H_2 concentration of the H_2 in the cell.

For example, the temperatures $T_{p\text{-}H_2}$ and $T_{n\text{-}H_2}$ reached in p-H_2 and n-H_2, respectively, are related to the corresponding heat conductivities in the following manner.

The heat given up (W) with the current i is expressed by

$$W_{p\text{-}H_2} = A \int_{T_0}^{T_{p\text{-}H_2}} \lambda_{p\text{-}H_2} dT = i^2 r_{p\text{-}H_2} \qquad \ldots\ldots(5),$$

and

$$W_{n\text{-}H_2} = A \int_{T_0}^{T_{n\text{-}H_2}} \lambda_{n\text{-}H_2} dT = i^2 r_{n\text{-}H_2} \qquad \ldots\ldots(5a),$$

A being a constant, depending on the geometrical dimensions of the vessel, T_0 the temperature of the wall, $r_{p\text{-}H_2}$ and $r_{n\text{-}H_2}$ the resistances of the wire at $T_{p\text{-}H_2}$ and $T_{n\text{-}H_2}$, respectively.

Using Eucken's approximate formula† for $\lambda_{n\text{-}H_2} = \alpha T$ and putting $r = \rho T$ (valid for platinum wires) we obtain

$$\frac{1}{T_{p\text{-}H_2}} \int_{T_0}^{T_{p\text{-}H_2}} \frac{C_v^{p\text{-}H_2} + 2{\cdot}25R}{C_v^{n\text{-}H_2} + 2{\cdot}25R} T\,dT = \frac{1}{T_{n\text{-}H_2}} (T_{n\text{-}H_2}^2 - T_{p\text{-}H_2}^2) \qquad \ldots\ldots(6).$$

* A. Schleiermacher, *Wied. Annalen*, **34**, 623 (1888).
† A. Eucken, *Physikal Z.* **14**, 324 (1913).

The cell actually used by Bonhoeffer and Harteck had the form shown in Fig. 2.

The platinum wire is about 20 cm. long and 0·01 mm. in diameter. It is soldered to 0·3 mm. copper wires and led through two glass eyes and held stretched by the weight of a small glass bead.

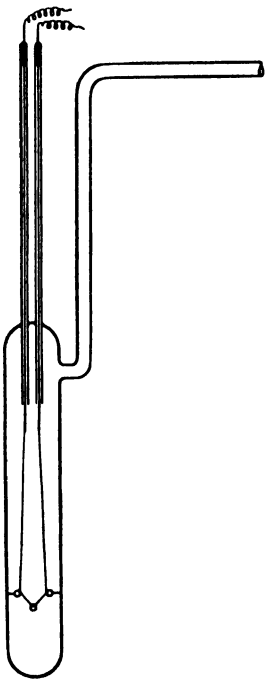


Fig. 2. Thermal conductivity cell of Bonhoeffer and Harteck.

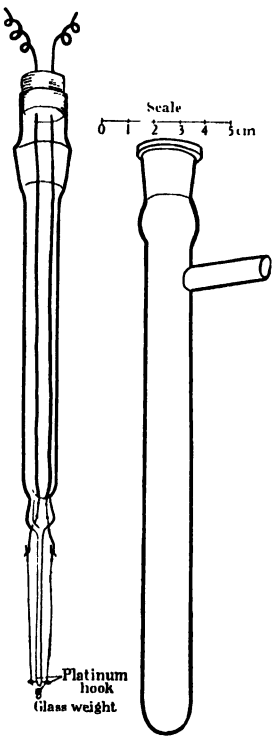


Fig. 3. Thermal conductivity cell.

The cell is immersed in liquid air or liquid hydrogen and filled to a definite pressure of 20–40 mm. Hg regulated by a precision valve or fine capillary to 0·1 mm.* (see Fig. 4).

Fig. 3 shows another practical form of a cell permitting a simple replacement if the wire is broken.

* At higher pressures heat convection may appear. At lower pressures the heat given up is considerably dependent on the pressure.

The resistance of the wire is measured by means of the Wheatstone bridge method (see Fig. 4). The heating current supplied by a storage battery of 8–12 volts is chosen to impart to the wire a temperature of 160–180° K., as the specific heats show the greatest difference in this temperature range.

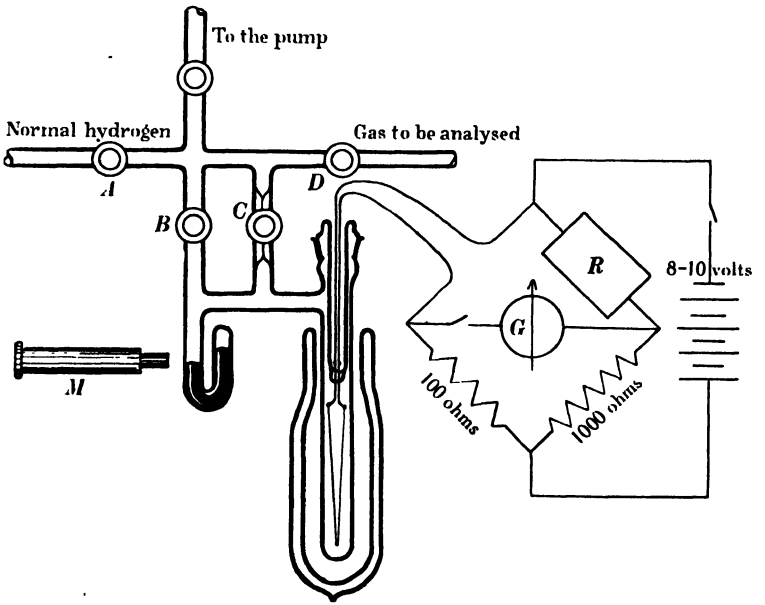


Fig. 4. Arrangement for the analysis of ortho-parahydrogen mixtures.

The following table gives some results obtained by Bonhoeffer and Harteck. The cell was immersed in liquid hydrogen ($r_0 = 32{\cdot}212$).

Percentage para H_2	Gas filled in the vessel	Resistance in ohms	Temperature °K
25	Normal H_2	111·85	203·9
99·7	Para H_2*	106·25	191·6

On the basis of these two values the composition of any ortho-parahydrogen mixture can be computed by linear inter-

* For preparation of parahydrogen, see next paragraph.

polation, for instance, a resistance of 107·13 ohms* corresponds to 88 per cent. p-H_2.

The following experiment [66] shows that this linear relation between resistance value and p-H_2 content is exactly fulfilled. Normal hydrogen (25 per cent. p-H_2) and 48 per cent. parahydrogen were mixed in different ratios. The p-H_2 concentrations of the mixtures computed by interpolation of the resistance values are practically identical with the concentrations calculated from the ratio of the mixed gases (see Fig. 5). (In this measurement a cell, type Fig. 3, immersed in

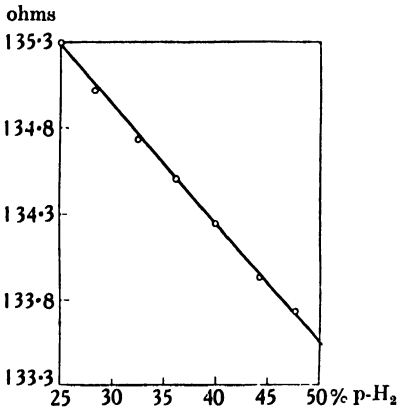


Fig. 5. Calibration curve for the determination of the ortho-parahydrogen concentration.

liquid air was used.) The sensitivity of the measurement is about 0·1 per cent.

This method was modified by Geib and Harteck [71] to measure p-o-H_2 concentration at a pressure of 0·5 mm. As at this pressure the heat given up is proportional to the pressure, the variation of the pressure was compensated in the following way.

One of the branches of the Wheatstone bridge was replaced by a second cell immersed in ice water (see Fig. 6). If the dimensions of the wires are suitably chosen the variation of

* Instead of the temperatures the resistances also can be used as a measure of the concentration.

the pressure causes the same relative change in the resistances of the cells 1 and 2, but does not influence the measurement of concentration. As the difference in the heat conductivity of the two hydrogen modifications is many times larger at low temperatures than at high temperatures the method is as sensitive as before.

For even lower pressures and for cases where only very small

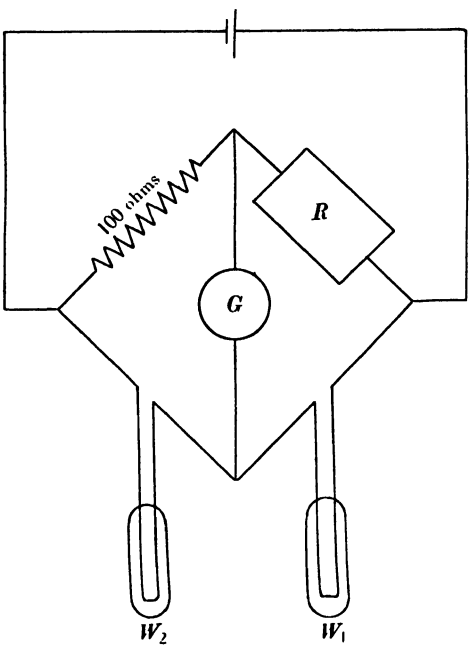


Fig. 6. Arrangement of Geib and Harteck for concentration measurements at low pressures.

amounts of gas are available the present method was improved by A. Farkas[31]. In his arrangement the cell immersed in liquid air has a volume of 2 c.c. and is provided with a platinum wire 50 mm. long and 0·01 mm. in diameter. The vessel is filled with the gas in question to a pressure of about 0·05 mm., at which the wire reaches the temperature T_1, using a heating current i_1; the current is then raised to i_2 and the temperature T_2 attained is measured. This temperature is the higher the

richer the gas in parahydrogen. Fig. 7 shows the situation for normal and parahydrogen.

The heat given up is proportional to the expression

$$\text{pressure} \cdot \int_{T_0}^{T_1} C_v dT^*$$

(T_0 = wall temperature), and, as at the temperature T_1 the

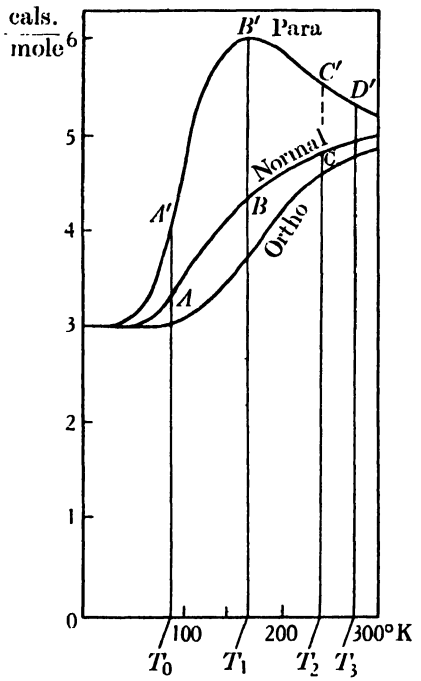


Fig. 7. The principle of Farkas' method for very low pressures.

pressure (P) is regulated to obtain the same amount of heat given up in both kinds of hydrogen, we have

$$P_{\text{p-H}_2} : P_{\text{n-H}_2} = \int_{T_0}^{T_1} C_v^{\text{n-H}_2} dT : \int_{T_0}^{T_1} C_v^{\text{p-H}_2} dT = T_0 T_1 BA : T_0 T_1 B'A' \quad \ldots\ldots(7).$$

If in normal hydrogen the temperature T_2 is attained using

* In this case the formula is valid, as the mean free path is very large compared with the dimension of the wire.

the current i_2, the corresponding temperature T_3 in para-hydrogen is given by

$$\frac{\int_{T_0}^{T_1} C_v^{\text{n-H}_2} dT}{\int_{T_0}^{T_1} C_v^{\text{p-H}_2} dT} = \frac{\int_{T_0}^{T_3} C_v^{\text{n-H}_2} dT}{\int_{T_0}^{T_3} C_v^{\text{p-H}_2} dT} \cdot \frac{T_3}{T_2} \qquad \ldots\ldots(8),$$

if it be taken that the heat given up is proportional to the resistance or in the case of platinum to the temperature of the wire.

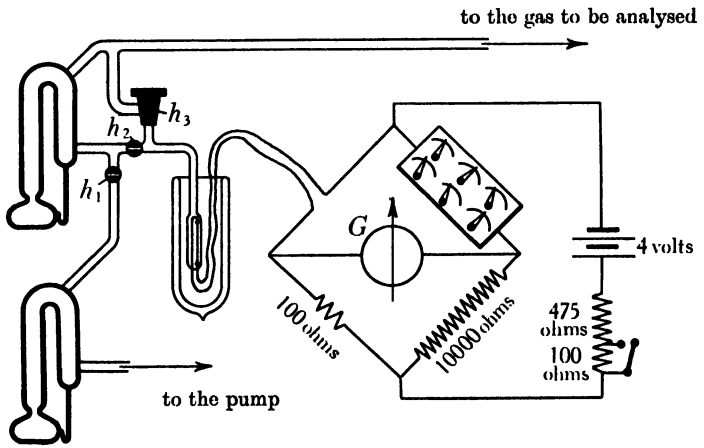


Fig. 8. The arrangement for concentration measurements at very low pressures.

If the wire is not overheated and its surface is not considerably changed by impurities (as grease, Hg, etc.) very accurate and reproducible results are obtainable. Since about 2–3 cm.^{3} H_2 (at N.T.P.) are enough for one measurement and since parahydrogen may be forced through a mercury pump practically without any conversion, and so introduced into the cell, the method can be used for any pressure provided the given amount of gas is available, as, for instance, a volume of 500 c.c. and a pressure of $4 \cdot 10^{-4}$ cm.

In a cell used,

$i_1 = 5{\cdot}2$ mAmp., $T_1 = 180°$ K., $r_1 = 84{\cdot}50$ ohms,

$i_2 = 5{\cdot}7$ mAmp., $T_2 = 250$–$260°$ K., $r_2 = 116$–122 ohms,

the latter two figures depending on the composition of the hydrogen. The experimental arrangement for this method is shown in Fig. 8.

The measurements made had to be compared with corresponding measurements of hydrogen with known composition, in the same way as in the original method of Bonhoeffer and Harteck. The computation of the concentration can again be made by linear interpolation (see Table 5).

Table 5

Gas	Percentage para H_2	r_2 in ohms
Normal H_2	25·0	115·99
	43·5	117·73
Para H_2	(97·3 computed)	122·78

2. Preparation of parahydrogen

Although at 20° K. equilibrium hydrogen consists of practically pure parahydrogen, simply cooling the hydrogen to this temperature or transitory liquefaction or solidification does not cause equilibrium to be established. The establishment of the equilibrium can, however, be catalyzed, as was discovered by Bonhoeffer and Harteck [15, 16, 17, 19]. If normal hydrogen is adsorbed on charcoal at 20° K. for some time, the gas given up on desorption is pure parahydrogen, corresponding to the thermal equilibrium.

The preparation of parahydrogen can be carried out as follows. A quartz or pyrex vessel containing 10 g. charcoal is baked out *in vacuo*. After cooling it is filled with hydrogen and saturated first at liquid air temperatures, then at liquid hydrogen temperatures. In this way several litres of hydrogen are taken up. The equilibrium is established in times ranging from some minutes to some hours,* depending on the activity† of the charcoal used. Table 6 gives the results of Bonhoeffer and Harteck's experiment. The thermal conductivity of a hydrogen

* See Keesom, Bijl and van der Horst[41].

† For the activity of different charcoals see Chapter IV, § 2(*a*).

sample drawn off from the charcoal vessel did not change after 20 minutes (constant resistance value), thus the equilibrium could be considered as established, i.e. the concentration corresponding to this resistance value could be taken to be 99·7 per cent. On this basis the other concentrations have been computed.

Table 6

Time	Resistance in ohms	Percentage para H_2 concentration
(Normal H_2	115·85	25·0)
5	107·13	88·0
10	106·35	98·3
15	106·27	99·3
20	106·25	99·7
120	106·25	99·7

Larger amounts of nearly pure parahydrogen can be obtained if the temperature of the adsorption vessel is raised a little by lowering the vessel containing the liquid hydrogen. Thus some litres of hydrogen are given up without much adjustment of the parahydrogen equilibrium to the higher temperatures. Table 7 gives the mean concentration of four portions of gas obtained in this way.

Table 7

Gas given up	Percentage para H_2 content
4 litres	97·7
1 litre	97·0
1 ,,	93·0
1 ,,	88·7

If larger amounts of pure parahydrogen are required continuously, the apparatus sketched in Fig. 9 may be used. (Cf. Farkas and Sachsse [70].) The Dewar-vessel is filled with liquid hydrogen and one part of the evaporating gas* is led directly into the adsorption vessel, the other escapes through a mercury bubbler. To obtain better insulation, the hydrogen

* The evaporating gas is very pure as all impurities are frozen out.

vessel is surrounded by a second flask containing liquid air. Such an apparatus does not need more than 1–2 litres of liquid hydrogen per week provided suitable deep and narrow vessels are used.

If liquid air only is available a gas with 42–48 per cent. p-H_2 (depending on the temperature of the liquid air) can readily be prepared in the vessel shown in Fig. 10, and by rapidly pump-

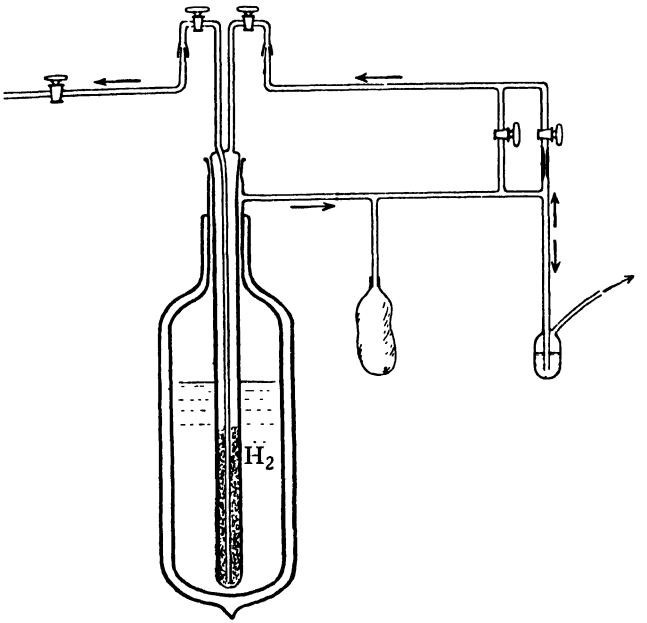


Fig. 9. Apparatus for the production of pure parahydrogen.

ing off the liquid air the parahydrogen content may be raised to 65 per cent.

According to Taylor and Sherman [78] the charcoal catalyst can be replaced by a nickel-Kieselgur preparation (obtained by reducing a NiO-Kieselgur mixture at 150° C. with hydrogen). 15 g. of this preparation containing 10 per cent. nickel produce at −183° C. up to 100 c.c. equilibrium hydrogen containing 43 per cent. per minute.

At ordinary temperatures parahydrogen is a very stable gas and can be stored in clean glass vessels for weeks without any

conversion, provided traces of oxygen are absent. In gas holders for parahydrogen mercury should be used for confining the gas, as parahydrogen is gradually converted in contact with water.* If parahydrogen is led through rubber tubing, greased taps or metal valves, no conversion is observed; at low pressures it can even pass suddenly through a mercury pump without being destroyed.

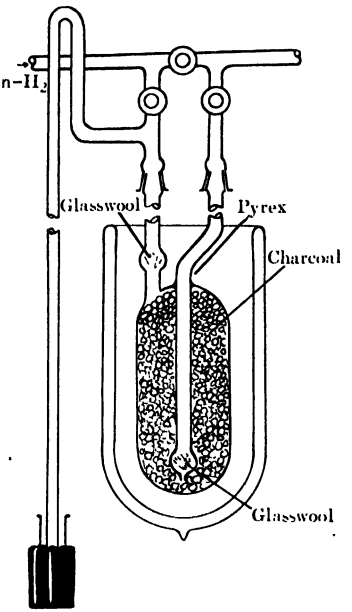


Fig. 10. The preparation of 42–48 per cent. parahydrogen.

In contact with metal catalysts (e.g. platinized asbestos), under the influence of an electrical discharge, or at temperatures of several hundred degrees, a more or less rapid reconversion occurs. Table 8 shows the influence of temperature on parahydrogen according to experiments of Bonhoeffer and Harteck [17] in which a gas containing 50 per cent. p-H_2 was streamed through a heated porcelain tube, the time of contact being one second.

Table 8

Temperature °C.	Concentration of the gas leaving the tube
700	50·0
750	49·5
800	48·0
850	47·0
900	38·0
950	31·0
1000	27·0
1050	25·5
1100	25·0

As a lecture experiment the ortho-parahydrogen conversion

* Cf. Chapter IV, § 1(*e*).

can be demonstrated in the following relatively simple way.*

Normal hydrogen, taken from a cylinder without further purification, can be converted to 45 per cent. p-H_2 in the adsorption vessel A (Fig. 11) cooled with liquid air. From the point C the hydrogen may be subjected to three different treatments:

(1) Through the tube 1,

(2) Through the porcelain or silica tube 2, heated to 900–1000° C.,

(3) Through the tube 3, filled with platinized asbestos.

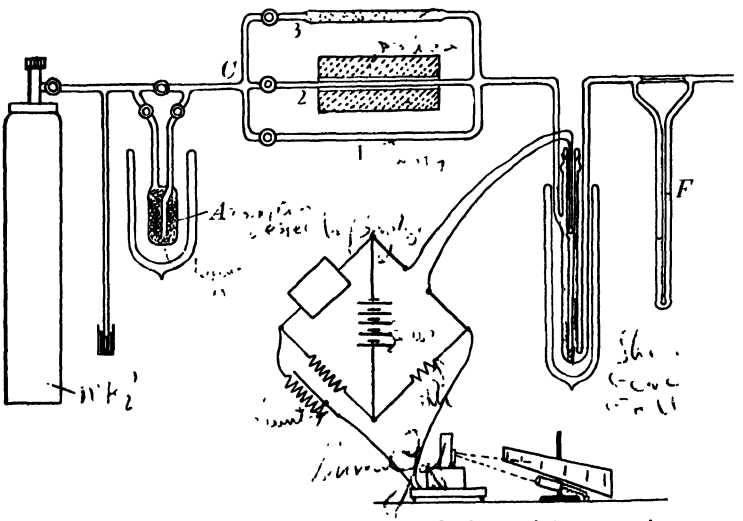


Fig. 11. Demonstration of the ortho-parahydrogen interconversion.

The conductivity cell is constructed as described on p. 22. The flow of the hydrogen amounts to 100 c.cm./minute and is controlled on the flow-meter F. In the Wheatstone bridge circuit a mirror galvanometer serves as zero instrument. If the bridge resistance and galvanometer shunt are suitably arranged, the light index of the galvanometer points to the number 25 or 45 of a large scale according as 25 or 45 per cent. p-H_2 is streaming through the cell. The demonstration of the

* These experiments are carried out by students in the physical chemistry classes of the Universities of Cambridge and of Frankfurt-am-Main.

conversion of normal hydrogen to 45 per cent. p-H_2 and the reconversion of the latter by catalysis or by high temperatures needs no further explanation.

Another experiment to demonstrate the ortho-parahydrogen conversion and re-conversion is described by Senftleben [51]. To detect a change in the ortho-parahydrogen conduction the thermal conductivity method is again used. The conductivity cell is in this case maintained at room temperatures, but the difference of 2 per cent. in the specific heats of the hydrogen modifications at this temperature still suffices to show the effect. This cell, made of quartz, is joined to a side tube containing charcoal and is filled with hydrogen at several cm. pressure. After adjustment of the Wheatstone bridge, the hydrogen is adsorbed on the charcoal by cooling the side tube with liquid air, and then again evaporated. The parahydrogen formation can be demonstrated by the deflection of the galvanometer. The re-conversion is attained by illuminating the hydrogen containing some mercury with a mercury arc. Within some minutes the deflection of the galvanometer vanishes (cf. p. 69).

While pure parahydrogen can be prepared without great difficulty, the isolation of orthohydrogen is not yet possible, as no temperature range exists in which pure orthohydrogen is the equilibrium gas. In principle it would be possible to isolate this modification by fractional distillation, but this operation could be only executed with great difficulty on account of the small difference in the heats of evaporation (cf. p. 42).

3. Specific heat

As early as 1912 Eucken [27] had observed that the specific heat of hydrogen having at room temperatures the value $\frac{5}{2}R$, in agreement with the classical theory for diatomic molecules, gradually decreased when the temperature was lowered, and below 50° K. had the value $\frac{3}{2}R$ characteristic of monatomic gases. It was soon recognized that this effect could be explained by means of the quantum theory, but no complete and exact formula representing the specific heat at low

temperatures was obtained.* The solution of this problem was achieved by Dennison [31], who pointed out that if the correct value for the moment of inertia and the correct statistical weights found from band spectra were employed, the formulae developed did not even represent qualitatively the form of the experimental curve. He showed, however, that perfect agreement between experiment and theory could be obtained if H_2 was considered as a mixture of two different modifications. His formulae have been treated in Chapter II, § 2. Curve 25 (indicating 25 per cent. p-H_2) in Fig. 12 shows

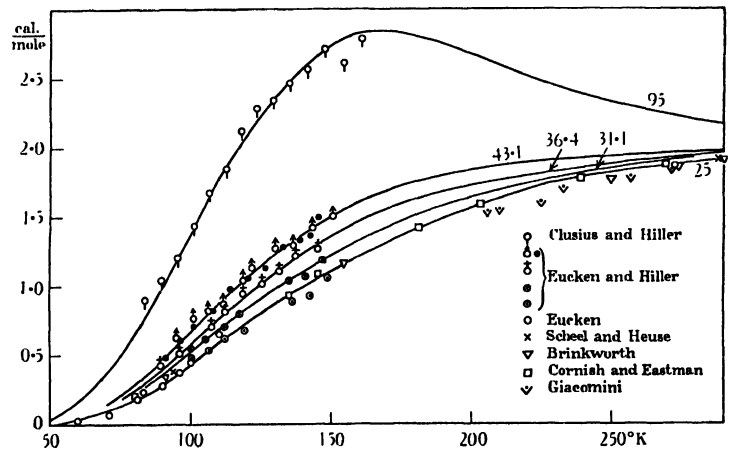


Fig. 12. The rotational specific heat of hydrogen.

the theoretical curve compared with the experimental results of Eucken [27], Scheel and Heuse [50], Partington and Howe [45], Giacomini [33], Brinkworth [20] and Cornish and Eastman [22] for normal hydrogen.

The difference between the specific heat of gaseous ortho-parahydrogen mixtures and normal hydrogen has been investigated by Eucken and Hiller [30] and Clusius and Hiller [21].

The experiments were carried out by Eucken and Hiller to prove that a change in the composition of ordinary hydrogen when kept at temperatures of about 90° K. actually took place,

* Cf. e.g. F. Krüger, *Ann. d. Physik*, **50**, 346, **51**, 450 (1916); F. Reiche, *ibid.* **58**, 657 (1919).

as predicted by theory. The apparatus was similar to that used by Eucken in 1912. The hydrogen was compressed to 50 atm. in a thin-walled steel vessel fitted with a heating coil and resistance thermometer and surrounded by an evacuated glass vessel immersed in liquid air. The specific heat was measured according to the methods of vacuum calorimetry. As the rotational heat capacity of the gas was only a small fraction of the heat capacity of the whole vessel, the precision of measurement had to be highly improved and amounted to 1–2 per cent. Immediately after filling the vessel with normal hydrogen the curve expressing the variation of the rotational specific heat with temperature was determined, and after one or two weeks the measurements were repeated. It was found that the resulting experimental curve was in good agreement with Dennison's formulae (27*a*, *b*, p. 18) provided a suitable p-H_2 concentration was used. For instance, the curves obtained after one or two weeks' storage at the temperature of liquid air corresponded to a p-H_2 concentration of 31·1 and 36·4 per cent., respectively. See Fig. 12, curves 31·1 and 36·4. Curve 43·1 refers to a hydrogen sample which contained 43·1 per cent. p-H_2 after having been kept for four days at 90° K. and under 180 atm. in contact with platinized asbestos.

The experiments of Clusius and Hiller on pure gaseous p-H_2 were carried out with the same apparatus, the p-H_2 being prepared according to Bonhoeffer and Harteck's method (see p. 28). The rotational specific heat curve of 95 per cent. p-H_2 (see Fig. 12, curve 95) is in quantitative agreement with theory. It is remarkable that the classical value of R is exceeded at 115° K. and that a maximum of 2·8 cal./degree is reached at 170° K.

The specific heat of liquid and solid p-H_2 was also measured by Clusius and Hiller [21] at 11–18° K. For this range of temperature their results (see Fig. 13) agree within the experimental error of 1–1·5 per cent. with the corresponding measurements of Simon and Lange [53] with normal H_2.

At even lower temperatures Simon, Mendelssohn and Ruhemann [54] investigated the specific heat of different ortho-para-hydrogen mixtures in the solid phase. The specific heat of the

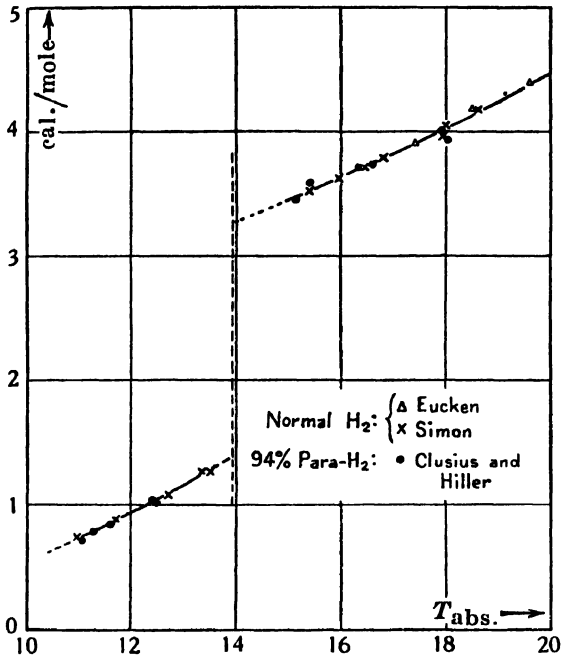


Fig. 13. The specific heat of liquid and solid hydrogen.

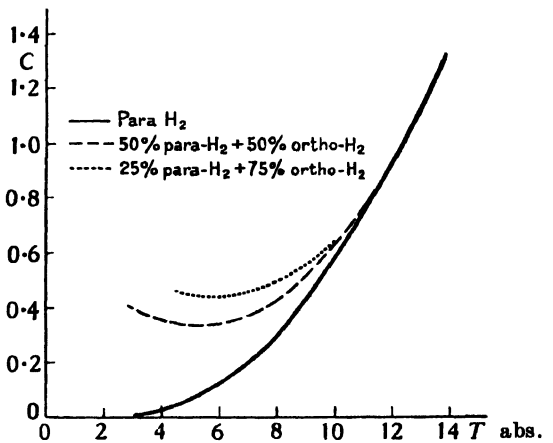


Fig. 14. The specific heat of solid hydrogen at very low temperatures.

parahydrogen crystal decreased with the temperature according to the Debye T^3 law and at 2° K. was immeasurably small. On the other hand, below 10° K. the specific heat of the mixtures rises (see Fig. 14). This anomaly can be explained on the assumption that in the crystal the lowest rotational level of the orthohydrogen ($J=1$) is split into three different levels corresponding to the statistical weight $g_J=3$ (see Chapter II, § 2, Formula 21, p. 13), and with decreasing temperature all ortho molecules revert to the lowest of these three levels. That the anomaly is actually due to this effect and not to the ultimate formation of a two-phase mixture is shown by the following fact: the deviation from the normal form of specific heat curve (ΔC) is the larger the higher the o-H_2 concentration and has no maximum at the mixture $\frac{1}{2}$o-H_2 + $\frac{1}{2}$p-H_2 as would be expected if there was a real separation into two single phases.

Assuming that the distances between the three split levels are equal, the energy difference amounts to 7·5 cal. (Private communication from F. Simon.) With this value the supplementary specific heat observed, ΔC, agrees fairly well with the theoretical formula (compare formulae (24) and (26), Chapter II)

$$\Delta C_x = -xR\frac{d}{dT}\frac{d\ln(1+e^{-\epsilon/kT}+e^{-2\epsilon/kT})}{d\,1/T} \quad \ldots\ldots(9),$$

x denoting the percentage of o-H_2.

4. Heat of conversion

The energy difference between the modifications of hydrogen computed in Chapter II cannot be confirmed spectroscopically as there are no energy levels combining both with the ortho and with the para states (see p. 45).

To measure this energy difference the heat of the ortho-parahydrogen conversion was determined by v. Elbe and Simon [24]. If normal hydrogen is adsorbed on charcoal at the temperature of liquid air, besides the heat of adsorption the heat of the conversion

$$\text{n-}H_2 \rightarrow \text{e-}H_2$$

is evolved on account of the catalytic transformation.* Desorbing the same amount of hydrogen, the heat of adsorption is taken up and the total thermal effect after the adsorption and desorption process is the heat of conversion.

The measurements have been made by means of accurate vacuum calorimetry. Liquid nitrogen or hydrogen was used as calorimetric and as thermostatic liquid.

The hydrogen or nitrogen evaporated by the heat of adsorption or conversion was collected in a burette and served as a measure of the heat effect. The heat taken up at the desorption was compensated by electric heating. The calorimeter was provided with a vacuum jacket and immersed in the liquid nitrogen or hydrogen.

The hydrogen to be adsorbed was measured in a burette and admitted to the charcoal partly (at 100 mm. Hg pressure) loaded with hydrogen. By means of a pressure regulator the same amount of hydrogen was always pumped off as had been previously adsorbed. In two series of experiments the heat of transformation of normal hydrogen to the equilibrium mixture was measured at 20·4° and 77·5° K. and in another series at 77·5° K. for the conversion from 45 to 50 per cent. p-H_2. The table gives the mean values obtained in the different series compared with the theoretical estimates.

Table 9

Temperature ° K.	Conversion in percentage para H_2	Heat effect, observed in cal.	Heat effect, theoretical in cal.
77·5	25→50	74 ± 16	78
77·5	45→50	15 ± 7	15
20·4	25→100	214 ± 4	253

As in this method small experimental errors have a large effect, the agreement between experiment and theory is as good as can be expected.

* It is evident that a charcoal of high activity must be used in these experiments.

5. Vapour pressure and melting point

The vapour pressure of parahydrogen was first measured by Bonhoeffer and Harteck[17] and compared with the vapour pressure of normal hydrogen.

At the boiling point of normal hydrogen, i.e. at 20·39° K., they found the following relationship between the para-hydrogen percentage of the gas sample and the vapour pressure of the liquid.

Table 10

Percentage para H_2	Vapour pressure at 20·39° K. in mm. Hg
98·5	786·5
98·0	786·3
92·5	785·5
80·5	781·0
25·0 (normal H_2)	760·0
100 (para H_2)	787 ±1
0 (ortho H_2)	751 ±1

The two final values were obtained by extrapolation from the linear relationship found in these experiments between the vapour pressure and the p-H_2 content.

At the triple point of normal hydrogen (13·95° K.)* there is a difference of 3 mm. between the vapour pressure of p-H_2 and n-H_2.

	Vapour pressure at 13·95° K. in mm.
Parahydrogen	57·0 ±0·1
Normal hydrogen	53·9 ±0·1

To measure the vapour pressure at the triple point H_2 was liquefied in a small vessel with a vacuum jacket cooled with liquid hydrogen. This sample was then solidified by pumping off the gas at 20 mm. pressure. Cutting off the pump the vapour pressure slowly increased on account of the very poor heat transfer from without and remained constant at the

* It was pointed out by Smits[55] that, strictly speaking, normal hydrogen being a mixture has no triple point.

triple point for about 15 minutes. The vapour pressure of p-H_2 was 0·9 mm. lower than that of n-H_2.

	Vapour pressure at the triple point in mm.
Parahydrogen	53·0 ±0·1
Normal hydrogen	53·9 ±0·1

These figures are in agreement with Giauque and Johnston's[35] observation that a hydrogen sample kept under high pressure for six months at liquid air temperatures showed a vapour pressure of 53·4 mm. at the triple point. Probably Giauque's sample contained about 50 per cent. p-H_2, and if we assume a linear relation between this vapour pressure and p-H_2 content it would actually be expected to be about 0·3 mm. less than the vapour pressure of n-H_2 at the triple point.

From their vapour pressure measurements Bonhoeffer and Harteck computed the boiling point and triple point of p-H_2 by interpolation,* finding them to be 0·13° lower than the corresponding values of n-H_2.

	Para H_2	Normal H_2
Boiling point	20·26° K.	20·39° K.
Triple point	13·82° K.	13·95° K.

The vapour pressure of parahydrogen was measured in 1931 with great precision in the Leyden laboratory. The results are in excellent agreement with the original figures of Bonhoeffer and Harteck.

Keesom, Bijl and van der Horst[41] obtained the following boiling points, vapour pressures and formulae.

	Para H_2	Normal H_2
Boiling point	−252·871° C.	−252·754° C.†

* Plotting log P (P = pressure) against $1/T$ an almost straight line is obtained in the temperature range in question.

† Heuse and Otto[37] find the boiling point of normal H_2 to be −252·780°. The difference of 0·026° is due partly to the different pressure coefficient for the helium thermometer and partly to the adjustment of the helium temperatures to the thermodynamical scale.

In the neighbourhood of the boiling point the formulae (10*a*) and (10*b*) are valid (precision $-0{\cdot}01°$), below the vapour pressure of an atmosphere the formulae (11*a*) and (11*b*) (precision $-0{\cdot}02°$).

Table 11. *Vapour pressures (interpolated)*

Temperature ° C.	Para H_2	Normal H_2
−253	732·9	708·2
−254	534·5	515·5
−255	381·7	365·0
−256	261·7	250·5
−257	174·0	166·7
−258	108·7	103·5

For p-H_2 $t = -252{\cdot}871 - 0{\cdot}00449\,(P_{\text{mm.}} - 760)$
$\quad - 4{\cdot}6 \cdot 10^{-6}\,(P_{\text{mm.}} - 760)^2$ .....(10*a*).

For n-H_2 $t = -252{\cdot}754 - 0{\cdot}00441\,(P_{\text{mm.}} - 760)$
$\quad - 5{\cdot}0 \cdot 10^{-6}\,(P_{\text{mm.}} - 760)^2$ .....(10*b*).

(The vapour pressures $P_{\text{mm.}}$ are given in mm.)

For p-H_2* $t = -260{\cdot}937 - 1{\cdot}0270 \log P_{\text{cm.}}$
$\quad - 1{\cdot}7303 \log^2 P_{\text{cm.}}$ .....(11*a*).

For n-H_2 $t = -260{\cdot}865 - 1{\cdot}0619 \log P_{\text{cm.}}$
$\quad - 1{\cdot}7233 \log^2 P_{\text{cm.}}$ .....(11*b*).

(The vapour pressures $P_{\text{cm.}}$ are given in cm.)

Since normal hydrogen in the liquid state is slowly converted to parahydrogen† a gradual increase in the vapour pressure of normal hydrogen can be observed (Keesom and co-workers [41]). This change amounts to 0·15 mm. per hour, corresponding to a change of 0·5 per cent. per hour in the p-H_2 concentration, and causes a lowering of the boiling point of normal hydrogen by 0·0008° per hour. This effect must be considered in very precise temperature measurements if the boiling point of normal hydrogen is used as fixed point of the temperature scale. If,

* On the bases of these formulae the triple points p-H_2 and n-H_2 are −259·28° and −259·17° C., respectively, i.e. the difference in the triple point amounts to 0·11°, in agreement with the figures given by Bonhoeffer and Harteck.

† Compare Chapter IV, § 1(*d*).

however, accuracy exceeding $\pm 0{\cdot}005°$ is not required, and the hydrogen is not kept more than six hours in the liquid phase, this effect may be neglected.

Considering the vapour pressure formula valid for hydrogen in the temperature range in question,

$$\log P_{\text{atm.}} = -\frac{\lambda_0}{4{\cdot}57T} + 2{\cdot}5 \log T - \frac{1}{4{\cdot}57} \int \frac{dT}{T^2} \int C_{\text{condens.}}\, dT + i \quad \ldots\ldots(12),$$

where λ_0 denotes the heat of evaporation at the absolute zero, $C_{\text{condens.}}$ the specific heat of condensed hydrogen and i the chemical constant, the cause of the different vapour pressure of para- and normal hydrogen may be recognized. The differences in the two chemical constants cancel with the terms for the heat content of the condensate (see Chapter III, § 10). Thus the difference in the vapour pressures is due to a difference in the heats of evaporation. According to calculation the heat of evaporation of p-H_2 is about 0·65 per cent. less than that of n-H_2, showing stronger van der Waals' forces between the rotating ortho molecules than between the non-rotating para molecules.* From the difference in the sublimation pressure curves a difference of the same magnitude in the heat of sublimation must also be expected.

The heat of fusion of p-H_2 according to Clusius and Hiller [21] is $28{\cdot}0 \pm 0{\cdot}3$ cal. The good agreement with the heat of fusion of n-H_2, 28·0 cal., obtained by Simon and Lange [53], may be accidental, for probably in this case, too, a small difference (of the magnitude of the experimental error) exists.

As the heat of fusion and the heat of evaporation of normal and parahydrogen agree to within 1 per cent., the energy difference between gaseous ortho- and parahydrogen, i.e. 337 cal., is maintained both in the liquid and in the solid phase. This can be explained by assuming that the ortho molecules are freely rotating in the liquid and in the crystal. This behaviour may be connected with the relatively small heat of fusion and of evaporation compared with the rotational energy.† The

* Corresponding to this fact a minute difference in the heat of adsorptions of o-H_2 and p-H_2 could be expected. Compare Ubbelohde [57].

† For theoretical treatment see Pauling, *Phys. Rev.* **36**, 473 (1930).

evidence for the unperturbed molecular rotation actually occurring in the liquid is given by the Raman effect observed by McLennan and McLeod[13] in liquid H_2.*

6. Spectra

In the normal state of the H_2 molecule the rotational levels with even quantum numbers are para states and the rotational levels with odd quantum numbers are ortho states. Similarly, ortho and para states can also be distinguished in the higher electronic levels of the excited molecule, in which the ortho states again have the higher statistical weights. Apart from the normal state the two lowest singlet levels of the excited

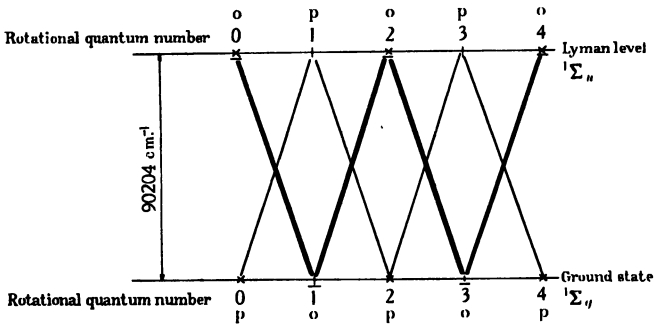


Fig. 15. Levels of the Lyman bands.

H_2 molecule are the simplest. The so-called Lyman and Werner bands, corresponding to the combination of the singlet levels with the normal state, have all the characteristics of the H_2 spectrum, which are due to the distinctive differences between the ortho and para states.

Fig. 15 shows the levels of the Lyman bands. The two horizontal lines represent the electronic levels and the successive rotational states are indicated horizontally (the distances are not proportional to energy differences). For the sake of clearness all vibrational levels are omitted. The normal state is a $^1\Sigma_g$ state,† the first excited state a $^1\Sigma_u$ state.

* See next paragraph.

† The symbols employed are those used by Ruark-Urey (cf. p. 4, footnote), W. Jevons, *Report on Band-spectra of Diatomic Molecules*, Cambridge University Press (1932), and Weizel, *Bandenspektren* [*Wien-Harms Handbuch der Experimentalphysik, Ergänzungsband*] (1933).

The subscripts g and u indicate "even" and "odd" (gerade and ungerade) levels whose electronic wave function (χ) retains or changes its sign respectively, if the electrons are reflected at the mid point of the molecule (Wigner and Witmer [13]).

The classification of the rotational levels into ortho and para states is based on the antisymmetry postulate of the total wave function represented approximately by $\psi = \chi . \psi_J . \Sigma$. The rotational wave function ψ_J retains its sign for even quantum numbers and changes it for odd ones if both electrons and protons are reflected at the mid point.* The corresponding levels are described as positive and negative and marked with $\times$ and |, respectively.† As an interchange of the nuclei is equal to a reflection of electrons and protons and to an additional reflection of electrons, the even positive and the odd negative states are symmetrical in the spatial co-ordinates of the nuclei, while the odd positive and even negative states are antisymmetrical (underlined).

To obtain a total wave function antisymmetrical in the spatial and spin co-ordinates of the nuclei the levels symmetrical in the spatial co-ordinates are to be connected with antiparallel nuclear spins having an antisymmetrical spin function and vice versa. Thus levels antisymmetrical in the spatial co-ordinates of the nuclei have parallel nuclear spins and are the ortho levels (underlined). Since there can only be combination between ortho levels and between para levels and the rotational quantum number may change at the most by unity,‡ the marked lines are obtained in the bands. The thick lines represent the ortho transitions and the thinner lines the para transitions. Owing to the higher statistical weight of the ortho states the ortho lines are more intensive than the para lines. This so-called alternation of intensities, discovered in 1924 by Mecke [11], is a very characteristic property of the band spectra emitted by homonuclear

* I.e. if the line joining the nuclei is turned in the opposite direction. See p. 8.

† Kronig, *Band Spectra and Molecular Structure*, Cambridge University Press (1930), designates them "even" ($\times$) and "odd" ($\circ$).

‡ For selection rules, see e.g. Kronig.

molecules possessing a nuclear spin. The alternation of intensity can be recognized distinctly in the Lyman bands. As a consequence of the selection rule ortho → ortho, para → para the energy difference of two successive rotational levels ($J-1$ and J) given by the formula (20), Chapter II, p. 13, as $2J\frac{h^2}{8\pi^2\bar{I}}$ cannot be found from the spectrum.

Fig. 16 shows an analogous scheme for the Werner bands representing a $^1\Pi_u \rightarrow {}^1\Sigma_g$ transition. The band lines are somewhat more numerous as in the $^1\Pi_u$ state two levels, one positive and one negative,* correspond to each rotational quantum number. In these bands the alternation of intensities is only slightly in evidence [49].

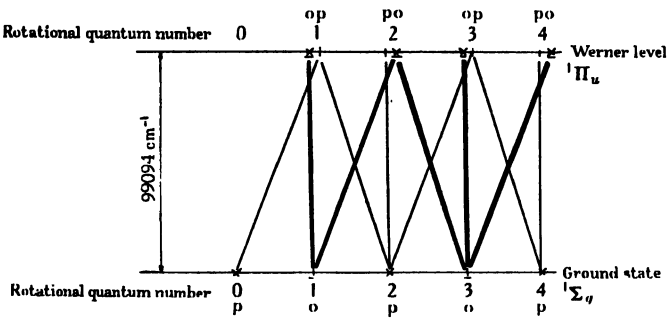


Fig. 16. Levels of the Werner bands.

The other bands of H_2† also show to a greater or less degree the alternation of intensity, but the treatment of these bands may be omitted on account of their complicated structure.

The intensity measurement of the band lines in the so-called many line spectrum of H_2 was carried out by Kapuczinski and Eymers [38]. On the basis of their measurements the intensity ratio of ortho to para lines is found to be equal to the theoretical value of 3 : 1.

The spectrum of nearly pure parahydrogen was compared with that of normal hydrogen by Bonhoeffer and Harteck. In

* The difference between the distance of two successive positive levels and the distance of two successive negative levels, the so-called combination defect, cannot be computed directly from the spectrum. Assuming the validity of formula (20), p. 13, for the normal state, it amounts to several cm.$^{-1}$

† See e.g. Weizel (footnote, p. 43).

the parahydrogen spectrum the para lines, weak in the normal spectrum, were very strong, while the normally intense ortho lines were but faintly visible. Fig. 17 shows the complete conversion of the intensity ratio in the so-called Fulcher bands. The para lines are marked with points. The spectrum was taken in emission in streaming gas to prevent a re-excitation of molecules which had already been converted to normal hydrogen by the electric discharge.*

Beutler[1] showed that the selection rule ortho→ortho, para→para is valid for excitation by collision even if both the electronic and vibrational quantum numbers are changed. The Lyman bands are selectively excited by argon atoms (in four different levels with an energy of about 94000 cm.$^{-1}$), when the

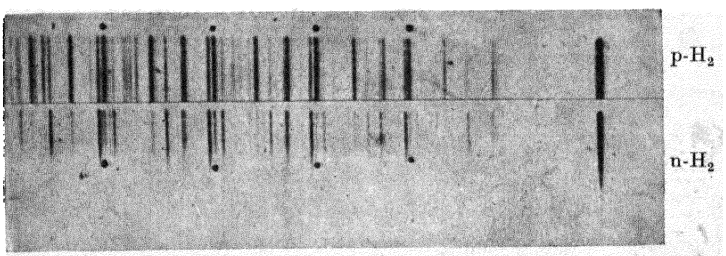


Fig. 17. The spectrum of parahydrogen.

transitions $^1\Sigma_g^0(2) \rightarrow {}^1\Sigma_u^3(6)$ and $^1\Sigma_g^0(4) \rightarrow {}^1\Sigma_u^3(6)$ are absent in spite of high resonance and resulting efficient transfer of energy. (The numbers in brackets indicate the rotational quantum number, the superscripts to the right of the Σ the vibrational quantum numbers.) According to the selection rule these combinations are actually forbidden, as in the normal $^1\Sigma_g$ state even rotational quantum numbers represent para levels, and in the $^1\Sigma_u$ state ortho levels (see Fig. 15).

The alternation of intensity is also observed in the Raman spectra of H_2, both in the liquid and in the gas. McLennan and McLeod[43] investigated liquid hydrogen, and, according to the selection rule of Raman spectra (in this case $\Delta J = +2$),† they found the transition $J = 0 \rightarrow 2$ with the frequency 354 cm.$^{-1}$ and the transition $1 \rightarrow 3$ with the frequency 588 cm.$^{-1}$

* See p. 31. † See Kronig, *Band Spectra*, p. 108.

It is remarkable that in spite of the condensation these frequencies do not deviate appreciably from the corresponding frequencies computed from band spectra (347 and 578 cm.$^{-1}$, respectively). The ortho transition $1 \rightarrow 3$ is more intense than the para transition $0 \rightarrow 2$, on account of the higher concentration of orthohydrogen in normal hydrogen when liquefied. McLennan, Smith and Wilhelm [44] observed that the intensity of the para transition $0 \rightarrow 2$ increased when the liquid hydrogen had been stored for some time, owing to the ortho-para conversion taking place gradually in the liquid.* The experiments of McLennan and McLeod are of great importance, as they showed for the first time that at 20° K. hydrogen molecules occupy the rotational levels 0 and 1, according to Dennison's theory, instead of all reverting to the lowest level as postulated by the equilibrium.

In his experiments on the Raman effect in gaseous H_2, Rasetti [47, 48] obtained the same results as McLeod and McLennan: the ortho transitions were more intense (cf. [11]) and the observed frequencies were in complete agreement with theory.

C. and M. Cuthbertson [23] compared the refractive index of 50 per cent. p-H_2 with that of n-H_2, but for the mercury line used no difference whatever was found.

7. Chemical properties

Chemical and electrochemical properties

In some cases a difference in the chemical reactivity of the two hydrogen modifications might be expected. For instance, the union of hydrogen and iodine, which takes place according to the equation

$$H_2 + I_2 = 2HI,$$

could proceed with different velocities for the two modifications.† This reaction, therefore, might be further investigated.

* See p. 76, Chapter IV, § 1(*d*).

† Rosenbaum and Hogness [48*a*] have investigated the reaction between I_2 and p-H_2 and found the p-H_2 being converted to n-H_2 during the reaction. This was mainly due to the reverse reaction $2HJ = H_2 + I_2$ and to the influence of the paramagnetic I-atoms (cf. Chapter IV, § 1 (*e*)). These experiments, however, do not allow conclusions to be drawn as to whether o-H_2 and p-H_2 react with the same speed.

On the other hand, the thermal dissociation of ortho- and of parahydrogen differs considerably (see § 10). This effect could be observed in reactions involving H atoms, (e.g. H_2-O_2 reaction), but as yet no suitable experiments to show this effect with certainty have been carried out.*

According to § 10 (p. 56) the difference of the free energy of p-H_2 and n-H_2 is large enough to cause a potential difference of 35 millivolts in suitable hydrogen electrodes. The absence of this effect, using platinized platinum electrodes, is due probably to the immediate catalytic transformation of p-H_2 in contact with the electrode (cf. Bonhoeffer and Harteck [17]).

8. Cross-sectional area, viscosity and crystal structure

The cross-sectional areas of normal and parahydrogen presented to 0·2–9 volt-electrons were measured by Ramsauer and Kollath [46] and were found to be equal within the experimental error of $\pm 2{\cdot}5$ per cent.

Harteck and Schmidt [86] came to the same conclusion with regard to the viscosity. The coefficient of viscosity η is given by the expression

$$\eta = \frac{M}{N} \cdot \frac{\bar{v}}{4\pi d^2} \cdot \frac{T}{C+T} \qquad \ldots\ldots(13),$$

M designating the molecular weight, $\bar{v}$ the root mean square velocity, d the molecular diameter, N Avogadro's number and C Sutherland's constant. A difference in the viscosity of para and normal H_2 would be caused by any difference in the corresponding Sutherland's constants, as might be expected on the basis of the vapour pressures.† Therefore, instead of measuring the viscosities directly, their variation with temperature was compared.

* The experiments of Goldmann, *Z. f. physikal. Chemie*, B, 5, 305 (1929), showing the same explosion limit for both modificatious, do not allow any conclusions to be drawn from them, as under his experimental conditions the p-H_2 was converted by the oxygen, before the measurements were made (cf. Chapter IV, § 1(*e*)).

† As is well known the Sutherland constant is determined by the mutual attraction of the molecules.

The apparatus used consisted of two capillary tubes with a pressure gauge between them. One of the capillaries was heated to 100° C., the second cooled to temperatures of 0°, −185° and −253° C. When hydrogen streamed through the apparatus the pressure measured was dependent on the temperature of the outlet capillary but independent of the composition of the gas in the wide range of temperatures investigated. From these results it follows that both modifications have the same Sutherland constant and therefore the same viscosity (within 1 per cent.).

The crystal structure of p-H_2 was investigated by Keesom, de Smedt and Mooy [39, 40] at 2° K. Their X-ray diagrams are in good agreement with a hexagonal close packing structure with $a = 3{\cdot}75$ Å. and $c/a = 1{\cdot}633$, the elementary cell containing two molecules. At 2° K. the computed density amounts to 0·088. This result is in disagreement with Wahl's* experiments, according to which (normal) hydrogen is isotropic at the melting point, i.e. it has a cubic structure (cf. *International Critical Tables*, **1**, 104 (1926)). This contradiction could be explained by assuming either that n-H_2 and p-H_2 have different crystal structures, or that between 2° and 14° K. a transformation cubic→hexagonal occurs, though the measurements of Simon (see p. 37) exclude such an effect, at all events for p-H_2.

9. Magnetic properties

The magnetic moment of the H_2 molecule is composed of two parts: one part originates from the nuclear spin, zero in p-H_2 molecules (antiparallel nuclear spins) and twice the value of the magnetic moment of the proton in o-H_2 molecules, the other part is caused by the rotational motion of the molecules and depends on the rotational quantum number.

The magnetic moment of ortho- and parahydrogen was measured by Estermann, Frisch and Stern [25, 26, 32] according to the Stern-Gerlach method.

This well-known method consists in deflecting a molecular

* W. Wahl, *Proc. Roy. Soc.* A, **88**, 61 (1913).

ray by an in-homogeneous magnetic field. Denoting by $\frac{dH}{dx}$ the in-homogeneity of the field, μ the magnetic moment, M the mass, v the velocity of the particle and l the length of the field, the deflection ΔS is given by

$$\Delta S = \frac{1}{2}\frac{dH}{dx}\cdot\frac{\mu}{M}\left(\frac{l}{v}\right)^2 \qquad \text{.....(14).}$$

In the apparatus used the in-homogeneity of the field was 2.10^5 gauss/cm. and its length $l = 10$ cm. For the mean velocity of 900 cm./sec. (at liquid air temperatures) this field gives a deflection of 0·04 mm. per nuclear magneton, a nuclear magneton being 1/1840 part of Bohr's magneton $= 0{\cdot}5.10^{-23}$ C.G.S. The intensity distribution in the deflected ray was measured by means of a minute Pirani gauge with a slit which could be moved perpendicularly to the beam.

At liquid air temperatures practically all para molecules occupy the rotational level zero and, therefore, at this temperature p-H_2 was found to be non-magnetic. From deflection experiments at 195° K. (23 per cent. of the molecules in the rotational level 2) and at 292° K. (46 per cent. in the level 2) the magnetic moment of the rotation with the quantum number 2 was found to be about 2 nuclear magnetons. Assuming that the magnetic moment of the rotation with the quantum number 1 is half this value, the deflection of the normal H_2 ray at liquid air temperatures gave as the nuclear moment of the orthohydrogen molecule 5 nuclear magnetons. Thus the magnetic moment of the proton is found to be equal to 2·5 nuclear magnetons*. This is a remarkable result, as the proton was supposed to have the moment of 1 nuclear magneton. While no explanation as yet exists for this discrepancy, Wick[58] succeeded in estimating the rotational magnetic moment. Assuming that the H_2 molecule is not rotating as a rigid body, but that the electron cloud is rotating slightly more slowly than the nucleus, he obtains 0·35–0·92 nuclear magnetons for the rotation with the quantum number 1, in adequate agreement with experiment.

* Rabi, Kellog and Zacharias (*Phys. Rev.* **45**, 761 (1934)) obtained the value $3{\cdot}15 \pm 0{\cdot}3$ using a similar method for atoms.

10. Entropy, free energy and chemical constant

(a) *Entropy*

The entropy of hydrogen in thermal equilibrium with regard to the ortho-para concentration (e-H_2) is given, in general, by the formula (cf. Giauque[31])

$$S_{\text{e-H}_2} = R\left[\frac{5}{2}\ln T - \ln P + \frac{5}{2} + \ln \frac{(2\pi M)^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3 N^{\frac{3}{2}}}\right] + R\left[\ln Q + T\frac{d\ln Q}{dT}\right] \quad \text{.....(15),}$$

with P = pressure, M = molecular weight and

$$Q = Q_e + Q_o = \sum_{J=0,2,4,\ldots} (2J+1)\, e^{-\frac{BJ(J+1)}{kT}} + 3 \sum_{J=1,3,5,\ldots} (2J+1)\, e^{-\frac{BJ(J+1)}{kT}} \quad \text{.....(16).}$$

In this expression the first term represents the translational entropy* ($S_{\text{trans.}}$) and the second the rotational entropy† ($S_{\text{rot.}}$).

Thus we find the entropy of hydrogen at N.T.P. ($P = 1$ atm., $T = 298{\cdot}1°$ K.)

$$S^\circ_{\text{e-H}_2} = 28{\cdot}090 + 5{\cdot}889 = 33{\cdot}98 \text{ cal./degree} \quad \text{.....(17).}$$

As at this temperature equilibrium hydrogen and normal hydrogen are practically identical, this is simultaneously the entropy of normal hydrogen.

* Cf. e.g. Lewis-Randall, *Thermodynamics and the free energy of chemical reactions*, McGraw-Hill Book Co., Inc., New York, 1923.

† This term is obtained from

$$dS_{\text{rot.}} = C_{\text{rot.}}\, d\ln T$$

with formula (24) and (26), Chapter II.

$$S - S_0 = -R\int_0^T \frac{d}{dT}\frac{d\ln Q}{d1/T}\, d\ln T = R\left[\ln Q + T\frac{d\ln Q}{dT}\right]_0^T = R\left[\ln Q - \ln Q_{T=0} + T\frac{d\ln Q}{dT}\right],$$

or as

$$S_0 = R\ln Q_{T=0}$$

$$S = R\left[\ln Q + T\frac{d\ln Q}{dT}\right].$$

Replacing Q by Q_e or by Q_o we obtain the entropy for parahydrogen or orthohydrogen, respectively:

$$S_{\text{p-H}_2} = S_{\text{trans.}} + R\left[\ln Q_e + T\frac{d\ln Q_e}{dT}\right] \quad \text{.....(15}a\text{)},$$

$$S_{\text{o-H}_2} = S_{\text{trans.}} + R\left[\ln Q_o + T\frac{d\ln Q_o}{dT}\right] \quad \text{.....(15}b\text{)}.$$

For any ortho-parahydrogen mixture containing a fraction x of parahydrogen the entropy at any temperature is given by

$$S_{x\text{-H}_2} = xS_{p\text{-H}_2} + (1-x)S_{\text{o-H}_2} - R[x\ln x + (1-x)\ln(1-x)] \quad \text{.....(18)},$$

the last term representing the entropy of mixing which always appears in gaseous mixtures.

At low temperatures (below 20° K.), indicated by suffix I for equilibrium hydrogen, i.e. for parahydrogen, the rotational entropy vanishes as $Q_{\text{I}} = 1$ and therefore

$$S_{\text{I}}^{\text{e-H}_2} = S_{\text{I}}^{\text{p-H}_2} = S_{\text{trans.}} \quad \text{.....(19)}.$$

For orthohydrogen, $Q_{\text{I}} = 9$ (i.e. the statistical weight of the lowest level), we obtain

$$S_{\text{I}}^{\text{o-H}_2} = S_{\text{I}}^{\text{p-H}_2} + R\ln 9 \quad \text{.....(19}a\text{)}.$$

According to the formula (18) for mixtures the entropy of normal hydrogen at low temperatures is given by

$$S_{\text{I}}^{\text{n-H}_2} = S_{\text{I}}^{\text{p-H}_2} + R\left(\tfrac{3}{4}\ln 3 + \ln 4\right) = S_{\text{I}}^{\text{p-H}_2} + 4{\cdot}39 \quad \text{.....(19}b\text{)},$$

i.e. this entropy exceeds the entropy of parahydrogen by 4·39 E.U. (cal./degree per mole). The same entropy difference exists between normal hydrogen and parahydrogen in the solid phase.

Of these 4·39 entropy units at temperatures below 12°, $\frac{3}{4}R\ln 3 = 1{\cdot}64$ E.U. are gradually given up by the transition of the ortho molecules to the lowest of the three rotational levels which result from the splitting up of the first ortho level in the solid. The entropy loss actually observed by Simon, Mendelssohn and Ruhemann ([54], cf. p. 35), amounted to 0·7 E.U. in the temperature range 2–12° K. (cf. p. 37, formula (9)).

The remainder, $R\ln 4 = 2{\cdot}75$ E.U., represents the entropy due to the nuclear spin and will probably be diminished at extremely low temperatures by a further $\frac{3}{4}R\ln 3$ by the transition of the molecules to the lowest of the three levels caused by the nuclear spin, while the entropy of mixing (1·11 E.U.) may persist until the ortho- and parahydrogen phases are separated.

At high temperatures (indicated by suffix II) above 300° K., when the ortho : para hydrogen ratio is equal to 3 : 1, i.e. $3Q_e = Q_o$, Q has the form

$$Q_{\mathrm{II}} = \tfrac{4}{2}\sum_{J=0,1,2,\ldots}(2J+1)e^{-\frac{BJ(J+1)}{kT}} = \int_0^\infty (2J+1)e^{-\frac{BJ(J+1)}{kT}}dJ = \frac{16\pi^2 IkT}{h^2} \quad \ldots\ldots(20),$$

and thus we obtain

$$S_{\mathrm{II}}^{\mathrm{e\text{-}H_2}} = S_{\mathrm{trans.}} + R\left[\ln\frac{16\pi^2 kI}{h^2} + 1 + \ln T\right] \quad \ldots(21)$$

or, with the numerical values,

$$S_{\mathrm{II}}^{\mathrm{e\text{-}H_2}} = R\left[\tfrac{7}{2}\ln T - \ln P - 2{\cdot}84\right] \quad \ldots\ldots(21a).$$

Since at high temperatures $Q_o = \frac{3Q_{\mathrm{II}}}{4}$ and $Q_e = \frac{Q_{\mathrm{II}}}{4}$, the following expressions are valid for the entropy of ortho-hydrogen and for the entropy of parahydrogen, respectively:

$$S_{\mathrm{II}}^{\mathrm{o\text{-}H_2}} = S_{\mathrm{II}}^{\mathrm{e\text{-}H_2}} - R\ln\tfrac{4}{3} = S_{\mathrm{II}}^{\mathrm{e\text{-}H_2}} - 0{\cdot}59\ \mathrm{E.U.} \quad \ldots\ldots(21b),$$

$$S_{\mathrm{II}}^{\mathrm{p\text{-}H_2}} = S_{\mathrm{II}}^{\mathrm{e\text{-}H_2}} - R\ln 4 = S_{\mathrm{II}}^{\mathrm{e\text{-}H_2}} - 2{\cdot}75\ \mathrm{E.U.} \quad \ldots\ldots(21c).$$

It must be added at once that the entropy values given above, representing the absolute entropies including the nuclear spin entropy, cannot be used in combination with entropy values of other gases for the calculation of gaseous equilibria, as the entropy due to the nuclear spin for the other gases is not always known.

Gibson and Heitler [36] showed, however, that in gaseous reactions at high temperatures the nuclear spins of the reactant gases mutually cancel, as each atom preserves its nuclear spin unchanged after the reaction has taken place. Therefore gaseous equilibria can be treated correctly, omitting the spin

entropy altogether, as has been done hitherto. Thus the spin entropy, amounting to $R \ln 4 = 2{\cdot}75$ E.U., has to be subtracted from the values given by formulae (21) and (17) if the entropy is to be used to calculate gaseous equilibria involving normal hydrogen at high temperatures. In the standard state the entropy of normal hydrogen is then

$$33{\cdot}98 - 2{\cdot}75 = 31{\cdot}23 \text{ E.U.}$$

Table 12

Change of state	Entropy change	
Solid heated from 0–13·95° K.	$\Delta S = \int_0^{13\cdot95} C_{\text{solid}}\, d \ln T$, $C_{\text{solid}} = 464{\cdot}5 \left(\frac{T}{\theta}\right)^3$, $\theta = 91$	0·52
Melting	$\Delta S = \frac{28{\cdot}0}{13{\cdot}95}$	2·01
Evaporation at 53·8 mm. pressure	$\Delta S = \frac{217{\cdot}8}{13{\cdot}95}$	15·61
Correction for ideal gas	According to Berthelot 0·13, van der Waals 0·03	0·08 ± 0·05
Compression to atmospheric pressure	$\Delta S = RT \ln \frac{53{\cdot}8}{760}$	− 5·26
Gas heated to 298·1° K.	$\Delta S = \int_{13\cdot95}^{298\cdot1} C_p\, d \ln T$ (according to Cornish and Eastman)	16·73
		29·69 ± 0·05
	Additional entropy of n-H_2 at 0° K.	4·39
		34·08 ± 0·05

On the other hand, the spin entropy must not be neglected if the reaction is taking place at low temperatures or if it involves ortho-parahydrogen mixtures differing from the high temperature ratio 3 : 1.*

To show that the value of the entropy $S^\circ_{\text{c-H}_2} = 33{\cdot}98$ (p. 51)

* Strictly speaking at high temperatures real equilibrium only exists if normal hydrogen is involved, e.g. in the case of the iodine-parahydrogen reaction we have

$$\text{p-H}_2 + \text{I}_2 \rightarrow 2\text{HI} \rightleftarrows \text{n-H}_2 + \text{I}_2.$$

The example of the H_2 dissociation will show, however, that the composition of the hydrogen must actually be taken into consideration. See p. 58.

was correct, the entropy change of hydrogen had to be determined experimentally from the absolute zero to 298·1° K., carrying out a change of state in which the ortho-parahydrogen equilibrium is always established at the prevailing temperature. Thus it was necessary to start with solid parahydrogen at the absolute zero, heat it to the melting point, melt, evaporate, compress to atmospheric pressure and finally heat the gas to 298·1° K., always establishing the actual ortho-parahydrogen equilibrium. The entropy change due to the last step, however, cannot be determined, as the corresponding specific heat curve (Fig. 1, curve e-H_2) has not yet been obtained experimentally. Therefore another method is chosen, starting with normal H_2 and adding the supplementary entropy of normal hydrogen at low temperatures (see formula (19*b*), p. 52) to the experimental value.* The table shows the result according to Giauque's computation [31].

As this value is in excellent agreement with the theoretical entropy, 33·98, the entropy problem of hydrogen, which caused so much misunderstanding and error, can be regarded as finally solved and the entropy given above represents the true value without doubt.

(*b*) *Free energy*

The free energy of hydrogen is expressed by the formula

$$F = E + RT - TS \qquad \text{.....(22),}$$

or, with

$$E = E_0 + \tfrac{3}{2}RT + RT^2 \frac{d \ln Q}{dT} \qquad \text{.....(23)}$$

(E_0 = zero point energy; the vibrational energy is omitted),

$$F = E_0 - RT\left[\frac{5}{2}\ln T - \ln P + \ln \frac{(2\pi M)^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3 N^{\frac{3}{2}}} + \ln Q\right] \qquad \text{.....(24).}$$

We obtain for the free energy difference of the two modifications

$$\Delta F = \Delta E_{\text{rot.}} - T\Delta S \qquad \text{.....(25)}$$

* The extrapolation is not correct as it is known that there is an anomaly in the specific heat of solid n-H_2 (see p. 37), but it is permissible since the whole entropy change due to this anomaly is contained in the supplementary term 4·39 E.U.

($\Delta E_{\text{rot.}}$ may be obtained from Table 4, p. 19), e.g. at 298·1° K., in the case of ortho- and normal hydrogen

$$\Delta F^\circ = 4\cdot45 - 298\cdot1\,(-R\ln\tfrac{1}{3}) = 22\cdot04\,\text{cal.}$$

or para- and normal hydrogen

$$\Delta F^\circ = -13\cdot35 - 298\cdot1\,(-R\ln 4) = 806\cdot42\,\text{cal.}*$$

(c) *Chemical constant*

In general the chemical constant† of hydrogen (i) is defined by the equation

$$i = \frac{S^*}{4\cdot57} - C_p \qquad \text{.....(26),}$$

where S^* represents the expression in the entropy formula (see formula (15), p. 51), which does not contain the temperature and the pressure and C_p the specific heat at constant pressure. Thus the chemical constants are obtained without any difficulty from the corresponding entropies:

Low temperatures (< 20° K.)

$$\begin{cases} i_{\text{I c-H}_2} = i_{\text{I p-H}_2} = \log\dfrac{(2\pi M)^{\frac{3}{2}}k^{\frac{5}{2}}}{h^3 N^{\frac{3}{2}}} = -1\cdot132, \\ i_{\text{I o-H}_2} = i_{\text{I p-H}_2} + \log 9 = -0\cdot177, \\ i_{\text{I n-H}_2} = i_{\text{I p-H}_2} + \log 4 + \tfrac{3}{4}\log 3 = -0\cdot171; \end{cases}$$

High temperatures (> 300° K.)

$$\begin{cases} i_{\text{II c-H}_2} = i_{\text{II n-H}_2} = i_{\text{I c-H}_2} + \log\dfrac{16\pi^2 Ik}{h^2} = -2\cdot759, \\ i_{\text{II p-H}_2} = i_{\text{II n-H}_2} + \log\tfrac{1}{4} = -3\cdot361, \\ i_{\text{II o-H}_2} = i_{\text{II n-H}_2} + \log\tfrac{3}{4} = -2\cdot884. \end{cases}$$

In intermediate temperature ranges naturally i_{I} is to be used, but the dependence of the rotational specific heat on temperature must be taken into consideration in the appropriate manner.

For ortho-parahydrogen mixtures containing the fraction x of parahydrogen the formula

$$i_{x\text{-H}_2} = x i_{\text{p-H}_2} + (1-x)\,i_{\text{o-H}_2} - [x\log x + (1-x)\log(1-x)] \qquad \text{.....(27)}$$

is again valid.

* As 23,000 cal. corresponds to 1 volt, this difference of free energy is equal to 35 Mv. (cf. p. 48).

† Cf. Simon[52], Eucken[29], Ludloff[42], Stern[56].

Strictly speaking, in the vapour pressure (P) formula of hydrogen,

$$\log P = \frac{-\lambda_0}{4{\cdot}57T} + \frac{5}{2}\log T - \frac{1}{4{\cdot}57}\int_0^T \frac{dT}{T^2}\int C_{\text{condens.}}\,dT + i_{\text{I}} \qquad \text{.....(28)}$$

(λ_0 = heat of evaporation at the absolute zero, $C_{\text{condens.}}$ = specific heat of the condensed H_2), the proper i_{I} constants are to be inserted, i.e. $-1{\cdot}132$ for parahydrogen and $-0{\cdot}171$ for normal hydrogen, provided the correct temperature function of the specific heat $C_{\text{condens.}}$ is used. Although the specific heat of solid parahydrogen corresponds only to a Debye function $464{\cdot}5\,(T/\theta)^3$ down to absolute zero, the same function may be used in the case of normal hydrogen if $i = -1{\cdot}132$ is simultaneously taken as the chemical constant, for the difference between this value and the correct chemical constant $-0{\cdot}171$ cancels out owing to the same difference in the value of the double integral. This state of affairs, which is due to the equality of the entropy difference between para and normal hydrogen in the gas and in the crystal, is the reason for the good agreement of the chemical constant $-1{\cdot}09$ computed from vapour pressure measurements with normal hydrogen (assuming of course a Debye function for the specific heat) with the theoretical value of $-1{\cdot}13$ obtained from Stern-Sackur-Tetrode's formula (formula (30)) without taking into consideration the nuclear spin.

What has been said with regard to the nuclear spin entropy, if the entropy is to be used to calculate gaseous equilibria, is naturally valid for the chemical constant as well. At high temperatures in the case of normal hydrogen that part of the chemical constant which is due to the nuclear spin may be omitted and the constant

$$i_{\text{II}} = i_{\text{II e-H}_2} - \log 4 = -3{\cdot}36 \qquad \text{.....(29)}$$

may be used, in agreement with the value hitherto calculated from Stern-Sackur-Tetrode's formula:*

$$i = +36{\cdot}81 + \tfrac{3}{2}\log M + \log I + \log g/s \quad \text{.....(30),}$$

* This formula, however, had no exact theoretical support.

where g = multiplicity of the normal electronic level = 2, s = "symmetry number" = 2, and with the experimental value of $-3{\cdot}44 \pm 0{\cdot}10$ obtained (omitting the spin complication) from chemical reactions (as $HgO + H_2 = H_2O + Hg$. Cf. Eucken [29]).

In the case of the thermal dissociation of hydrogen it can be shown according to Gibson and Heitler [36] that the same H atom concentration is obtained whether the nuclear spin is neglected or not, if normal hydrogen is considered, but that normal hydrogen gives a different H concentration from para-hydrogen.

The equilibrium constant for the dissociation of hydrogen is given by the equation (at high temperatures)

$$\log K_p = -\frac{q_0}{4{\cdot}57T} + \tfrac{3}{2}\log T - \frac{1}{4{\cdot}57}\int_0^T \frac{dT}{T^2}\int C_{\text{vibr.}}\,dT + 2i_{\text{H}} - i_{\text{H}_2} \quad \ldots\ldots(31),$$

where $K_p = \frac{P_{\text{H}}^2}{P_{\text{H}_2}}$, q_0 = heat of dissociation at absolute zero, and $C_{\text{vibr.}}$ = the vibrational specific heat of H_2. The chemical constant of the H atom i_{H} is given by

$$i_{\text{H}} = -1{\cdot}588 + \tfrac{3}{2}\log 1{\cdot}0078 + \log g \quad \ldots\ldots(32),$$

where $g = 4$ or 2, according as the nuclear spin is taken into consideration or is omitted.

Therefore

$$i_{\text{H}} = -0{\cdot}98 \text{ (with nuclear spin)},$$
$$i_{\text{H}}' = -1{\cdot}28 \text{ (without nuclear spin)},$$

or we obtain the term $\Sigma i = 2i_{\text{H}} - i_{\text{H}_2}$ of the formula

$$\text{with nuclear spin} \quad = -2.0{\cdot}98 + 2{\cdot}76 = 0{\cdot}80,$$
$$\text{without nuclear spin} \quad = -2.1{\cdot}28 + 3{\cdot}36 = 0{\cdot}80,$$

i.e. the same result in both cases.

On the other hand, this equality does not hold for the dissociation of normal and of parahydrogen. In this case the nuclear spin must be considered, and there is obtained

$$\text{for normal } H_2 \quad 2i_{\text{H}} - i_{\text{II}}^{\text{n-H}_2} = +0{\cdot}80,$$
$$\text{for para } H_2 \quad 2i_{\text{H}} - i_{\text{II}}^{\text{p-H}_2} = -1{\cdot}96 + 3{\cdot}36 = 1{\cdot}40,$$

i.e. the dissociation constant of parahydrogen is four times larger than that of normal hydrogen or the H atom concentration* in parahydrogen is twice the H concentration in normal hydrogen.

On the basis of the foregoing discussion Nernst's theorem can be applied to the hydrogen question.

Nernst's theorem states that at the absolute zero a state with the lowest energy and with the entropy zero is established, provided the zero-point energy and entropy are suitably chosen.† Considering both hydrogen modifications separately, it is evident that Nernst's theorem is valid for parahydrogen, as at the absolute zero all molecules cease to rotate and pass into the (absolutely) lowest energy level having the entropy zero. In the case of orthohydrogen the lowest energy level and the entropy zero are reached after the removal of the threefold rotational degeneracy and threefold nuclear spin degeneracy. The experimental evidence for the latter effect has not yet come to hand. Moreover, in ortho-parahydrogen mixtures the entropy of mixing should vanish at the absolute zero point.

As other molecules will probably behave in the same way, maintaining their nuclear spin entropy even at the lowest temperatures experimentally attainable, this entropy can always be included in the zero-point entropy without committing any error, and thus the practical applicability of Nernst's theorem will be guaranteed.

* In the case of parahydrogen this H atom concentration is not a real equilibrium concentration, as there is a gradual conversion into normal H_2 due to the dissociation and recombination ($p\text{-}H_2 \rightarrow 2H \rightleftarrows n\text{-}H_2$) and to another even faster reaction described in Chapter IV, § 1(*a*), p. 60. The H concentration given consequently represents an initial concentration which, however, can be maintained for a considerable time provided the temperature is low enough (conversion slow).

† For instance, the behaviour of the diamond corresponds to Nernst's theorem, although the absolutely lowest energy level would be only reached by rearranging the C atoms in a graphite lattice. As at the absolute zero practically no transformation diamond → graphite occurs, both modifications can be regarded to possess a level with the lowest energy and entropy. The same consideration is valid in the case of the states "gas mixture" and "compound" ($2H_2 + O_2$, $2H_2O$).

CHAPTER IV

THE KINETICS OF THE ORTHO-PARAHYDROGEN CONVERSION

THE kinetics of the ortho-parahydrogen conversion have been studied in homogeneous and heterogeneous systems. The result obtained is that in general there are two different mechanisms for conversion. One of these represents a real chemical reaction in which the transformation occurs by interchange of atoms between molecules, while the other is based on the influence of physical forces on the orientation of the nuclear spins. The special investigation of the homogeneous "chemical" conversion seemed attractive, since it is the simplest of all chemical reactions and amenable to theoretical treatment.

1. THE HOMOGENEOUS CONVERSION

(*a*) *The thermal reaction*

The simplest mechanism of the homogeneous ortho-para-conversion is the spontaneous transition between ortho and para levels by radiation. As the first rough estimation (before Wigner's calculation, see p. 10) showed that the probability of this transition, although very small compared with the usual probability of optical transition, could bring about a conversion in some weeks, Bonhoeffer and Harteck [16, 17] carried out the following experiments. Several conductivity cells, as described on p. 22, were filled with normal hydrogen at 200 mm. pressure and immersed in liquid air. To detect a change in the ortho-para-H_2 concentration, the thermal conductivity of the gas was measured daily for four weeks. The anticipated effect, however, was completely absent, showing that the half life-time of the conversion by radiation, if this occurs, is greater than a year. This result agrees with Wigner's estimation.

Another homogeneous conversion might be brought about by impacts between gas molecules and should become

manifest at high pressures. The first ortho-para-H_2 transformation was actually detected by Bonhoeffer and Harteck when they kept hydrogen under (150 atm.) pressure in a brass vessel at liquid air temperature. This reaction, however, is not a homogeneous reaction, as was shown by Farkas and Bonhoeffer [68], but a catalytic wall reaction,* because the velocity of the transformation depends on the material and dimensions of the reaction vessel used. The conversion effect observed by Eucken and Hiller [30] is likewise due to catalysis. The following table shows the results obtained by Farkas and

Table 13

Pressure in atm.	Brass vessel 400 c.c.	Brass vessel 60 c.c.	Glass vessel†	Brass vessel 400 c.c. (Bonhoeffer and Harteck)	Steel vessel 45 c.c. (Eucken and Hiller)
1	-	4·0	—	-	—
2	5·0	—	6·0	-	-
5	3·7	—	6·5		-
10	—	3·5	—	—	—
25	1·5	—	1·0	—	—
50	2·0	0·75	0·5	—	5·0
75	1·2	0·3	—	—	—
110	1·5	—	—	1·0	—

Bonhoeffer compared with the original experiments of Bonhoeffer and Harteck and those of Eucken and Hiller. The numbers in columns 2–6 represent the days required for the p-H_2 percentage to increase from 25 to 30 at $-185°$ C. H_2S inhibits the conversion in a brass vessel (at 30 atm. 30 per cent. p-H_2 attained in 5 days). Treatment with emery accelerates it. In the same vessels the re-conversion occurs about 2–5 times faster at 20° C.

On the other hand the thermal conversion of p-H_2 to n-H_2 occurring at 700–800° C. proved to be a homogeneous reaction since Bonhoeffer and Harteck [17] showed that the velocity

* It is possible that paramagnetic gaseous catalysis caused by traces of O_2 (cf. p. 79) also occurs.

† The high pressure experiments in the glass vessel were carried out by enclosing the glass vessel in a brass bomb and keeping the external and internal pressures equal.

of this conversion is reproducible in quartz or in glazed* porcelain tubes and remains unchanged when the surface of the reaction tube is increased by putting another tube inside the first.

An exhaustive study of this reaction was carried out by A. Farkas[65, 66]. His apparatus consisted of three parts: (1) the apparatus for preparing 47 per cent. p-H_2, (2) the quartz reaction vessel with electric furnace and (3) the thermo-conductivity cell. The homogeneous nature of the conversion was proved in three series of experiments carried out

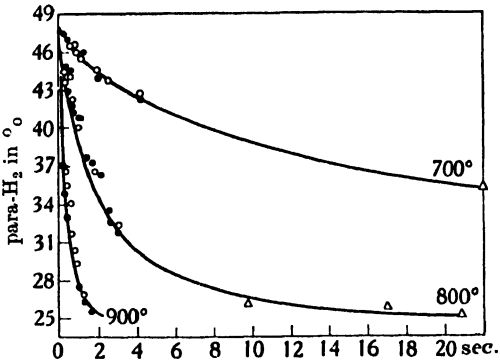


Fig. 18. The homogeneous re-conversion of parahydrogen.

in vessels with a different surface/volume ratio according to the streaming method at atmospheric pressure. Fig. 18 shows the constancy of the reaction velocity, the points, circles and triangles referring to experiments in vessels with the surface/volume ratios 23·2, 2·7 and 0·6 cm.$^{-1}$, respectively.

The main experiments were carried out by the static method. The progress of the conversion is given by the equation

$$p_t - p_\infty = (p_0 - p_\infty)\, e^{-kt} \qquad \ldots\ldots(1),$$

p_0, p_t and p_∞ denoting the p-H_2 percentage at the time $t = 0$, t and $t = \infty$, i.e. in equilibrium, or by

$$u_t = u_0 e^{-kt} \qquad \ldots\ldots(1a),$$

u denoting the parahydrogen percentage in excess of the

* In rough unglazed tubes the re-conversion proceeds much faster and exclusively at the wall.

equilibrium value of 25. Fig. 19 shows the validity of this equation, for straight lines are obtained by plotting $\log u_t$ against t.

The pressure dependence of the velocity constant k is shown by Table 14: k is proportional to the square root of the pressure (see column 3) or to the root of the concentration (in moles/litre) (see column 4). Column 5 gives the "half life period" $\tau_{\frac{1}{2}}$ in which u_0 falls to $u_0/2$.

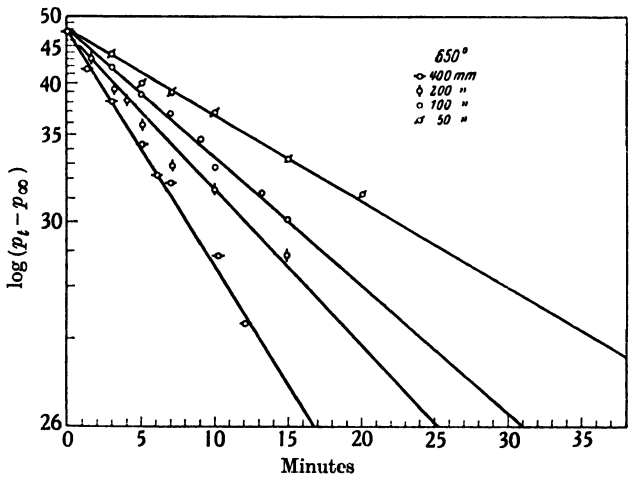


Fig. 19. The re-conversion of parahydrogen at 650° C.

Table 14. *Temperature* = 923° K.

P pressure in mm. Hg	k	$k' = \frac{k}{\sqrt{P}}$	$k'' = \frac{k}{\sqrt{(H_2)}}$ *	$\tau_{\frac{1}{2}}$ in sec.
50	0·00106	0·000150	0·0358	648
100	0·00153	0·000153	0·0365	450
200	0·00217	0·000154	0·0368	318
400	0·00310	0·000155	0·0371	222

The order of this reaction (n), determined by the well-known relation

$$\tau_{\frac{1}{2}} P^{n-1} = \text{constant} \qquad \ldots\ldots(2),\dagger$$

* In Farkas's paper[66] (Table 2) these figures are by mistake four times too low.

† C. N. Hinshelwood, *The Kinetics of Chemical Change in Gaseous Systems*, Oxford (1933).

is $\frac{3}{2}$, and since the square root proportionality indicates that H atoms are involved, we obtain the equation of the conversion

$$H + p\text{-}H_2 \rightleftarrows o\text{-}H_2 + H^* \qquad \ldots\ldots(3).$$

According to this a conversion occurs as a result of successful collisions between H_2 molecules and H atoms resulting from the thermal dissociation of H_2. In these collisions the free atom and one bound atom interchange forming ortho- and parahydrogen in the equilibrium ratio 3 : 1. By this mechanism the prohibition of the ortho → para transition is avoided, the total symmetry of the system $H + H_2$ being unchanged by the conversion as expressed by

$$H + p\text{-}H_2 = o\text{-}H_2 + H\dagger \qquad \ldots\ldots(3),$$

$$\uparrow + \uparrow\cdot\downarrow = \uparrow\uparrow + \downarrow \qquad \ldots\ldots(3a),$$

the arrows representing the nuclear spins of the molecule and of the atom.

Table 15

Temperature ° K.	k''	k^*‡ in (mole^{-1} litre sec.$^{-1}$)	Collision efficiency	Steric factor
873	0·0083	$1{\cdot}37.10^9$	0·00287	0·06
923	0·0365	$1{\cdot}22.10^9$	0·00257	0·05
973	0·263	$2{\cdot}00.10^9$	0·00400	0·06
1023	1·188	$2{\cdot}38.10^9$	0·00463	0·05

The increase of the k'' constants with temperature is chiefly due to the increased concentration of H atoms. The temperature coefficient of the H-concentration [H] can be eliminated by replacing $k'' = \frac{k}{\sqrt{[H_2]}}$ by $k^* = \frac{k}{[H]}$. (The hydrogen

* For the reaction between three H atoms $n = 3/2$, but such collisions are extremely rare at the very low H concentrations at this temperature.

† According to Beutler and Eisenschimmel, *Z. f. physikal. Chemie*, B, **10**, 89 (1930), an analogous process in the case of electrons is the cause of the triplet → singlet transition of Hg by collision with excited Kr atoms, i.e.

$$(2^3P_2)\,Kr + (1^1S_0)\,Hg \rightarrow (1^1S_0)\,Kr + (5^3D)\,Hg + 0{\cdot}038 \text{ volt.}$$

‡ These figures vary slightly from Farkas's figures as the dissociation equilibrium was calculated on the basis of somewhat different data.

concentration is computed from the H_2 dissociation equilibrium. p. 58, formula (31).)

Table 15 shows these constants (columns 4 and 5, see p. 64): in the temperature range 873–1023° K.

The remaining small temperature dependence of the constant k^* is due to the activation energy of the interchange reaction

$$H + p\text{-}H_2 = o\text{-}H_2 + H.$$

According to the modified Arrhenius equation,

$$k^* = \text{prop.} \sqrt{T}\, e^{-E/RT} \qquad \ldots\ldots(4),$$

E amounts to 5500 cal.

It can be easily shown that the above mechanism is in agreement with the experimental result. The reaction velocity is expressed by

$$\frac{-dp[H_2]}{dt} = k_1 p [H_2][H] - k_2 o [H_2][H] \qquad \ldots\ldots(5),$$

or as $o = 100 - p$, and in equilibrium, when $\frac{dp}{dt} = 0$,

$$\frac{p}{100-p} = \frac{1}{3},$$

by

$$-\frac{dp}{dt} = 4k_2[H](p - 25) \qquad \ldots\ldots(6).$$

Integrating, we obtain

$$(p - 25) = (p_0 - 25)\, e^{-4k_2[H]t} \qquad \ldots\ldots(7),$$

since for $t = 0$, $p = p_0$. Thus the velocity constant

$$k^* = 4k_2 = k_1 + k_2$$

is the sum of the velocity constants of the partial reaction o → p and of that of the reaction p → o.

The collision efficiency Z, expressed by

$$Z = \frac{v}{n} = \frac{\text{number of molecules reacting}}{\text{number of molecules entering into collision}} \qquad \ldots\ldots(8),$$

or with

$$v = \frac{k^* z_1 z_2}{6{\cdot}06 \,.\, 10^{20}} \text{ (per c.c. and per sec.)} \qquad \ldots\ldots(9)$$

and $$n = 2\sqrt{2\pi}\left(\frac{d_1+d_2}{2}\right)^2\sqrt{\frac{M_1+M_2}{M_1M_2}RT}.z_1z_2$$

$$= 2{\cdot}64.10^{-11}\sqrt{T}.z_1z_2 \qquad \text{.....(10).}$$

z_1, z_2 } number of {atoms per c.c., molecules per c.c.,

d_1, d_2 } diameter of {$H = 2{\cdot}14.10^{-8}$,* $H_2 = 2{\cdot}3.10^{-8}$,†

M_1, M_2 } molecular weight of {H, H_2,

by $Z = \frac{k^*}{1{\cdot}6.10^{10}.\sqrt{T}}$ is given in Table 15, column 4. This collision efficiency is the sum of the collision efficiencies of the conversion o→p and p→o.‡ On the other hand Z represents directly the probability of an atomic interchange in the reaction $H + H_2 = H_2 + H$, if we refer to all interchanges, including those not leading to conversion (e.g. ↑ + ↓ ↑ = ↑ ↓ + ↑). Comparing this yield with the activation energy we obtain the steric factor S of this reaction according to the relation $Z = S.e^{-5500/RT}$. S has the value 0·05–0·06 (see Table 15, column 5).

(*b*) *The interaction of parahydrogen with hydrogen atoms*

The same mechanism as for the thermal conversion was found by Geib and Harteck [71] for the interaction of p-H_2 and H atoms.

The atomic H§ was prepared in the usual way by an electric discharge and streamed through a reaction vessel to the pump after having passed a U-tube immersed in liquid air to destroy

* Cf. Harteck, *Z. f. physikal. Chemie*, A, **139**, 98 (1928).

† Landolt-Bornstein, *Physik.-Chem. Tabellen*, 5th edition, p. 121.

‡ The probability of the para-ortho conversion is three times larger than the probability of the ortho-para conversion. The reason for this ratio is that the nuclear spin both of the free atom and of the molecule's atom turned towards the free atom have two orientations, each giving four different states. Three of these states are ortho states with the nuclear spin components +1, 0, −1, and one is a para state with the spin 0. Cf. Pelzer and Wigner[74].

§ The concentration of H atoms was measured by the Harteck-Wrede capillary method.

the H atoms. The stream of parahydrogen could be mixed with the active hydrogen either before it entered the reaction vessel or after it left the U-tube; in the former case the p-H_2 was exposed to the influence of the H atoms, and in the latter not at all.

The p-H_2 percentage of the H_2 passing to the pump was determined by the method given on p. 24.

When the p-H_2 was exposed to the H atoms, a decrease in the p-H_2 concentration of the gas was observed, due to the reaction

$$\text{p-H}_2 + \text{H} \rightarrow \text{H} + \text{o-H}_2 \qquad \text{.....(3).}$$

The velocity constant of this reaction was calculated from the formula

$$k = \frac{1}{t} . ln \frac{u_0}{u_t} \qquad \text{.....(11),}$$

where u_0 and u_t have the same meaning as on p. 63, and t* is the time of the H–H_2 interaction, and according to the formula

$$k = \frac{u_0 - u_t}{u_t . t} \qquad \text{.....(12),}$$

which takes into account that the fresh gas entering the reaction zone is continuously mixed with the partly converted gas.†

Table 16 shows the results obtained in different series of experiments at 0·56 mm. Hg pressure.

The k values are independent of the initial p-H_2 concentration and nearly proportional to the H atom concentration used, thus demonstrating the validity of the mechanism

$$\text{p-H}_2 + \text{H} \rightleftarrows \text{H} + \text{o-H}_2 \qquad \text{.....(3).}$$

Table 17 contains the energies of activation, collision efficiencies, yields and steric factors, calculated in the same way as in the thermal conversion from the velocity constant k.

It seems that formula (12) is to be preferred, as an extrapolation to high temperatures agrees quite well with Farkas' results. Thus at 973° C. the collision efficiency 3.10^{-3} is

* In performing the calculations, several corrections were made to allow for the diffusion of the H atoms against the stream and the interaction outside the reaction vessel.

† Cf. M. Bodenstein, *Z. f. physikal. Chemie*, **61**, 422 (1908).

obtained compared with the experimental value 4.10^{-3} (see p. 64, Table 15).

Table 16

No.	Temperature ° C.	Percentage para H_2	Percentage H atoms	Relative amount converted $=\frac{u_0-u_t}{u_0}100$	k Formula (11)	k Formula (12)
1	10	100	18·8	34·8	0·44	0·55
2	57	100	18·8	65·3	1·80	3·17
3	100	100	18·8	84·0	4·12	11·70
6	11	53	18·8	36·9	0·506	0·645
7	56·5	53	18·8	64·8	1·91	3·38
8	100	53	18·8	85·2	4·73	14·25
9	10	100	3·0	5·6	0·059	0·062
10	57	100	3·0	16·6	0·312	0·341
11	100	100	3·0	35·2	0·986	1·22

Table 17

Temperature ° K.	Formula (11) Collision efficiency	Steric factor	Activation energy	Formula (12) Collision efficiency	Steric factor	Activation energy
283	$2{\cdot}75.10^{-7}$	0·11	5150 cal.	$3{\cdot}41.10^{-7}$	0·136	7110 cal.
330	$1{\cdot}12.10^{-6}$	0·07		$1{\cdot}98.10^{-6}$	0·126	
373	$2{\cdot}56.10^{-6}$	0·046		$7{\cdot}3\ .10^{-6}$	0·130	

Table 18 compares the kinetic data of the reaction

$$H + p\text{-}H_2 \rightleftarrows o\text{-}H_2 + H \qquad \ldots\ldots(3)$$

obtained by Farkas and by Geib and Harteck.

Table 18

Author	Temperature range	Energy of activation	Steric factor
Geib and Harteck	10–100° C.	7000 ± 500	0·13
Farkas	600–750° C.	5000 ± 500	0·06

An exact decision between these values is impossible without further experimental data, but the higher energy of activation seems to be more probable. In any case the agreement is as good as can reasonably be expected taking into consideration the very different experimental conditions (10^{-8}–10^{-6} per cent. H atoms, 50–760 mm. pressure and 600–900° C. in Farkas' experiment, 3–19 per cent. H atoms, 0·5 mm. pressure and 10–100° C. in Geib-Harteck's experiments).

Naturally the same reaction

$$H + p\text{-}H_2 \rightleftarrows o\text{-}H_2 + H$$

occurs if the H atoms are produced photochemically. Thus the experimental demonstration of the conversion by illumination (described on p. 33) is based on the reactions

$$Hg + h\nu \rightarrow Hg^*,$$

$$Hg^* + H_2 \rightarrow Hg + 2H,$$

$$H + p\text{-}H_2 \rightarrow o\text{-}H_2 + H,$$

the H atoms being produced by collisions with excited Hg (Hg^*) atoms. Moreover, a conversion by dissociation and recombination is taking place. This reaction is, however, very slow on account of the small H atom concentration (see p. 104).

On the other hand, in the conversion by an electric discharge the latter reaction may play a considerable part. In this connection it may be mentioned that according to Bonhoeffer and Harteck [15, 16, 17] an electric discharge does not cause parahydrogen formation in a tube filled with normal H_2 immersed in liquid air, although it would be expected that the hydrogen molecules formed from H atoms at liquid air temperature would be in the equilibrium corresponding to this temperature. Evidently the newly formed molecules are so "hot" (in the nascent state) owing to the heat of formation that the low temperature equilibrium cannot be established.

(c) *Theoretical treatment of the reaction* $H + p\text{-}H_2 \rightleftarrows o\text{-}H_2 + H$

The ideal simplicity of the reaction

$$H + p\text{-}H_2 \rightleftarrows o\text{-}H_2 + H$$

permits a theoretical treatment. According to London [73] the total energy of three H atoms is approximately given by the expression

$$-W_{abc} = F(a) + F(b) + F(c) + \sqrt{f^2(a) + f^2(b) + f^2(c) - f(a)f(b) - f(b)f(c) - f(c)f(a)} \quad \ldots\ldots(13),$$

where F and f are functions of the distances (a, b, c) of the atoms from each other. The F terms are integrals of the squares of the eigenfunctions; they represent the mutual electrostatic interaction of the electrons and protons and are accordingly called "Coulomb" terms. These terms are additive, as shown by the formula. The f terms contain the products of the eigenfunctions of the three pairs of electrons and are called "exchange or resonance energies", representing, as was shown by Heitler and London [7], the valence forces.

Provided no quantum jump occurs, the energy of activation is the energy required to transform the configuration $a = \infty$, $b = r_0$, $c = \infty$ into the configuration $a = \infty$, $b = \infty$, and $c = r_0$, r_0 designating the equilibrium distance of the H atoms in the H_2 molecule. Both the initial and final state represent a hydrogen molecule and a free atom and the total binding energy is given in both cases by

$$-W_0 = F(r_0) + f(r_0) = 102 \text{ kg. cal.} \quad \ldots\ldots(14).$$

As pointed out by London, the approach of the third atom to the molecule can take place most easily along the molecular axis, while the most unfavourable mode of attack is to bring up the atom perpendicular to the axis of the molecule. In practice the former will occur when $a = b + c$.

In order to estimate the energy of activation the Coulomb terms F may be neglected, as they amount to only 5–10 per cent. of the total binding energy, and the f terms representing

the interaction of the two lateral atoms having the distance $a=b+c$. Thus we obtain

$$-W_0' = f(r_0) \qquad \text{.....(15),}$$

and

$$-W'_{abc} = \sqrt{f^2(b)+f^2(c)-f(b)f(c)} \qquad \text{.....(16).}$$

If we assume that the distance $b=r_0$ in the original molecule is at first not altered very much by the influence of the approaching atom, the energy $-W'$ attains its maximum value when $f(c)=f(b)/2$. In this case

$$-W'_{\max.} = \frac{\sqrt{3}}{2} f(r_0),$$

or the energy of activation

$$E = -W_0' + W'_{\max.} \simeq f(r_0)\left[1-\frac{\sqrt{3}}{2}\right] = 0{\cdot}13 f(r_0),$$

or as $\quad f(r_0) = -W_0' = 102$ kg. cal., $\quad E = 13$ kg. cal.

Even this very rough approximation does not differ much from the experimental value of 7000 cal., and it explains the well-known fact that reactions involving one atom have, in general, a low energy of activation compared with reactions involving molecules.

Eyring and Polanyi [63, 61, 75] extended London's theory by taking into account the neglected terms. They proceeded as follows.

The total energy W_{abc} of the three H atoms lying in a straight line may be represented as a three-dimensional surface in terms of the distances b and c according to formula (13). To a first approximation the Coulomb terms are again omitted, and as the resonance energy $f(r)$ is not exactly known it is replaced by the total binding energy $\epsilon(r)=f(r)+F(r)$. The $\epsilon(r)$ function is well known from band spectra and is given by Morse's formula.* Fig. 20 shows the surface given by

$$-W''_{abc} = \sqrt{\epsilon^2(b+c)+\epsilon^2(b)+\epsilon^2(c)-\epsilon(b)\epsilon(c)-\epsilon(b)\epsilon(b+c)-\epsilon(b+c)\epsilon(c)} \qquad \text{.....(17),}$$

the value of the energy being represented by the contour lines.

* *Phys. Rev.* **34**, 57 (1929).

In Fig. 21 the same "energy mountain" is shown photographed from a plastic model.* The initial state is to be found at the bottom of the energy valley, where c is very large and $b = r_0 = 0{\cdot}75$ Å., while the final state is at the bottom of the corresponding energy valley with b very large and $c = 0{\cdot}75$ Å.

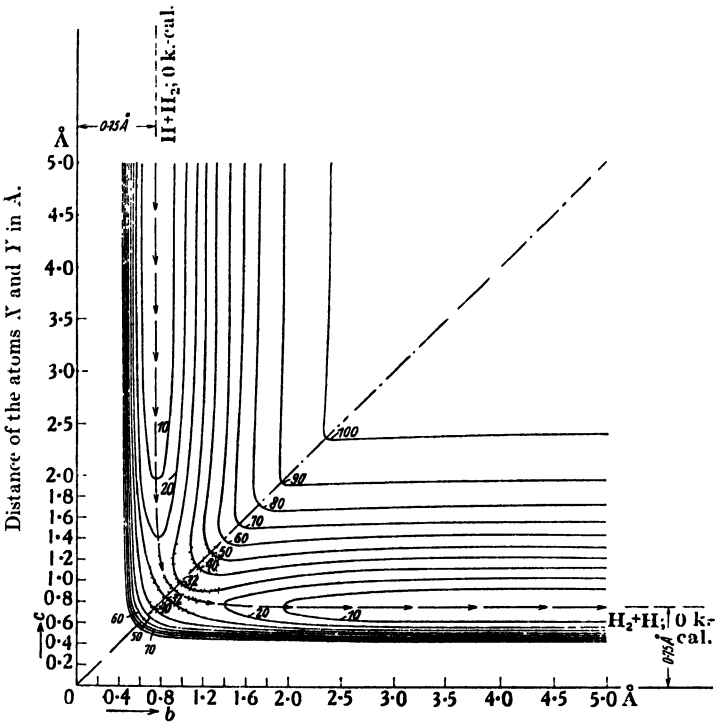


Fig. 20. The energy mountain of the reaction $H + H_2 = H_2 + H$.

The chemical reaction can be visualized as the movement of a point along the dotted line. This "reaction path" leads from the initial valley to the final valley, passing the minimum height. At the beginning the path is parallel to the axis; this means that the H–H distance in the molecule is uninfluenced. In the vicinity of the "saddle point", however, the deviation of the reaction path from the axis constantly increases up to

* The author is very much indebted to Mr C. F. Goodeve for the photograph.

a right angle, when the molecule is decomposed and the remote atom breaks away with the simultaneous formation of a new molecule.

The saddle point of the energy surface corresponds to a symmetrical transition state H–H–H with $b = c = 0{\cdot}9$ Å. The energy of activation, i.e. the height of the saddle point measured from the bottom of the initial valley, amounts to 32 cal.

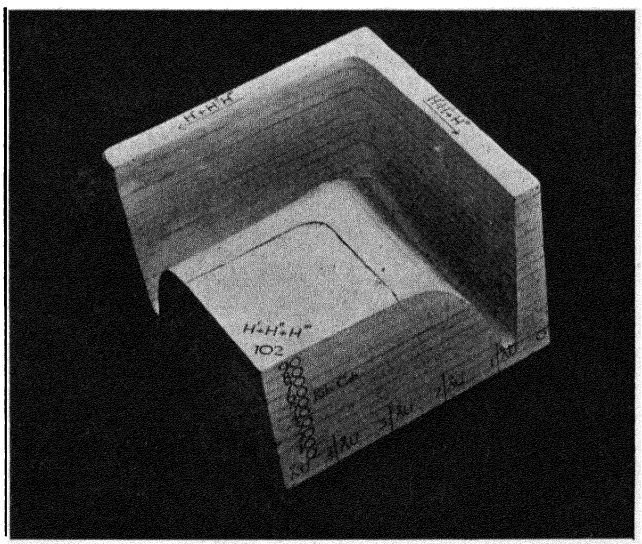


Fig. 21. Plastic model of the energy mountain of the reaction $H + H_2$.

This value is considerably diminished when the Coulomb terms are considered. This correction is made according to a theoretical formula for $F(r)$ computed by Sugiura.* By a superposition of the Coulomb energy on Fig. 20 the surface given in Fig. 22 is obtained, demonstrating (on a larger scale) how the saddle point is deformed. The energy of activation is now reduced to about 20 kg. cal.

This amount, however, is further lowered by the zero-point energy.† The zero-point energy is much less in the transitional

* *Z. f. Physik*, **45**, 484 (1927).

† The zero-point energy is that part of the vibrational energy which is preserved at the absolute zero (cf. Part II, p. 152).

state than in the initial state and thus a great amount of the initial zero-point energy (6·2 kg. cal.) can contribute to the activation. The final value of the energy of activation may therefore be lowered to 15 kg. cal.

Eyring and Polanyi's calculations have been extended by Pelzer and Wigner[71] in two directions. At first London's assumption that the interchange reaction proceeds adiabatically, i.e. without quantum jump, was demonstrated. The

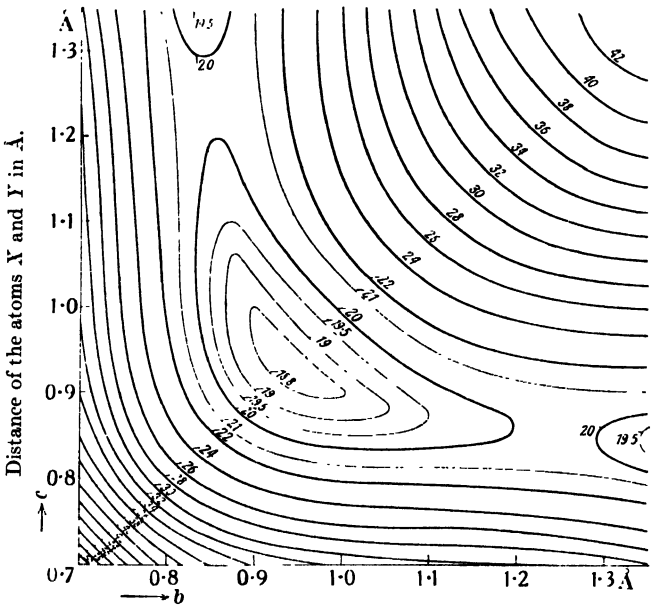


Fig. 22. The energy mountain of the reaction $H + H_2$.

criterion for such a reaction is that the lowest energy level of the system is situated at a sufficient distance from a higher level. This condition is fulfilled in the case of hydrogen, the energy of excitation being very high compared with the energy of activation. Further, the absolute velocity constants of the reaction

$$H + p\text{-}H_2 = o\text{-}H_2 + H$$

have been computed. Besides the most favourable, "straight-line" reaction, treated by Eyring and Polanyi, cases were also

considered in which the atom does not attack the molecule in the direction of the molecular axis. It was shown that the energy of activation is now to be increased by $\frac{\delta^2 D}{10}$, δ denoting the angle between the direction of the approaching atom and the molecular axis, and D the heat of dissociation, including the zero-point energy.

As the average energy of the molecules possessing energy greater than W amounts to $W + RT$, the maximum angle δ up to which the supplementary energy of activation can be supplied is expressed by

$$\frac{\delta^2 D}{10} = RT \qquad \text{.....(18),}$$

or with $D = 108$ kg. cal.

and $T = 300°$ K.,

$$\delta^2 \sim 0{\cdot}05 \quad \text{and} \quad \delta \sim 13°.$$

The steric factor (S) is given by the ratio of the surface of the spherical cap subtended by the angle δ to the surface of the hemisphere, i.e. $S = \frac{1 - \cos\delta}{1}$, or

$$S = 0{\cdot}025 \text{ at } 300° \text{K.},$$

$$S = 0{\cdot}08 \text{ at } 1000° \text{K.},$$

in agreement with the experimental results (Table 18).

To determine the velocity constant, i.e. the number of the transitions from the initial valley into the final valley in the presence of one mole H atoms/litre, the equilibrium is considered in which the number of processes leading from the initial valley into the final valley is equal to the number of reverse processes. Then according to Boltzmann's formula the distribution of the molecules in the saddle region and their velocity component perpendicular to the energy crest which divides the two valleys is computed. This velocity constant is given by the expression

$$k = C \,.\, T^{\frac{1}{2}} e^{-W/RT} \qquad \text{.....(19),}$$

C denoting a magnitude equal to 10^6 containing only molecular

constants. Table 19 shows the C values (column 3) calculated from the experimental velocity constants on the basis of this equation with $W = 6600$ cal. The agreement with the theoretical value (10^6) is evident.

Table 19

Temperature °K.	k in (sec. mole/litre)$^{-1}$	C	C'
283	$8{\cdot}5.10^4$	$2{\cdot}0.10^6$	$2{\cdot}0.10^6$
373	$2{\cdot}4.10^6$	$2{\cdot}5.10^6$	$3{\cdot}0.10^6$
873	$1{\cdot}3.10^9$	$1{\cdot}7.10^6$	$2{\cdot}6.10^6$
1023	$2{\cdot}4.10^9$	$1{\cdot}9.10^6$	$2{\cdot}8.10^6$

Wigner [80] improved formula (19) by taking into consideration in addition processes which may occur through a quantum mechanical "tunnel" effect, even if the energy of activation required to go over the barrier is lacking.*

This quantum mechanical correction, however, does not change the results much (see column 4, Table 19).

In view of the excellent agreement between the experimental and theoretical results for the reaction

$$H + p\text{-}H_2 = o\text{-}H_2 + H,$$

this simple bimolecular process can be regarded as completely cleared up.

(*d*) *The conversion in the liquid and the solid phase*

An increase of the p-H_2 percentage in the liquid H_2 due to gradual ortho-parahydrogen conversion† was first observed by Bonhoeffer and Harteck [16]. They found that in liquid hydrogen kept for five and for thirty hours the p-H_2 content amounted to 29 and 40 per cent., respectively. Measuring the vapour pressure of H_2, Keesom, Bijl and van der Horst [41] observed

* According to quantum mechanics there is a finite probability for the penetration of an energy barrier even if its height considerably exceeds the actual energy of the molecules in question.

† As the heat of the conversion normal-para (see p. 38) is nearly the same as the heat of evaporation of H_2 the conversion of a given amount of gas causes a supplementary evaporation of the same amount.

the same effect as the p-H_2 concentration increased 0·5 per cent. per hour, causing a slow increase in the vapour pressure.*

This conversion both in the liquid and the solid phase was more fully investigated by Cremer and Polanyi [62]. They used as reaction vessel a large Dewar beaker (immersed in liquid N_2) in which condensed H_2 could be kept for eighteen days. If the conversion in the solid was to be studied the H_2 was solidified by continuous pumping at 6–40 mm. pressure.

The progress of the conversion corresponds to the equation

$$-\frac{do}{dt} = k.o^2 \qquad \text{.....(20)}$$

(o = ortho H_2 percentage), as is evident from the constancy of k in Table 20.

Table 20

Time in hours	Liquid		Solid	
	Percentage ortho H_2	k	Percentage ortho H_2	k
0	75·0	—	75·0	—
5	72·3	10.10^5	69·5	20.10^5
15	67·0	11.10^5	61·6	18.10^5
25	62·5	12.10^5	55·2	18.10^5
40	56·5	12.10^5	47·8	20.10^5
60	50·0	12.10^5	40·0	20.10^5
80	44·4	12.10^5	34·2	21.10^5
100	40·0	13.10^5	30·0	20.10^5
115	37·5	12.10^5	27·7	19.10^5
125	35·8	12.10^5	26·5	14.10^5
135	34·3	11.10^5	25·5	12.10^5
145	32·8	13.10^5	24·7	11.10^5

In the case of solid H_2 a remarkable result was obtained; at the beginning a conversion was observed which was considerably faster than in the liquid and corresponded to the formula

$$-\frac{do}{dt} = k.o^2.$$

* Meissner and Steiner, *Z. f. Physik*, **79**, 601 (1932), observed that the vapour pressure of H_2 samples fractionated to enrich the H^2 isotope (cf. p. 118) increased more slowly than the vapour pressure of an unfractionated sample, which would indicate that the ortho-para conversion took place more slowly. This effect is not yet cleared up.

When a concentration of about 70 per cent. p-H_2 (=30 per cent. o-H_2) was attained the velocity constant began to decrease and became even less than the constant for the liquid. After melting and solidifying the H_2 sample, the conversion started with its original velocity.

Both in the liquid and in the solid the reaction velocity was independent of the temperature (Table 21).

Table 21

	Temperature ° K.	k
Solid	4	19.10^{-5}
	11–13	19.10^{-5}
	13–14	19.10^{-5}
Liquid	14–15	12.10^{-5}
	20	12.10^{-5}

The conversion is caused by the interaction of two ortho-hydrogen molecules. According to the orientation of the nuclear spins either two parahydrogen molecules or one para and one ortho molecule* may result.

The conversion, however, is not due to a chemical reaction corresponding to the scheme



since according to the calculation of Eyring [62a] the activation energy of this reaction would amount to 100 kg. cal., while the

* Two ortho molecules each having the nuclear spin 1, can form nine different states corresponding to the three different orientations of their nuclear spins. These states have the spin components:

+2			The first column represents the configuration o-H_2+o-H_2 (the
+1	+1		resulting nuclear spin is 2 and has therefore five orientations),
0	0	0	i.e. no reaction has taken place, the second the configuration
−1	−1		o-H_2+p-H_2 (with the resulting spin 1, three orientations) and
−2			the third the configuration p-H_2+p-H_2. Thus we obtain

$$\text{o-H}_2+\text{o-H}_2=\begin{cases}\frac{5}{9}\ (\text{o-H}_2+\text{o-H}_2),\\ \frac{3}{9}\ (\text{o-H}_2+\text{p-H}_2),\\ \frac{1}{9}\ (\text{p-H}_2+\text{p-H}_2).\end{cases}$$

temperature independence of the velocity indicates the absence of any energy of activation.

On the other hand, the overcoming of such a large energy barrier in a quantum mechanical tunnel effect (Born and Weisskopf*) has a very small probability on account of the unfavourably large distance between the H_2 molecules (2·2 Å.). The conversion is caused by the reversal of the nuclear spin under the influence of molecular (magnetic) forces which become effective if the molecules are packed very closely together. This behaviour is similar to the conversion found by Farkas and Sachsse in the gas phase in the presence of paramagnetic molecules (see below).

The "falling asleep" of the conversion in the solid is explained as follows: on account of the small mobility of the H_2 molecules in the lattice more and more isolated orthohydrogen molecules arise as the conversion proceeds, and these orthohydrogen molecules are not capable of further conversion as a second orthohydrogen molecule is missing in the vicinity.† When the solid is melted, the orthohydrogen molecules have the opportunity to form pairs of ortho molecules (according to the statistical distribution), and thus the conversion can start with the high velocity if the hydrogen is again solidified.

(e) *Homogeneous catalysis by paramagnetic substances*

While engaged in an investigation of detonating-gas mixtures containing para H_2, L. Farkas and H. Sachsse [69,70] observed that the para H_2 was converted to normal H_2 with a considerable velocity in the presence of O_2. A closer study showed that besides O_2 other paramagnetic molecules and ions were effective. In this case the ortho-para-H_2 transformation is rendered possible, since the prohibition of the intercombination is to some extent removed on account of the large perturbation caused by the extremely in-homogeneous magnetic field of molecules or ions‡ (see below).

* M. Born and V. Weisskopf, *Z. f. physikal. Chemie*, B, **12**, 206, 478 (1931).

† According to Cremer's theoretical considerations this residual o-H_2 should amount to 10–20 per cent., in agreement with the experimental value.

‡ A homogeneous magnetic field of 1000–2000 gauss is ineffective.

The experiments were carried out in the same way as described in the foregoing kinetic studies. Using the micro method (see p. 25) the samples drawn off from the reaction vessel for the purpose of analysis could be made so small that no pressure change was brought about. Before entering the concentration cell the samples passed through a trap cooled with liquid hydrogen in order to remove the added O_2 (or other gases).

The homogeneity of the conversion was demonstrated by comparing the reaction velocities in the empty vessel and in the vessel packed with glass tubes (see Fig. 23).

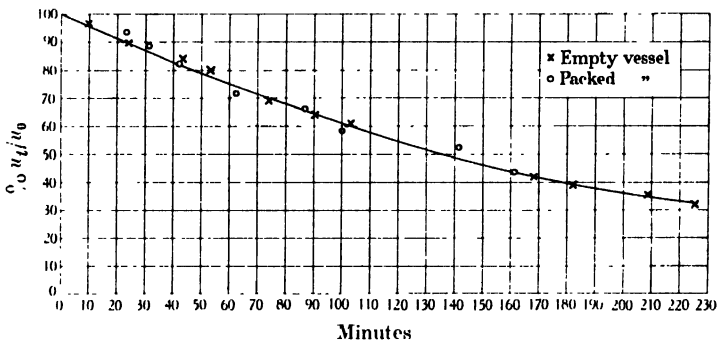


Fig. 23. The re-conversion of parahydrogen catalyzed by O_2.

The conversion proceeds according to the equation

$$u_t = u_0 e^{-k[O_2]t} \qquad \ldots\ldots(21),$$

i.e. the reaction velocity is independent of the H_2 pressure and proportional to the O_2 pressure (see Figs. 24 and 25 and Table 22).

Table 22. *Temperature* = 293° K.

O_2 pressure in mm.	$\tau_{\frac{1}{2}}$ in min.	k in (mole^{-1} litre min.$^{-1}$)
172·0	8·3	9·20
120·0	12·0	9·14
31·0	46·0	9·22
10·0	143·0	9·20
1·1	1290·0	9·27

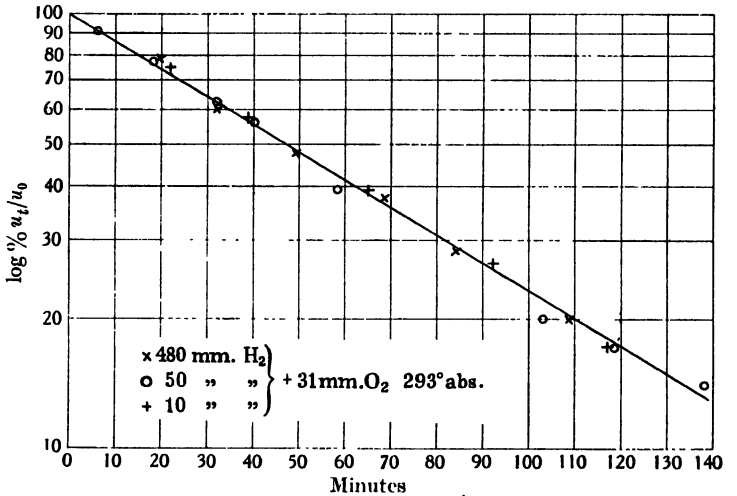


Fig. 24. The re-conversion of parahydrogen catalyzed by O_2.

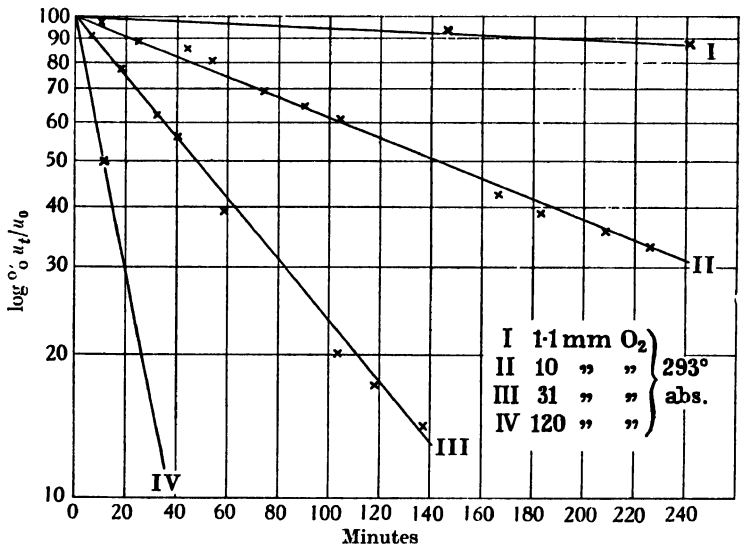


Fig. 25. The re-conversion of parahydrogen catalyzed by O_2.

Table 23 shows the velocity constants k, and the collision efficiencies Z in the temperature range 77·3–623° K.

Table 23

Temperature ° K.	k mole^{-1} litre min.$^{-1}$	Z	$Z_{p\to o}$	$Z_{o\to p}$
77·3	2·81	$2{\cdot}38.10^{-13}$	$1{\cdot}19.10^{-13}$	$1{\cdot}19.10^{-13}$
86	2·94	$2{\cdot}61.10^{-13}$	$1{\cdot}44.10^{-13}$	$1{\cdot}17.10^{-13}$
193	7·10	$5{\cdot}86.10^{-13}$	$4{\cdot}34.10^{-13}$	$1{\cdot}52.10^{-13}$
293	9·16	$6{\cdot}80.10^{-13}$	$5{\cdot}10.10^{-13}$	$1{\cdot}70.10^{-13}$
373	10·00	$6{\cdot}85.10^{-13}$	$5{\cdot}13.10^{-13}$	$1{\cdot}72.10^{-13}$
493	11·10	$7{\cdot}13.10^{-13}$	$5{\cdot}26.10^{-13}$	$1{\cdot}77.10^{-13}$
623	12·75	$7{\cdot}61.10^{-13}$	$5{\cdot}71.10^{-13}$	$1{\cdot}90.10^{-13}$

This reaction is formally completely analogous to the thermal conversion according to the formula

$$-\frac{dp}{dt} = k_1 p\,(O_2) - k_2\,(100-p)\,(O_2) \qquad \ldots\ldots(22),$$

and the constants k given above represent the sum of the constants $k_1 + k_2$. The conversion is caused by the non-homogeneous magnetic field of the O_2 molecules in the collision. The given collision efficiencies Z are the sum of the collision efficiencies for the p→o reaction and for the o→p reaction (columns 4 and 5 of the table). The collision efficiencies are calculated as indicated on pp. 65–66.

While a great many diamagnetic gases (as N_2, N_2O, CO_2, NH_3, HI, SO_2, $Fe(CO)_5$) do not cause any parahydrogen conversion, the effect of the paramagnetic gases NO and NO_2 is similar to that of O_2. The progress of the reaction caused by NO and NO_2, and its dependence on temperature and pressure, correspond completely to the experiments with O_2, and even the absolute magnitudes of the collision efficiencies do not differ much.

In the experiments with NO the fact must be taken into consideration, that out of the two lowest levels, $^2\Pi_{\frac{1}{2}}$ and $^2\Pi_{\frac{3}{2}}$, NO is only paramagnetic in the latter, which lies 354 cal. higher than the ground level.*

* The concentration of the paramagnetic NO is given by

$$[NO]_{^2\Pi_{\frac{3}{2}}} = \frac{e^{-354/RT}}{1+e^{-354/RT}}.$$

On the other hand NO_2 is only effective as such and ineffective in the associated form N_2O_4.

Table 24 gives the results for NO.

Table 24

Temperature ° K.	Percentage $(NO)_{paramagn.}$	k_1+k_2 mole^{-1} litre min.$^{-1}$	Z	$Z_{p\to o}$	$Z_{o\to p}$
143	20·8	40·6	$3{\cdot}40.10^{-12}$	$2{\cdot}40.10^{-12}$	$1{\cdot}00.10^{-12}$
199	28·0	41·6	$3{\cdot}34.10^{-12}$	$2{\cdot}46.10^{-12}$	$0{\cdot}90.10^{-12}$
293	34·0	37·9	$2{\cdot}59.10^{-12}$	$1{\cdot}94.10^{-12}$	$0{\cdot}65.10^{-12}$
373	37·4	40·0	$2{\cdot}76.10^{-12}$	$2{\cdot}07.10^{-12}$	$0{\cdot}69.10^{-12}$
493	40·2	39·0	$2{\cdot}54.10^{-12}$	$1{\cdot}90.10^{-12}$	$0{\cdot}64.10^{-12}$
793	43·5	49·4	$2{\cdot}75.10^{-12}$	$2{\cdot}06.10^{-12}$	$0{\cdot}69.10^{-12}$

The velocity constant for NO_2 amounts to 12·5–13 at temperatures 293–373° K.

Orthohydrogen also has a magnetic moment, though a very small one (about 1/2000 of the O_2 moment, see p. 50), and therefore a slow conversion (half lifetime some years at atmospheric pressure) in ortho-parahydrogen mixtures due to this effect is also to be anticipated.

The catalysis of the p-o-H_2 conversion by paramagnetic substances is not limited to the gaseous state, it occurs also in solution as caused by either the solvent itself or by paramagnetic gases or ions solved.

If parahydrogen is dissolved in H_2O a considerable conversion to normal hydrogen is observed. In this case the reaction is due to the nuclear moment of the protons in the water molecules. That this assumption is correct is shown by the fact that the conversion takes place in other solvents containing H atoms, and the velocity constant for the same hydrogen-concentration is of the same order of magnitude. See Table 25.

Whether the conversion in CS_2 is due to impurities or to induced moments is not yet settled.

Oxygen dissolved in H_2O also causes a conversion,* and thus it is possible to compare the effect of O_2 in the gas phase

* In these and all other experiments in solutions the rate of conversion due to the water alone was taken into account and subtracted from the observed rate.

and in solution. Using the collision formula valid for the gas, at 20° C. the velocity constant of 10·5 is obtained, in good agreement with the corresponding figure of 9·16 in the gas phase.

Table 25

Solvent	Half lifetime in min.	k in mole $(H)^{-1}$ litre $min.^{-1}$
H_2O	134	$4{\cdot}64.10^{-5}$
C_6H_6	350	$2{\cdot}92.10^{-5}$
$C_6H_5NH_2$	270	$3{\cdot}32.10^{-5}$
CH_3OH	230	$3{\cdot}04.10^{-5}$
C_6H_{12}	452	$1{\cdot}36.10^{-5}$
CS_2	1000	—

A considerable conversion proceeds under the influence of paramagnetic ions, the velocity increasing in solutions with the magnetic moment of the ion. Table 26 gives the results obtained in half-molar solutions of the sulphates of the iron group [87a] and Tables 27 and 28 the result of measurements carried out with the trivalent ions of the rare earths.

Table 26

Ion	μ magnetic moment in magnetons	k in $mole^{-1}$ litre $min.^{-1}$
Zn^{++}	0	0
Cu^{++}	3·53	1·15
Ni^{++}	5·56	1·95
Co^{++}	6·56	5·56
Fe^{++}	6·54	6·05
Mn^{++}	5·92	8·05

Table 27. $NdCl_3$, *temperature* = 293° K.

Concentration in 10^{-3} mole/litre	2·53	4·04	5·24	15·4	21·4
Velocity constant in (mole $litre^{-1}$ $min.)^{-1}$	2·46	2·19	2·30	2·78	2·76

The theoretical treatment of the paramagnetic ortho-para-hydrogen conversion has been developed by Wigner [81]. While

the energy of interaction between the nuclear spins of the H_2 molecules and a homogeneous magnetic field is not changed by interchanging the nuclei, this is not valid for a field which is in-homogeneous in molecular dimensions.

Table 28

Ion	Half lifetime in mins. in a 10^{-3} mole/litre solution	k in mole^{-1} litre min. $^{-1}$	μ magnetic moment in magnetons*	$\frac{k}{\mu^2}$
Pr^{+++}	304	2·26	3·62	0·181
Nd^{+++}	290	2·37	3·68	0·168
Sm^{+++}	·1080	0·64	1·60	0·250
Gd^{+++}	39·4	17·50	7·94	0·276
Er^{+++}	18·0	38·20	9·70	0·416
Yb^{+++}	67·5	10·20	4·50	0·502

In such a field, which is obtained in the vicinity of paramagnetic molecules, ortho-parahydrogen conversion may take place. At a distance r from the paramagnetic molecule the part of the magnetic moment (Z-component) causing the conversion is given by

$$U_Z = \frac{3\mu_a \mu_p S_Z Z}{2r^4} \qquad \text{.....(23),}$$

μ_p designating the magnetic moment of the proton, μ_a that of the paramagnetic molecule, $S_Z = S_{1Z} - S_{2Z}$ the difference of the spin co-ordinates and $Z = Z_1 - Z_2$ the difference of the spatial co-ordinates. Then the matrix element connecting the states J and $J \pm 1$, i.e. corresponding to an ortho→para transition, has the form

$$M_{J\,m, J\pm 1\,m'} = \int \psi_{J\,m} U_Z \psi^*_{J+1\,m'} \qquad \text{.....(24),}$$

m and m' designating the magnetic quantum number before and after the transition. (In this case the selection rule $\Delta m = 0$, $\Delta J = \pm 1$ is valid.)

On computing the value of the integral according to the intensity formula (see e.g. Kronig, *Bandspectra*) and intro-

* van Vleck, *Theory of Magnetic Susceptibilities*, Oxford (1932).

ducing r_H, the distance of the H atoms, the following formulae are obtained:

$$M_{J\,m,J-1\,m} = \frac{3 r_H \mu_a \mu_p}{r^4} \sqrt{\frac{J^2 - m^2}{(2J+1)(2J-1)}} \quad \ldots\ldots(25),$$

$$M_{J\,m,J+1\,m} = \frac{3 r_H \mu_a \mu_p}{r^4} \sqrt{\frac{(J+1)^2 - m^2}{(2J+1)(2J+3)}} \quad \ldots(25a).$$

To calculate the probability of transition the collision is to be replaced by the following process: the paramagnetic molecule under consideration is supposed to be brought with infinite velocity within distance of collision (r_s), supposed to stay there, at rest, during the time of collision and removed again with infinite velocity. During the collision the Schroedinger wave equation is valid:

$$\Delta\psi - \frac{8\pi^2 m_{H_2}}{h^2}(U^0 - U)\psi + \frac{4i\pi m_{H_2}}{h}\frac{\partial\psi}{\partial t} = 0 \ldots\ldots(26),$$

U designating the variable perturbation potential caused by the collision. Putting (cf. p. 11)

$$\psi(q,t) = \Sigma a_n(t)\psi_n(q)e^{-\frac{2i\pi E_n t}{h}} \quad \ldots\ldots(27),$$

and considering that ψ_n satisfies the unperturbed Schroedinger equation, we obtain

$$U\Sigma a_n e^{-\frac{2i\pi E_n t}{h}}\psi_n = \frac{hi}{2\pi}\Sigma\frac{\partial a_n}{\partial t}e^{-\frac{2i\pi E_n t}{h}}.\psi_n \ldots\ldots(28).$$

If this equation is multiplied by ψ^*_{J+1} and integrated over the whole range, using the relationships

$$\int \psi^*_{J+1}\psi_n d\tau = \begin{cases} 0 \text{ if } n \neq J+1 \\ 1 \quad n = J+1 \end{cases} \quad \ldots\ldots(29)$$

and

$$\int \psi^*_{J+1} U\psi_n = \begin{cases} 0 & \text{if } n \neq J \\ M_{J,J+1} & n = J \\ M_{J+2,J+1} & n = J+2 \end{cases} \quad \ldots\ldots(30),$$

the equation

$$\frac{hi}{2\pi}\frac{\partial a_{J+1}}{\partial t}e^{-\frac{2i\pi E_{J+1}t}{h}} = a_J M_{J,J+1}e^{-\frac{2i\pi E_J t}{h}} + a_{J+2}M_{J,J+2}e^{-\frac{2i\pi E_{J+2}t}{h}} \quad \ldots\ldots(31)$$

is obtained. Assuming that at $t=0$ all molecules are in the state J, i.e. $a_n(0)=0$, for $n \neq J$,

$$\left|\frac{a_{J+1}(t)}{a_J(0)}\right|^2 = W_{J,J+1} \quad \ldots\ldots(32)$$

is the probability of the transition $J \to J+1$ taking place during the time interval.

Taking the mean of all the values of m in the formulae (25) and (25a), and integrating equation (28), we obtain, with the collision time $t=\frac{r_S}{v}$ and $E_J=\frac{h^2}{8\pi^2 I}J(J+1)$,

$$W_{J,J+1}=\frac{192 r_{\mathrm{II}}^2 \mu_a^2 \mu_p^2 I^2 \pi^4}{h^4 r_S^8 (J+1)(2J+1)}\sin^2\frac{h(J+1)}{4\pi I v}r_S \quad \ldots(33),$$

or replacing the sines by the angle and with

$$m_{\mathrm{II}_2} r_{\mathrm{II}}^2 = 2I,$$

$$m_{\mathrm{H}_2} v^2 = 3kT,$$

$$W_{01}=\frac{8\mu_a^2\mu_p^2 I\pi^2}{h^2 r_S^6 kT} \quad \ldots\ldots(34),$$

$$W_{J,J+1}=W_{01}\frac{J+1}{2J+1} \quad \ldots\ldots(35),$$

$$W_{J,J-1}=W_{01}\frac{J}{2J-1} \quad \ldots\ldots(35a).$$

The probability of transition must be multiplied by one-third in the case of the ortho-parahydrogen conversion.

In order to obtain from these transition probabilities the collision efficiencies, the expressions $W_{J,J+1}$ must be multiplied by a factor $e^{-\frac{E_{J+1}-E_J}{kT}}$, allowing for the endothermicity of these transitions.

Comparing the theoretical collision efficiencies with the experimental values it is necessary to consider the exact equation for the ortho-parahydrogen conversion

$$-\frac{dp[H_2]}{dt} = \{k_{01}b_0 + (k_{21}+k_{23})b_2 + (k_{43}+k_{45})b_4 + \ldots - [(k_{10}+k_{12})b_1 + (k_{32}+k_{34})b_3 + \ldots]\}[X] \quad \ldots\ldots(36),$$

where $b_0, b_1, \ldots$, etc. denote the concentration of the H_2 molecules present in the rotational level 0, 1, ..., etc., and k_{lm} the velocity constants of the transitions $l \rightarrow m$. From this equation we obtain

$$k_1 = \frac{k_{01} + (k_{21}+k_{23})\,5e^{-E_2/kT} + \ldots}{1 + 5e^{-E_2/kT} + 9e^{-E_4/kT} + \ldots} \quad \ldots\ldots(37),$$

$$k_2 = \frac{(k_{10}+k_{12})\,9e^{-E_1/kT} + (k_{32}+k_{34})\,21e^{-E_3/kT} + \ldots}{9e^{-E_1/kT} + 21e^{-E_3/kT} + \ldots} \quad \ldots(37a),$$

and replacing k_1 by $Z_{p\rightarrow o}$ and k_{01}, k_{21}, etc. by Z_{01}, Z_{21}, etc., we find that the collision efficiency of the whole para-ortho reaction is theoretically given by

$$Z_{p\rightarrow o} = W_{01}\left(\frac{e^{-E_1/kT} + 2e^{-E_2/kT} + 3e^{-E_3/kT} + \ldots}{1 + 5e^{-E_2/kT} + 9e^{-E_4/kT} + \ldots}\right) \ldots(38).$$

An exact comparison between theory and experiment can not be made since the distance of the nearest approach r_s appearing to the sixth power in formula (34) is not necessarily the same as that in gas kinetic collisions.

The theory gives, however, both the right order of magnitude for the collision efficiency and its correct dependence on temperature.

Thus we obtain for $\mu_a = 1$ Bohr magneton and for room temperature when the expression in brackets in formula (38) is about 0·4, $Z = 10^{-12}$ to 10^{-14} if r_s is taken as 1 to 2 Å.

According to theory k should be proportional to μ_a^2. The variation of the expression k/μ_a^2 with the ions of the different rare earths in Table 28 can be accounted for, assuming that with increasing nuclear charge of the ion the distance of

nearest approach decreases which is in qualitative agreement with the results of other investigation concerning the radii of these ions.

Table 29 shows the theoretical dependence of the collision efficiency of O_2 and NO on temperature. It will be seen that there is a fairly good agreement with the experimental values of the Tables 23 and 24 provided the respective r_S values are suitably chosen (cf. figures in brackets) and their dependence on temperature according to the well-known Sutherland formula is taken into account. In the case of NO also the fact must be considered that the paramagnetic NO molecules have an energy excess of 354 cal. which can be transferred in the collision to the hydrogen molecule, thus diminishing the endothermicity of certain transitions.

Table 29

Temperature ° K.	Z for O_2	Z for NO
77	$1{\cdot}9.10^{-13}$	—
143	$5{\cdot}3.10^{-13}$	$3{\cdot}5.10^{-12}$
193	$6{\cdot}1.10^{-13}$	$3{\cdot}3.10^{-12}$
293	$(6{\cdot}8.10^{-13})$	$(2{\cdot}6.10^{-12})$
373	$7{\cdot}4.10^{-13}$	$2{\cdot}5.10^{-12}$
493	$6{\cdot}8.10^{-13}$	$2{\cdot}3.10^{-12}$

2. The heterogeneous conversion

The catalysis of the ortho-parahydrogen conversion was first observed by Bonhoeffer and Harteck using charcoal at liquid air temperatures. The investigation of the temperature coefficient of this catalysis and of the effect of other catalysts led to a very remarkable result. Charcoal is a better catalyst at low temperatures than at high temperatures, while for other substances such as platinum black, the reverse is true. If several c.c. of normal hydrogen are passed per minute through a tube containing about 10 g. of charcoal, the ortho-parahydrogen equilibrium is completely established at liquid air temperatures, but no conversion is observed if parahydrogen is passed through the charcoal at room temperatures. If the charcoal is

replaced by platinum black complete conversion occurs at room temperatures, but practically none at low temperatures.

A closer study has shown that a positive or a negative temperature coefficient is not characteristic of particular groups of catalysts. The same catalyst may exhibit both positive and negative temperature coefficients according to the temperature range investigated. This is generally the case if charcoal, metals or salts are used as catalysts. The negative temperature coefficient is usually found at low temperatures and the positive one at higher temperatures (Bonhoeffer, Farkas and Rummel[61]). Some examples of this behaviour are given in

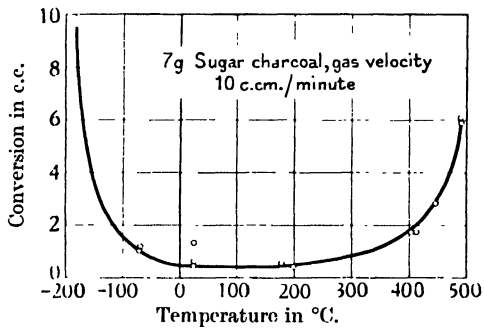


Fig. 26. The ortho-parahydrogen conversion on charcoal (7 g.).

Fig. 26 and in Table 30. Fig. 26 shows the catalytic activity of charcoal at temperatures from -185 to 450° C. with a gas velocity of 10 c.c./minute. Table 30 refers to stationary experiments at a few hundredths of a mm. pressure and gives the half lifetime of the conversion for a sample of 0·0025 c.c. H_2.

The negative temperature coefficient of the conversion is not always observed, e.g. using electrically heated wires as catalysts at low temperatures the velocity of the conversion becomes immeasurably small.

The double temperature coefficient of the conversion causes a minimum activity at a certain temperature, consequently there are two independent mechanisms by which conversion takes place: one of them is effective at low temperatures and is responsible for the negative temperature coefficient, while

the other predominates at high temperatures and has a positive temperature coefficient (Bonhoeffer and Farkas[60]). These two mechanisms (under the headings "low temperature mechanism" and "high temperature mechanism") are discussed separately (pp. 92 and 96).

Table 30

Temperature ° C.	Half lifetime $\tau_{\frac{1}{2}}$ in sec.
Nickel film prepared by evaporation*	
−133	12
− 80	54
20	30
Copper powder prepared by reduction of CuO	
−183	9
20	4200
260	300
Sodium chloride sublimed	
−183	10800
− 80	36000
20	50000
146	1050
205	348
246	192
300	66
340	42

It may be pointed out at once that there is a striking similarity between the temperature dependence of the catalytic ortho-parahydrogen conversion and the temperature dependence of the hydrogen sorption on the different catalysts observed within the last few years.† Starting at −185° C. the adsorption at first decreases as the temperature is raised. Above a certain temperature, depending on the catalyst used, the adsorption begins to increase. Taylor‡ explained this behaviour by postulating two different kinds of adsorption: the molecular or van der Waals' adsorption and the activated adsorption, which are effective in different temperature ranges.

* The nickel film was obtained by heating a nickel wire to 1100–1200° C. *in vacuo* for a few minutes. The film is invisible, but a very effective catalyst.

† "Adsorption of Gases by Solids", *Transact. Faraday Soc.* **28**, 131–437 (1932).

‡ H. S. Taylor, *Journ. Am. Chem. Soc.* **53**, 578 (1931).

While van der Waals' adsorption proceeds with a high speed independent of temperature, the activated adsorption is subject to an activation energy (like that of a chemical reaction) and it is only at fairly high temperatures that the speed is sufficient to cause a measurable adsorption.*

The following discussion will show that there is a close connection between the two mechanisms of the catalytic para-hydrogen conversion and the two kinds of adsorption.

(*a*) *Low temperature mechanism*

It was shown by Rummel[76] that the low temperature catalysis represents the heterogeneous analogue of the conversion occurring in liquid and solid hydrogen or of that caused by paramagnetic substances.

The low temperature conversion was investigated mainly on charcoals of different kinds. On account of the relatively high adsorptive capacity of the charcoals used as catalysts practically all the hydrogen introduced into the reaction vessel (filled with charcoal) was present in the adsorption layer.

Owing to this fact the main experiments could be carried out in a static system by taking the gas samples directly from the adsorption layer. Thus it was possible to investigate the progress of the conversion in the adsorption phase itself and to exclude all complications due to different transport processes (adsorption, desorption, diffusion) that occur in streaming systems.

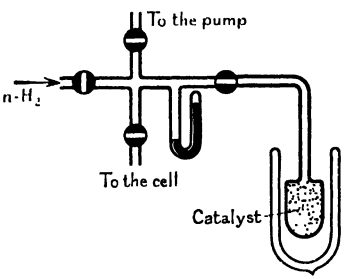


Fig. 27. Experimental arrangement for the investigation of the catalytic ortho-parahydrogen conversion according to the stationary method.

The experimental arrangement is sketched in Fig. 27.

Fig. 28 shows the course of the conversion in the adsorption layer of six different sorts

* According to Harkness and Emmett [72*a*] there are on the surface of a promoted iron catalyst two types of activated adsorption coming into operation at −78 to 0° and above 100° C., respectively.

of charcoal at $-183°$ C. and at atmospheric pressure. It is evident that hydrogen can be adsorbed and desorbed without the ratio of ortho-parahydrogen adjusting itself to the equilibrium corresponding to the temperature of the charcoal. This shows that hydrogen is adsorbed on charcoal in the form of molecules which are not considerably perturbed by the adsorption forces.

The catalytic activities of the different kinds of charcoal vary very much. In general, technical charcoals (curves II and III) are more effective than sugar charcoals (curves V and VI).

Further investigation showed that the different activity is not due to different ash content, and that an addition of platinum to the charcoal does not appreciably change the

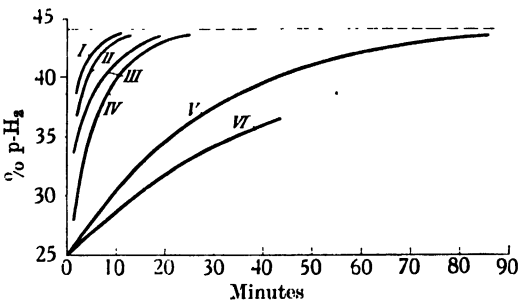


Fig. 28. The activity of different specimens of charcoal.

efficiency. Neither is there a correlation between adsorptive and catalytic activity, e.g. bone charcoal, although a very poor adsorbent, shows greater catalytic activity than the highly adsorbent sugar charcoal. The main experiments were carried out with an ash-free sugar charcoal.

As the reaction proceeds according to the expression $u_t = u_0 e^{-kt}$, the reaction velocity can be characterized by giving the half lifetime of the conversion or the velocity constant k. k is again the sum of the reaction velocity constant of the ortho-para reaction and of the constant of the para-ortho reaction.

The half lifetime of the conversion is independent of the pressure above 7 mm. (Table 31) and, thus, also independent of the concentration in the adsorption layer. This means

that the conversion is of the first order, i.e. the absolute amount of gas converted is proportional to the concentration in the adsorption layer. At low pressures, however, the half lifetime of the conversion decreases indicating that the first small amounts of H_2 taken up by the charcoal are adsorbed on parts of the surface of high catalytic activity.

Table 31. *Sugar charcoal* 90° K.

Pressure in mm. Hg	Half lifetime $\tau_{\frac{1}{2}}$ in sec.	$k=\frac{\ln 2}{\tau_{\frac{1}{2}}}$
0·03	210	$32{\cdot}8\ .10^{-4}$
0·25	492	$14{\cdot}0\ .10^{-4}$
0·54	875	$7{\cdot}90.10^{-4}$
7	1170	$5{\cdot}90.10^{-4}$
60	1200	$5{\cdot}75.10^{-4}$
102	1170	$5{\cdot}90.10^{-4}$
170	1260	$5{\cdot}48.10^{-4}$
760	1200	$5{\cdot}75.10^{-4}$

The half lifetime of the conversion is also independent of the temperature at 63–106° K. See Table 32.*

Table 32. *Cocoanut charcoal ash-free. Pressure* 260 *mm.*

Temperature ° K.	Half lifetime $\tau_{\frac{1}{2}}$ in sec.	$k=k_{o\rightarrow p}+k_{p\rightarrow o}$	$k_{o\rightarrow p}$	$k_{p\rightarrow o}$
106	1260	$5{\cdot}48.10^{-4}$	$2{\cdot}00.10^{-4}$	$3{\cdot}48.10^{-4}$
90	1200	$5{\cdot}25.10^{-4}$	$2{\cdot}48.10^{-4}$	$3{\cdot}27.10^{-4}$
63	1140	$5{\cdot}05.10^{-4}$	$3{\cdot}71.10^{-4}$	$2{\cdot}24.10^{-4}$

At first sight this result seems to be in disagreement with the experiments in streaming systems, which showed a negative temperature coefficient. The data of the streaming method, however, give the absolute amount of gas converted, while the above velocity constants represent the relative change in the concentration and give absolute amounts only if multiplied by the actual concentration in the adsorption layer. Consequently both methods agree, and the negative

* Naturally in this range the ortho-parahydrogen equilibrium is dependent on the temperature and this must be taken into account in calculating the half lifetime and velocity constants.

temperature coefficient is caused by the decrease in adsorption.

The experiments described above refer to a sugar charcoal baked out at 1000° C. *in vacuo*. If the charcoal is brought into contact with hydrogen above 20° C. or with O_2 above −80° C., the catalytic activity is lowered. If the charcoal is again out-gassed the higher activity is restored. This poisoning effect* is not proportional to the amount of gas taken up, showing that the surface of the charcoal is not of uniform activity.†

Oxygen adsorbed at liquid air temperatures, however, increases the efficiency of the charcoal [61, 76], so much that the equilibrium is established within two or three minutes (see Table 33).

Table 33

	Half lifetime $\tau_{\frac{1}{2}}$ in sec.
Sugar charcoal (7 g.)	1620
Addition of 1 cm.³ O_2	450
Addition of 15 cm.³ O_2	< 180

This effect is caused only by the paramagnetic O_2 and not by N_2, for example. This indicates, in connection with the observed first order of reaction, that the conversion involves isolated H_2 molecules and is effected by the magnetic forces of the adsorbing surface in a similar way to the homogeneous magnetic conversion. The magnetic forces are probably due to unsaturated C atoms with free valencies. The O_2 taken up at low temperatures is adsorbed in the form of molecules and the promoting effect is due to its magnetic moment. On the other hand, the poisoning at higher temperatures is caused by a reaction with the charcoal, which saturates the free valencies.

* The same poisoning effect of H_2 for the low temperature catalysis was found by Burstein and Kashtonov [61 *a*] using a charcoal catalyst, and by Harkness and Emmett [72] using a promoted iron synthetic ammonia catalyst.

† That in spite of this inhomogeneity of the charcoal a first order reaction is found can be explained by the assumption that the parts of the surface exhibiting high catalytic activity are not necessarily parts of high adsorptive activity.

Taylor and Diamond [79] recently succeeded in bringing forward experimental evidence for this assumption. They were able to show that the ortho-parahydrogen conversion is really much more rapid on catalysts having a paramagnetic moment, such as Cr_2O_3, Gd_2O_3, etc. (see Table 34).

Table 34. *Temperature* = 86° K.

Catalyst in g.	Pressure in mm.	Time of contact or rate of flow	$\frac{u_t}{u_0}$ 100, %	Specific susceptibility
Cr_2O_3 12·5	760	175 c.c./min.	100	20·1
Gd_2O_3 20·0	760	76 c.c./min.	57	130·1
		3 min.	100	
Nd_2O_3 20·0	555	75 c.c./min.	42	30·3
		3 min.	100	
V_2O_3 80·0	760	76 c.c./min.	63	13·9
	630	5 min.	100	
V_2O_5 9·5	550	34 min.	61	0·85
CeO_2 7·5	560	150 min.	9	0·39
		430 min.	19	
ZnO 10·0	625	130 min.	32	−0·362
La_2O_3 5·0	700	360 min.	17	−0·40

The explanation of the temperature dependence of the conversion is the same as in the case of the paramagnetic homogeneous catalysis: the transitions para→ortho have a positive temperature coefficient on account of the endothermic nature of this step, while the transitions ortho→para are favoured at lower quantum numbers according to Wigner's formula (35, 35*a*, p. 87), and have, therefore, a negative temperature coefficient. As the velocity of the total conversion represents the sum of the velocities of these partial reactions its independence of temperature may be considered as more or less accidental.

(*b*) *High temperature mechanism*

The catalytic ortho-parahydrogen conversion corresponding to the high temperature mechanism has been investigated on

different substances: on metals (in the form of wires, powders and films) [59, 60, 61, 67], on salts [61] and on oxides [77, 78].

The apparatus employed was similar in principle to that used in the experiments with charcoal.

Without previous treatment most substances have no catalytic activity at all, as they are poisoned by surface layers (organic compounds or oxygen). This poisoning layer can be removed by evaporation of several atom layers in the case of metals or by sublimation in the case of salts. Moreover, metals are very sensitive to typical catalyst poisons such as H_2S and to tap grease. For example, it was not possible to obtain reproducible results with a platinum wire in the presence of greased taps and ground joints as its catalytic activity gradually diminished. The activity of a clean platinum wire at 135° C. is equal to that of a poisoned wire at 500° C. [59]. In order to avoid the effect of the grease a trap cooled with liquid air was inserted between the reaction vessel containing the catalyst and the rest of the apparatus. In this case the catalytic activity was reproducible.

The poisoning effect of oxygen is very marked with tungsten [67]. This is due to the great affinity of tungsten for oxygen. The oxygen surface layer lowers the activity of a wire in the ratio 1:200 or more. It can be completely removed by heating the wire to 2200° C. for some minutes.

Both nickel and iron are also poisoned by oxygen, but these metals can be easily reactivated by reduction with hydrogen.

Only platinum is insensitive* to oxygen [59]. It was even rendered more active by contact with oxygen. This promoting effect of oxygen, which has been frequently observed in hydrogenation catalysis, is not yet explained.

The metals copper, silver and gold in the form of wires have a considerably lower activity than the metals mentioned above. In the form of sublimed films or powder there is also a remarkable difference between silver or copper and nickel. Thus an evaporated silver film is practically inactive at

* The high catalytic activity of platinum compared with other metals in the untreated state, as described by Bonhoeffer and Harteck [16, 17] in their first paper, is probably explained by this insensitiveness to O_2.

room temperature; the efficiency of copper powder at 20° C. (see Table 30) is also very poor compared with nickel powder, which brings about immediate establishment of the equilibrium.

The salts NaCl and KI can also be poisoned by oxygen, which is held rather strongly and given up only gradually at higher temperatures.

Table 35

Pressure in mm.	Half lifetime $\tau = \frac{\ln 2}{k}$ in sec.	Apparent order
−100° C. Tungsten wire. 200 mm. long, 0·1 mm. diameter. Volume ~ 500 c.c.		
25	150	0·3
50	240	
100	510	
200	720	
400	1110	
12° C. Nickel tube. 150 mm. long, 7 mm. diameter. Volume ~ 400 c.c.		
0·004	138	0·6
0·04	294	
0·44	780	
4·5	1980	
230° C. NaCl (3–4 g.). Volume ~ 50 c.c.		
0·02	276	1·0
0·04	264	
0·06	282	
0·10	270	
0·20	270	

The conversion proceeded in all cases according to the formula

$$u_t = u_0 e^{-kt}.$$

The apparent order* of the reaction, as indicated by the dependence of the reaction velocity on the pressure, is between

* Inasmuch as the concentration change is measured in the gas phase and not in the adsorption layer (as was done in the investigation of the low temperature mechanism on charcoal) the apparent and the true order of a heterogeneous reaction are to be distinguished. The apparent order shows the dependence of the velocity on the pressure, while the true order shows its dependence on the concentration in the adsorption layer.

0 and 1. It has the lowest value at low temperatures and high pressures and the highest value at high temperatures and low pressures (see Table 35).

The dependence of the reaction velocity on temperature is given in Table 36 for tungsten, platinum and nickel wires of about the same area ($\frac{1}{2}$ cm.^{2}) in a reaction vessel of about 500 c.c.

Table 36

Temperature ° C.	Half lifetime in sec.
Tungsten wire, pressure 50 mm.	
−110	920
100	340
75	59
50	24
25	15
0	8
Platinum wire, pressure 30 mm.	
100	420
120	126
140	48
170	18
210	8
245	5
Nickel wire, pressure 100 mm.	
50	5000
125	2000
150	800
175	500
200	150

The experiments on the catalytic activity of metallic oxides were carried out by H. S. Taylor and A. Sherman [77, 78], who proved that all oxides effecting a parahydrogen conversion at temperatures above 100° C. also show activated H_2 adsorption in the same temperature range according to measurements previously made by Taylor and his collaborators.*

The fact that the apparent order of the high temperature catalysis is less than unity indicates that the conversion proceeds exclusively in the adsorption layer. It is not, for example, based on a reaction between adsorbed and impinging

* H. S. Taylor, *Journ. Am. Chem. Soc.* **53**, 578 (1931).

molecules, as in this case the order should exceed unity. The progress of the reaction shows that the true order with regard to the parahydrogen concentration is equal to 1. The simplest mechanism agreeing with these experimental results is as follows (Bonhoeffer and Farkas [59, 60, 61, 67]).

When hydrogen molecules strike a solid surface, they are either reflected or adsorbed. In the reflection process the speed and direction of the impinging molecule in general are somewhat changed. Adsorption occurs if the impinging molecule loses so much of its kinetic energy in the elastic collision that it cannot overcome the attraction of the surface atoms of the solid. Hydrogen adsorbed in this way is taken up in the form of molecules (molecular adsorption or van der Waals' adsorption).

As the heat of adsorption in this state is very low the molecules remain adsorbed only a short period and are soon desorbed. Neither the reflection processes nor the molecular adsorption* and re-evaporation processes cause para-ortho-hydrogen conversion in agreement with the stability of parahydrogen with respect to collisions in the gas phase (except in the case of collisions with paramagnetic gases).

But not all molecules adsorbed will evaporate as such; some of them will pass into the state of activated adsorption after having received the energy of activation from the solid. In this state the bond between the atoms in the molecule becomes loosened to such an extent that the individual atoms are bound more firmly to the solid than to each other. Due to the loosening of the bond in this state the ortho- and parahydrogen molecules cannot be distinguished. Because of the higher energy of adsorption in the activated adsorption layer as compared with the adsorption energy of the molecular layer, most of the adsorbed molecules are in the activated state. The hydrogen evaporates from the activated layer by way of the molecular layer. In this process a molecule is formed from two atoms which may have belonged originally to two different molecules. The ortho-parahydrogen content of the gas leaving

* That the molecular adsorption does not necessarily cause a conversion is directly shown by the experiments on charcoal (p. 93).

the activated layer corresponds to the equilibrium at the temperature of the surface.

The temperature coefficient of the high temperature catalysis is thus due to the heat of activation which is necessary to cause the hydrogen to pass from the state of molecular adsorption to the state of activated (atomic) adsorption. If the concentration in the adsorption layer is low, the apparent order 1 is found; in the region of saturation zero order prevails.

The scheme is somewhat simplified if it is assumed that the duration of adsorption in the molecular layer is not much longer than the period of the oscillation of the adsorbed molecule attached to the adsorbent. In this case the molecular adsorption processes may be considered as reflection processes. This is probably true at high temperatures.*

Thus the high temperature mechanism of the para-ortho-hydrogen conversion involving exchange of atoms may be considered as a reaction of the chemical type in contrast to that at low temperatures.

* In their first papers this simplified theory was discussed by Bonhoeffer and Farkas[59].

CHAPTER V

APPLICATIONS

BOTH the mutual transformation of the two hydrogen modifications and their different behaviour can be applied to the investigation of different physical and chemical problems.

Thus it is possible by comparing the catalytic parahydrogen conversion with other catalytic processes to draw conclusions with regard to the mechanism of the latter. For example, Emmett and Harkness[82] observed a fast parahydrogen conversion on synthetic ammonia catalysts even at room temperature, and as the NH_3 formation does not begin on the same catalyst below temperatures of 300–400° C., they concluded that the N_2 must also be activated before ammonia is formed.

Farkas and Sachsse[83a] made use of the ortho-parahydrogen conversion to determine the magnetism of B_2H_6, since in this case the ordinary method of measuring magnetic susceptibilities is hardly applicable owing to the difficulty in handling a substance like B_2H_6. If B_2H_6 were paramagnetic it should cause a conversion when mixed with parahydrogen with a collision efficiency of 10^{-14} to 10^{-12} as given by formula (38), p. 88. In the actual experiments, however, the observed rate of conversion was so much smaller that one had to conclude that B_2H_6 in the ground level is diamagnetic.

Since all radicals having a free valency are paramagnetic the presence of such radicals in reactions in progress could be demonstrated by the ortho-parahydrogen conversion caused by them.

Three series of experiments which led to some interesting results are discussed below at greater length.

1. Determination of the H atom concentration in chemical reactions

Since both the energy of activation and the steric factor of the reaction $H + p\text{-}H_2 \rightleftarrows o\text{-}H_2 + H$ are well known, this process can be applied to determine the H atom concentration present during a chemical reaction. This is carried out by adding $p\text{-}H_2$ to the other substances as they undergo the reaction in question, and measuring the change in the $p\text{-}H_2$ percentage induced by the H atoms present.

Naturally only reactions can be investigated which are uninfluenced by the addition of $p\text{-}H_2$ and in which any other processes causing a $p\text{-}H_2$ conversion (wall reaction or influence of paramagnetic gases) are excluded.

The H atom concentration present during the photochemical union of chlorine and hydrogen was investigated by Geib and Harteck [84]. For this reaction, Nernst suggested the well-known chain mechanism

$$Cl_2 + h\nu \rightarrow 2Cl \qquad \ldots\ldots(1),$$

$$Cl + H_2 \rightarrow HCl + H + 0\,\text{kg. cal.} \qquad \ldots\ldots(2),$$

$$H + Cl_2 \rightarrow HCl + Cl + 4\,\text{kg. cal.} \qquad \ldots\ldots(3).$$

As according to Bodenstein (*Transact. Farad. Soc.* **23**, 413 (1931)) the latter reaction proceeds at room temperature at every 100th collision, while the reaction

$$H + p\text{-}H_2 = o\text{-}H_2 + H \qquad \ldots\ldots(4)$$

only at every $3 . 10^6$th collision, so all H atoms will be removed by reaction (3) in an illuminated $p\text{-}H_2$–Cl_2 mixture before they can convert a measurable amount of $p\text{-}H_2$. (This is the explanation for Bonhoeffer and Harteck's [17] observation that any parahydrogen in excess is unchanged after the union of H_2 and Cl_2 has taken place.)

To obtain a great number of H–$p\text{-}H_2$ collisions the chlorine was admitted through a capillary tube into the middle of a large bulb containing several hundred mm. of $p\text{-}H_2$. By using intense illumination all the chlorine was used up at the inlet and thus no H atoms were destroyed by Cl_2 molecules in the

remainder of the bulb. The calculation was made according to the formula

$$\ln \frac{u_0}{u_t} = k\,[\mathrm{H}]\,t \qquad \ldots\ldots(5).$$

If [H] is measured in mm. Hg, t in seconds, at 20° C. $k = 8$.

The stationary H atom concentrations obtained ranged between 1 and 5.10^{-5} mm., depending on the H_2 pressure and the intensity of the illumination.

These figures must be regarded, however, as not very accurate, since according to Sommer* in this particular case the parahydrogen conversion appears to be increased by the reaction

$$\mathrm{H} + \mathrm{HCl} = \mathrm{H_2} + \mathrm{Cl},$$

which produces an additional amount of n-H_2.

In the same way the presence of H atoms was shown in the photochemical decomposition of HBr and H_2O, and the stationary hydrogen concentration produced by the radiation of a mercury arc in H_2 containing some Hg was measured. The latter amounted in 200 mm. H_2 to $1{\cdot}5.10^{-4}$ mm.

According to Haber and Oppenheimer [85] a tungsten arc produced 2.10^{-4} per cent. H atoms in a stream of hydrogen at 150 mm. pressure. This concentration of H atoms causes an explosion at 280° C. if the H_2 is mixed with O_2 after having passed the arc. Without atoms the explosion does not occur below 500° C.

L. Farkas and P. Harteck [83] investigated the concentration of the H atoms and their rôle in the photochemical decomposition of NH_3, using the same method. The kinetic study has shown

$$\mathrm{NH_3} + h\nu = \mathrm{NH_2} + \mathrm{H}$$

to be the primary reaction. The photochemically produced H atoms have a very short lifetime, since they react with NH_3 according to

$$\mathrm{NH_3} + \mathrm{H} + \mathrm{M} \rightleftharpoons \mathrm{NH_4} + \mathrm{M}.$$

This is the cause of the low stationary H atom concentration amounting to some 10^{-5} mm. (H_2 and NH_3 pressure some hundred mm.). From the temperature coefficient of the parahydrogen conversion induced by illuminating NH_3 the energy

* Dissertation, Berlin, 1934.

of activation of 7000 cal. is obtained, i.e. the same as found directly for the reaction

$$H + p\text{-}H_2 = o\text{-}H_2 + H.$$

This means that the stationary H atom concentration is practically independent of temperature and therefore the primary processes involving the consumption of the H atoms proceed without appreciable energy of activation.

The same method of $p\text{-}H_2$ conversion by H atoms was used by Cremer, Curry and Polanyi[81a] for the investigation of the relative reactivity of simple organic compounds with H atoms.

2. Energy exchange between hydrogen and metals

In the investigation of the catalytic ortho-parahydrogen conversion on electrically heated platinum or tungsten wires it was found that at higher temperatures more energy was necessary for the attainment of a given temperature with active wires than with poisoned wires[59, 67]. Fig. 29 shows the heat given up in hydrogen (20 mm. pressure) by active and poisoned platinum wires plotted as a function of the temperature.* The explanation of this behaviour is as follows:

The hydrogen molecules impinging on the metal are partly reflected and partly adsorbed.† The heat exchange between gas and solid is incomplete, since in these impacts the energy of the impinging molecules is only altered to correspond with the temperature of the solid if adsorption takes place, while for reflection processes this is not the case. On the poisoned wire no adsorption processes occur, as indicated by the lack of the parahydrogen conversion, and the heat exchange is due to the inelastic collision processes only. The same statement applies also to the active surface for low temperatures until the number of the molecules adsorbed (i.e. converted) is small

* Cf. also Blodgett and Langmuir, *Phys. Rev.* **40**, 78 (1932).

† This statement is limited to activated adsorption processes, since probably in molecular adsorption processes, at higher temperatures, the time of contact is so short that such adsorptions are practically identical with reflection processes.

compared with the total number of impinging molecules. At higher temperatures the number of the adsorbed molecules increases, and when it becomes comparable with the collision number an additional energy exchange due to this process appears.*

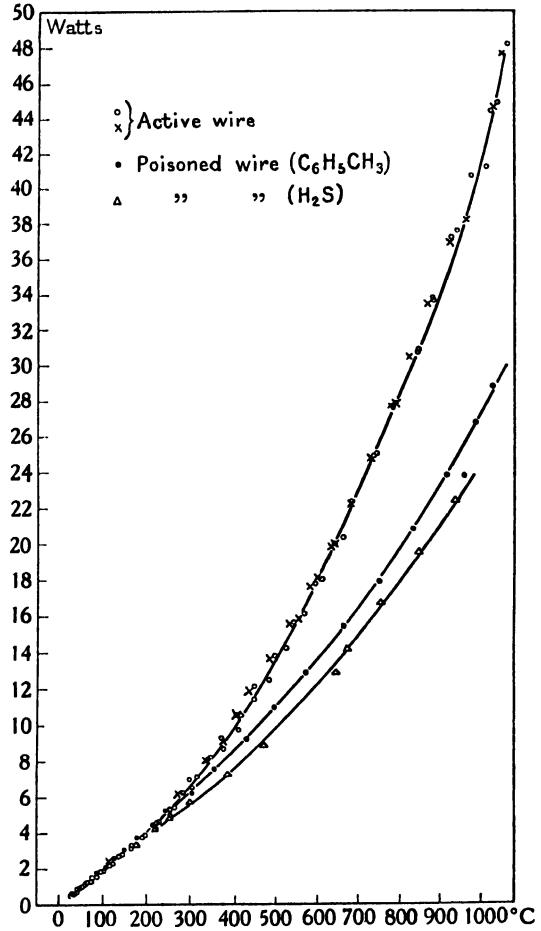


Fig. 29. The heat consumption of active and poisoned wires.

* Naturally this is the case only at very high conversion rates which are not directly measurable but can be extrapolated. For example, at 750° K., when the higher energy consumption of the active wire is already noticeable, we can calculate that $\frac{1}{4}$ of the impinging molecules are actually converted.

The comparison of the accommodation coefficient of normal and of parahydrogen gives more information about the mechanism of the energy exchange between hydrogen and metals.

The accommodation coefficient is a measure of the energy exchange between gas and solid and is defined by the expression

$$a = \frac{T_g - T_g'}{T_g - T_s} \qquad \ldots\ldots(6),$$

T_g, T_g' and T_s denoting the mean temperatures of the impinging molecules, of the molecules leaving the solid and of the solid, respectively.* Rowley and Bonhoeffer[87] have found that the accommodation coefficient of parahydrogen is some-

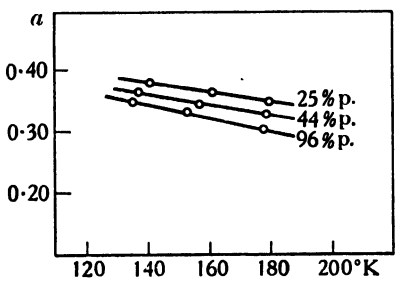


Fig. 30. The accommodation coefficient of parahydrogen on Pt.

what lower than that of ordinary hydrogen (see Fig. 30). As the translational specific heats of normal and parahydrogen are equal and only their rotational specific heats are different (being larger for parahydrogen), it may be concluded that the accommodation for the rotational energy is different compared with that for the translational energy. Table 37 shows the translational and rotational accommodation coefficients calculated from those determined for mixtures of ortho- and parahydrogen of known concentration.

* The accommodation coefficient can be measured by determining the heat given up per sq. cm. per second (W) by an electrically heated wire. For low pressures $a = \frac{WN}{nC\Delta T}$, n denoting the number of impinging molecules per sq. cm. per second, C the specific heat, ΔT the temperature difference between the impinging molecules and the wire and N Avogadro's number.

This result indicates that in the temperature range investigated the energy exchange is mainly due to inelastic reflection processes, for if the energy exchange had occurred by means of adsorption and desorption processes it would be expected that the same value for the accommodation coefficient for the rotational energy and for the translational energy would have been obtained.

Table 37

Temperature ° K.	$a_{trans.}$	$a_{rot.}$
140	0·43	0·26
170	0·44	0·18

3. Self-diffusion of hydrogen

The existence of the two hydrogen modifications permits an investigation to be made of the self-diffusion of hydrogen (Harteck and Schmidt[86]).

Hitherto the self-diffusion constant of H_2 (D) has been calculated indirectly from the diffusion coefficient of three diffusion couples, giving 1·26–1·34. An exact determination seemed desirable to verify the important relation deduced from the kinetic theory of gases:

$$D = f\frac{\eta}{\rho} \qquad \text{.....(7),}$$

η being the viscosity,* ρ the density and f a factor depending on the law of force between the molecules (e.g. if the law of force is given by Kr^{-S}, $f = 1{\cdot}55$ for $S = 5$, or $f = 1{\cdot}20$ for $S = \infty$).

The self-diffusion coefficient was measured by two methods. In the first, two equal tubes of uniform bore, joined by a stopcock, were filled with normal H_2 and with para H_2 respectively. The stopcock was opened and the diffusion allowed to proceed for about 600 seconds. If a be the gas remaining in the tube and b the amount which has diffused

* The viscosity is the same for normal and parahydrogen. Cf. Chapter III, § 8, p. 48.

out, l the length of the tube and t the time, the diffusion constant is given by

$$D=\frac{l^2}{t\pi^2}\ln\left(\frac{\pi^2}{8}\cdot\frac{a+b}{a-b}\right) \qquad \ldots\ldots(8).$$

This method gives very exact results.

The second method* is based on the following fact. If to a stream of gas (say normal H_2) another gas (say para H_2) is added at a certain place, the added gas also diffuses in the opposite direction to that of streaming. Denoting the concentration after complete mixture is attained by c_0, the concentration x cm. from the inlet in the direction opposite to that of the stream by c_x and the velocity of the gas stream by V, the diffusion constant is given by

$$D=\frac{Vx}{\ln c_0/c_x} \qquad \ldots\ldots(9).$$

Although this method is not very accurate it permits of a large variation of the temperature. Table 38 shows the results obtained.

Table 38

Method	Temperature ° K.	D	$f=\frac{D\rho}{\eta}$
I	273†	1·280 ±0·0025	1·37
II	273	1·28	1·37
	85	0·172 ±0·015	1·32±0·11
	20·4	0·00816±0·002	1·28±0·03

Assuming spherical molecules and the law of force Kr^{-s}, the f value 1·37 gives $S=15$.

* Hertz, *Z. f. Physik*, **19**, 35 (1923).

† The actual measurements were made at 293°. These figures are calculated according to Sutherland's equation

$$\frac{D}{D_0}=\left(\frac{T}{T_0}\right)^{\frac{3}{2}}\frac{C+T_0}{C+T}.$$

CHAPTER VI

ORTHO AND PARA SYSTEMS IN OTHER MOLECULES

ORTHO and para modifications are shown by all molecules which contain at least two identical* atoms having a nuclear spin, as the prohibition of the ortho-para intercombination is of general validity. If there is no nuclear spin one set of molecules is missing. This happens in the case of the molecules He_2, C_2^{12}, O_2^{16}, S_2^{32}, etc.

As the state of affairs is very complicated in polyatomic molecules†, the present discussion will be limited to diatomic molecules only.

The normal (high temperature) ratio of ortho to para molecules is determined by the nuclear spin. As the ortho states have the higher statistical weight they correspond to the symmetrical spin function, while the para states represent the levels with the antisymmetrical spin function. Let t be the nuclear spin of the atom. Then the resulting spin of the molecule (T) may have $2t+1$ values,

$$T = 2t,\ \underline{2t-1},\ 2t-2,\ \underline{2t-3},\ \ldots\ 2,\ 1,\ 0.$$

The values underlined correspond to the antisymmetrical spin function, i.e. to the para states. As each resulting nuclear spin T is $(2T+1)$-fold, the normal ortho-para ratio is given by the ratio of the total multiplicity of the ortho states to that of the para states, viz.

$$\frac{g_{\text{ortho}}}{g_{\text{para}}} = \frac{\sum_{n=0,2,4\ldots} 2(2t-n)+1}{\sum_{n=1,3,5\ldots} 2(2t-n)+1} = \frac{(2t+1)(t+1)}{(2t+1)t} = \frac{t+1}{t}.$$

This expression gives at the same time the theoretical in-

* Naturally there are no ortho and para modifications of molecules like $Cl^{35}Cl^{37}$.

† See e.g. Weizel, *Bandenspektren*; Wien-Harms, *Handbuch der Experimentalphysik Ergänzungsband* (1933); and Hund[97].

tensity ratio for the corresponding ortho and para lines in the molecular spectrum.

Table 39 gives the resulting nuclear spins for $t=0$ to $t=\frac{5}{2}$ and the corresponding ortho-para ratios.

Table 39

t	Resulting nuclear spin	$g_{\text{ortho}} = (2t+1)(t+1)$	$g_{\text{para}} = (2t+1)t$	$\frac{t+1}{t}$
0	0	1	0	1:0
$\frac{1}{2}$	1 0	3	1	3:1
1	2 1 0	6	3	2:1
$\frac{3}{2}$	3 2 1 0	10	6	1·67:1
2	4 3 2 1 0	15	10	1·5:1
$\frac{5}{2}$	5 4 3 2 1 0	21	15	1·4:1
∞	— —	—	—	1:1

The electronic and rotational levels with which the ortho and para systems are connected depend on the symmetry of the total wave function, since the latter is not always antisymmetrical as in the case of hydrogen. A general rule with regard to this symmetry is not yet settled,* but it seems that symmetrical total eigenfunctions occur if the nuclei contain an even number of protons + neutrons, i.e. if the atomic weight is even, and antisymmetrical eigenfunctions if the nuclei contain an odd number of protons + neutrons, i.e. if the atomic weight is odd. This can be expressed in other terms by saying that the statistics of Bose and Einstein apply to nuclei with even atomic weight and the statistics of Dirac and Fermi to nuclei with odd atomic weight.†

Table 40 shows the co-ordination of the different levels.

In Table 41 the molecules having ortho and para systems are given. The nuclear spins are obtained according to Table 39 from the intensity ratio of the ortho and para lines observed in the spectrum.

Hitherto the existence of ortho and para modifications in

* This rule cannot be tested in many cases since the normal state and its symmetry property are not always known.

† Dirac, *Proc. Roy. Soc.* A, **112**, 661 (1926); Fermi, *Z. f. Physik*, **36**, 902 (1926); Bose, *ibid.* **26**, 178 (1924); Einstein, *Berl. Akad.* 261 (1924), 3, 18 (1925).

other molecules* has been shown only by the alternation of intensity in band spectra.

Table 40

Statistics	Symmetry of the total eigenfunction	Electronic level	Rotational level	Spin function	System
Bose-Einstein	Symmetrical	Even	Positive	Symmetrical	Ortho
			Negative	Antisymmetrical	Para
		Odd	Positive	Antisymmetrical	Para
			Negative	Symmetrical	Ortho
Dirac-Fermi	Antisymmetrical	Even	Positive	Antisymmetrical	Para
			Negative	Symmetrical	Ortho
		Odd	Positive	Symmetrical	Ortho
			Negative	Antisymmetrical	Para

In the case of iodine the non-occurrence of the ortho-para-hydrogen conversion was shown by Wood and Loomis [112, 113] in the fluorescent spectrum. When iodine vapour is illuminated with monochromatic light in the presence of helium, a number of new bands appear in the fluorescent spectrum. These additional bands are due to the fact that the rotational quantum number of the excited I_2 molecules is changed by collisions with He atoms. In the resultant spectrum, however, every second line is missing, since by collision even rotational quantum numbers are not changed to odd (and vice versa), showing that ortho-para transitions do not occur.

The isolation of one modification or the change of the normal ortho-para ratio fails on account of the high moment of inertia of the molecules in question (except H_2[2], p. 157). The characteristic temperature where the change of the equilibrium can be expected is thereby lowered to a point at which the molecules do not exist in the gas phase. Nevertheless, there is a finite probability of conversion in the solid phase.† Such a conversion could then be demonstrated spectroscopically by the change in the intensity ratio of the ortho and para lines.

* Among the polyatomic molecules the existence of ortho and para molecules was proved by Mecke and his co-workers in the case of C_2H_2[103] and H_2O[104]. They showed by very careful analysis of the rotational structure of the spectra that an alternation of intensity occurs.

† Bonhoeffer and Harteck[88] tried to separate the modifications of H_2O by fractional sublimation and distillation, but without success.

Table 41

Atom	Intensity ratio	t	Total wave function	References
H^1	3:1	$\frac{1}{2}$	Antisymmetrical	[38]
H^2	2:1	1	Symmetrical	[206] [220]
He^4	1:0	0	Symmetrical	—
Li^6	Hyperfine structure	0	—	—
Li^7	1·63:1 1·78:1	$\frac{3}{2}$	—	v. Wijk and v. Koeveringe [111*a*]; Harvey and Jenkins [94]
	Hyperfine structure	$\frac{3}{2}$	—	Breit and Doermann, *Phys. Rev.* **36**, 1732 (1930)
C^{12}	1:0	0	—	—
N^{14}	(N_2^{+}) 2:1 (Raman) 2:1	1	Symmetrical	Ornstein and v. Wijk[106]; v. Wijk[110, 111]; Rasetti [107, 108]; Kronig[100]; Heitler and Herzberg[95]
O^{16}	1:0	0	Symmetrical	—
F^{19}	3:1	$\frac{1}{2}$	—	Gale and Monk[92, 93]
Na^{23}	1·71:1 1·74:1	$\frac{3}{2}$	—	Joffe [99*a*]; Joffe and Urey [99]
	Magnetic deflection	$\frac{3}{2}$	—	Rabi and Cohen, *Phys. Rev.* **43**, 582 (1933)
Al^{27}	Hyperfine structure	$\frac{1}{2}$	—	Ritschl, *Nature*, **31**, 58 (1933)
P^{32}	3:1	$\frac{1}{2}$	—	Jenkins and Ashley[98]; Herzberg[96]
S^{32}	1:0	0	—	Naudé and Christy[105]
Cl^{35}	1·36:1	$\frac{3}{2}$	—	Elliott[90, 91]
K^{39}	3:1	$\frac{1}{2}$	—	Loomis and Wood[102]
Br^{79} Br^{81}	$\fallingdotseq$ 1·67:1 Hyperfine structure	$\frac{3}{2}$ $\frac{3}{2}$	— —	Brown[89] T. L. de Bruin, *Naturwiss.* **18**, 265 (1930); *Nature*, **125**, 414 (1930)
I^{127}	1:1	$\frac{5}{2}$	—	Loomis[101]

PART II

HEAVY HYDROGEN

CHAPTER I

THE DISCOVERY OF HEAVY HYDROGEN

THE discovery of the heavy hydrogen isotope provides a further typical example of the fruitfulness of exact experimental technique applied with confidence in theory.

In 1927 the atomic weight of hydrogen was measured by Aston* with his mass spectrograph in comparing the masses of H and O. The ratio obtained,

$$\frac{\text{Mass H}}{\text{Mass O}} = \frac{1{\cdot}00778}{16{\cdot}0000},$$

seemed to be in perfect agreement with the chemists' value

$$\frac{\text{Mass H}}{\text{Mass O}} = \frac{1{\cdot}00777}{16{\cdot}0000},$$

determined in the usual way of measuring atomic weights. This agreement was somewhat disturbed when, in 1929, Giauque and Johnston† showed that the molecules of ordinary oxygen do not consist exclusively of oxygen atoms of mass 16 (O^{16}), as taken hitherto, but also contain atoms of masses 17 and 18 (O^{17} and O^{18}). The natural abundance of these three atoms in atmospheric oxygen was found to be‡

$$O^{16}:O^{17}:O^{18} = 3150:1:5,$$

and therefore the average atomic weight of the "mixed" oxygen ($\bar{O}$) is given by

$$\bar{O} = \frac{3150\times 16 + 1\times 17 + 5\times 16}{3156} = 16{\cdot}0035,$$

* F. W. Aston, *Proc. Roy. Soc.* A, **115**, 487 (1927).
† W. F. Giauque and H. W. Johnston, *Nature*, **123**, 318, 831 (1929).
‡ R. Mecke and H. W. J. Childs, *Z. f. Physik*, **68**, 362 (1931).

i.c. it is 1·00022 times larger than 16·0000.

Thus the chemical determination of the atomic weight has really given the ratio

$$\frac{\text{Mass H}}{\text{Mass O}} = \frac{1{\cdot}00777}{16{\cdot}0000}$$

or

$$\frac{\text{Mass H}}{\text{Mass O}^{16}} = \frac{1{\cdot}00777 \times 1{\cdot}00022}{16{\cdot}0000} = \frac{1{\cdot}00799}{16{\cdot}0000},$$

whereas Aston's value was

$$\frac{\text{Mass H}^1}{\text{Mass O}^{16}} = \frac{1{\cdot}00778}{16{\cdot}0000}.$$

After a careful consideration of the limits of error (in Aston's measurements 1:20,000) Birge and Menzel [120] concluded that the minute discrepancy of 2 in 10,000 between the atomic weights of hydrogen, measured by chemical and by mass spectrographic methods, might be due to the presence of a heavier isotope of hydrogen in the ordinary gas. If the mass of the heavy isotope was 2, one part in five thousand would cause the observed discrepancy.

In December 1931, Urey, Brickwedde and Murphy [160] succeeded in discovering two very faint lines near the well-known Balmer lines of ordinary hydrogen, the wave lengths of which were in exact agreement with those calculated for the Balmer lines of hydrogen with mass 2. Their hydrogen sample was the residue of a large amount of liquid hydrogen which had been evaporated in order to concentrate the isotope.

An unexpected development in the investigation of the heavy hydrogen isotope occurred when Washburn and Urey [170] discovered in July 1932 that when ordinary water is electrolyzed under suitable conditions the light hydrogen is about six times more readily liberated than its heavy isotope, and thus the latter remains preferentially in the residual water. Sometime later Lewis and MacDonald [116] succeeded by the continuous electrolysis of a very large amount of water in preparing some tenth of a cubic centimetre of water which contained practically only hydrogen atoms of mass 2. The specific gravity of this water was about 10 per cent.

greater than that of the ordinary water, in accordance with the fact that its molecular weight is 20 instead of 18.

The discovery of a convenient way of producing the heavy hydrogen has stimulated a very large number of investigations in this field, which seems to present one of the most interesting chemical problems of recent years.* (Cf. [133*a*, 135*a*].)

* The existence of the hydrogen isotope was predicted by Allison using his magneto-optic method[115, 116].

CHAPTER II

THE PREPARATION AND DETERMINATION OF HEAVY HYDROGEN

1. Nomenclature

In view of the great differences in the properties of light and heavy hydrogens and of their compounds, Urey, Brickwedde and Murphy [163, 164] suggested special names for the isotopes H^1 and H^2, namely, "protium" and "deuterium" respectively, from the Greek words "protos" and "deuteros", meaning the first and second. These names permit the formation of the prefixes and suffixes used in chemistry, e.g. protides and deuterides, protoxyl and deuteroxyl, protates and deutrates, proto- and deutero-compounds analogous to hydrides, hydroxyl, hydrates and hydro-compounds.

For the nucleus of the heavy hydrogen isotope Lewis proposed the name "deuton" (or deuteron), analogous to the name "proton".

In English literature we also find the names "diplogen" and "diplon" used instead of "deuterium" and "deuton", following a suggestion of Lord Rutherford [151, 152].

It also seemed important that the heavy hydrogen isotope should have a definite symbol, and so far the symbol "D" has attained a fairly general use.

2. The preparation of heavy hydrogen

The heavy hydrogen content of ordinary water is about one part in five thousand, and this small amount may be concentrated in many different ways, by partial evaporation of liquid hydrogen, by diffusion methods or by electrolysis.

(*a*) *Fractional distillation of liquid hydrogen*

In the first hydrogen sample in which the heavy hydrogen could be detected the heavy isotope was enriched by evaporation of liquid hydrogen. In their original experiment Urey,

Brickwedde and Murphy[160–162] evaporated 4 litres of liquid hydrogen and found that the relative abundance of heavy hydrogen in the last cubic centimetre was increased about five or six times compared with the original gas, the estimation being made by spectroscopic methods (see p. 132). Separation of the isotopes occurred, since the heavy hydrogen has a lower vapour pressure than the light isotope, a fact, which has been predicted theoretically (p. 168, Chapter III, § 9).

A more effective concentration of the heavy hydrogen present in ordinary hydrogen was performed by Keesom, van Dijk and Haantjes[144], using a specially designed rectifier column. Starting with 40 litres of ordinary liquid hydrogen the final residue of 2 litres of gas had a specific gravity which was 1·5 per cent. higher than that of ordinary hydrogen, showing that the sample contained 1·5 per cent. of the heavy isotope.

According to Taylor, Gould and Bleakney[155] a slight separation of the hydrogen isotopes also occurs by fractional desorption from charcoal at liquid air temperature.

(*b*) *Diffusion methods*

The preparation of the heavy hydrogen by diffusion is based on the different molecular velocities of the isotopes. The mean velocities (w) of H_2, HD and D_2, being inversely proportional to the square root of the mass, are in the ratio

$$w_{H_2} : w_{HD} : w_{D_2} = \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}} : \frac{1}{\sqrt{4}}.$$

If a mixture of, say, H_2 and D_2 is pumped out from a vessel through a fine nozzle the separation is given by the Rayleigh formula provided that the mean free path is large compared with the dimension of the nozzle:

$$\frac{(H)_0}{(H)}\left[\frac{(D)}{(D)_0}\right]^s = \left(\frac{p_0}{p}\right)^{s-1} \qquad \ldots\ldots(1),$$

p_0 and p denoting the initial and the final pressure in the vessel, $(H)_0$, $(D)_0$, (H) and (D) the initial and the final con-

centration of the light and the heavy hydrogen, respectively, and $s = \frac{\sqrt{4}}{\sqrt{2}} = 1{\cdot}41$.

Although this separation factor is relatively low Hertz [143] succeeded by an ingenious combination of several diffusion stages in preparing absolutely pure D_2. His apparatus (Fig. 31) consisted of a large number of porous clay tubes sealed in glass and several diffusion pumps connected up in a suitable way to effect a multiple separation. When the mixture of the isotopes enters, say the third diffusion unit of the system at

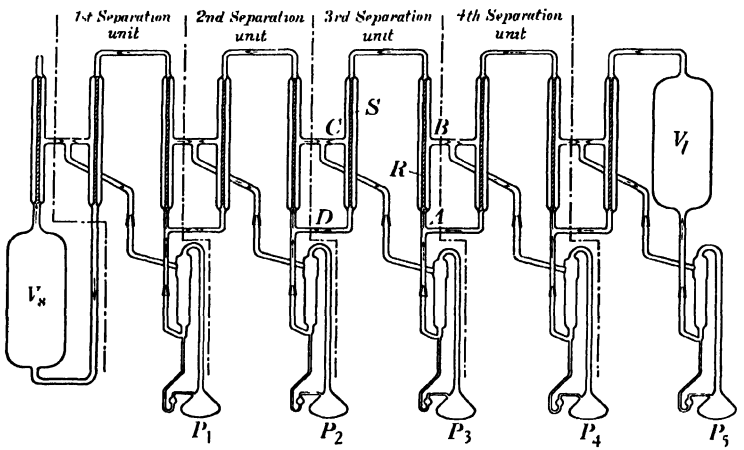


Fig. 31. Hertz' diffusion apparatus for the separation of isotopes.

A, one fraction containing more light hydrogen diffuses through the clay tube R and enters the fourth unit. Another somewhat heavier fraction diffuses through the tube S and is pumped back to A by pump P_3, while the heaviest fraction enters at D, the second unit, etc. In the steady state, when all the pumps are working, the light isotope collects in the vessel V_l and the heavier in the vessel V_s. In the actual apparatus 48 units were used, and starting with the hydrogen containing 0·1 per cent. of the heavy isotope, Hertz prepared heavy hydrogen of such a purity that spectral tubes filled with the gas did not show the Balmer lines of ordinary hydrogen at all. As in the original gas only H_2 and HD were present with practically no D_2 molecules,

it was necessary to apply an electric discharge at a suitable point in the system in order to establish the equilibrium

$$H_2 + D_2 \rightleftarrows 2HD \quad \text{(see p. 176)}.$$

A separation of the hydrogen isotopes also occurs when a mixture diffuses through palladium, but in this case the separation is not due to the different molecular velocities alone.

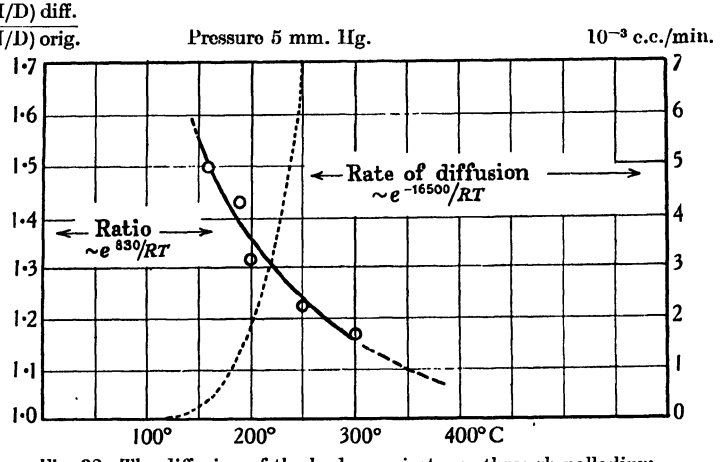


Fig. 32. The diffusion of the hydrogen isotopes through palladium.

The diffusion of the hydrogen isotope through palladium was investigated by A. and L. Farkas [132, 253], who measured the H/D ratio of the gas diffusing from a vessel which contained hydrogen of known H/D ratio (about 40–50 per cent. D). The dependence of the separation factor

$$s = \frac{(H/D)_{\text{diffused}}}{(H/D)_{\text{original}}} \qquad \ldots\ldots(2)$$

and of the rate of diffusion on temperature are given in Fig. 32;* the former can be represented by the expression $e^{-16500/RT}$, the latter by $e^{830/RT}$. The lower the temperature the higher is the separation factor, i.e. the lower is the D content of diffused gas compared with that of the original gas.

* The absolute value of s may be somewhat larger since in these experiments the different solubilities of the hydrogen isotopes have not been taken into account.

The explanation of this behaviour is as follows. The hydrogen diffuses through palladium in the atomic form, and this process has an activation energy, like other chemical reactions, of about − 16500 cal., i.e. the rate of diffusion is proportional to $e^{-16500/RT}$. This activation energy (see Fig. 33) appears to be higher for D_2 and HD than for H_2 owing to the smaller zero-point energies (E_0) (see p. 155) of D_2 and HD compared with H_2. It can be easily shown that assuming an atomic mechanism for the diffusion process, the dependence of the separation factor on temperature is given by

$$s = e^{(E_{0H_2} - E_{0D_2})/2RT},$$

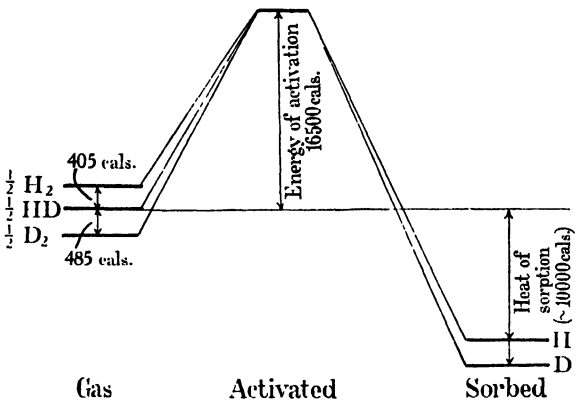


Fig. 33. The energy levels in the adsorption of the hydrogens.

i.e. using the theoretical values

$$E^0_{0H_2} = 6183{\cdot}5 \text{ and } E^0_{0D_2} = 4394{\cdot}5 \text{ cal.}$$

$$s = e^{890/RT},$$

which is in good agreement with the experimental value of

$$s = e^{830/RT}.$$

The diffusion of hydrogen through palladium is however not very efficient as a means of concentrating the isotope. At lower temperatures, when the separation factor is relatively great, the amount of gas passing through is very small, whereas at higher temperatures the diffusion rate is large but the separation is very poor. Nevertheless, Harris, Jost and Pearse [141]

succeeded in effecting eight–tenfold concentration of D by diffusion through palladium at about 300° C. when the pressure was decreased by a factor of 100 (cf. also [131] and [261 *a*]).

(c) *Electrolysis of water*

The most important source of heavy hydrogen is ordinary water and the best method of its preparation is the electrolytic.

The electrolytic separation of the hydrogen isotopes was discovered by Washburn and Urey [170], who found that when ordinary water was subjected to electrolysis the last portion of the residual water had a somewhat higher specific gravity than the original: for example, when 98 per cent. of the water was decomposed the specific gravity was higher by 164 parts in a million. That the higher specific gravity was really due to an enrichment of the hydrogen isotope with mass 2 owing to a slower liberation of the latter in the electrolysis was confirmed by spectroscopic observation, which showed a higher D content as compared with ordinary water. Since the specific gravities of water containing exclusively light and heavy hydrogens, respectively, are in the same ratio as their molecular weights, i.e. 18:20, the observed increase in the specific gravity corresponded to an increase of 0·16 per cent. in the D content of the water.

The electrolytic method for the production of heavy hydrogen was taken up on a larger scale by Lewis and MacDonald [146], who were the first to succeed in preparing water containing practically only heavy hydrogen. The electrolysis was carried out in several stages in alkaline solution (0·5 *N*) using nickel electrodes. In the first stage 10 litres of water from an old electrolytic cell (cf. also [149]) containing about 1:3000 D were electrolyzed in a large tube using a current of 250 amps. until the volume was reduced to 1 litre. In order to avoid great losses by evaporation the electrolyte was cooled by running water. After having neutralized 900 c.c. of the residual litre with CO_2 it was distilled and again made alkaline by adding the other 100 c.c. This solution was then electrolyzed in a smaller cell until

100 c.c. were left. In two other still smaller cells the volume of the water was reduced to 0·5 c.c. containing already 31·5 per cent. D. In another run starting with 20 litres of the same original water the residual 0·5 c.c. of water contained 65·7 per cent. D. By continued electrolysis of such samples, 0·3 c.c. of water was finally obtained with a specific gravity of $d_4^{25} = 1{\cdot}1059$, which did not increase when the volume of the water was further reduced by electrolysis to 0·12 c.c.; indicating that this sample contained practically only heavy hydrogen.

Table 42 contains the results of a complete electrolysis carried out by Taylor, Eyring and Frost [154] in seven stages.

Table 42

Stage	Amount electrolyzed	Specific gravity (d_4^{20}) of the residue	D content of the residue
I	2310 litres*	0·998	—
II	340 litres	0·999	0·5
III	52 litres	1·001	2·5
IV	10·15 litres	1·007	8·0
V	2 litres	1·031	30·0
VI	420 cm.³	1·098	93·0
VII	83 cm.³	1·104	99·0

At the beginning of the electrolysis the hydrogen evolved contains only very little D, but in the later stages of the electrolysis, when the solution is already considerably enriched with respect to the heavy hydrogen, it is advisable to recover the D content of the gas liberated by burning it to water.

This can be done very efficiently by passing the electrolytic gas over an incandescent platinum spiral and condensing the steam formed. In order to avoid explosions mercury bubblers, capillary tubes and sand valves are employed.

A convenient way for the electrolytic concentration of heavy water suitable for use in the laboratory is described by Taylor, Eyring and Frost [154] (cf. also [116*a*, 139, 142, 151*a*, 158*a*]). The solution of 0·5 mol. NaOH is electrolyzed in a battery of 210 cells made from hydrometer jars of 200 c.c. capacity cooled

* D content about 1:3000.

by immersion in flowing water. The electrodes are made from nickel strips and bent twice at right angles in order to form cathode and anode for two neighbouring cells. The current taken up is 6–7 amperes and the battery is subdivided in a number of cells which permit direct connection with the electric supply. The electrolysis is continued until the electrolyte is reduced to 1/6–1/7 of its original volume.

Fig. 34 shows an arrangement for the production of heavy water of high D_2O content to be used in the last stage of the concentration process. The electrolytic cell has a volume of

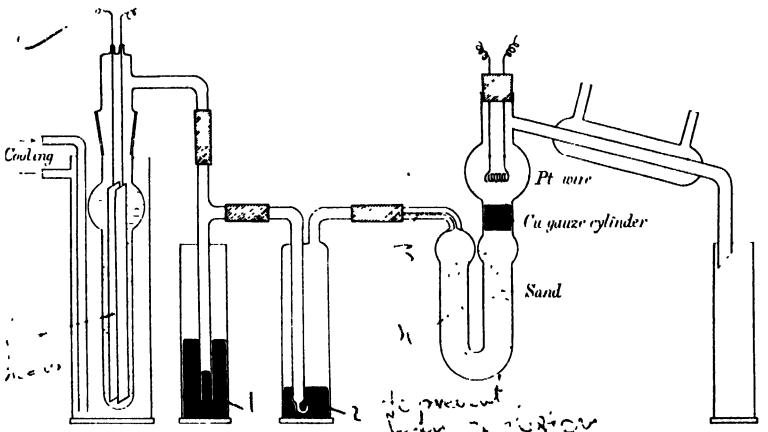


Fig. 34. Experimental arrangement for the concentration of heavy water by electrolysis.

50–100 c.c. and is fitted with Ni-cathode and a platinum anode, since a nickel anode has a tendency to corrode.

Formally the electrolytic enrichment of heavy hydrogen proceeds according to the expression

$$d \ln a_H = s\, d \ln a_D \qquad \ldots\ldots(3),$$

where a_H and a_D are respectively the total amount of H and D present in the electrolyte and s is the so-called "separation factor" or "separation coefficient"* indicating how many times the light hydrogen is liberated more readily than the heavy one.

* Some authors use its reciprocal value.

Introducing the volume of the electrolyte (V) and the concentrations of H and D,

$$(\mathrm{H}) = \frac{a_{\mathrm{H}}}{V} \quad \text{and} \quad (\mathrm{D}) = \frac{a_{\mathrm{D}}}{V};$$

and considering that at the beginning of the electrolysis $V = V_0$, $(\mathrm{H}) = (\mathrm{H})_0$ and $(\mathrm{D}) = (\mathrm{D})_0$, the equation (3) is easily transformed into a form similar to Rayleigh's formula:

$$\frac{(\mathrm{H})_0}{(\mathrm{H})}\left[\frac{(\mathrm{D})}{(\mathrm{D})_0}\right]^s = \left(\frac{V_0}{V}\right)^{s-1} \qquad \ldots\ldots(4).$$

From these equations formula (5) follows directly, giving the connection between the isotopic composition of the gas liberated and that of the original liquid:

$$\frac{\left[\frac{(\mathrm{H})}{(\mathrm{D})}\right]_{\mathrm{gas}}}{\left[\frac{(\mathrm{H})}{(\mathrm{D})}\right]_{\mathrm{liquid}}} = s \qquad \ldots\ldots(5).$$

This equation explains immediately the discrepancies in the first estimation of the D-content in ordinary hydrogen by different investigators, when values obtained for the ratio D:H varied between 1:5000 and 1:30,000. The ratio 1:5000 represents the natural abundance of D in ordinary water (cf. p. 139), whereas the electrolytic hydrogen developed from the same water contains, according to formula (5), five to six times less D, the electrolytic separation factor s being about 5–6 (see p. 127). If the electrolytic hydrogen generator is, however, used for a longer period and the water decomposed replaced by fresh water the electrolyte is gradually enriched about six times with respect to its D content, the steady state being attained when the hydrogen evolved contains the same amount of D as the ordinary water itself.

The separation factor is practically independent of the D content of the electrolyte for a given cell (see Table 43), but depends somewhat on the metal of the electrode (see Table 44) and on the other conditions of electrolysis, as p_{H}, current density, etc. With increasing temperature the separation factor tends to decrease (Urey [159*a*]).

In Fig. 35 the curves representing equation (4) are shown for $s = 5$, the logarithm of the concentration of H and D being plotted against the logarithm of the decrease in the volume of the electrolyte. For example, with the usual efficiency in electrolysis the volume of ordinary water containing 0·02 per cent. of D must be decreased by the factor 100 to obtain 1 per cent. D, by the factor 2000 to obtain 10 per cent. D and by a factor of about 100,000 to obtain 90 per cent. D in the residual water.

Table 43. *Efficiency of separation according to Harteck* [112]

V_0 in c.c.	V in c.c.	D_0 in %	D in %	s
3000	300	0·33	2·3	6·7
2500	22·5	0·48	27·0	6·0
120	6	12·00	91·5	5·5
3000	100	0·33	5·3	6·0

Table 44

Metal of cathode	s	References
Ni	4·5	Bell and Wolfenden [119]
Pt	5·3	
Cu	5·3	
Pt	7·6–6·5	Topley and Eyring [156, 157, 158]
Pt activated	3·6	
Cu	6·8	
Ni	5·5	
Ag	5·3–5·0	

The mechanism of the electrolytic separation is not yet completely cleared up [130, 131, 153]. So far relatively few data about the influence of the different experimental conditions are available and the process of the electrolysis is rather complex. There are four different processes involved in the actual electrolysis, each demanding separate consideration (cf. Fowler [135]):

(1) The transport of the ions from the electrolyte to the electrodes.

(2) The discharge of the ions at the electrodes.

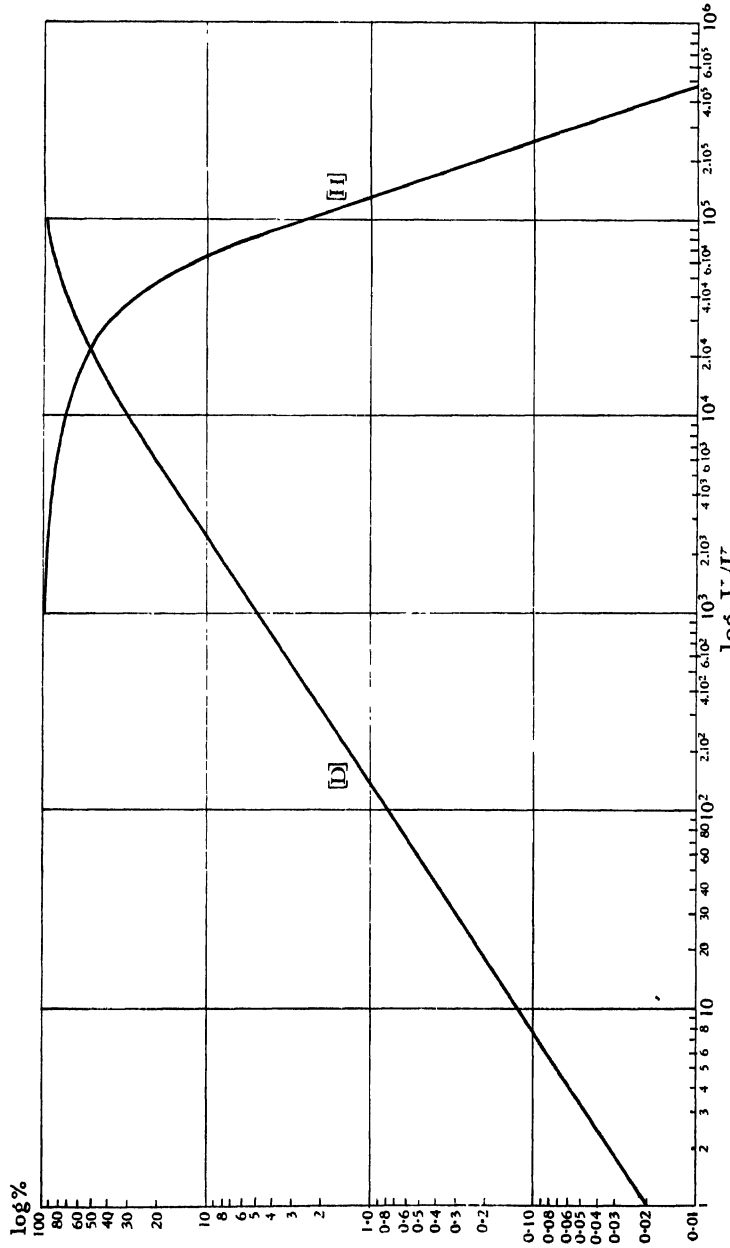


Fig. 35. The enrichment of the heavy hydrogen in the electrolysis.

(3) The formation and liberation of molecular gases at the electrodes.

(4) The exchange reaction

$$H_2O + HD \rightleftharpoons HDO + H_2 \quad \text{.....(6)}$$

between light and heavy hydrogens and water at the surface of the electrodes (A. and L. Farkas[256]).

The transport of ions cannot effect any separation in alkaline electrolytes, since only the alkali and hydroxyl ions then take part in the current-carrying process. But even in acid solutions (where the moving of the hydrogen ions and acid ions is responsible for the current) separation of the hydrogen isotopes due to the different mobilities of their ions (see p. 172) could only occur in the transport process if the natural diffusion did not keep the two hydrogens in normal concentration ratios on the cathode boundary. This condition is, however, never fulfilled (Fowler[135]).

The discharge of the ions at the electrodes might cause a separation in both acid and alkaline solutions. Quantum mechanical considerations* have shown that the transition of an electron from the cathode metal to a hydrogen ion in the boundary layer proceeds by a jump over an energy barrier; it is very probable that the height of this barrier is different for the light and the heavy hydrogen ions, thus giving a different probability of discharge (Polanyi[150]). This is also applicable for alkaline electrolytes, where the process of discharge is

$$(NaOH_2)^+ + e^- \rightarrow Na^+ + OH^- + H \quad \text{.....(7)}$$

and different rates of discharge are to be expected for light and heavy hydrogens. Bell[118] showed that this theory gives the right order of magnitude for the separation coefficient and accounts for the experimental fact that the efficiency of separation is nearly independent of the electrode metal, since it is not the absolute heights of the energy barriers which are to be considered but their differences for the two isotopes.

Similarly, the formation and liberation of molecular gas from the discharged and adsorbed atoms may have different

* R. W. Gurney, *Proc. Roy. Soc.* A, 134, 137 (1931).

velocities for light and heavy hydrogens. From adsorption measurements and catalytic experiments it is known that the recombination of hydrogen atoms on metal surfaces proceeds with an activation energy. In Chapter IV (p. 186) we shall see that in a great number of chemical reactions the respective activation energies are different for the hydrogen isotopes; the same might be anticipated for the processes involved in the electrolysis.

Finally, we have to consider the exchange reaction between water and hydrogen:

$$H_2O + HD \rightleftharpoons HDO + H_2 \qquad \ldots\ldots(6).$$

The equilibrium constant of this reaction,

$$K = \frac{[HDO][H_2]}{[H_2O][HD]},$$

is about 3 at 20° C. (Bonhoeffer and Rummel [248a] and A. and L. Farkas [133] and [259a]). This means that if the hydrogen is liberated from a mixture of light and heavy water under equilibrium conditions, the D content of the gas is much less than that of the liquid, yielding a separation of the isotopes with a "separation coefficient" which is equal to the equilibrium constant (see p. 185).

It is fairly certain that this exchange reaction between hydrogen and water takes place to a certain extent in the electrolysis, since most metals used as electrodes will catalyse even the exchange reaction between molecular hydrogen and water. One would expect it to occur more probably in the actual electrolysis on account of the high reactivity of the hydrogen *in statu nascendi*. In certain cases (e.g. on activated platinum electrodes) the equilibrium (6) was observed to be completely established.

It is clear, however, that this exchange reaction, although an important factor, cannot be the only cause of the isotopic separation, since separation factors much higher than the equilibrium constant K are observed. Further investigation is required to determine to what extent this exchange reaction modifies the primary separation caused by the different rates

of discharge of the H and D ions and by the different rates of recombination of the H and D atoms formed.*

(*d*) *Other methods*

Among other methods for the production and concentration of heavy water the fractional distillation of water and chemical methods may be mentioned.

Washburn and Smith [165] and Lewis and Cornish [207] tried to utilize the difference in the vapour pressure of light and heavy water (cf. p. 172) for the enrichment of the small amount of heavy water present in ordinary water, but the resulting fractionation was rather small: the difference in the specific gravity of the "top" and "bottom" layers of water in a 20-foot column corresponded to an approximately two-fold increase in the D content. A more effective fractionation is to be expected if the distillation is carried out at lower temperatures at reduced pressure when the relative difference in the vapour pressures of light and heavy water is much greater (cf. [195] and [252*a*]).

It is of some interest that in the fractional distillation of water besides the heavy hydrogen isotope the heavy oxygen isotope O^{18} is also somewhat concentrated [272].

For the concentration of heavy hydrogen by chemical means in principle any chemical reaction could be used in which the hydrogen isotopes are produced or consumed with different speeds. Although this happens in most of the chemical reactions involving light and heavy hydrogen, so far no chemical process has been adapted for the production of heavy hydrogen or its compounds.

3. The estimation of heavy hydrogen

In the following pages several methods for the quantitative estimation of heavy hydrogen are described. Some of these methods can be applied only to gaseous hydrogen, others only

* Bowden and Kenyon (in the press) have made a direct comparison of the overpotential of the two isotopes at a mercury cathode and have shown that the irreversible potential of deuterium is *ca.* 0·12 volt more negative than that of hydrogen.

to water; according to the method used it may therefore be necessary to transform the total amount of hydrogen in the sample to be analysed into water or to liberate it all as gas. Some of the methods are absolute, giving directly the ratio of light and heavy hydrogens in the sample; others need an empirical calibration with samples of known composition.

(*a*) *Spectroscopic method*

The first quantitative estimation of heavy hydrogen was carried out by the spectroscopic method by Urey, Brickwedde and Murphy [160]. The measurement was based on the different wave lengths of the corresponding lines in the atomic spectra of light and heavy hydrogens (p. 148), and was carried out by comparing the intensities of the so-called β and γ lines of the Balmer spectrum. Table 45 shows the wave lengths of these lines in Ångström units.

Table 45

	H_β	H_γ
Light hydrogen	4861·3	4340·4
Heavy hydrogen	4860·0	4339·3

The time of exposure was varied until in two different spectrograms of a discharge through the gas to be analysed the intensities of the "light" and "heavy" lines were equal; then the concentration ratio of the isotopes was approximately equal to the reciprocal ratio of the times of exposure; e.g. in one sample the lines of the light hydrogen appeared after an exposure of one second, whereas the lines of the heavy hydrogen were only visible after an hour's exposure, showing that the ratio of heavy hydrogen to light hydrogen was about 1 to 4000. In another sample the respective times of exposure were 1 second and 10 minutes, i.e. the concentration of the heavy hydrogen was about 1 in 600. The spectroscopic method is not very accurate but allows absolute measurements in relatively small amounts of gas even if the concentration of the heavy hydrogen is very low. It can only be applied if a suitable spectrograph of high dispersion (about 1 Å./mm.) is available.

(*b*) *Mass spectroscopic method*

A very accurate absolute method requiring small amounts of gas is the mass spectrographic method worked out by Bleakney [121] (cf. also [147*a*]).

The principle of this method is as follows. In a discharge operated at low pressures in hydrogen containing some of the heavy isotope a great variety of monatomic, diatomic and triatomic ions is formed.* From these ions those having mass 3 and charge 1, i.e. H_3^+ and HD^+, are separated by using suitable electric and magnetic fields which permit only these ions to pass through a system of slits. Their amounts can be determined by varying the pressure, since the concentration of the H_3^+ ions is proportional to the square of the pressure (p^2), whereas that of the HD^+ ions is proportional to the pressure p itself. Thus the number of ions of mass 3 (I) is given by $I = ap + bp^2$. The equation $I/p = a + bp$ represents a straight line whose intercept a is the ratio $HD:H_2$. The ratio D:H is of course half of this value. In the actual experiment the pressure is measured by estimating either the amount of the H_2^+ ions or the total positive ion current.

In the first experiments the following measurements were made with this method [122]:

Table 46

Source	D:H ratio
Sample of liquid hydrogen somewhat enriched by evaporation	1:1050
Rain water	1:5000
Electrolytic hydrogen†	1:30,000 to 1:20,000

This method also permits us to estimate the relative amounts of the ions H_2^+, HD^+ and D_2^+ formed, and thus the concentration of the corresponding molecular species, since the probability of ionization proved to be the same for all three hydrogen molecules [286].

* Cf. also Zeeman and J. de Gier[239].

† On p. 126 we have already referred to the explanation of this discrepancy between the D content of natural water and electrolytic H_2.

(c) *Thermoconductivity method*

The micro-thermoconductivity method for the determination of ortho- and parahydrogen (described on p. 25) has been applied by A. and L. Farkas [132, 253] to estimate the heavy isotope in hydrogen. In Fig. 36 the specific heat curves for the three different sorts of hydrogen, H_2, D_2 and HD (cf. p. 164), are represented, showing that the situation is in principle the same as for the system ortho- and parahydrogen. The apparatus was calibrated using samples of hydrogen containing known amounts of the heavy isotope. The calibration curves are given in Fig. 37, the changes in the resistance value relative to ordinary hydrogen being plotted against the D content. The straight line (*b*) was obtained by mixing different amounts of light hydrogen with pure heavy hydrogen, the sample then containing the molecules H_2 and D_2. The curve (*a*) refers to a mixture containing all three molecules H_2, D_2 and HD in equilibrium with one another (cf. p. 176). This curve is obtained by making measurements on hydrogen samples prepared from water with different D contents or on samples in which the equilibrium $H_2 + D_2 \rightleftarrows 2HD$ has been established by contact with a catalyst. In the latter case the determination is made by measuring the resistance value of the sample before and after contact with a suitable catalyst (e.g. hot nickel wire). The change in the resistance value is a measure of HD defect in the original sample relative to its equilibrium concentration.

The method can only be used if the D content of the sample is not too low, e.g. not less than 1 per cent. and has an accuracy of about $\pm 0{\cdot}1$ per cent. The amount of gas required is about 2–3 $mm.^3$ (N.T.P.) for one measurement, which can be carried out in a few minutes. If the D content of water is to be analysed the sample of hydrogen can be prepared by decomposing the water on a tungsten wire. This method has several advantages, for complete out-gassing at 2000° C. eliminates the possibility of any contamination of the gas recovered, and the tungstic oxide is volatile and distils off so that a fresh metal surface is always being presented to the water.

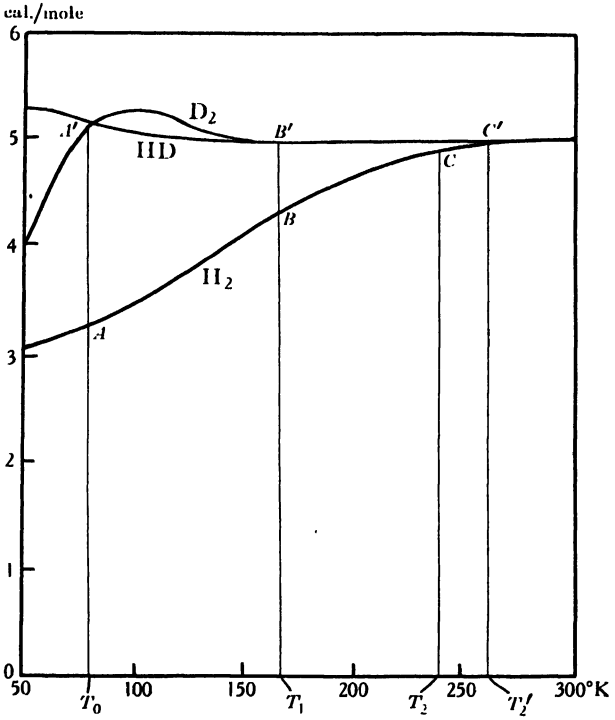


Fig. 36. The principle of the micro-thermal conductivity method for the estimation of heavy hydrogen.

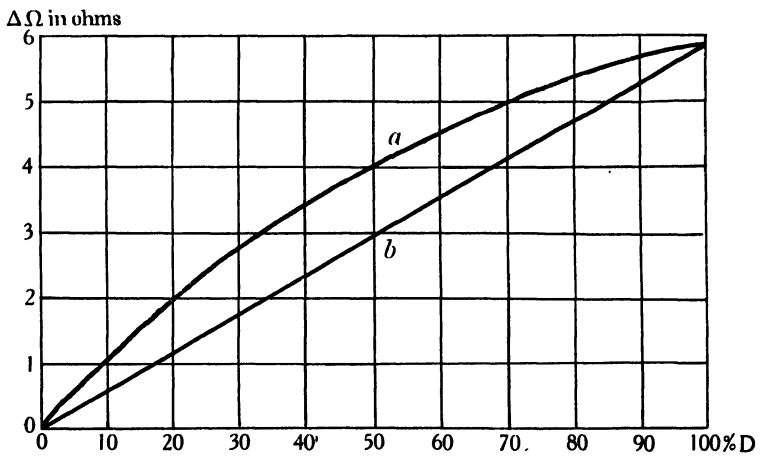


Fig. 37. Calibration curve.

It is also possible to determine the concentrations of the ortho and para modifications of deuterium in a similar way as for ortho- and parahydrogen and thus to carry out in principle a complete analysis of a sample containing the five molecular species o-H_2, p-H_2, HD, o-D_2 and p-D_2 [193] (cf. p. 157).

(*d*) *Specific-gravity method*

The most important and the most widely used method for the estimation of heavy hydrogen is based on the variation of the specific gravity of water* with its heavy hydrogen content. Since the hydrogen contained in any compound can be easily transformed into water this method can be generally applied.

The actual determination of the specific gravity is carried out either by the pyknometer method or by the float method.

With the pyknometer method the weight of water in a given volume is measured. The precision of the determination is much increased by using silica pyknometers, with strict temperature control and balances of high sensitivity. Thus Washburne, Smith and Frandsen [165*a*, 169] succeeded in determining the densities of their samples with a precision of one part per million. With the float method the measurement is performed by varying either the temperature of the water to be analysed or the pressure above it until the float neither sinks nor rises. The float method requires a calibration with solutions of known specific gravity. The former method was used by Lewis and his co-workers [145, 146]. Using a 10 c.c. float at 16° C. a change in the specific gravity of 1 in 10^6 corresponded to a change in the buoyancy temperature of 0·006°. A still higher precision (0·2 part per million) was obtained by Briscoe and his co-workers [128]. Gilfillan [136] used the latter method; in his

* It is perhaps worth while to remember the distinction between specific gravity and density. The specific gravity of a substance is a pure number (without dimension) indicating how many times the substance is heavier than the same volume of a standard substance, generally of ordinary water at 4° C. The density, however, is the mass of substance contained in the unit of volume and has the dimension g./cm.^{3} Specific gravity and density stand in the same relation to one another as litre and cubic decimetre. The specific gravity of ordinary water at 4° C. is 1·000000 (per definition) and its density 1/1·000028 = 0·999972 g./cm.^{3}

arrangement, with floats of 35–0·1 c.c. volume, 1 mm. Hg change in the pressure corresponded to a change of 0·03 to 7 parts per million in the specific gravity, the accuracy obtained being 0·3 to 4 parts per million.

For measurements on a few milligrams of water the float method was improved by Gilfillan and Polanyi [137]. Their float consists of a capillary tube of a few cubic millimetres volume attached to a small glass sphere (Fig. 38). The capillary, with a fine opening of 0·02 mm., is filled, after having been exhausted, with the water to be analysed; the float is then put in distilled water and the pressure above the water varied until the float neither sinks nor rises. The volume of the glass sphere and hence the buoyancy alter with the pressure. 1 mm. change in the pressure corresponds to a change in the buoyancy of 10^{-5} mg. (cf. also [138]).

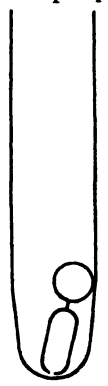


Fig. 38. Micro-float of Gilfillan and Polanyi.

The specific-gravity method required calibration with respect to the abundance of heavy hydrogen in natural water and to the exact dependence of the specific gravity on the isotopic constitution of the water. The determination of the heavy hydrogen content of natural water was made by Bleakney and Gould [122], who found the D:H ratio in rain water to be 1:5000 by means of the mass spectrographic method. The second calibration was performed by Lewis and Luten [145, 148] in determining the specific gravities of the mixtures of light and heavy water. They found that the dependence of the specific gravity on composition differs somewhat from linearity, the specific gravity at 25° C. being given by

$$d_4^{25} = 0{\cdot}9970 + 0{\cdot}1078X - 0{\cdot}0012X(1-X) \ldots\ldots (8),$$

$1-X$ and X designating the mole fractions of light and heavy water respectively.*

* In formulae (8) and (9) the specific gravity for D_2O $d_4^{25} = 1{\cdot}1048$ given by Taylor and Selwood [234] is used (cf. p. 173).

From the difference in the specific gravity Δd, X the mole fraction of the heavy water can be obtained from the formula

$$X = 9{\cdot}381\Delta d_4^{25} - 0{\cdot}97\,(\Delta d_4^{25})^2 \qquad \ldots\ldots(9).$$

It should be emphasized that in specific-gravity measurements precise temperature control is of great importance on account of the peculiar temperature dependence of the specific gravities of light and heavy waters (see p. 172, different temperature of maximum specific gravity).

(e) *Refractometric method*

Another convenient method for the estimation of the heavy hydrogen content of water, based on the refractive index, was worked out by Lewis and Luten [115, 148] and Crist, Murphy and Urey [125, 126]. The difference in the refractive indices of light and heavy waters is 0·00449 for the Na-D line (5893 Å.) at 25° C., the light water having the higher index. By special experiments it was proved that there is a linear connection between the change in the refractive index (Δn) and the mole fraction of heavy water present (X):

$$\left.\begin{aligned} &\Delta n = -0{\cdot}00449X \text{ (for 5893 Å. and 25° C.)} \\ \text{and} \quad &\Delta n = -0{\cdot}00456X \text{ (for 5893 Å. and 20° C.)} \end{aligned}\right\} \ldots\ldots(10).$$

The estimation is easily carried out in a Zeiss interferometer after an empirical calibration. For samples with lower D content than 20 per cent. a longer cell is necessary (e.g. 40 mm., containing 1·5 c.c.). For higher concentrations either a smaller cell (e.g. 10 or 1 mm. cell of 0·3 or 0·05 c.c.) may be used or a small amount of the sample can be accurately diluted. The accuracy of the measurement is 0·01–0·02 per cent. Small amounts of concentrated heavy water must be handled and kept in water-free air, in order to prevent dilution, since heavy water behaves as a hygroscopic substance.

It is interesting to note that by measuring simultaneously the specific gravity and refractive index of a given sample of water it is possible to perform a complete isotopic analysis, including the estimation of the amount of O^{18} present in water, as was shown by Lewis and Luten [145]. From measurements

on a sample containing 0·5 per cent. of the oxygen isotope O^{18} they derived the formulae valid for 25° C.

$$\left.\begin{aligned} X &= 1{\cdot}342\,\Delta d_4^{25} - 190{\cdot}5\,\Delta n \\ Y &= 7{\cdot}535\,\Delta d_4^{25} + 180{\cdot}9\,\Delta n \end{aligned}\right\} \quad \ldots\ldots(11),$$

Δd_4^{25} and Δn denoting the observed change in the specific gravity and refractive index relative to ordinary water, and X and Y the amount of D and O^{18} present.

(*f*) *Other methods*

In general the difference in any property of light and heavy hydrogen or light and heavy water may be utilized for the determination of heavy hydrogen provided this difference is large enough to be conveniently measured. Such differences exist between the freezing points [203], viscosities [213], vapour pressures of light and heavy water [212], between the potentials of the "light" and "heavy" hydrogen electrodes [234*b*] and so forth.

4. Abundance of heavy hydrogen in natural sources

Since the first estimation of the natural abundance of heavy hydrogen made by the discoverers [160–162] a great many samples of water and other substances from various sources have been investigated with respect to their D content (cf. [117, 124, 129, 159, 165*a*]).

The measurements were made by comparing the specific gravities of the water sample in question with a standard. Ordinary tap water was used as a standard and was proved to have a constant specific weight over a long period and identical, according to Briscoe and his co-workers [128], for specimens from London, South Wales, Sumatra and America. Since no pure H_2O (free from D) has so far been prepared (e.g. by electrolysis) the exact D content of the standard is not known;* most probably it will not differ much from the value obtained by Bleakney and Gould for rain water [122] by means of their mass spectroscopic method, i.e. 1:5000.

* According to recent measurements of Ingold and co-workers (*Nature*, **134**, 661 (1934)) the D content of tap water is 1:9000.

Table 47 contains the results obtained for some samples from animal, vegetable and mineral sources.* The differences in specific gravity relative to the standard are given in parts per million. (1 part per million corresponds to a D content of 1:100,000.)

Table 47

Origin	Δd in parts per million	References
	Water	
1. Rain water From Princeton	Mass spectroscopic method 1:5000	Bleakney and Gould [122]
Surface water		
2. From London	0	Briscoe and his co-workers[128]
3. From South Wales	0	,, ,,
4. From Sumatra	0	,, ,,
5. Sea water	2·3	Gilfillan[136]
6. From the Tibetan lake	1·5	Briscoe and his co-workers[128]
7. From the Dead Sea	3·0	,, ,,
	In animal sources	
8. Human blood	1·5	Briscoe and his co-workers[128]
9. Human milk	3·0	,, ,,
10. Human urine	0	,, ,,
11. Cow's milk	−1·0	,, ,,
12. Ox blood	3·0	,, ,,
	In vegetable sources	
13. Willow tree sap water	2·8	Washburn and Smith[166]
14. Willow tree from combined H	5·4	,, ,,
15. Fruits	0–5	Briscoe and his co-workers[128]
16. Honey	4	Dole[127]
	In mineral sources	
17. Hydration water of minerals	3–7·5	Briscoe and his co-workers[128]
18. Kerosene (Oklahoma)	7	Dole[127]
19. Benzene from destructive distillation of coal	8	,,

* In this connection it might be mentioned that according to Lozier, Smith and Bleakney's[147] and Bleakney and Gould's[123] measurements heavy water (91 per cent. D) contains about 1 part in 200,000 hydrogen of mass 3 (H^3), whereas the ratio of the abundancies of $O^{18}:O^{16}$ is practically the same as in ordinary water.

The varying distribution of the heavy hydrogen may be due to a number of causes. A physical process, such as fractional evaporation of the light water, may play a part in entries 6, 7. The higher D content of the hydration water of some minerals may be due to a chemical equilibrium, the heavy water being held more strongly than the light.* Similar factors are probably responsible for the excess of D content in some fruits; in Chapter IV, § 2, p. 200, it will be seen, for instance, that when acetone is in contact with heavy water the heavy hydrogen is present preferentially in the acetone. To what extent the speeds of the uptake of light and heavy waters by the organism are different, causing a different distribution, is still a matter for investigation.

* According to Erlenmeyer and Gärtner [252*a*, *b*] and Friend [193*a*] the hydration water of Na_2SO_4 crystallized from a mixture of light and heavy water has the same D content as the solution.

CHAPTER III

THE PROPERTIES OF HEAVY HYDROGEN

1. Mass, spin and magnetic moment

The atomic weight of heavy hydrogen was determined with very great precision by Bainbridge [172] by means of his highly sensitive mass spectrograph. The most reliable figures are

$$H^2 = 2{\cdot}01363 \pm 0{\cdot}00004 \text{ for } He = 4{\cdot}00216,$$

$$H^2 = 2{\cdot}01363 \pm 0{\cdot}00008 \text{ for } O^{16} = 16{\cdot}0000,$$

$$H^1 = 1{\cdot}007775 \pm 0{\cdot}000035.$$

The heavyhy drogen nucleus, the deuton, is composed of one proton and of one neutron (n), as was shown directly by Chadwick and Goldhaber [181a] who succeeded in disintegrating the deuton by the γ-rays of ThC″ according to

$$_1D^2 + h\nu = {}_1H^1 + {}_0n^1$$

(the left-hand subscripts denote the nuclear charge, the right-hand superscripts the mass). The mass for the neutron obtained from these experiments was $1{\cdot}0080 \pm 0{\cdot}0005$ and leads to a mass defect of 0·002 for the deuton corresponding to a binding energy of about 2×10^6 electron volts which is rather small compared, for example, with the binding energy of 28×10^6 electron volts for He.

According to Wigner [235] this relatively small binding energy in the D nucleus results, because the single potential energy between the neutron and the proton is nearly compensated by the kinetic energies of these two particles. In the case of He however there are four potential energies between the two neutrons and the two protons and only four kinetic energies for these particles.

With reference to this small binding energy Ladenburg [202] investigated the question whether heavy hydrogen is stable or whether it undergoes radioactive decay. According to his measurements heavy hydrogen proved to be an absolutely

stable element, the decay, if any, occurring in a period longer than 10^{15} years.

The spin of the heavy hydrogen nucleus was first estimated by Lewis and Ashley [206]. They observed that in the bands of the D_2 spectrum the lines corresponding to transitions involving even rotational levels are about twice as intense as those connected with the odd ones, and they concluded that the spin of the deuton is 2/2 (in $h/2\pi$ units), in accordance with the rule that nuclei with even atomic weight have integral spins. This result was confirmed by Murphy and Johnston [220], who found 1·95 to 2·02 for the intensity ratio, and is further supported by the investigation of the para-ortho equilibrium (see p. 157) carried out by Farkas, Farkas and Harteck [192, 193]. Since the nucleus of the heavy hydrogen is most probably composed of a proton and a neutron it seems that its spin 2/2 is the resultant of the proton spin 1/2 and of the neutron spin 1/2.

The magnetic moment of the deuton was determined by Estermann and Stern [190 191] using the same method as for the proton (cf. p. 49), and by Rabi, Kellogg and Zacharias [222] using the method of deflecting the atoms in a weak magnetic field. Farkas, Farkas and Harteck [193] deduced the ratio

$$\frac{\text{Magnetic moment of the proton}}{\text{Magnetic moment of the deuton}}$$

by comparing the rate of re-conversion of parahydrogen to normal hydrogen catalyzed by collisions with oxygen molecules (see p. 79) with the corresponding reactions for heavy hydrogen, the collision efficiency of the re-conversion being according to Wigner [81], *ceteris paribus*, proportional to the square of the magnetic moment of the hydrogen nucleus.

The values obtained are given in Table 48.

Table 48

Author	Magnetic moment (μ) of		Ratio $\frac{\mu_H}{\mu_D}$
	H	D	
Estermann and Stern [191]	2·5	0·7	3·6
Rabi, Kellogg and Zacharias [222]	3·15 ± 0·3	0·75 ± 0·2	4·2
Farkas, Farkas and Harteck [193]	—	—	4·25

Exact knowledge of the magnetic moment of the deuton is of the greatest importance for the theory of the nuclei. (Theory, cf. [227].)

2. Transmutations produced by deutons [225]

Cockcroft and Walton have shown in their pioneer experiments [*Proc. Roy. Soc.* A, **137**, 230 (1932)] that high speed protons can penetrate inside the atomic nucleus and change its structure. Such a nuclear reaction occurs for example with lithium when bombarded with protons at accelerating potentials of 100,000 volts,

$$_3Li^7 + _1H^1 = _2He^4 + _2He^4.$$

The energy set free in this reaction is 17×10^6 electron volts and the resultant α-particles have a mean range of 8·4 cm. in air.

The use of deutons instead of protons in transmutation experiments has become a powerful tool for the study of the nuclear reactions, since the deuton has proved to be a much more efficient projectile in bombarding other atoms than protons of the same energy.

Thus the transmutation of lithium when bombarded with deutons becomes more complex and yields a great number of fast protons, α-particles and neutrons according to the following formulae:

$$_3Li^6 + _1D^2 = _2He^4 + _2He^4 + 22 \times 10^6 \text{ electron volts}$$

(Lewis, Livingston and Lawrence [211], Oliphant, Kinsey and Rutherford [221*a*], cf. also [221*b*]),

$$_3Li^6 + _1D^2 = _3Li^7 + _1H^1 + 4{\cdot}8 \times 10^6 \text{ electron volts}$$

(Cockroft and Walton [183*b*], Lewis, Livingston and Lawrence),

$$_3Li^7 + _1D^2 = _2He^4 + _2He^4 + _0n^1 + 14{\cdot}9 \times 10^6 \text{ electron volts}$$

(Oliphant, Kinsey and Rutherford [221*a*], Crane, Lauritsen and Soltan [184]).

Figs. 39 and 40* show the Wilson chamber tracks of particles produced in the disintegration of lithium by protons and deutons (Dee and Walton [187]). The characteristic difference

* The author is very much indebted to Dr Dee for the original photographs.

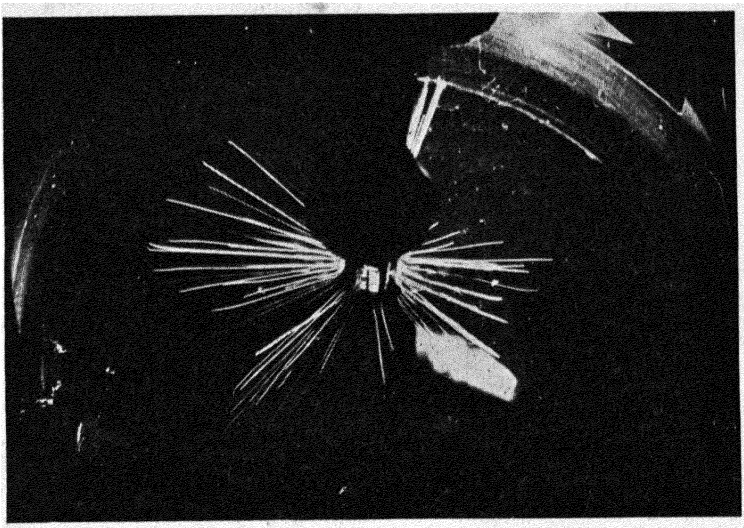


Fig. 39. The disintegration of lithium by protons according to $Li^7 + H^1 = 2He^4$ (Dee).

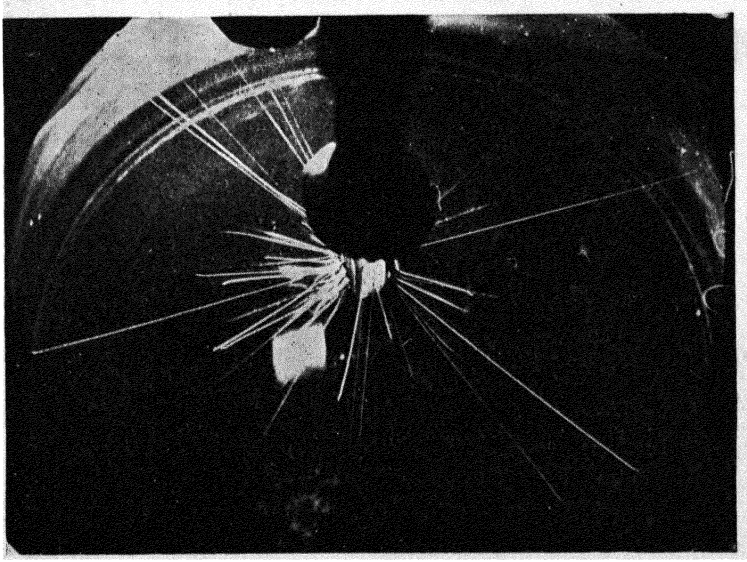


Fig. 40. The disintegration of lithium by deutons. The long-range α-particles flying in opposite directions are due to the reaction $Li^6 + D^2 = 2He^4$ (Dee and Walton).

between the two reactions is obvious. The protons produce only α-particles having a mean range of 8·4 cm. in air, whereas the deutons give rise to the emission of very fast α-particles of 13·4 cm. range.

Similar nuclear reactions occur with other elements such as Be[183*b*, 184, 185, 204, 211, 218], B[183*b*, 203*a*], C[183*b*, 203*a*, 211] and O[183*b*] when bombarded with deutons.

A very remarkable result was obtained by Oliphant, Harteck and Rutherford[221] when bombarding heavy hydrogen

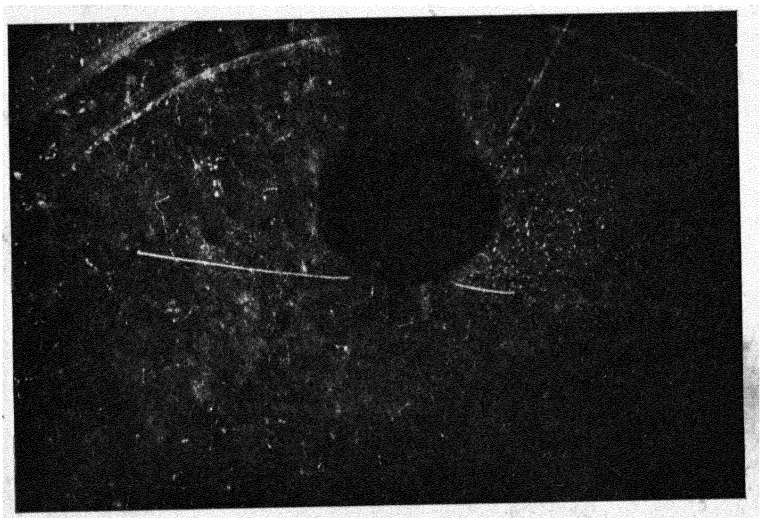


Fig. 41. The tracks of H^3 and H^1 flying in opposite directions formed in the reaction $D^2 + D^2 = H^3 + H^1$ (Dee).

in the form of the compound $(ND_4)_2SO_4$ with deutons. In these experiments an enormous number of fast protons and neutrons could be observed even when the relatively low potential of 100,000 volts was used for accelerating the deutons. The nuclear reactions occurring were

$$ {}_1D^2 + {}_1D^2 \rightarrow ({}_2He^4) \rightarrow {}_1H^3 + {}_1H^1, $$

$$ {}_1D^2 + {}_1D^2 \rightarrow ({}_2He^4) \rightarrow {}_2He^3 + {}_0n^1. $$

The tracks of the resulting H^3 and H^1 flying in opposite directions are shown in Fig. 41* (Dee[186]). From the range of

* The author is very much indebted to Dr Dee for the original photograph.

these particles (14 cm. for H^1 and 1·6 cm. for H^3) it was possible to deduce the mass of this new artificially produced hydrogen isotope $H^3 = 3{\cdot}10151 \pm 0{\cdot}0001$.

The production of H^3 was also observed by Harnwell, Smyth, van Voorhis and Kuper [197] when heavy hydrogen was bombarded by a very strong beam of deutons (cf. also [178a]).

3. Kinetic properties

As already mentioned (see p. 119) the molecular velocities of deuterium and hydrogen are in the ratio of the reciprocal square root of their masses, i.e.

$$w_{H_2} : w_{HD} : w_{H_2} = \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}} : \frac{1}{\sqrt{4}}.$$

This difference in the molecular velocities becomes apparent when a mixture of the isotopes is pumped at low pressures through narrow tubes or fine openings, as used in a laboratory vacuum apparatus. In Table 49 some results of A. and L. Farkas [132, 255] are given, showing the variation of the isotopic composition of an H_2-D_2 mixture when the original pressure p_0 is reduced to p by pumping through a fine nozzle. The results obtained are in good agreement with the values calculated on the basis of the theoretical equation (1) (p. 119), the dimension of the opening being large compared with the mean free path.

Table 49

p_0/p	Percentage D_2 observed	Percentage D_2 calculated
1·0	47·0	—
1·5	50·7	50·7
2·0	53·0	53·0
3·25	56·0	57·8

Some other kinetic properties of deuterium, which are directly related with the molecular velocity, are compared with those of hydrogen in Table 50.

The symbols used have the following meanings: c, concentration in moles cm.$^{-3}$; d, molecular diameter; N, Avogadro's number; M, molecular weight; C_v, specific heat.

Table 50

Property	Approximate formula	Ratio $\frac{\text{property of } D_2}{\text{property of } H_2}$
Number of collisions	$\frac{N^2 c'^2}{2} \bar{w} . \pi . d^2$	$1/\sqrt{2}$
Mean free path	$\Lambda = \frac{1}{\sqrt{2} N c \pi d^2}$	1
Viscosity	$\eta = \frac{1}{3} M . \bar{w} c . \Lambda$	$\sqrt{2}$
Heat conductivity*	$\lambda = k\eta \frac{C_v}{M}$	$1/\sqrt{2}$
Diffusion coefficient†	$D = f \frac{\bar{w}}{3} \Lambda$	$1/\sqrt{2}$

4. Spectrum of D, HD, D_2 and other D-compounds

Treating the spectrum of heavy hydrogen, in general we have to consider three different groups of spectra:

(*a*) The atomic spectrum of D.
(*b*) The spectra of the molecules HD and D_2.
(*c*) The spectra of other D-compounds.

(*a*) *The atomic spectrum*

The atomic spectrum of heavy hydrogen is a good example of the isotopic effect which can be derived directly from the well-known Bohr expression for the Rydberg formula.

The frequencies ν of the different lines in the spectrum of atomic hydrogen are given by

$$\nu = R\left(\frac{1}{n_1} - \frac{1}{n_2}\right), \quad n_1 = 1, 2, 3, \ldots, n_2 > n_1 \quad \ldots\ldots(1);$$

* Cf. p. 20. † Cf. p. 108.

with the Rydberg constant

$$R = \frac{2\pi^2 \mu e_0^4}{h^3 w_l} \qquad \ldots\ldots(2),$$

$$\frac{1}{\mu} = \frac{1}{m_0} + \frac{1}{m_{\mathrm{H}}} \qquad \ldots\ldots(2a),$$

m_0 and e_0 denoting the mass and charge of the electron, m_{H} the mass of the proton, h Planck's constant and w_l the velocity of light. The Rydberg constant for H is $R_{\mathrm{H}} = 109677{\cdot}76$, whereas for D the value $R_{\mathrm{D}} = 109707{\cdot}56$ results when m_{H} is replaced by m_{D} in formula $(2a)$.

The lines of the Balmer series are obtained from formula (1) with $n_1 = 2$ and $n_2 = 3, 4$, etc. Table 51 contains the calculated wave lengths $(\lambda = 1/\nu)$ for the first four lines of this series together with the calculated and observed isotopic shift $(\Delta\lambda)$.

Table 51

Wave length λ in Ångström units calculated for	$n_2=3$ H_α	$n_2=4$ H_β	$n_2=5$ H_γ	$n_2=6$ H_δ
H	6562·793	4861·326	4340·467	4101·738
D	6561·000	4860·000	4339·282	4100·619
$\Delta\lambda$ calculated	1·793	1·326	1·185	1·119
$\Delta\lambda$ observed (Urey and his co-workers[160, 161]	1·791	1·346	1·206	1·145
	—	1·330	1·199	1·103
	1·820	1·313	1·176	1·088
$\Delta\lambda$ observed (Rank[224])	—	—	1·211	—

Fig. 42 shows the first spectrogram on which the lines of the heavy hydrogen isotope were discovered by Urey, Brickwedde and Murphy[160]. Fig. 43 shows two photographs of the Hα line in two spectral tubes taken by Hertz[143],* one of the tubes being filled with ordinary hydrogen and the other with deuterium prepared by the diffusion method. The purity of this deuterium sample is remarkable since no trace of the $H^1\alpha$ line can be detected in its spectrum.

Table 52 contains similar data for the Lyman spectrum $(n_1 = 1)$ of light and heavy hydrogens according to the measurements of Ballard and White[172a].

* The author is very much indebted to Prof. Hertz for the original photograph.

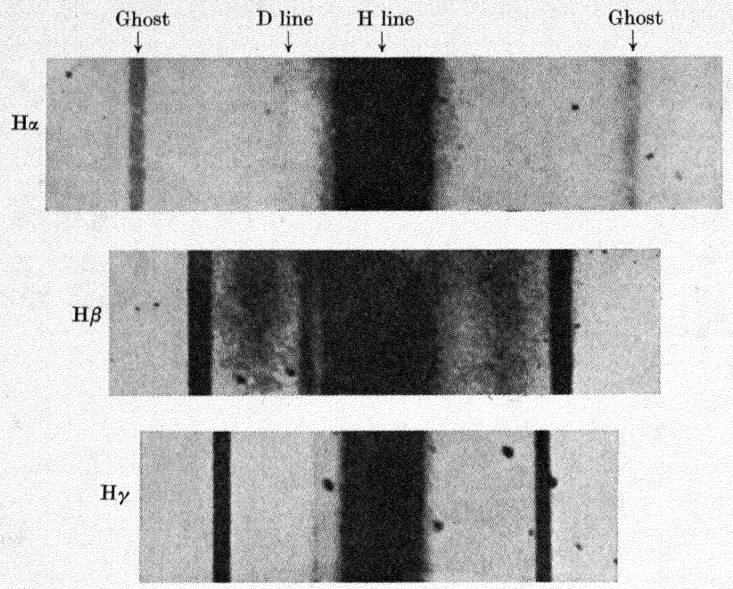


Fig. 42. Hα, Hβ, and Hγ lines. The faint lines appearing on the left-hand side of the over-exposed H^1 lines are the lines due to D. (The symmetrical pair of lines in each case are ghosts.)

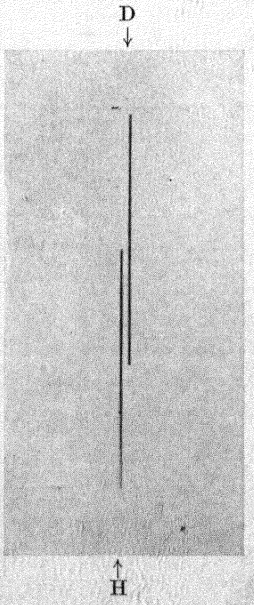


Fig. 43. The Hα lines of light and heavy hydrogen (Hertz).

It is evident that in both series the agreement between theory and experiment is excellent.

Table 52

	λ calculated		Δλ	
	For H	For D	Calculated	Observed
$n_2=2$	1215·664	1215·334	0·330	0·330
3	1025·718	1025·439	0·279	0·276
4	972·533	972·269	0·264	0·266
5	949·739	949·481	0·258	0·262
6	937·800	937·545	0·255	0·274
7	930·744	930·491	0·253	0·258

(*b*) *Molecular spectra of* HD *and* D_2

Somewhat more complicated is the isotopic effect in molecular spectra.* In general we can write for the isotopic displacement of a given line

$$\nu^i - \nu = (T^{i'} - T^{i''}) - (T' - T'') \qquad \ldots\ldots(3),$$

T denoting the energy term E/hw_l and the superscript i indicating that the given symbol refers to the isotope. Since E is the sum of electronic, vibrational and rotational energies,

$$E = E_{el} + E_v + E_r \qquad \ldots\ldots(4),$$

we may expect an isotopic effect in the electronic, vibrational and rotational structures of the spectrum. The isotopic shift in the electronic levels is generally small; in the case of the molecules HD and OD, however, it amounts to 135 and 20 cm.$^{-1}$ respectively (Jeppesen [200], Beutler and Mie [177] and Johnston [201]). The effect for the vibrational and rotational structures can be derived in the following way. To a first approximation E_v is given by

$$\frac{E_v}{hw_l} = \omega\,(v + \tfrac{1}{2}) \qquad \ldots\ldots(5),$$

where ω is the frequency of vibration, v the vibrational quantum number, taking the successive integral values 0, 1, 2, ... The additional $\frac{1}{2}$ in formula (5) accounts for the fact that even

* Cf. Jevons, *Report on Band Spectra of Diatomic Molecules*, University Press, Cambridge (1932).

in the lowest vibrational state when $v = 0$ the molecules contain a certain amount of energy,

$$E_0^0 = \tfrac{1}{2}\omega h w_l \qquad \text{.....(6),}$$

called the zero-point energy, since it remains preserved even at the absolute zero point. (In Chapter IV we shall see that this zero-point energy is of great importance in dealing with both chemical equilibria and kinetics.)

The dependence of ω on the masses (m_1, m_2) of the atoms in the molecule is governed by the expression (supposing the vibrations are harmonic)

$$2\pi\omega = \sqrt{\frac{K}{\mu}} \qquad \text{.....(7),}$$

where μ is the reduced mass defined by

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \qquad \text{.....(8).}$$

Replacing the atom with mass m_2 by its isotope with mass $m_2{}^i$, we obtain for the new frequency

$$\omega^i = \omega\sqrt{\frac{\mu}{\mu^i}} = \omega\rho^i \qquad \text{.....(9),}$$

where $\dfrac{1}{\mu^i} = \dfrac{1}{m_1} + \dfrac{1}{m_2{}^i}$, and

$$\sqrt{\frac{\mu}{\mu^i}} = \rho^i \qquad \text{.....(10).}$$

This equation is valid if the law of force in the molecule does not change on introducing the isotope, and this condition is practically always fulfilled.

The rotational energy is defined (cf. p. 13) by

$$E_r = B.J(J+1) = h^2/8\pi^2 I.J(J+1) \quad \text{.....(11).}$$

Since the moment of inertia (I) is given by

$$I = \mu r^2$$

(r = internuclear distance), the factor B in formula (11) changes by the factor $(\rho^i)^2$ on replacing one atom by its isotope.

The formulae (5) and (11) for the vibrational and the rotational energy are not exact and need some correction, since

the vibration is anharmonic and the moment of inertia is somewhat altered by the vibration and by the expansion of the molecule under the centrifugal force caused by the rotation. The exact formulae are (putting B_v instead of B/hw_l)

$$\frac{E_v}{hw_l} = \omega_e(v+\tfrac{1}{2}) - x_e\omega_e(v+\tfrac{1}{2})^2 + y_e\omega_e(v+\tfrac{1}{2})^3 + \ldots \quad \ldots(5a),$$

$$\left.\begin{aligned} \frac{E_r}{hw_l} &= B_v J(J+1) + D_v J^2(J+1)^2 + \ldots \\ B_v &= B_e - \alpha_e(v+\tfrac{1}{2}) + \ldots \\ D_v &= D_e + \beta_e(v+\tfrac{1}{2}) + \ldots \end{aligned}\right\} \quad \ldots\ldots(11a).$$

On the basis of the law of force one can express these correction factors in terms of ω_e and B_e, e.g.

$$x_e = \frac{IB_e}{\omega_e}, \quad \alpha_e = \frac{6B_e^2}{\omega_e}, \quad D_e = \frac{4B_e^3}{\omega_e^2},$$

and thus derive their dependence on the factor ρ^i. These results are summarized in Table 53.

Table 53

Constant	ω_e	$x_e\omega_e$	$y_e\omega_e$	B_e	α_e	D_e	β_e
Mass factor	$\mu^{-\frac{1}{2}}$	μ^{-1}	$\mu^{-\frac{3}{2}}$	μ^{-1}	$\mu^{-\frac{3}{2}}$	μ^{-2}	$\mu^{-\frac{5}{2}}$
Ratio	ρ^i	$(\rho^i)^2$	$(\rho^i)^3$	$(\rho^i)^2$	$(\rho^i)^3$	$(\rho^i)^4$	$(\rho^i)^5$

From this table we are able to calculate the spectra for diatomic hydrogen compounds containing D atoms instead of H atoms from the spectrum of the corresponding H compound.

Table 54 contains these constants for H_2* in the normal state and the calculated values for HD and D_2, ρ^i being for HD 0·86617 and for D_2 0·70744 (Johnston and Long [201*b*]).

It will be noticed that owing to the large ratio of the masses H and D the isotopic displacement in the molecules HD and D_2 is abnormally large compared with that in other isotopic molecules, for example in $O^{16}O^{16}$ and $O^{16}O^{18}$.

* C. R. Jeppesen, *Phys. Rev.* **44**, 165 (1933).

C. R. Jeppesen [200] has investigated the emission spectrum of HD in the extreme ultraviolet which corresponds to a transition between an excited $^1\Pi$ level and the ground state $^1\Sigma$. The observed lines of twelve bands were in perfect agreement with those calculated from the constants of Table 54.

Table 54

	H_2	D_2	HD
ω_e	4417·19 cm.$^{-1}$	3125·4 cm.$^{-1}$	3826·6 cm.$^{-1}$
$x_e\omega_e$	131·315 cm.$^{-1}$	65·72 cm.$^{-1}$	98·52 cm.$^{-1}$
B_e	60·872 cm.$^{-1}$	30·465 cm.$^{-1}$	45·668 cm.$^{-1}$
α_e	3·0671 cm.$^{-1}$	1·0859 cm.$^{-1}$	1·9931 cm.$^{-1}$
$-D_e$	0·04652 cm.$^{-1}$	0·001165 cm.$^{-1}$	0·002618 cm.$^{-1}$
β_e	0·00101 cm.$^{-1}$	0·00018 cm.$^{-1}$	0·000495 cm.$^{-1}$

Dieke and Blue [188] have analysed the spectra of HD and D_2 corresponding to transitions between two excited levels and compared the calculated coefficients with those actually observed. Table 55 contains their results for the upper and lower states of certain bands analogous to the Fulcher bands of H_2 and shows the excellent agreement with theory (cf. also [171], [177]).

Table 55

	H_2	HD	D_2	$(\rho^i_{HD})^n$		$(\rho^i_{D_2})^n$		n
				Observed	Calculated	Observed	Calculated	
ω'	2373·18	2055·52	1678·70	0·86615	0·86617	0·70737	0·70744	1
ω''	2665·34	2308·39	1885·80	0·86608	0·86617	0·70753	0·70744	1
$x'\omega'$	66·32	49·68	32·90	0·7490	0·7502	0·4960	0·5005	2
$x''\omega''$	72·09	53·73	35·93	0·7454	0·7502	0·4985	0·5005	2
B''	34·216	25·685	17·109	0·7507	0·7502	0·5000	0·5005	2
α''	1·671	1·099	0·606	0·658	0·650	0·363	0·354	3
D''	0·0216	0·0128	0·0055	0·590	0·563	0·25	0·250	4

Fig. 44 shows the band spectra of H_2, of D_2 and of a mixture $H_2 + D_2 + HD$ in the spectral range 4570 to 4960 Å. (Hertz [143]).* The difference in the vibrational and rotational structures of the H_2 spectrum and of the D_2 spectrum will be easily re-

* The author is very much indebted to Prof. Hertz for the original spectrogram.

cognized. The enormous number of lines present in the second spectrogram is very characteristic for the spectrum of the mixture containing three different sorts of hydrogen molecules.

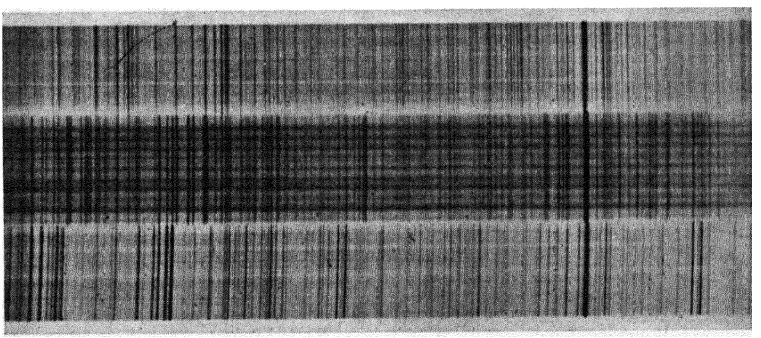
From the ω_e and $x_e\omega_e$ values given in Table 54 we can calculate the zero-point energies

$$E_0^0 = hw_l\left(\tfrac{1}{2}\omega_e - \tfrac{1}{4}\omega_e x_e\right) \qquad \ldots\ldots(12)$$

for the different hydrogen molecules and find for

H_2 6183·5 cal., HD 5366·4 cal., D_2 4394·5 cal.*

On account of this difference in the zero-point energies of these molecules there is the same difference in the dissociation energies. The dissociation energy for H_2 is 101·9 kg. cal.†, and we have to expect for HD and D_2 dissociation energies which are respectively 0·8 and 1·8 kg. cal. higher [177].



4570 Å. 4960 Å.

Fig. 44. The spectra of the hydrogen molecules (Hertz).

(c) *Spectra of other* D-*compounds*

The isotopic effect observed in the spectra of other diatomic molecules such as OH [182, 201, 201*a*, 230], HCl [196], NH [189] and AlH [199, 199*a*] is also in agreement with the general theory.‡ Fig. 45 shows the spectra of the molecules AlH and AlD according to Holst and Hulthén [199*a*].§ The large displacement of the AlD spectrum relative to the AlH spectrum is a striking

* 1000 cm.$^{-1}$ = 2842 calories.

† R. T. Birge, *Proc. Nat. Acad. Sci.* **14**, 12 (1928).

‡ R. de L. Kronig, *Physica*, **1**, 617 (1934).

§ The author has to thank Prof. Hulthén for the original spectrogram.

feature of the isotopic effect occurring in diatomic hydrogen compounds.

The investigation of the isotopic effect in the spectrum of polyatomic molecules gives us some information about the structure of these molecules which could not be deduced from the spectra of the hydrogen compounds alone. Thus it is possible to calculate the internuclear distances in the acetylene molecule from the moment of inertia of the C_2HD molecule and from the moment of inertia of the C_2H_2 molecule [178*c*, 194*a*, 198, 223]. Cf. also [173].

In general there are

$$(3n-6)(3n-5)/2$$

constants necessary in order to describe completely the vibrations of a molecule composed of n atoms, whereas the spectrum contains only $3n-6$ frequencies. The missing constants were eliminated by certain assumptions with regard to the forces acting between the atoms in the molecule. Replacing an H atom in a polyatomic molecule by a D atom, new frequencies are obtained which enable us to investigate the correctness of the hypothetical assumptions.

From this standpoint the vibrational spectra of the molecules HDO and D_2O have been compared with that of H_2O, by studying their infrared [175, 178*b*, 181, 189*b*] and Raman spectra [224*a*, 236, 237, 238].

The fundamental frequencies for

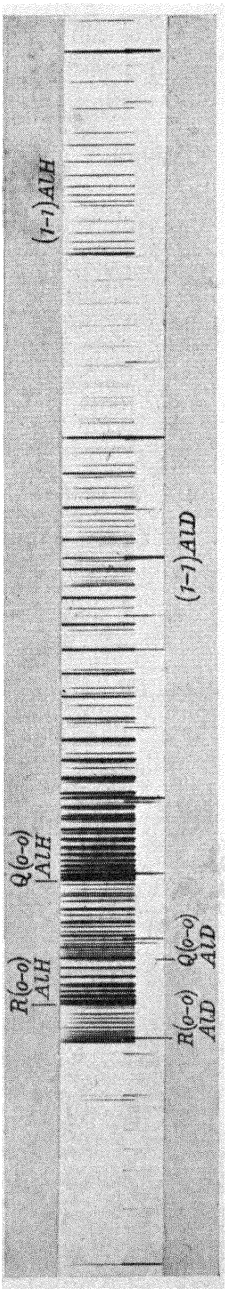


Fig. 45. The spectrum of AlD according to Holst and Hulthén.

these three molecules given in Table 56, according to the measurements of Bartholomé and Clusius [175] and Wood [238a], are in good agreement with those anticipated on the theory of the H_2O molecule as developed by Teller,* proving its correctness (the frequencies in brackets are not yet measured accurately).

Table 56. *Fundamental frequencies for the water molecules in cm.*$^{-1}$

	ω_σ	ω_π	ω_δ
H_2O	3895	3803	1655
HDO	3844	(2848)	1424
D_2O	2850	(2707)	1218

The isotopic effect has been also studied in the spectra of the molecules ND_3 [174, 189, 231], CH_3D [173].

5. Ortho-para equilibrium

The ortho-para equilibrium in deuterium was investigated by Farkas, Farkas and Harteck [192, 193], the measurements being made according to the same technique as described for hydrogen (p. 28). The attainment of the ortho-para equilibrium was catalyzed by charcoal and three runs were made, at 20·4° K., 53° K. and 78° K., in order to determine the temperature dependence of the equilibrium.

The observed changes in the resistance value of the heavy hydrogen (90 per cent. D) before and after the adsorption on charcoal are given in Table 57.

Table 57

Temperature ° K.	Change in the resistance value in ohms, $\Delta\Omega$	Ratio $\frac{\Delta\Omega_T}{\Delta\Omega_{78}}$
20·4	1·40	9·2
53·0	0·51	3·4
78·0	0·15	1·0

Since the changes in the resistance value were proved for hydrogen to be proportional to the changes in concentration

* E. Teller, *Det Kgl. Danske Videnskabernes Selskab* (1934).

of the parahydrogen, it was possible to determine from these results the spin and the statistics of the deuton in the following way, which is independent of spectroscopic measurements.

The temperature dependence of the ortho-para equilibrium for deuterium is governed by the same law as for hydrogen (cf. p. 13):

$$\frac{[\text{p-D}_2]}{[\text{o-D}_2]} = \frac{\sum_{\text{para}} p_{\text{para}}\, e^{-E_J/kT}}{\sum_{\text{ortho}} p_{\text{ortho}}\, e^{-E_J/kT}} \qquad \text{.....(13),}$$

where g is equal to $2J+1$ multiplied by a factor depending on the spin (t) and statistics of the deuton. From Chapter VI, Part I, p. 110, it is evident that for the Bose-Einstein statistics

$$\left.\begin{aligned} p_{\text{para}} &= (2t+1)\,t\,(2J+1), & J &= \text{odd} \\ p_{\text{ortho}} &= (2t+1)\,(t+1)\,(2J+1), & J &= \text{even} \end{aligned}\right\} \text{.....(14),}$$

and for the Dirac-Fermi statistics

$$\left.\begin{aligned} p_{\text{para}} &= (2t+1)\,t\,(2J+1), & J &= \text{even} \\ p_{\text{ortho}} &= (2t+1)\,(t+1)\,(2J+1), & J &= \text{odd} \end{aligned}\right\} \text{.....(14}a\text{).}$$

(In the formula for E_J the moment of inertia for the D_2 molecule is naturally twice as large as for H_2.)

Table 58 contains the ratios of the excess concentration relative to the normal equilibrium of ortho- or paradeuterium, i.e. the expressions

$$\frac{(\text{p-D}_2)_T - (\text{p-D}_2)_n}{(\text{p-D}_2)_{78} - (\text{p-D}_2)_n} = \frac{(\text{o-D}_2)_T - (\text{o-D}_2)_n}{(\text{o-D}_2)_{78} - (\text{o-D}_2)_n} \qquad \text{.....(15),}$$

calculated for both statistics and $t=\frac{1}{2}$ and $t=1$; $(\text{p-D}_2)_n$, $(\text{p-D}_2)_T$ and $(\text{p-D}_2)_{78}$ denoting the equilibrium concentration at normal temperature, at the temperature T and at 78° K. respectively.

Table 58

Temperature ° K.	Dirac-Fermi statistics		Bose-Einstein statistics	
	$t=\frac{1}{2}$	$t=1$	$t=\frac{1}{2}$	$t=1$
20·4	31·2	14·7	8·4	9·5
53	3·8	3·2	3·1	3·2
78	1·0	1·0	1·0	1·0

Comparing these values with the ratios given in Table 57 we can certainly exclude the Dirac-Fermi statistics; further, we find the observed ratios agree best with $t = 1$ (higher values for t are very improbable). This result is in agreement with the general rule that nuclei with even atomic weight follow the Bose-Einstein statistics (p. 111) and have an integral spin (p. 143), and also with the spectroscopic experiments of Lewis and Ashley [206] and Murphy and Johnston [220].

If we compare the temperature dependence of the ortho-deuterium concentration with that for hydrogen we note a remarkable difference due to the different statistics. In hydrogen the ortho component is present in excess at high temperatures and disappears as the temperature is lowered; in deuterium, however, the ortho modification is the stable form at low temperatures, the lowest rotational level with $J = 0$ (and all other levels with even J) being ortho states.

Table 59

Temperature ° K.	Percentage orthodeuterium	Percentage paradeuterium
0	100·00	0·00
10	99·97	0·03
15	99·51	0·49
20	97·97	2·03
25	95·29	4·71
30	92·07	7·93
40	85·12	14·78
50	79·19	20·81
60	74·79	25·21
70	71·78	28·22
80	69·82	30·18
90	68·58	31·42
100	67·82	32·18
120	67·07	32·93
140	66·81	33·19
160	66·72	33·28
190	66·67	33·32
220	66·66	33·33
260	66·66	33·33
300	66·66	33·33

Table 59 shows the dependence of the orthodeuterium concentration on temperature calculated by Johnston and Long [201*b*] (cf. also [219]).

Thus normal deuterium is a mixture of $\frac{2}{3}$ orthodeuterium and $\frac{1}{3}$ paradeuterium.

The kinetics of ortho-paradeuterium conversion have been compared in two respects with the corresponding reactions in hydrogen; firstly for the heterogeneous ortho-paradeuterium conversion at 20·4° K., and secondly for the re-conversion catalyzed by oxygen at room temperature. The latter experiment was made in order to gain some information about the magnetic moment of the deuton. Fig. 46 shows the rates of formation of orthodeuterium and parahydrogen at 20·4° K. in a glass tube which catalyzed the conversion with a con-

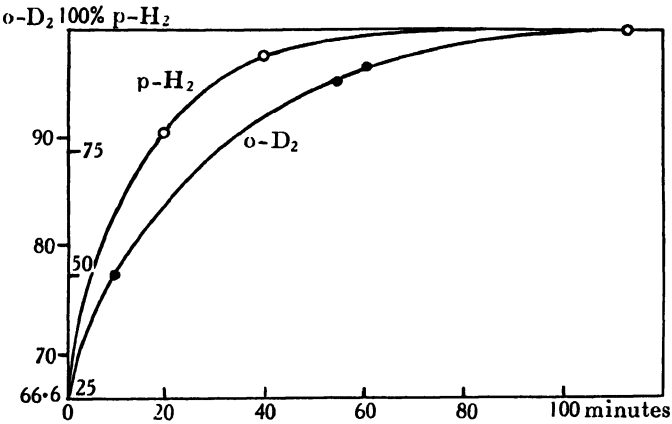


Fig. 46. The formation of orthodeuterium and parahydrogen.

veniently measurable speed owing to the presence of some solid O_2.* On this catalyst the rate of the orthodeuterium formation was somewhat slower than that of parahydrogen, the respective half-conversion times being 19 and 11 minutes.

The mechanism of the heterogeneous ortho-paradeuterium conversion is probably the same as that of the corresponding ortho-parahydrogen conversion, and we have again two different mechanisms: thelow-temperature and the high-temperature mechanism (cf. pp. 92 and 96).

The homogeneous re-conversion of orthodeuterium by collisions with oxygen molecules proceeds sixteen times more

* The conversion on the charcoal used was too rapid to be measured.

slowly than the corresponding reaction with hydrogen, the velocity constant being 0·57 litre/mole minute at 20° C. compared with 9·16 litre/mole minute for hydrogen.

Applying the formula derived on p. 87 to these velocity constants, the ratio of the collision efficiencies for the two conversions

$$p\text{-}H_2 + O_2 \rightleftharpoons o\text{-}H_2 + O_2 \qquad \text{.....(16)}$$

and

$$o\text{-}D_2 + O_2 \rightleftharpoons p\text{-}D_2 + O_2 \qquad \text{.....(16}a\text{)}$$

is found to be

$$\frac{Z^{H_2}_{p\to o}}{Z^{D_2}_{p\to o}} = \frac{\frac{3}{4}\cdot 9{\cdot}16\sqrt{\frac{32\cdot 2}{34}}}{\frac{2}{3}\cdot 0{\cdot}57\sqrt{\frac{32\cdot 4}{36}}} = 13,$$

the square root factors allowing for the different collision numbers for H_2 and D_2. According to Wigner's formula (pp. 87 and 88, formulae (34) and (38)) this ratio is connected with the nuclear magnetic moment of the proton (μ_P) and of the deuton (μ_D) by the relation

$$\frac{Z^{H_2}_{p\to o}}{Z^{D_2}_{p\to o}} = \frac{\mu^2_P \cdot I_{H_2}\cdot \alpha_{H_2}}{\mu^2_D \cdot I_{D_2}\cdot \alpha_{D_2}}\cdot (\tfrac{1}{3})^2,$$

where I designates the moment of inertia, α_{H_2} and α_{D_2} the expressions given for H_2 in formula (38), p. 88, allowing for the fact that the ortho-para transitions occur between a number of different rotational states and the factor $(\frac{1}{3})^2$ arises on account of the different nuclear spins of the proton and deuton (Kalckar and Teller [201c]). Using the numerical value of $\frac{\alpha_{H_2}}{\alpha_{D_2}} = 0{\cdot}8$ we obtain for the ratio

$$\frac{\mu_P}{\mu_D} = 4{\cdot}25.$$

6. Rotational energy and specific heat

The rotational energy of D_2 and HD can be calculated according to the formula which has been used for the calculation of the rotational energy of H_2 (cf. p. 16) provided that the following differences are taken into account.

The moments of inertia of the molecules H_2, D_2 and HD are different, being

$$I_{H_2} = 4{\cdot}67 \,.\, 10^{-41}\,\text{g.cm.}^{-2},$$
$$I_{D_2} = 9{\cdot}31 \,.\, 10^{-41}\,\text{g.cm.}^{-2},$$
$$I_{HD} = 6{\cdot}21 \,.\, 10^{-41}\,\text{g.cm.}^{-2}$$

The ortho states of the D_2 molecule are those with the even rotational quantum numbers and have the nuclear statistical weight 6, whereas the para states are connected with the odd rotational quantum numbers and have the statistical weight 3. For the unsymmetric HD molecules there is no distinction between ortho and para states, since transitions between levels having odd and even rotational quantum numbers are not forbidden (cf. p. 110). All rotational levels of HD have the statistical weight 6.

Thus we have the following formulae for the rotational energies and specific heats:

$$E_{\text{rot.}}^{\text{e-D}_2} = -R\frac{d\ln(Q_e+Q_o)}{d\,1/T},$$

where

$$Q_e = \sum_{J=\text{even}} 6\,(2J+1)\,e^{-J(J+1)\frac{h^2}{8\pi^2 I_{D_2}}},\quad Q_o = \sum_{J=\text{odd}} 3\,(2J+1)\,e^{-J(J+1)\frac{h^2}{8\pi^2 I_{D_2}}},$$

$$E_{\text{rot.}}^{\text{o-D}_2} = -R\frac{d\ln Q_e}{d\,1/T},\qquad E_{\text{rot.}}^{\text{p-D}_2} = -R\frac{d\ln Q_o}{d\,1/T},$$

$$E_{\text{rot.}}^{\text{n-D}_2} = \tfrac{2}{3}E_{\text{rot.}}^{\text{o-D}_2} + \tfrac{1}{3}E_{\text{rot.}}^{\text{p-D}_2},$$

$$E_{\text{rot.}}^{\text{HD}} = -R\frac{d\ln\sum 6\,(2J+1)\,e^{-J(J+1)\frac{h^2}{8\pi^2 I_{HD}}}}{d\,1/T},$$

$$C_{\text{rot.}}^{\text{e-D}_2} = \frac{dE_{\text{rot.}}^{\text{e-D}_2}}{dT},\qquad C_{\text{rot.}}^{\text{o-D}_2} = \frac{dE_{\text{rot.}}^{\text{o-D}_2}}{dT},$$

$$C_{\text{rot.}}^{\text{p-D}} = \frac{dE_{\text{rot.}}^{\text{p-D}_2}}{dT},\qquad C_{\text{rot.}}^{\text{n-D}_2} = \tfrac{2}{3}C_{\text{rot.}}^{\text{o-D}_2} + \tfrac{1}{3}C_{\text{rot.}}^{\text{p-D}_2},$$

$$C_{\text{rot.}}^{\text{HD}} = \frac{dE_{\text{rot.}}^{\text{HD}}}{dT}.$$

The values for the rotational energy and specific heat are given in Tables 60 and 61 according to calculations of Johnston and Long[201 *b*]. Fig. 47 shows the rotational specific heat for

the seven hydrogens n-H_2, o-H_2, p-H_2, n-D_2, o-D_2, p-D_2 and HD.

Table 60. *Rotational energy for gaseous D_2 and HD in calories/mole*

Temperature ° K.	o-D_2	p-D_2	e-D_2	n-D_2	HD
0	0·00	170·22	0·00	56·74	0·00
20	0·01	170·22	3·46	56·74	1·27
25	0·09	170·22	8·10	56·80	4·50
50	14·62	170·61	46·74	66·62	49·31
100	143·54	197·20	160·81	161·43	154·15
150	265·38	274·32	268·35	268·36	232·99
200	369·41	370·54	369·79	369·79	355·39
250	470·16	470·30	470·21	470·21	455·77
300	570·61	570·62	570·62	570·62	556·27
400	771·86	771·86	771·86	771·86	757·70

Table 61. *Rotational specific heats of the heavy hydrogens in cals./mole degree*

Temperature ° K.	o-D_2	p-D_2	e-D_2	n-D_2	HD
0	0·000	0·000	0·000	0·000	0·000
10	0·000	0·000	0·039	0·000	0·000
15	0·000	0·000	0·316	0·000	0·083
20	0·002	0·000	0·726	0·000	0·401
25	0·034	0·000	1·078	0·022	0·902
30	0·137	0·000	1·307	0·091	1·406
40	0·656	0·011	1·659	0·440	2·026
50	1·455	0·064	1·973	0·991	2·179
60	2·206	0·189	2·205	1·533	2·154
70	2·693	0·383	2·325	1·923	2·106
80	2·894	0·622	2·355	2·137	2·066
90	2·889	0·874	2·325	2·217	2·042
100	2·775	1·116	2·273	2·222	2·028
120	2·477	1·502	2·162	2·152	2·014
140	2·249	1·745	2·084	2·081	2·009
160	2·120	1·878	2·040	2·040	2·006
190	2·037	1·964	2·013	2·013	2·004
220	2·012	1·991	2·005	2·005	2·005
260	2·006	2·002	2·005	2·005	2·006
300	2·007	2·007	2·007	2·007	2·008

The rotational specific heats of HD and n-D_2 have been determined experimentally by Clusius and Bartholomé [183], using two samples of heavy hydrogen: one containing 1·3 per cent. D_2, 77·9 per cent. H_2 and 20·7 per cent. HD, and the other

73·9 per cent. D_2, 1·9 per cent. H_2 and 24·1 per cent. HD (for method see p. 35). The specific heats of HD and of D_2 were computed from that of the mixture ($C_{\text{rot.}}^{\text{mix.}}$) according to the relation

$$C_{\text{rot.}}^{\text{mix.}} = mC_{\text{rot.}}^{\text{n-H}_2} + rC_{\text{rot.}}^{\text{n-D}_2} + (1-m-r)\,C_{\text{rot.}}^{\text{HD}},$$

m and r designating the mole fractions of H_2 and D_2 present.

The specific heats obtained in the temperature range 30–120° K. are in good agreement with the theoretical values shown in Fig. 47 and listed in Table 61.

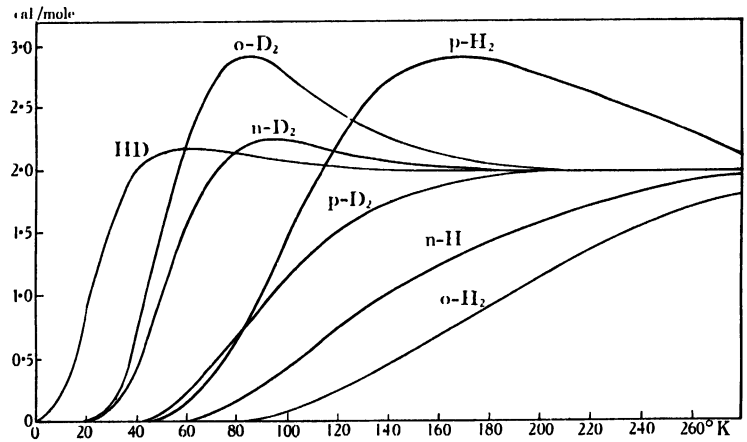


Fig. 47. The specific heat curves for the molecules H_2, D_2 and HD.

The results of these experiments are of some importance. The HD molecule is the only example for the classical rotator (transitions between levels with even and odd rotational quantum numbers not forbidden), the specific heat curve of which has been hitherto experimentally verified. The measurements concerning the specific heat of D_2 give further experimental evidence for the nuclear spin of D being one (cf. pp. 143 and 159).

According to Clusius and Bartholomé [183a] in the temperature region 10–14° K. the specific heat of solid D_2 is practically the same as that of H_2, the characteristic temperature for Cp being for D_2 $\theta = 89$ (for H_2 $\theta = 91$, see p. 37). This is a very remarkable result since hitherto it has been assumed that the

frequencies in the lattice of two isotopes are proportional to the reciprocal square roots of the masses (cf. p. 171).

7. Entropy and free energy

The entropies and free energies (F^0) for HD and D_2 and atomic D have been calculated by Johnston and Long [201 *b*] and are given in Tables 62 and 63 together with the corresponding values for H_2 and atomic H calculated by Giauque [34] (cf. p. 51). (E_0^0 = zero-point energy.)

What has been said with regard to the entropies of ortho- and parahydrogen (p. 51) applies also to ortho- and paradeuterium. Thus at low temperatures below 10° K. the entropies are given by

$$S_{\mathrm{I}}^{\mathrm{e\text{-}D_2}} = S_{\mathrm{I}}^{\mathrm{o\text{-}D_2}} = S_{\mathrm{trans.}} + R \ln 6,$$

$$S_{\mathrm{I}}^{\mathrm{p\text{-}D_2}} = S_{\mathrm{trans.}} + R \ln 9,$$

$$S_{\mathrm{I}}^{\mathrm{n\text{-}D_2}} = S_{\mathrm{trans.}} + R\left(\tfrac{1}{3} \ln 3 + \ln 9\right).$$

Table 62. *Entropies of* e-H_2, e-D_2 *and* HD *in the ideal gaseous state in calories/mole degree (nuclear spin entropy included)*

Temperature ° K.	e-H_2	e-D_2	HD
298·1	—	38·731	37·954
300	34·025	—	—
400	36·023	41·054	39·972
500	37·582	42·616	41·532
600	38·857	43·901	42·810
700	39·940	44·999	43·896
800	40·871	45·965	44·844
1000	42·477	47·621	46·458
1250	—	49·346	48·124
1500	45·495	50·813	49·537
2000	47·782	53·227	51·877
2500	49·647	55·177	53·780
3000	51·227	56·814	55·836

In the last expression the term $R \ln 9 = 4{\cdot}366$ represents the nuclear spin entropy which is to be subtracted from the values given in Tables 62 and 63 in order to obtain the entropies or

free energies of D_2 with the nuclear spin contribution excluded. The contribution of the nuclear spin is

for HD $R\ln 6 = 3{\cdot}560$ E.U.,

for D $R\ln 3 = 2{\cdot}183$ E.U.,

for H $R\ln 2 = 1{\cdot}378$ E.U.

Table 63. *Values of* $-\frac{F^0 - E_0^0}{T}$ *for* e-H_2, e-D_2, HD, *atomic* H *and atomic* D *in the ideal gaseous state at* 1 *atmosphere* (*nuclear spin contribution included*)

Temperature ° K.	e-H_2	e-D_2	HD	H	D
298·1	27·191	32·133	31·099	23·818	26·680
300	27·235	32·176	31·137	23·849	26·712
400	29·193	34·157	33·110	25·278	28·141
500	30·720	35·698	34·645	26·387	29·249
600	31·973	36·961	35·902	27·292	30·155
700	33·035	38·033	36·968	28·058	30·921
800	33·959	38·965	37·895	28·721	31·584
900	34·775	39·792	38·715	29·306	32·169
1000	35·507	40·536	39·451	29·830	32·692
1250	37·069	42·131	41·025	30·938	33·801
1500	38·360	43·459	42·329	31·844	34·706
2000	40·440	45·610	44·435	33·273	36·136
2500	42·100	47·335	46·119	34·391	37·244
3000	43·514	48·782	47·533	35·287	38·149

The experimental value for the entropy of D_2 can be obtained by means of the same scheme given for H_2 (see p. 54). Using the characteristic temperature $\theta = 89$ for solid D_2 (p. 164) the heat of fusion of 47 cal. (p. 169), the specific heat for n-D_2 as obtained by Clusius and Bartholomé [183a] and the heat of sublimation calculated from the vapour pressure measurements (p. 169), the value of 33·65 E.U. is obtained at 298·1° K. which is in excellent agreement with the theoretical value of 38·73 if we allow for the additional entropy of n-D_2 at absolute zero amounting to $R(\ln 9 + \frac{1}{3}\ln 3) = 5{\cdot}093$ E.U.

8. The chemical constants and the dissociation of heavy hydrogen

The chemical constants of D_2, HD and of atomic D have the following values (the same notation is used as for H_2 on p. 56).

(a) *Nuclear spin contribution included*

At temperatures below 10° K.

$$i_{\text{Ic-D}_2} = i_{\text{Io-D}_2} = \log \frac{(2\pi M_{D_2})^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3 N^{\frac{3}{2}}} + \log 6$$
$$= -0{\cdot}6807 + 0{\cdot}7781 = 0{\cdot}0974,$$

$$i_{\text{Ip-D}_2} = \log \frac{(2\pi M_{D_2})^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3 N^{\frac{3}{2}}} + \log 9 = 0{\cdot}2735,$$

$$i_{\text{In-D}_2} = \log \frac{(2\pi M_{D_2})^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3 N^{\frac{3}{2}}} + \log 9 + \tfrac{1}{3}\log 3 = 0{\cdot}4325,$$

$$i_{\text{IHD}} = \log \frac{(2\pi M_{\text{HD}})^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3 N^{\frac{3}{2}}}$$
$$+ \log 6 = -0{\cdot}8679 + 0{\cdot}7781 = 0{\cdot}0898.$$

At temperatures above 200° K.

$$i_{\text{IIc-D}_2} = i_{\text{IIn-D}_2} = i_{\text{Ic-D}_2} + \log \frac{36\pi^2 I_{D_2} k}{h^2}$$
$$= -0{\cdot}6807 - 0{\cdot}9755 = -1{\cdot}6562,$$

$$i_{\text{IIo-D}_2} = i_{\text{IIc-D}_2} - \log \tfrac{3}{2} = -1{\cdot}8323,$$

$$i_{\text{IIp-D}_2} = i_{\text{IIc-D}_2} - \log 3 = -2{\cdot}1333,$$

$$i_{\text{IIHD}} = i_{\text{IHD}} + \log \frac{48\pi^2 I_{\text{HD}} k}{h^2} = -0{\cdot}0898 - 1{\cdot}0265 = -1{\cdot}1163,$$

$$i_{\text{D}} = \log \frac{(2\pi M_{\text{D}})^{\frac{3}{2}} k^{\frac{5}{2}}}{h^3 N^{\frac{3}{2}}} + \log 6$$
$$= -1{\cdot}1316 + 0{\cdot}7781 = -0{\cdot}3535.$$

(b) *Nuclear spin contribution excluded*

$$i'_{D_2} = i_{\text{IIc-D}_2} - \log 9 = -1{\cdot}6562 - 0{\cdot}9542 = -2{\cdot}6104,$$

$$i'_{\text{HD}} = i_{\text{IIHD}} - \log 6 = -1{\cdot}1163 - 0{\cdot}7781 = -1{\cdot}8944,$$

$$i'_{\text{D}} = i_{\text{D}} - \log 3 = -0{\cdot}3535 - 0{\cdot}4771 = -0{\cdot}8306.$$

The equilibrium constant $K_P = \frac{P_H^2}{P_{H_2}}$ for the dissociation of the hydrogen molecule is given by (cf. p. 58)

$$\log K_P = -\frac{q_0}{4{\cdot}57T} + \tfrac{3}{2}\log T - \frac{1}{4{\cdot}57}\int_0^T \frac{dT}{T^2}\int C_{\text{vibr.}}\,dT + 2i_H - i_{H_2}.$$

For the molecules D_2 and HD this equilibrium constant changes for several reasons: the heat of dissociation at absolute zero (cf. p. 155), the vibrational frequency determining the vibrational specific heat $C_{\text{vibr.}}$ (cf. p. 154) and the chemical constants have different values for the three molecular species H_2, D_2 and HD, and also the chemical constants for atomic H and D are different. The dissociation constants are given in Table 64 according to calculations of Johnston and Long [201*b*].

Table 64

Temperature ° K.	H_2	HD	D_2
1000	$6{\cdot}499.10^{-18}$	$2{\cdot}478.10^{-18}$	$3{\cdot}708.10^{-18}$
1500	$3{\cdot}600.10^{-10}$	$1{\cdot}566.10^{-10}$	$2{\cdot}699.10^{-10}$
2000	$2{\cdot}960.10^{-6}$	$1{\cdot}362.10^{-6}$	$2{\cdot}491.10^{-6}$
2500	$6{\cdot}915.10^{-4}$	$3{\cdot}276.10^{-4}$	$6{\cdot}168.10^{-4}$
3000	$2{\cdot}687.10^{-2}$	$1{\cdot}295.10^{-2}$	$2{\cdot}475.10^{-2}$

It will be seen that for H_2 and D_2 the differences in the chemical constants and in the vibrational specific heat cancel at high temperatures when the vibration is fully excited. Since in this temperature range the small difference in the heat of dissociation of H_2 and D_2 does not affect very much the equilibrium constants, the equilibrium constants for H_2 and D_2 tend to the same value. On the other hand, the limiting value for the dissociation constant of HD is half that for H_2 and D_2 on account of the asymmetry of this molecule.

9. Vapour pressure

The vapour pressure of heavy hydrogen was measured by Brickwedde, Scott, Urey and Wahl [179, 228] and by Lewis and Hanson [209], the temperatures being determined with a vapour-

pressure thermometer filled with normal or parahydrogen. Table 65 shows the results obtained.

Table 65

Temperature °K.	Vapour pressure in mm. Hg.	
	n-H_2	n-D_2
20·334	749·8	252·0
19·330	550·3	168·5
18·953	486·5	143·2
18·182	372·8	97·7
17·479	287·3	65·5
16·463	190·6	35·0
15·188	106·2	14·2

These experimental data can be represented by the empirical equations (P in mm. Hg.)

$$\text{Liquid } D_2\text{: } \log P = 4{\cdot}7459 - 58{\cdot}5951/T + 0{\cdot}02650T,$$

$$\text{Solid } D_2\text{: } \log P = 5{\cdot}1995 - 68{\cdot}6144/T + 0{\cdot}03103T.$$

In Table 66 are listed the boiling points and the triple points, and in Table 67 the latent heats and molar volume of H_2 and D_2.

Table 66

Temperature °K.		Vapour pressure in mm. Hg.	
		H_2	D_2
23·5	Boiling point of D_2	1740	760
20·38	Boiling point of H_2	760	257
18·58	Triple point of D_2	429	121
13·92	Triple point of H_2	54	5

Table 67

	H_2	D_2	Reference
Heat of vaporization at absolute zero in cals./mole	183	276	Scott, etc. [228]
Heat of fusion in cals./mole	28	47	Clusius and Bartholomé [183*a*]
Molar volume at the triple point	26·15	23·17	Clusius and Bartholomé [183*a*]

According to Brickwedde, Scott and Taylor (cf. [228]) the

vapour pressure of orthodeuterium at 20·4° K. is 5 mm. higher than the vapour pressure of normal deuterium.

The vapour pressures of mixtures of H_2 and D_2 were measured by Lewis and Hanson [209] and were found to vary almost linearly with the mole fraction (see Table 68).

Table 68

Percentage D_2	Vapour pressure at 18·65° K. in mm. Hg
0	450
50	290
75	210
85	180
100	130

The same relation holds for the freezing points of these mixtures.

The vapour pressure did not change appreciably when the equilibrium

$$H_2 + D_2 = 2HD$$

was established in mixtures of H_2 and D_2 by means of a hot platinum wire, showing that the vapour pressure of HD is approximately midway between that of H_2 and D_2.

The observed differences in the vapour pressures of light and heavy hydrogens can be accounted for in the following way (cf. Urey, Brickwedde and Murphy [160]).

According to equation (12) (p. 42) the vapour pressure of solid hydrogen is given by

$$\log P_{\text{atm.}} = -\frac{\lambda_0}{4{\cdot}57T} + \tfrac{5}{2}\log T - \frac{1}{4{\cdot}57}\int\frac{dT}{T^2}\int C_{\text{condens.}}\,dT + i'_{\text{I}},$$

where λ_0 is the heat of evaporation at the absolute zero, $C_{\text{condens.}} = D(\theta)$ (D meaning the Debye function) the specific heat of the solid and i'_{I} the chemical constant (nuclear spin excluded, cf. p. 42).

It was shown by Clusius and Bartholomé [183a] that the specific heats (at saturation pressure) of solid D_2 and H_2 are practically equal. Scott, Brickwedde, Urey, and Wahl have

come to the same conclusion when calculating the specific heats from their vapour-pressure measurement. Hence we can write as first approximation

$$\log \frac{P_{H_2}}{P_{D_2}} = -\frac{\lambda_{0H_2} - \lambda_{0D_2}}{4{\cdot}57T} + i_{IH_2} - i_{ID_2},$$

where

$$i_{H_2} - i_{D_2} = \tfrac{3}{2} \log \frac{M_{H_2}}{M_{D_2}} = -0{\cdot}452.$$

The difference of the heat of evaporation of H_2 and D_2, amounting to 93 cals., is due to the different zero-point energies of solid H_2 and D_2. It was pointed out by Scott, Brickwedde, Urey, and Wahl that the frequencies to be used for the calculation of the zero-point energy of the crystal are those corresponding to the specific heat at constant volume instead of those deduced from specific heat measurements made at constant pressure. It is to be expected that these frequencies are considerably different for H_2 and D_2, since the coefficient of expansion is larger for H_2 than for D_2. This effect and the larger molar volume of solid H_2 is due to the fact that the vibrations in the H_2-crystal are more anharmonic than in D_2 (Clusius and Bartholomé, *Göttinger Nachrichten*, III, 29 (1934)).

10. Properties of heavy water

The best studied compound of heavy hydrogen is heavy water, D_2O. Some of its most important physical constants are summarized in Table 69. Bernal and Fowler [176, 191] have shown that the differences in the properties of heavy water as compared with normal water can be accounted for theoretically (especially where volume effects are involved, i.e. for entries 1–7) on the assumption that cold water is a sort of non-rigid "ice" in which the majority of the water molecules are surrounded by their four nearest neighbours in a more or less regular tetrahedral arrangement. The main difference between light water and heavy water is that in the latter the molecules are better co-ordinated.

Table 69

Property	Value for H_2O	Value for D_2O	References
1. Lattice constants of ice near melting point in Å.	$a=4{\cdot}514$ $c=7{\cdot}352$	4·517 7·354	*
2. Specific gravity at 20° C.	0·9982	1·1059	[146, 234]
3. Relative molecular volumes at 20° C.	1	1·0037	
4. Freezing point ° C.	0	3·82	[212, 234]
5. Boiling point ° C.	100	101·42	[212]
6. Temperature of maximum density	4	11·6	[212]
7. Heat of vaporization cals./mole	9700	9960	[212]
8. Dielectric constant	82	80·5	[215]
9. Viscosity at 20° C.	10·09	12·6	[213, 234]
10. Surface tension 20° C. dynes/cm.	72·75	67·8	[229]
11. Magnetic susceptibility	$-0{\cdot}72.10^{-6}$	$-0{\cdot}65.10^{-6}$	[180, 229]
12. Refractive index n_D^{20} †	1·33300	1·32844	[148, 234]
13. Ionic mobilities at 18°			[234 *a*]
K^+	64·2	54·5	[208]
Cl^-	65·2	55·3	
H^+, D^+ respectively	315·2	213·7	
14. Solubility at 25° C. in g. per g. water			
NaCl	0·359	0·305	[232]
$BaCl_2$	0·357	0·289	

The vapour pressures of heavy water (p_2) at different temperatures are given (in mm. Hg) in Table 70, together with the corresponding values for light water (p_1) (Lewis and MacDonald [212]).

Table 71 shows the dependence of the specific gravity of D_2 (cf. footnote, p. 136) on temperature calculated from the data of Lewis and MacDonald [212]. On account of the different temperatures of maximum density for light and heavy water the difference in the specific gravity appears to have a maximum at 25° C.

The physical properties of mixtures of light water and heavy water containing the three molecular species H_2O, HDO and D_2O in the equilibrium $H_2O+D_2O=2HDO$ show a nearly

* Miss Megaw (*Nature*, in the press).

† The refractive indices are equal for H_2O and D_2O vapour (Cuthbertson [185*a*]).

linear dependence on concentration for the specific gravity [145, 148], refractive index [125, 126, 145, 178, 205], viscosity [213] and melting point [203]. This shows that only small heat effects appear when H_2O and D_2O are mixed (cf. also Doehlemann and Lange [189*a*] and p. 181). The electrolytic dissociation constant of heavy water has not yet been measured accurately, but from preliminary experiments Abel, Bratu and Redlich [170*a*] conclude that it is about three times smaller than that of H_2O (cf. also Gross, Suess and Steiner [261*b*], and Topley and Wynne-Jones [234*b*]).

Table 70

Temperature ° C.	p_1	p_2	$p_1 - p_2$	p_1/p_2
20	17·5	15·2	2·3	0·87
30	31·8	27·9	3·9	0·99
40	55·3	49·2	6·1	0·89
50	92·5	83·4	9·1	0·90
60	149·4	136·3	13·1	0·913
70	233·7	215·7	18·0	0·923
80	355·1	331·2	23·9	0·933
90	525·8	495·1	30·7	0·942
100	760·0	721·6	38·4	0·949
110	1074·6	1027·6	47·0	0·956

Table 71

Temperature ° C.	d_4 for H_2O	d_4 for D_2O	Δd_4
4	1·00000	—	—
5	0·99999	1·10622	0·10623
10	0·99972	1·10665	0·10693
15	0·99912	1·10654	0·10742
20	0·99822	1·10590	0·10768
25	0·99706	1·10486	0·10780
30	0·99567	1·10339	0·10772
35	0·99405	1·10150	0·10745
40	0·99224	1·09943	0·10719

11. Properties of some D compounds

In addition to D_2O the following compounds have been studied: deuteroammonia ND_3 (Taylor and Jungers [233]), deutochloric acid DCl (Lewis, MacDonald and Schutz [214]), deutocyanic

acid DCN (Lewis and Schutz [217]), deutacetic acid CH_3COOD (Lewis and Schutz [216, 217]), and deutofluoric acid (Claussen and Hildebrand [182a]).

ND_3 was prepared by the interaction of D_2O (99 per cent. D) and Mg_3N_2. It melts at 199° K. (NH_3 at 195·2) and boils at 242·1° K. (NH_3 at 239·75).

The latent heat of evaporation calculated from its vapour pressure (see Table 72) is 5990 cal. (NH_3 5797 cal.).

Table 72

Temperature ° K.	202·3	213·0	226·1	232·1	238·6
p_{NH_3} in mm. Hg	77	184	367	511	714
p_{ND_3} in mm. Hg	63	154	313	475	628

DCl was obtained by allowing anhydrous $MgCl_2$ to react with D_2O at 600° C. Its vapour pressure is not very different from that of HCl and is given by the equations

$$\log \frac{p_{HCl}}{p_{DCl}} = \frac{15{\cdot}4}{T} - 0{\cdot}075 \text{ in the liquid state}$$

and

$$\log \frac{p_{HCl}}{p_{DCl}} = -\frac{57{\cdot}7}{T} + 0{\cdot}387 \text{ in the solid state.}$$

Table 73 shows the heat of evaporation and of fusion.

Table 73

	Heat of evaporation		Heat of fusion
	In the liquid	In the solid	
HCl	4081	7557	476
DCl	4151	4292	171

As with HCl and DCl the vapour pressures of HCN and DCN lie close together. The freezing point of DCN is 261° K., i.e. 2° higher than that of HCN.

The deutacetic acid was prepared by the interaction of deutochloric acid and silver acetate:

$$DCl + CH_3COOAg = CH_3COOD + AgCl.$$

CH_3COOD melts at 13·3° C. (CH_3COOH at 16·6° C.) and has a higher vapour pressure than CH_3COOH (see Table 74).

Table 74

Temperature ° C.	49·7	52·2	64·4	65·3	73·4	74·4	86·0	86·9	94·2
p_{CH_3COOH} in mm. Hg	--	66·1	—	117·8	--	172·7	—	272·9	—
p_{CH_3COOD} in mm. Hg	63·2	—	120·4	—	171·0	—	271·5	—	366·4

The dissociation constant of CH_3COOD (in D_2O) is much smaller than that of CH_3COOH (in H_2O), being $0{\cdot}59.10^{-5}$ at 25° C. compared with $1{\cdot}84.10^{-5}$ for CH_3COOH. This result shows that the deuton is held more tenaciously by a pair of electrons than the proton. (Cf. Lewis and Schutz [217, 217*a*].)

The vapour pressure of DF is slightly higher than that of HF [182*a*], whereas the vapour pressure of acetylene is lowered if its H atoms are replaced by D [201*d*].

It is not so easy to explain theoretically the differences in the vapour pressures of the hydro- and deutero-compounds as it is for hydrogen and deuterium (see p. 171). According to Lewis the great differences between the isotopic forms of substances such as water and ammonia can be chiefly ascribed to an increase in strength of the D bond compared with the H bond. This effects the lowering of the vapour pressure of the D compound when these bonds only occur in the liquid. On the other hand, a higher vapour pressure results for the deut-acetic acid compared with acetic acid, since these substances are completely associated in the vapour phase in consequence of similar hydrogen bonds operative in the vapour. In the case of hydrochloric and deutochloric acid there is not much tendency to form the hydrogen bond, and this behaviour explains the small difference in the vapour pressure of these compounds. The same holds also for HCN and DCN.

CHAPTER IV

THE CHEMISTRY OF HEAVY HYDROGEN

1. Equilibria

(a) *The equilibrium* $H_2 + D_2 \rightleftharpoons 2HD$

The equilibria in chemical reactions involving the heavy hydrogen isotope were first treated theoretically by Urey and Rittenberg [294].

The equilibrium constants of these reactions can be easily calculated on the assumption that the binding energy in the molecules involved is not changed if H atoms are replaced by D atoms, i.e. the total heat effect at absolute zero is the change in the zero-point energies. This assumption is most probably fulfilled for reactions involving only one sort of molecules, such as, for example, $H_2 + D_2 \rightleftharpoons 2HD$, but one might expect deviations if different sorts of molecules take part in the reaction (cf. p. 185).

The simplest equilibrium is that between the three different hydrogen molecules

$$H_2 + D_2 \rightleftharpoons 2HD \qquad \text{.....(1).}$$

The equilibrium constant

$$K_1 = \frac{[HD]^2}{[H_2][D_2]} \qquad \text{.....(1}a\text{),}$$

for this reaction is given by the expression

$$-\ln K_1 = \frac{\Delta E_0^0}{RT} - \tfrac{3}{2} \ln \frac{M_{HD}^2}{M_{H_2} M_{D_2}} - \ln \frac{Q_{HD}^2}{Q_{H_2} Q_{D_2}} \qquad \text{.....(2),}$$

ΔE_0^0 denoting the difference of the zero-point energies of the reaction partners (cf. p. 155), i.e.

$$\Delta E_0^0 = 2E_{0HD}^0 - E_{0H_2}^0 - E_{0D_2}^0 = 155 \text{ cals.},$$

M the masses and Q the summation of state:

$$Q = \Sigma p_J e^{-E/kT}.$$

The statistical weights for H_2 and D_2 are given on pp. 9 and 162; for HD it is

$$p_J = 6(2J + 1).$$

The summation for Q must be extended over the rotational and vibrational levels, and thus the energy E is given by

$$E = \omega_e h w_e (v + \tfrac{1}{2}) + B_e (J+1) J h w_e \quad \ldots\ldots(3),$$

the first term representing the vibrational energy, the second the rotational energy. (The higher terms accounting for the anharmonic character of the vibration and for the effect of the centrifugal force in the rotation are omitted.) The values for ω_e and B_e are given in Table 54 (p. 154).

In the temperature range 200–800° K., when the rotation is completely excited and the vibration is negligible, the equation (2) has the form

$$-\ln K_1 = \frac{\Delta E_0^0}{RT} - \tfrac{3}{2} \ln \frac{M_{HD}^2}{M_{H_2} M_{D_2}} - \ln \frac{4 I_{HD}^2}{I_{H_2} I_{D_2}} \quad \ldots(2a),$$

or with the numerical values

$$-\log K_1 = \frac{155}{4{\cdot}57 T} - 0{\cdot}6276 \quad \ldots\ldots(2b).$$

Table 75 contains the equilibrium constants calculated for temperatures 20–700° K.

Table 75

Temperature ° K.	K
20·4	0·151
50	1·345
100	2·265
200	2·903
298·1	3·269
400	3·494
575	3·710
700	3·800

The position of this equilibrium was experimentally investigated by A. and L. Farkas [132, 253, 255], using the thermoconductivity method. Pure H_2 and D_2 were mixed in known proportions and their resistance values determined before and after contact with a hot nickel wire (600° C.). The equilibrium $H_2 + D_2 \rightleftharpoons 2HD$ was readily established with this catalyst and the observed increase in the resistance value was therefore due to the formation of HD molecules. The results were

consistent with an equilibrium constant $K = 3$ to 4 and the equilibrium was found to vary little with temperatures above room temperature, indicating a very small heat of reaction, as expected from theory.

A more accurate determination of this equilibrium constant was made by Rittenberg, Bleakney and Urey [286], using the mass spectroscopic method to measure the relative amounts of

Table 76

Temperature ° K.	Source of hydrogen sample	K observed	K calculated
83	Catalysis of $H_2 + D_2 \rightleftharpoons 2HD$	2·18 2·30	2·2
195	Catalysis of $H_2 + D_2 \rightleftharpoons 2HD$	2·89 3·01	2·88
273	Catalysis of $H_2 + D_2 \rightleftharpoons 2HD$	2·96	3·19
298	Reaction HI + DI + Hg	3·28 3·28	3·27
670	Decomposition of HI + DI	4·20 3·35	3·78
741	Decomposition of HI + DI	3·82 3·68	3·82

Table 77

Percentage D	Percentage H_2	Percentage HD	Percentage D_2
0	100·0	0·0	0·0
10	81·1	17·7	1·1
20	64·5	31·0	4·5
30	49·9	40·2	9·9
40	37·1	45·7	17·1
50	26·2	47·5	26·2
60	17·1	45·7	37·1
70	9·9	40·2	49·9
80	4·5	31·0	64·5
90	1·1	17·7	81·1
100	0·0	0·0	100·0

H_2, HD and D_2. The same method was used by Gould, Bleakney and Taylor [243, 261*a*] for the investigation of this equilibrium at low temperatures, the equilibrium between H_2 and D_2 being established by very active Cr_2O_3 and supported nickel catalysts (other catalysts which are very effective for catalyzing the o-p-H_2 conversion, such as charcoal, failed to catalyze this reaction, cf. p. 188).

Table 76 gives the results obtained which are in perfect agreement with theory.

Table 77 shows the dependence of the concentration of the molecular species H_2, HD and D_2 on the total D content of the gas (per cent. D content = per cent. $D_2 + \frac{1}{2}$ per cent. HD) calculated according to the equilibrium $H_2 + D_2 \rightleftharpoons 2HD$ at 20° C. for $K_1 = 3{\cdot}27$.

(*b*) *The equilibria* $H_2 + DCl \rightleftharpoons HD + HCl$ *and* $H_2 + DI \rightleftharpoons HD + HI$

The equilibria $H_2 + DCl \rightleftharpoons HD + HCl$ .....(4)

and $H_2 + DI \rightleftharpoons HD + HI$ .....(5)

may be treated in a similar way [290]. For example, the equilibrium constant for the former reaction is given by

$$-\ln K = \frac{\Delta E_0^0}{RT} - \tfrac{3}{2}\ln\frac{M_{HD}M_{HCl}}{M_{H_2}M_{DCl}} - \ln\frac{Q_{HD}Q_{HCl}}{Q_{H_2}Q_{DCl}} \quad .....(6);$$

the first term, ΔE_0^0, is 367 cal. for the HCl-DCl reaction and 119 cal. for the HI-DI reaction, the zero-point energies being

HCl 4214·4 cal., HI 3245·7 cal.,

DCl 3030·4 cal., DI 2310·0 cal.

The coefficients for the vibrational and the rotational energy in the summation of state Q are to be taken from spectroscopic data.

Table 78 gives the equilibrium constants of these reactions.

Table 78

Temperature ° K.	$K = \frac{[HD].[HCl]}{[H_2].[DCl]}$	$K = \frac{[HD].[HI]}{[H_2].[DI]}$
200	0·947	—
298·1	1·281	1·950
400	1·504	2·058
575	1·730	2·140
700	1·822	2·155

The values for the reaction $H_2 + DI \rightleftharpoons HD + HI$ were experimentally confirmed by Rittenberg and Urey [287] by mea-

suring the thermal decomposition of different HI-DI mixtures. In Table 79 the experimental values for

$$h = \frac{2[I_2]}{2[I_2] + [HI + DI]}$$

($[I_2]$ and $[HI + DI]$ denoting the equilibrium concentrations) and those calculated from the theoretical equilibria are given together with Bodenstein's original values for pure HI.

Table 79

Temperature ° K.	Percentage D	$h_{\text{Bodenstein}}$	$h_{\text{exp.}}$	$h_{\text{calc.}}$
398	0	0·20703	0·20719	—
398	13·5	—	0·20838	0·20878
468	0	0·22772	0·22724	—
468	40	—	0·23287	0·23326
468	72	—	0·23877	0·23904

(c) *The equilibria* $H_2O + HD \rightleftharpoons HDO + H_2$ *and* $H_2O + D_2O \rightleftharpoons 2HDO$

The importance of the equilibrium between light and heavy hydrogen and water has already been mentioned in the discussion of the electrolytic separation of the hydrogen isotopes (see p. 130).

The complete equilibrium between the molecular species H_2, HD, D_2, H_2O, HDO and D_2O is defined by the equations

(1) $H_2 + D_2 \rightleftharpoons 2HD$, $\qquad K_1 = \dfrac{[HD]^2}{[H_2][D_2]}$ .....(1),

(2) $H_2O + D_2O \rightleftharpoons 2HDO$, $\qquad K_2 = \dfrac{[HDO]^2}{[H_2O][D_2O]}$ ...(7),

(3) $H_2O + HD \rightleftharpoons HDO + H_2$, $\qquad K_3 = \dfrac{[HDO][H_2]}{[H_2O][HD]}$ ...(8).

From these three equilibria all other equilibria involving the six molecular species can be derived:

$$H_2O + D_2 \rightleftharpoons D_2O + H_2, \qquad K_4 = \frac{[D_2O][H_2]}{[H_2O][D_2]} = \frac{K_3^2 K_1}{K_2} \quad \ldots\ldots(9),$$

$$H_2O + D_2 \rightleftharpoons HDO + HD, \qquad K_5 = \frac{[HDO][HD]}{[H_2O][D_2]} = K_3 K_1 \quad \ldots(10),$$

$$HDO + HD \rightleftharpoons D_2O + H_2, \qquad K_6 = \frac{[D_2O][H_2]}{[HDO][HD]} = \frac{K_3}{K_2} \quad \ldots(11),$$

$$D_2O + HD \rightleftharpoons HDO + D_2, \qquad K_7 = \frac{[HDO][D_2]}{[D_2O][HD]} = \frac{K_2}{K_1 K_3} \quad \ldots(12).$$

For a temperature range up to 500–600° K. (vibration negligible) the equilibrium constant K_2 is given by

$$-\ln K_2 = \frac{2E^0_{0HDO} - E^0_{0H_2O} - E^0_{0D_2O}}{RT} - \tfrac{3}{2}\ln\frac{M^2_{HDO}}{M_{H_2O}M_{D_2O}} - \ln\frac{4\bar{I}^2_{HDO}}{\bar{I}_{H_2O}\bar{I}_{D_2O}} \quad \ldots\ldots(7a),$$

where $$\bar{I} = \sqrt{I_A . I_B . I_C},$$

I_A, I_B and I_C denoting the three momenta of inertia of the water molecule. From the frequencies given in Table 56 and the corresponding anharmonic constants the following zero-point energies are obtained for H_2O, HDO and D_2O:

$$E^0_{0H_2O} = 13097 \text{ cal.},$$

$$E^0_{0HDO} = 11393 \text{ cal.},$$

$$E^0_{0D_2O} = 9527 \text{ cal.}$$

If we use these values and calculate the moment of inertia for HDO and D_2O from those for H_2O, assuming that the geometrical configuration of the water molecule is not altered by replacing H by D, we obtain

$$-\log K_2 = \frac{162}{4{\cdot}57T} - 0{\cdot}6231 \quad \ldots\ldots(7b)$$

or $K_2 = 3{\cdot}26$ at 25° C. and $K_2 = 3{\cdot}37$ at 100° C.

(Cf. also Topley and Eyring [158].)

Similarly we obtain for the equilibrium constant of reaction

$$H_2O + HD \rightleftharpoons HDO + H_2$$

$$-\log K_3 = -\frac{887}{4{\cdot}57T} + 0{\cdot}1335 \qquad \ldots\ldots(8a).$$

The equilibrium (8) was first investigated by Bonhoeffer and Rummel [248a], who measured the change in the specific gravity of dilute heavy water when in contact with the equivalent amount of ordinary hydrogen under pressure in the presence of a catalyst (see p. 190). At the D concentrations used (less than 0·6 per cent.) practically the whole of the deuterium was present either as HD or as HDO with no appreciable amounts of D_2 and D_2O; the equilibrium between light and heavy hydrogens and water was therefore defined by equilibrium (8) alone, and the equilibrium constant could be calculated directly from the final D content in the water (W_D) and the decrease observed owing to the formation of the HD molecules. From these experiments

$$K'_3 = \frac{W_D}{G_D} = 3{\cdot}8 \text{ at } 20^\circ \text{ C.},$$

K'_3 being the equilibrium constant of the reaction

$$(H_2O)_{liquid} + [HD]_{gas} = (HDO)_{liquid} + [H_2]_{gas} \ldots\ldots(8b)$$

and G_D the D content of the gas in equilibrium. From this value the equilibrium constant for the gaseous reaction

$$[H_2O]_{gas} + [HD]_{gas} = [HDO]_{gas} + [H_2]_{gas} \quad \ldots\ldots(8)$$

is obtained as $K_3 = 3{\cdot}1$ if we allow for the fact that the D content of the vapour is less than that of the liquid owing to the smaller vapour pressure of heavy water compared with ordinary water (cf. p. 173). This result seems to be in good agreement with the theoretical formula (8a) which gives $K_3 = 3{\cdot}4$ for 20° C.

A slightly different result was obtained by A. and L. Farkas [259a], who measured the increase in the D content of ordinary hydrogen in contact with heavy water in presence of palladium black. Since these experiments were carried out (at reduced pressure) with an excess of water, the original D content of the water was not appreciably altered by the forma-

tion of heavy hydrogen gas. Table 80 shows the rate of attainment of equilibrium between ordinary hydrogen and heavy water containing 26·2 per cent. D.

Table 80

Time in min.	Percentage D in the gas
0	0·0
30	5·0
48	7·5
55	9·5
93	10·2
120	10·1

From these two figures, 10·1 per cent. D in the hydrogen gas (G_D) and 26·2 per cent. D in the water (W_D), the equilibrium constant K_3 can be calculated, using the following relations (the concentrations being given in per cent.):

$$K_3 = \frac{[HDO][H_2]}{[H_2O][HD]} \qquad \text{.....(8),}$$

$$[HDO] = -\frac{K_2}{4-K_2} + \sqrt{\left(\frac{K_2}{4-K_2}\right)^2 + \frac{4K_2}{4-K_2} V_D . V_H} \qquad \text{.....(13),}$$

$$[H_2O] = V_H - \tfrac{1}{2}[HDO] \qquad \text{.....(14),}$$

$$[HD] = -\frac{K_1}{4-K_1} + \sqrt{\left(\frac{K_1}{4-K_1}\right) + \frac{4K_1}{4-K_1} G_D . G_H} \qquad \text{.....(15),}$$

$$[H_2] = G_H - \tfrac{1}{2}[HD] \qquad \text{.....(16),}$$

where the D content of the vapour

$$V_D = \frac{W_D}{W_H \frac{P_{H_2O}}{P_{D_2O}} + W_D} \qquad \text{.....(17)}$$

(P_{H_2O} and P_{D_2O} the vapour pressure of H_2O and D_2O respectively) and G_H, W_H and V_H denote the H content of gas, water and vapour respectively.

Table 81 contains the equilibrium constants K_3 and K'_3 obtained at 20° C. with samples of water of different D content, and Table 82 shows the dependence of the equilibrium constant

on temperature. The ratio $\frac{G_H \cdot W_D}{G_D \cdot W_H}$ given in colum 2, Table 82, has a similar value to K_3 owing to the fact that both K_1 and K_2 are not very much different from 4. A simple calculation shows that $K_1 = K_2 = 4K_3 = \frac{G_H \cdot W_D}{G_D \cdot W_H}$.

Table 81. *Temperature* = 20° C.

Percentage D in			Water (%)		Vapour (%)		Gas (%)		K'_3	K_3
Water	Vapour	Gas								
W_D	V_D	G_D	HDO	H_2O	HDO	H_2O	HD	H_2		
20·5	18·4	7·4	31·4	63·8	29·1	67·0	13·5	85·85	3·12	2·76
25·9	23·2	9·8	36·8	55·7	34·3	59·65	17·36	81·52	3·10	2·70
41·0	37·5	17·9	45·9	36·1	44·6	40·2	28·5	67·85	3·02	2·64
66·8	63·6	38·5	42·2	12·1	44·0	14·4	45·2	38·9	3·01	2·63
73·6	70·8	46·8	37·2	7·8	39·5	9·4	47·2	29·6	2·99	2·64
								Mean	3·05	2·67

Table 82

Temperature ° C.	Ratio $\frac{G_H \cdot W_D}{G_D \cdot W_H}$	K'_3	K_3 (obs.)	K_3 (calc.)
3	3·6	3·46	2·97	2·89
20	3·2	3·05	2·67	2·67
40	2·8	2·64	2·46	2·46
65	2·6	2·57	2·37	2·24
100	2·2	2·13	2·00	1·98
450	—	—	1·15	1·23

Experiments at high temperatures were made by establishing the equilibrium in a mixture of vapour containing a known amount of D and hydrogen (cf. also [251*a*]).

Both the absolute value and the dependence of the equilibrium constants on temperature can be represented by the formula

$$\log K_3 = \frac{750}{4{\cdot}57T} - 0{\cdot}1335$$

as shown by Table 82, column 5.

The discrepancy between the heat effect of 750 cal. given by

these experiments and that deduced from the zero-point energies of 887 cal. is most probably due to a slight change in the binding energy of hydrogen or water caused by the introduction of the D atoms. That this might happen is made probable by the relatively large isotopic shift in the electronic levels of molecules such as H_2 and OH (cf. [200] and [201a]).

A. and L. Farkas [256] have shown that in a number of processes in which gaseous hydrogen is liberated from aqueous solutions equilibria are actually established, and that in these processes the observed isotopic separation is due only to the position of the equilibria.

Such processes are

(1) The electrolysis of water under certain conditions (see p. 130).

(2) The liberation of hydrogen by the interaction of salts such as $K_4Co(CN)_6$ with water according to the equation

$$K_4Co(CN)_6 + H_2O = K_3Co(CN)_6 + KOH + \tfrac{1}{2}H_2.$$

(3) The decomposition of sodium formate by palladium black or by *Bacterium coli* [258] in the presence of heavy water according to the equation

$$HCOONa + H_2O = H_2 + CO_2 + NaOH.$$

Table 83 contains the results for the latter process, which are of interest since the equilibrium is established by an enzymatic process.

Table 83

Percentage D in water	Percentage D in the hydrogen liberated	Equilibrium constant K'_3
19·5	6·5	3·59
25·0	10·0	2·92
30·7	12·5	3·02
77·5	49·1	3·41
		Mean 3·24

Furthermore, we shall expect the equilibrium to be established in all processes involving hydrogen and water which proceed at higher temperatures, especially in the presence of a catalyst. Such processes are the interaction of steam with

iron, the reduction of oxides such as copper oxide ([122, 271]), or the water gas process. In all these reactions the relative concentrations of H_2O, HDO, D_2O, H_2, HD and D_2 will be defined by equilibria (1), (2) and (3), which can cause an isotopic separation. (Naturally the ratio water/hydrogen depends not only on temperature but also on the actual reaction involved.)

2. Kinetics

The kinetics of reactions involving light and heavy hydrogen is for several reasons an attractive subject for study. Firstly, it furnishes information about reactions which we can hardly detect otherwise. Further, by "labelling" one or more hydrogen atoms in a compound, through replacement by their heavy isotope we are able to follow them up during a complicated reaction and to draw conclusions regarding the mechanism of the process (cf. Taylor and Jungers[291]). The comparison of the reactivity of light and heavy hydrogen widens our knowledge about reaction kinetics and enables us to refine the theoretical treatment.

Another wide field of application for heavy hydrogen as a research tool in chemical kinetics is opened up in organic chemistry, a field so far not much investigated on account of the small quantities of heavy hydrogen at present available. Nevertheless, the "labelling" of the hydrogen atoms in organic chemistry has already given some remarkable results concerning the structure and reactivity of certain compounds. Probably the most striking results are, however, to be expected in biological chemistry.

In the following we shall treat first the reactions of hydrogen itself and then the reactions of heavy water, including some biological processes.

In considering the relative velocities of reactions involving light and heavy hydrogen of the type

$$H_2 + XY = HX + HY \qquad \text{.....(18),}$$

$$D_2 + XY = DX + DY \qquad \text{.....(19),}$$

we have to distinguish three different effects (Cremer and Polanyi [250], Eyring [130], Eyring and Sherman [131]):

(1) The collision number is smaller in the case of D_2 owing to the smaller molecular velocity of D_2.

(2) The activation energy is larger for D_2 than for H_2 owing to the smaller zero-point energy of the heavy isotope.

(3) If an energy barrier is passed by the quantum mechanical tunnel effect (cf. p. 76) the probability of transition is different for light and heavy hydrogen [212]. Effects (1) and (3) will also influence the reaction rate in reactions involving hydrogen atoms, e.g.

$$H + XY = HX + Y \qquad \ldots\ldots(20),$$

on replacing the H atom by D, but the effect (2) will not be operative, since the hydrogen atoms have no zero-point energy.

In general, these three effects will lower the reaction velocity of D_2 compared with H_2.* For many reactions this has been found experimentally. So far no experimental evidence has been brought forward for the quantum mechanical tunnel effect, but it is most probable that it plays an important part in such processes as the discharge of the ions of light and heavy hydrogens (cf. also [284]).

The situation is somewhat more complicated in reactions involving hydro- or deutero-compounds or in reactions proceeding in aqueous solution, but again one will expect the D compounds to react more slowly than the H compounds (cf. also p. 201). Thus for example the photosensitized decomposition of ND_3 proceeds ten times more slowly than that of NH_3 (Jungers and Taylor [271 *a*] and Evans [252 *c*]).

(*a*) *The interaction of light and heavy hydrogen*

The kinetics of the simplest chemical reaction involving heavy hydrogen,

$$H_2 + D_2 = 2HD \qquad \ldots\ldots(21),$$

were investigated by A. and L. Farkas (in the press), using

* Pace and Taylor [280 *a*] have found that H_2 and D_2 are adsorbed on hydrogenation catalysts with the same speed at 110–180° C. This is an unexpected result compared with the diffusion of the hydrogen isotopes through palladium (cf. p. 121).

the micro-thermoconductivity method. The reaction was found to proceed at temperatures 600–750° C. about 1·5 times more slowly than the thermal p-H_2 conversion (cf. p. 62) but according to the same mechanism, the apparent heat of activation being about 56 kg. cal. and the order of the reaction 3/2. The individual reactions involved are

$$D + H_2 \rightleftharpoons HD + H \qquad \text{.....(22)}$$

and

$$H + D_2 \rightleftharpoons HD + D \qquad \text{.....(22}a\text{)},$$

the former having about the same activation energy as

$$H + H_2 \rightleftharpoons H_2 + H \quad \text{(cf. p. 65)} \qquad \text{.....(22}b\text{)},$$

whereas the activation energy of the latter is about 1·2 kg. cal. higher on account of the smaller zero-point energy of the D_2 molecule compared with the H_2 molecule. The apparent heat of activation is composed (as in the parahydrogen conversion) of the energy necessary to form a hydrogen atom and of the true activation energy for the interaction between the hydrogen atom and the molecule. Table 84 shows the times of half change at 10 mg. Hg pressure for $\frac{1}{2}H_2 + \frac{1}{2}D_2$ mixtures.

The reaction $H_2 + D_2 \rightleftharpoons 2HD$ proceeds readily on a catalyst, such as, for example, a hot nickel wire, but does not occur through adsorption on charcoal at liquid air temperatures [255]. This behaviour is to be expected from the experiments on the catalytic ortho-parahydrogen conversion. The high-temperature mechanism of the o-$H_2 \rightarrow$ p-H_2 reaction involves dissociation of the adsorbed molecules and is able therefore to bring about the $H_2 + D_2 \rightleftharpoons 2HD$ reaction, since on desorption the H and D atoms formed in the adsorption layer combine to give H_2, D_2 and HD molecules whose relative amounts are determined by the position of this equilibrium at the temperature of the catalyst. On the other hand, in the low-temperature ortho-parahydrogen conversion the adsorption and desorption on charcoal cause no rupture of the molecules and in consequence cannot effect an exchange reaction like $H_2 + D_2 \rightleftharpoons 2HD$.

The catalytic HD formation was directly compared with the ortho-parahydrogen conversion by Bonhoeffer, Bach and

Fajans[245] on a nickel catalyst (cf. p. 98). They found that these two reactions always show parallel behaviour on varying the activity and temperature of the catalyst and the pressure, the ortho-parahydrogen conversion being about three times faster than the reaction $H_2 + D_2 \rightleftharpoons 2HD$. The apparent order is for both reactions between 0 and 1. The apparent heat of activation is (between 0–100° C.) about 6000 cal. for p-$H_2 \rightarrow$ o-H_2 and about 7400 cal. for $H_2 + D_2 \rightleftharpoons 2HD$. These results show conclusively that in both reactions the same mechanism is involved.

Table 84.

Temperature ° K.	Time of half changes in minutes
582	282
620	82
673	15
735	2·5

(b) The hydrogen-water reaction

The homogeneous exchange reaction between light and heavy hydrogen and water proceeds much more slowly than the $H_2 + D_2$ reaction, indicating an apparent heat of activation of about 65 kg. cal.) (A. and L. Farkas [in the press], Crist and Dalin[251], Gould and Bleakney[261].)

For the mechanism we have two possible schemes:

(*a*) the atomic reactions, e.g.

$$D + H_2O \rightleftharpoons H + HDO \qquad \text{.....(23)}$$

or

$$H + D_2 \rightleftharpoons HD + H \qquad \text{.....(22}a\text{)},$$

the atoms (or radicals OH) being formed by thermal dissociation of D_2 or H_2O;

(*b*) the molecular reactions

$$H_2O + D_2 \rightleftharpoons \begin{cases} HDO + HD & \text{.....(24)}, \\ D_2O + H_2 & \text{.....(24}a\text{)}. \end{cases}$$

It is reserved for further investigation to determine to what extent these particular reactions take part in the actual mechanism.

It may be mentioned that the study of the homogeneous exchange reaction between hydrogen and water is somewhat difficult, since in quartz vessels a heterogeneous reaction catalyzed by the walls also becomes apparent, proceeding with a speed similar to that of the homogeneous reaction. (The wall reaction does not affect the $H_2 + D_2$ reaction, the latter being much quicker.)

It was shown by Horiuti and Polanyi[266,267] that the exchange reaction between water and hydrogen according to the equation

$$HD + H_2O \rightleftharpoons HDO + H_2 \qquad \ldots\ldots(26)$$

can be readily catalyzed by platinum black* and proceeds in the following way. The hydrogen is split up into ions on the surface of the catalyst and these go into solution. At the same time an equivalent number of ions coming from the solution are discharged to form hydrogen. If hydrogen on the catalyst is replaced by heavy hydrogen these two processes cause an exchange of D atoms between gas and water until the equilibrium is established.

According to Horiuti and Polanyi[266,267b] this ionic reaction proceeds on unpoisoned catalysts in acid solutions with such a speed that the rate of the exchange

$$H_2O + HD \rightleftharpoons HDO + H_2$$

is determined by the diffusion of the hydrogen to the catalyst. In alcoholic solutions the exchange reaction is slow enough to be measured, and it is found that the exchange reaction proceeds at a rate proportional to the square root of the hydrogen pressure and has an energy of activation of 10,000 calories. It is assumed that the rate determining step in this reaction is not the dissociation of H_2 or D_2 but the ionization and discharge of the ions, these processes being inhibited by a potential barrier of 10,000 calories situated between the metal and solution. This mechanism is supported by the well-known fact that platinum is a good hydrogen electrode,

* According to Taylor and Diamond[290] this exchange reaction takes place also at higher temperatures on catalysts such as Cr_2O_3-gel, ZnO, etc.

i.e. it brings about the equilibrium between gaseous hydrogen and hydrogen ions. It may be mentioned that an enzyme present in the *B. coli* also catalyzes the exchange reaction (Farkas, Farkas and Yudkin [258]), and, according to Strickland and Green,* may act as a hydrogen electrode. Although it is so far not certain that these two enzymes are identical the analogy with the case of platinum is obvious (cf. also [249]).

(c) *The hydrogen-chlorine and the hydrogen-bromine reactions*

The photochemical interaction with chlorine is a good example of the different reactivities of the two hydrogen isotopes. The experiments were carried out by Rollefson [288] by comparing the rate of union of chlorine with hydrogen and deuterium in the presence of CO,† and by A. and L. Farkas [259] by measuring the change of the D concentration in a mixture of light and heavy hydrogen during the reaction with chlorine.‡ Tables 85 and 86 show the results.

Table 85

Temperature ° C.	k_{H_2}§	k_{D_2}	k_{H_2}/k_{D_2}
0	3·7	0·275	13·4
32	16·6	1·70	9·75

The difference in the reaction rates of light and heavy

* *Nature*, **133**, 573 (1934).

† The addition of CO was necessary in order to obtain a convenient reaction rate.

‡ It may be pointed out that this method of measuring the change in the D content is to be preferred to a direct comparison of the reaction velocities of light and heavy hydrogen in cases when the experimental conditions are not always very well reproducible (e.g. catalytic and photochemical experiments), since with this method both hydrogen isotopes react simultaneously and are affected in the same way by slight changes. In the present experiment samples of 0·2 c.c. were withdrawn at intervals from the reaction vessel; first the total hydrogen present (light and heavy) was determined after freezing out HCl and Cl_2, and then the H-D ratio.

§ If a mixture of $CO + Cl_2 + H_2$ is illuminated the pressure decrease is given by

$$\frac{\Delta H_2 + \Delta CO}{\Delta H_2} = 1 + k\frac{(CO)}{(H_2)}.$$

hydrogen with chlorine is caused chiefly by the different velocities of the reactions:

$$Cl + H_2 = HCl + H \quad \text{.....(26),}$$

$$Cl + HD = DCl + H \quad \text{.....(26}a\text{),}$$

$$Cl + D_2 = DCl + D \quad \text{.....(26}b\text{),}$$

forming the first step in the well-known Nernst chain. Since it was pointed out by Eyring and Polanyi [64] that the zero-point energy of a molecule contributes also to the activation (cf. p. 74), it is evident that the activation energies of the reactions (26a) and (26b) will be higher by the difference in the zero-point energies of the molecules H_2, HD and D_2, i.e. by 817 and 1789 cal. respectively.

Table 86. *Temperature* = 30° C.

Time in min.	Percentage D	ΔD in mm.	ΔH in mm.	$s = \frac{\Delta H}{\Delta D}\frac{D_0}{H_0}$
0	29·0	0·00	0·00	—
6	31·9	0·2	1·81	3·7
14	35·2	0·55	4·46	3·3
18	36·3	0·60	5·00	3·4
21	37·5	0·68	5·52	3·3
31	39·7	1·02	6·78	2·8
∞	44·2	1·69	8·81	2·1

On the other hand, we cannot expect a great difference in the velocity of the second step in the chain reaction,

$$H + Cl_2 = HCl + Cl \quad \text{.....(27)}$$

and

$$D + Cl_2 = DCl + Cl \quad \text{.....(27}a\text{),}$$

since these reactions involve only hydrogen atoms. But it is possible that the decrease of s (see Table 86) during the reaction is caused by the difference in the reaction velocities of the reactions

$$H + HCl = H_2 + Cl \quad \text{.....(28)}$$

and

$$D + DCl = D_2 + Cl \quad \text{.....(28}a\text{),}$$

the former being the faster (cf. Ritche and Norrish*).

A quantitative comparison between theory and experiment shows a fairly good agreement after taking into account the

* *Proc. Roy. Soc.* A, **140**, 112 (1933).

smaller collision number in the reaction involving heavy hydrogen (effect 1, p. 187). From Rollefson's values for k_{H_2}/k_{D_2} we find for the difference in the activation energies of the decisive reaction the value $RT \ln k_{H_2}/k_{D_2} = 1630$ cal., and from Farkas' figures $RT \ln s/1{\cdot}25 = 600$ cal. Bearing in mind that in Rollefson's experiment the reactions

$$Cl + H_2 = HCl + H \qquad \text{.....(26)}$$

and

$$Cl + D_2 = DCl + D \qquad \text{.....(26}b\text{)}$$

were involved, whereas in Farkas' experiments the reactions

$$Cl + H_2 = HCl + H \qquad \text{.....(26)}$$

and

$$Cl + HD = DCl + H \qquad \text{.....(26}a\text{)}$$

predominated, owing to the relatively small D content,* the agreement of these figures with the above-mentioned values of 1789 and 817 cal. may be regarded as satisfactory.

The reaction rate of the thermal hydrogen bromide formation was compared by Bonhoeffer and Bach [245] with the corresponding reaction involving heavy hydrogen. The results obtained are similar to those for the union with chlorine, since again the H_2 proved to be the faster reactant. At 581° K. the heavy hydrogen reacts five times slower, and the cause for this is that the reaction

$$Br + D_2 = DBr + D \qquad \text{.....(29}a\text{)}$$

has an activation energy which is 1500 cal. higher than the activation energy of the reaction

$$Br + H_2 = HBr + H \qquad \text{.....(29).}$$

(*d*) *The hydrogen-ethylene reaction*

A very interesting exchange reaction between ethylene and heavy hydrogen was discovered by Farkas, Farkas and Rideal [257] when investigating the catalytic hydrogenation of ethylene on a nickel wire by a mixture of light and heavy hydrogen. By measuring simultaneously the change in the pressure and the change in the D content of the mixture, it

* Heavy hydrogen with 30 per cent. D contains 9 per cent. D_2 + 42 per cent. HD and 49 per cent. H_2.

could be shown that under certain conditions an exchange reaction according to

$$C_2H_4 + HD \rightleftharpoons C_2H_3D + H_2 \qquad \text{.....(30)}$$

took place before the hydrogenation

$$C_2H_4 + H_2 \rightleftharpoons C_2H_6 \qquad \text{.....(31)}$$

occurred. In general, both reactions (30) and (31) proceeded simultaneously, but at low temperature (20° C.) on an active catalyst the hydrogenation was predominant (see Table 87), whereas at higher temperatures the exchange reaction was the faster (see Table 88), causing a considerable decrease in the D content of the hydrogen.

Table 87. *Temperature* = 20° C.

Time in min.	Ethylene pressure in mm. Hg	Hydrogen pressure in mm. Hg	Percentage D content of the hydrogen
0	21·5	32·5	30·6
10	13·6	24·5	30·0
25	5·5	16·5	33·2
37	1·0	12·0	33·8

Table 88. *Temperature* = 120° C.

Time in min.	Ethylene pressure in mm. Hg	Hydrogen pressure in mm. Hg	Percentage D content of the hydrogen
0	12	14	30·1
7	8	10	18·9
13	5	7	15·4
21	4	6	12·9
46	2	4	11·1

Table 89 shows the relation of the final D concentration after the exchange reaction to the ratio hydrogen/ethylene. The heavy hydrogen is nearly equally distributed between ethylene and hydrogen. (The figures given in column 5 are calculated assuming an equilibrium constant 1 for the reaction (30).)

The equilibrium

$$C_2H_4 + HD \rightleftharpoons C_2H_3D + H_2 \qquad \text{.....(30)}$$

is only established when the exchange reaction proceeds much faster than the hydrogenation reaction, since the ethane formed does not exchange with heavy hydrogen. Table 90 shows the approach to equilibrium at different temperatures, see column 6 in terms of $100\left(\frac{D_{initial}-D_{final}}{D_{initial}-D_{calc.}}\right)$.

Table 89. *Temperature* = 120–150° C.

Ethylene pressure in mm. Hg	Hydrogen pressure in mm. Hg	Percentage initial D content	Percentage final D content	Final percentage D calculated
8·7	11·8	30·0	11·0	11·5
10·0	21·0	30·0	13·5	15·4
7·0	19·0	30·0	15·2	17·3
15·0	25·0	63·8	26·0	29·1

Table 90

Temperature ° C.	Ethylene / Hydrogen ratio	Percentage initial D content	Percentage final D content	Final percentage D calculated	Percentage equilibrium attained
20	1·0 : 1	29·7	35·4	9·9	~ 0
58	0·6 : 1	65·9	48·5	30·0	48
78	0·5 : 1	63·6	43·5	31·8	65
120	0·58 : 1	65·0	28·0	30·2	~100

This behaviour shows distinctly that the hydrogenation and the exchange reaction have different mechanisms. The latter proceeds most probably in a manner similar to the high-temperature mechanism of the catalytic parahydrogen conversion (see p. 100): the ethylene is dissociated on the surface of the catalyst into hydrogen atoms and the radical $\rangle C=C\langle$, and the exchange reaction occurs when the $\rangle C=C\langle$ radical picks up new H and D atoms corresponding to their concentration in the adsorption layer.

(e) *The hydrogen-oxygen and the hydrogen-nitrous oxide reactions*

Melville [277] has compared the interaction of light and heavy hydrogen with O_2 and N_2O on a nickel catalyst and finds that at temperatures of 150–250° C. the heavy hydrogen reacts

about 2–2·5 times more slowly than the light one. This difference is not to be explained by the different rate of impacts of light and heavy hydrogen on the catalyst (this would give only a factor $\sqrt{2}$), since the rate-determining step in these reactions is the migration of the hydrogen atoms in the surface. The activation energies for the migration of the H and D atoms should then differ by the difference of the zero-point energies of the Ni-H and Ni-D complexes formed on the surface of the catalyst. The difference in the activation energies calculated on this assumption agrees very well with the theoretical value for the zero-point energy difference computed of 700 cals. by Eyring and Sherman [131] (see Table 91).

Table 91

Reaction	Temperature °C.	Ratio	ΔE in cal.
H_2–N_2O	159	2·47	750
	192	2·10	690
H_2–O_2	177	2·42	780
	226	2·09	740
	255	2·31	880

The homogeneous hydrogen-oxygen reaction was investigated by Melville [277, 277*a*, 278], Frost and Alyea [260] and Hinshelwood, Williamson and Wolfenden [265] (cf. also [249*a*]).

Melville has shown that H and D atoms produced photochemically react with the same speed with oxygen. It is assumed that the rate determining step in this reaction is the formation of HO_2 and DO_2 in ternary collisions and that the higher collision frequency of the H atoms compared with the D atoms is compensated by the lower H concentration due to the greater diffusion of the H atoms to the wall. At higher temperatures, however, when chains are being propagated, a different speed of reaction is observed for the hydrogen isotopes, indicating that molecules or radicals are involved in the chains.

Frost and Alyea have observed that the lower pressure limit of explosion is the same for D_2 as for H_2; the upper explosion limit however is higher. This latter observation is in agreement with Hinshelwood's theory of deactivation by collisions, since

the D_2 is less efficient in deactivation owing to its smaller molecular velocity. On the other hand, the fact that the low pressure limit is the same for H_2 and D_2 shows that the probability of branching is the same for both hydrogen isotopes. This seems to indicate that the branching mechanism does not involve breaking of hydrogen bonds.

(*f*) *The dissolution of metals in water or acids*

A. and L. Farkas[251] observed that if metals such as zinc, aluminium, calcium or sodium were dissolved in water or in dilute acids containing a certain amount of heavy hydrogen, the hydrogen liberated had always a lower D content than the liquid, the separation factor

$$s = \frac{(H/D)_{gas}}{(H/D)_{liquid}} \qquad \ldots\ldots(32)$$

being about 4 to 1·5.

In Table 92 the dependence of this separation factor on the metal dissolved is shown according to investigations of Hughes, Ingold and Wilson[269, 270].

Table 92

	Medium	Separation coefficient	Notes
Li	Water	1·5	
Na	,,	2·8	As 3 per cent. amalgam 3·4. (Cf. also Davis and Johnston[252], Horiuti and Szabó[268])
K	,,	1·9	
Mg	,,	2·1	
Ca	Water or H_2SO_4	1·3	
Si	NaOH	2·3	
Al	NaOH	4·3	
	H_2SO_4	4·0	
Zn	H_2SO_4	5·6	With impurities or Cu couple 7–8
Cr	,,	4·5	
Mn	,,	5·1	
Fe	,,	4·3	
Co	,,	4·1	
CaC_2	Water	1·5	D content of the liberated C_2H_2 analysed
Al_4C_3	,,	2·0	D content of the liberated CH_4 analysed

It is remarkable that in all processes in which presumably a direct interaction between water and metal takes place the separation coefficient is smaller than the equilibrium constant of the reaction

$$H_2O + HD \rightleftharpoons HDO + H_2 \qquad \text{.....(33),}$$

whereas the processes occurring only in acid solution yield in general a higher separation factor.

This behaviour suggests that in these two groups of processes there are two different mechanisms which we could tentatively take to be

$$\text{I.}\ (a)\quad Me + H_2O \rightarrow Me^+ + OH^- + H$$
$$(b)\quad Me + D_2O \rightarrow Me^+ + OD^- + D \qquad \text{.....(34)}$$

and

$$\text{II.}\ (a)\quad Me + H^+ \rightarrow Me^+ + H$$
$$(b)\quad Me + D^+ \rightarrow Me^+ + D \qquad \text{.....(35).}$$

The relative rates of the reactions (*a*) and (*b*) define the primary separation of the hydrogen isotopes, which is however modified to a certain extent by the exchange reaction (33). That the exchange reaction actually takes place is made probable by the presence of the metallic surface acting as a catalyst and by the well-known high reactivity of hydrogen in the nascent state.

Since this latter reaction—as already mentioned in the discussion on electrolysis (p. 130)—tends to bring about a "separation factor" equal to the equilibrium constant, the primary separation in mechanism I will be smaller than that observed, but in mechanism II even larger than the observed value.

Urey and Price [293] observed that at 80° C. the liberation of methane by the interaction of aluminium-carbide and pure D_2O took place 23 times more slowly than that by the interaction between Al_4C_3 and H_2O. On the other hand, there is no separation of this magnitude if methane is evolved from a mixture of light and heavy water (*v.* Table 92), showing that in the latter case some sort of exchange reaction occurs besides the primary reaction which lowers the high separation caused by the primary reaction.

(*g*) *Exchange reactions with heavy water*

It was shown firstly by Bonhoeffer and Brown [216] and by Lewis [272] that substances containing hydrogen, such as ammonia, ammonium chloride or sucrose, undergo an exchange reaction of the type

$$XH + HDO \rightleftharpoons XD + H_2O \qquad \ldots\ldots(36)$$

when dissolved in water containing heavy hydrogen. It is obvious that in the case of NH_3 or NH_4Cl the exchange reaction is of the ionic type, including the steps

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad \ldots\ldots(37)$$

or

$$NH_4^+ \rightleftharpoons NH_3 + H^+ \qquad \ldots\ldots(37a).$$

A closer investigation of the exchange reaction with sugar has shown that not all the hydrogen atoms exchange but only about half of them, namely, those which are present in the OH groups; the H atoms linked directly to the carbon remain unaffected. The extension of the investigations to other organic compounds has given essentially the same result. Besides the hydroxyl-H, the H linked to N undergoes an exchange in aqueous solutions, a behaviour analogous to that of NH_3.

Very interesting is the exchange reaction with acetone [247, 262, 289*b*]: practically no reaction occurs in neutral solution, whereas in alkaline solution a rapid exchange of the hydrogen atoms takes place. Table 93 shows the rates of these exchange reactions according to Klar [271*c*].

Table 93. 38*g*. *acetone* + 25 *c.c. water*. *Temperature* = 100° C.

Neutral		1/50 mol. KOH	
Time in hours	D:H in the water	Time in hours	D:H in the water
0	1:200	0	1:200
12	1:210	0·08	1:245
24	1:240	3	1:370
36	1:260	6	1:415

This behaviour is connected with establishment of the keto-enol equilibrium

$$CH_3COCH_3 \rightleftharpoons CH_2 = C(OH).CH_3 \quad \ldots\ldots(38)$$

in alkaline solution, when the exchange can proceed through the OH radicals. The position of the equilibrium

$$CH_3COCH_3 + HDO \rightleftharpoons CH_3COCH_2D + H_2O \quad \ldots(39)$$

was measured by Halford, Anderson and Bates [262], who found that the equilibrium constant is about 2, the heavy hydrogen being present preferentially in the acetone.

The interchange of hydrogen atoms between acetylene and heavy water takes place in alkaline solution but not in neutral medium, indicating the acidic nature of the hydrogen bond in the acetylene molecule (Reyerson and Yuster [285]).

It may be pointed out in this connection that although this exchange reaction can be used as a "reagent" for OH and NH groups in organic compounds, the equilibrium constant of the reaction in question must be taken into consideration in drawing quantitative conclusions; this is not necessarily 1, as we have seen in the case of acetone.

The following table summarizes the exchange reactions of some other compounds with heavy water (cf. Bonhoeffer [214], Klar [271*c*], Hall, Bowden and Jones [263], Erlenmeyer and Gärtner [252*a*, *b*]).

Table 94

Benzene C_6H_6	No exchange
Glucose Sucrose	Exchange of the H atoms of the hydroxyl group
Acetaldehyde	Slow exchange
Formaldehyde	Exchange of all H atoms
Acetylacetone	Exchange of all H atoms
Ethyleneglycol	Immediate exchange of the H atoms in the hydroxyl group
Sodium acetate	No exchange
Ovalbumine	Exchange of H linked to N
Cellulose	In some days all H atoms of the hydroxyl groups are exchanged at 100° C.
H_2O_2	Rapid exchange
KH_2PO_2	No exchange
$Co(NH_3)_6(NO_3)_6$	Exchange of all H atoms

It was shown by Horiuti, Ogden and Polanyi [265a] that other exchange reactions of water with hydrogen, ethylene (cf. also p. 194) and benzene which do not proceed homogeneously can be catalyzed by hydrogenation catalysts such as nickel, platinum or palladium.

These experiments are of importance for the synthesis of organic deutero-compounds.

(*h*) *Some reactions in aqueous solution*

As a very simple case of a reaction in aqueous solution, Pacsu [281, 283] and Moelwyn-Hughes and Bonhoeffer [279, 279a] have investigated the mutarotation of α-*d*-glucose in light water and heavy water. At 20° C. the reaction proceeds three times more slowly in heavy water than in light water. Since in this reaction the absolute velocity can be directly calculated from the temperature coefficient making simple assumptions, it can be shown that the slower rate in heavy water is due to a higher activation energy (after allowing for the different viscosities of light water and heavy water). Essentially the same holds for the reaction catalyzed by hydrogen ions [279, 279a].

An unexpected result was obtained in studying the hydrolysis of sucrose catalyzed by D ions (Moelwyn-Hughes and Bonhoeffer [279]), when it was found that the D ions were 1·6–1·7 times more effective than the H ions. This peculiar result is not yet completely cleared up, but is probably due to the higher stability of some intermediate D complex compared with the corresponding H complex, the concentration of which determines the rate of hydrolysis (cf. also Gross, Suess and Steiner [261b]).

A similar result was found by Schwarz [289a] when investigating the hydrolysis of esters catalyzed by hydrogen ions.

The alcoholic fermentation of *d*-glucose in heavy water was compared by Pacsu [282] with that in ordinary water. Measuring the amount of CO_2 formed, he found that the fermentation proceeds eight to nine times more slowly in heavy water. Essentially the same result was obtained by Yudkin [268a], who worked under controlled p_H.

The effect of replacing light water by heavy water in other

reactions proceeding in aqueous solutions was investigated by Abel, Redlich and Stricks [239a], Hughes, Yudkin, Kemp and Rideal [268a] and Wynne Jones [295].

(i) *Biological experiments with heavy water*

Since most living processes are necessarily connected with water, the question soon arose whether ordinary water could be replaced in organisms by heavy water. The first and most striking experiments were performed by Lewis [273] and Taylor and his co-workers [292]. Lewis showed that in pure heavy water tobacco seeds failed to germinate, and Taylor detected the lethal effect of heavy water on water organisms such as tadpoles, goldfish, flatworms and protozoa. On the other hand, diluted 30 per cent. heavy water (or ordinary distilled water) had no effect within a day or so (cf. also Taylor [289], Lewis [274] and Macht and Davis [275]).

This latter result shows distinctly that we have not to deal here with a poisoning effect but rather with an upset of those delicately balanced equilibria which are necessary for living processes. Bonhoeffer [244] has found that yeast and *Bombardia* grow about four times more slowly in 90 per cent. heavy water than in ordinary water.

That heavy water or heavy hydrogen can be taken up into the organism was shown by Washburn and Smith [165a, 166] for willow and by Bonhoeffer [244] for yeast growing in dilute heavy water (cf. also [288a]).

In this connection a very instructive experiment carried out by Hevesy and Hofer [261] may be mentioned, which is at the same time a good example of the utilization of heavy hydrogen as a research tool for the investigation of a process otherwise not accessible: namely, the exchange of water between fish and their surroundings. Several goldfish (corresponding to 8 c.c. water; fish containing about 80 per cent. water) were put in 60 c.c. of water containing 0·5 per cent. D, and the decrease of the D content in the water was measured from time to time. After $4\frac{1}{2}$ hours no further change could be observed in the D content of the "aquarium water", indicating that in this time a complete exchange had taken place between the water in the

body of the fish and in the tank. On putting the "heavy" fish into normal water the excess of the D content was given up in the same time.

The question whether the small amount of heavy hydrogen present in normal water is a necessary factor for the organism is not yet solved.*

* There may be some connection between this question and the results of some investigators [240, 241, 276], who found that dilute heavy water (1:200) accelerates the growth of micro-organisms (cf. also [241*a*] and [271*b*]).

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