THE HYDROGEN ISOTOPES IN THE GASEOUS AND LIQUID STATES

H. F. P. KNAAP

21/5

THE HYDROGEN ISOTOPES IN THE GASEOUS AND LIQUID STATES

[illegible] LABORATORIUM
DER RIJKSUNIVERSITEIT
te LEIDEN

THE HYDROGEN ISOTOPES
IN THE GASEOUS AND LIQUID STATES

BIOCHEMISCH LABORATORIUM
DER RIJKSUNIVERSITEIT
LEIDEN

THE HYDROGEN ISOTOPES IN THE GASEOUS AND LIQUID STATES

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN
DOCTOR IN DE WIS- EN NATUURKUNDE
AAN DE RIJKSUNIVERSITEIT TE LEIDEN
OP GEZAG VAN DE RECTOR MAGNIFICUS
DR. G. SEVENSTER, HOOGLERAAR IN DE
FACULTEIT DER GODGELEERDHEID
PUBLIEK TE VERDEDIGEN OP WOENSDAG
30 MEI 1962 TE 11 UUR

DOOR

HENRICUS FRANCISCUS PETRUS KNAAP

GEBOREN TE LEIDEN IN 1936

Promotor: PROF. DR. K. W. TACONIS

Dit proefschrift is bewerkt onder leiding van Dr. J. J. M. BEENAKKER

Aan mijn ouders
Aan mijn vrouw

Promotor: PROF. DR. H. W. TALSMA

Dit proefschrift is bewerkt onder leiding van Dr. J. J. M. [illegible]

Ten einde te voldoen aan het verzoek van de Faculteit der Wis- en Natuurkunde volgt hier een overzicht van mijn studie.

Na in 1953 aan het Stedelijk Gymnasium te Leiden het eindexamen afgelegd te hebben, begon ik de studie in de Wis- en Natuurkunde te Leiden. In 1956 behaalde ik het candidaatsexamen D, waarna ik werkzaam was op het Kamerlingh Onnes Laboratorium in de werkgroep voor Molecuulphysica. De leiding van deze groep berustte tot 1960 bij Prof. Dr. A. van Itterbeek en daarna bij Prof. Dr. K. W. Taconis en Dr. J. J. M. Beenakker.

Gedurende een jaar assisteerde ik Dr. J. M. J. Coremans bij metingen van de viscositeit van gassen. In 1957 werkte ik drie maanden aan het "Instituut voor Lage Temperaturen en Technische Physica" te Leuven. Sindsdien heb ik mij bezig gehouden met onderzoekingen aan de toestandsvergelijking van gassen en de thermodynamische eigenschappen van vloeistofmengsels bij lage temperaturen.

Van 1957 af heb ik geassisteerd op het practicum voor prae-candidaten. Na de vereiste tentamens bij Prof. Dr. S. R. de Groot, Prof. P. Mazur, Prof. Dr. C. Visser en Dr. J. van Kranendonk te hebben afgelegd deed ik in februari 1959 het doctoraalexamen experimentele natuurkunde.

In december 1959 ben ik aangesteld als wetenschappelijk medewerker van de Stichting F.O.M.

In 1960 werkte ik een maand in het Laboratorium voor Physische Chemie te Brussel.

Bij het totstandkomen van dit proefschrift heb ik veel steun ondervonden van de intensieve samenwerking met Dr. J. J. M. Beenakker. De experimenten die in dit proefschrift beschreven worden zijn verricht in samenwerking met de heren F. H. Varekamp, Dr. C. M. Knobler, Drs. M. Knoester, R. J. J. van Heijningen en J. Korving.

Ten einde te voldoen aan het verzoek van de Faculteit der Wis- en Natuurkunde volgt hier een overzicht van mijn studie.

Na in 1953 aan het Stedelijk Gymnasium te Leiden het eindexamen afgelegd te hebben, begon ik de studie in de Wis- en Natuurkunde te Leiden. In 1956 behaalde ik het candidaatsexamen D, waarna ik werkzaam was op het Kamerlingh Onnes Laboratorium in de werkgroep voor Molecuulphysica. De leiding van deze groep berustte tot 1960 bij Prof. Dr. A. van Itterbeek en daarna bij Prof. Dr. K. W. Taconis en Dr. J. J. M. Beenakker.

Gedurende een jaar assisteerde ik Dr. J. M. J. Coremans bij metingen van de viscositeit van gassen. In 1957 werkte ik drie maanden aan het "Instituut voor Lage Temperaturen en Technische Physica" te Leuven. Sindsdien heb ik mij bezig gehouden met onderzoekingen aan de toestandsvergelijking van gassen en de thermodynamische eigenschappen van vloeistofmengsels bij lage temperaturen.

Van 1957 af heb ik geassisteerd op het practicum voor prae-candidaten. Na de vereiste tentamens bij Prof. Dr. S. R. de Groot, Prof. P. Mazur, Prof. Dr. C. Visser en Dr. J. van Kranendonk te hebben afgelegd deed ik in februari 1959 het doctoraalexamen experimentele natuurkunde.

In december 1959 ben ik aangesteld als wetenschappelijk medewerker van de Stichting F.O.M.

In 1960 werkte ik een maand in het Laboratorium voor Physische Chemie te Brussel.

Bij het totstandkomen van dit proefschrift heb ik veel steun ondervonden van de intensieve samenwerking met Dr. J. J. M. Beenakker. De experimenten die in dit proefschrift beschreven worden zijn verricht in samenwerking met de heren F. H. Varekamp, Dr. C. M. Knobler, Drs. M. Knoester, R. J. J. van Heijningen en J. Kerssing.

CONTENTS

INTRODUCTION 1

CHAPTER I. *The second virial coefficient of the hydrogen isotopes between 20 and 70°K* 5

1. Introduction 5
2. Experimental method and apparatus 5
3. Experimental results 7
4. Discussion 9
   a. The temperature dependence of B 10
   b. The absolute value of B 11
   c. Comparison with theory 15

CHAPTER II. *The second virial coefficient of binary mixtures of the hydrogen isotopes and helium at 20.4°K* 17

1. Introduction 17
2. Method and apparatus 17
3. Results 19
4. Conclusions 20

CHAPTER III. *The second virial coefficient of ortho- and para hydrogen at liquid hydrogen temperatures* 21

1. Introduction 21
2. Experimental method 23
3. Experimental results 24
4. Conclusions 28

CHAPTER IV. *The Lennard-Jones 6–12 potential parameters of H_2 and D_2* 29

1. Introduction 29
2. H_2 and D_2 29
3. The ortho and para modifications 31
4. Calculation of the properties 33

CHAPTER V. *The volume change on mixing for several liquid systems and the difference in molar volume between the ortho and para modifications of the hydrogenic molecules* 37

1. Introduction 37
2. Experimental method 37
3. Calculations and experimental results 40
4. Discussion 42

CHAPTER VI. *The heat of mixing of the liquid systems H_2–D_2, H_2–HD and HD–D_2* 47

1. Introduction 47
2. Apparatus 48
3. Measuring procedure 49
4. Experimental results and discussion 25

CONCLUSIONS 57

SAMENVATTING 59

INTRODUCTION

In the last fifteen years two important advances have been made in the field of molecular physics. The availability of computers made it possible to determine the complicated collision-integrals, which appear in the calculation of the transport properties and of the deviations from the ideal gas law, if realistic models are introduced for the intermolecular interaction. In this respect we can mention the work of Hirschfelder and coworkers, who strongly stimulated the work in this field by their very comprehensive book: "Molecular Theory of Gases and Liquids" 1).

The second important advance was the application of quantum mechanics to the collisions of molecules in the case of the realistic interactions. On this subject much work has been done by De Boer and coworkers 2). As will be shown later, the quantum mechanical and classical treatment differ only at sufficiently low temperatures (in general below 100°K). Therefore it is obvious that, when the "Werkgemeenschap voor Molecuulphysica van de Stichting voor Fundamenteel Onderzoek der Materie" was founded, the work of the Leyden Group for Molecular Physics would be primarily devoted to collecting sufficient experimental data at low temperatures 3).

Here it may be advantageous to discuss the circumstances under which the quantum-mechanical treatment predicts deviations from the classical behaviour. To estimate the influence of the quantum-effects on the properties of gases at low density, it is reasonable to compare the De Broglie wave length Λ, associated with the relative motion of the molecules, with the classical collision diameter σ of the molecules. For $\Lambda/\sigma \ll 1$, the collision may be treated classically, but when this is no longer valid, deviations from the classical description will appear and since

$$\Lambda = \frac{h}{mv_r} \approx \frac{h}{\sqrt{mKT}}$$

it is clear that the deviations will be more pronounced for light molecules and at low temperatures. The situation is particularly interesting for isotopes; they have the same intermolecular potential, but show different deviations from classical behaviour depending on their different masses.

Hence, a study of the helium and hydrogen isotopes seemed rather promising. Because of the scarcity of data in the case of the hydrogen isotopes, the main work of the Leyden group for molecular physics has been directed toward these isotopes. The complete set of possibilities is: H_2, D_2, T_2, HD, HT and DT. Since molecules containing tritium are experimentally difficult to handle, because of instability ($^3_1T \rightarrow {}^3_2He + \beta^-$) and because only small amounts are available, we have limited our studies to H_2, D_2 and HD.

In addition some subtle effects will be caused by the different modifications of the homonuclear hydrogen isotopes (the ortho and para modifications) and these are certainly worthy of investigation.

These considerations led Van Itterbeek and Beenakker to the development of a program for experiments on the equation of state, the thermal diffusion, the normal diffusion and the viscosity. We shall discuss in this thesis the work on the equation of state. Research on the viscosity of pure gases and gaseous mixtures is already published in detail in the theses of Coremans [4]) and Rietveld [5]), while the program for the thermal diffusion is now nearly completed by the work of Van Ee e.a. In the first stage of this project Beenakker and Varekamp performed isotherm determinations at the hydrogen boiling point for H_2, HD, D_2 and their mixtures with He. Subsequently for the same gases the temperature dependence of the second virial coefficient was measured between 14 and 20°K. The results for H_2 deviated appreciably from theory and also from the older experimental data at 20°K. We therefore considered the possibility of a systematical error in the measurements at 20°K. By measuring the temperature dependence of the second virial coefficient between 20 and 70°K, we could link up with the existing high temperature data and check whether the value at 20°K was consistent with these data (see Chapter I).

A further check on the isotherm determinations at 20°K was obtained by investigating the second virial coefficient for mixtures with He, using a differential method of improved accuracy (Chapter II). The developed apparatus allowed precise determinations of the excess second virial coefficient, which could be compared with the results of theoretical calculations.

For the ortho and para modifications of H_2 and D_2 small differences in the viscosity have been found by Becker e.a. As his results were not in disagreement with the calculation of Cohen e.a. it seemed important as a check on the theory to investigate also the ortho-para effect for the second virial coefficient, where theory predicted an effect of less than 0.1%. Earlier attempts of other investigators to measure the ortho-para effect in the second virial coefficient had failed.

To reach a higher precision we developed here also a differential method. A difference in second virial coefficient between ortho and para H_2 of the order of 1% was found (Chapter III).

Michels e.a. concluded from their recent isotherm work at higher temperatures to a small difference in the interaction between H_2 and D_2. In Chapter IV we show that such a difference should be expected from the small difference in polarizability. On the same grounds we concluded to a small difference in interaction between the ortho and para modifications. In this way we are able to account for the major part of the experimentally found differences between these modifications both in the gaseous and the liquid state.

In the course of our work on the gas properties we developed an extensive set up for the preparation of rather large amounts of isotopes of high purity with their ortho and para modifications. We constructed e.g. an automatically controlled electrolysis cell for the production of D_2 from heavy water, a rectification column for the purification of the gases and an apparatus to make para H_2. This made it possible to start a research on the properties of liquids for which large amounts of gas are needed; sometimes 100 liters of gas per week were necessary.

Our interest in the liquids was stimulated by the theoretical predictions of Prigogine and coworkers [6]), while further interest arose in connection with the work of Taconis e.a. [7]) on the properties of liquid mixtures of the helium isotopes.

Just as in the case of gases at low temperatures, the properties of the liquid helium and hydrogen isotopes are largely influenced by the deviations from classical behaviour. The deviation will become important when the zero point energy is no longer small in comparison with the interaction energy. For a liquid made up of cells of linear dimension l, the zero point energy is proportional to h^2/l^2m, while the interaction energy for a molecule (at the centre of the cell) with its neighbours is $(z\varepsilon/2)$. So we have a characteristic ratio $h^2/\sigma^2m\varepsilon$ as l is of the order of σ the diameter of the molecule. From this it is clear that also for liquids small mass and small interaction energy favour quantum deviations. De Boer and Lünbeck [8]) showed that for pure liquids the deviations from classical behaviour by quantum effects can be described rather well in terms of $\Lambda^{*2} = h^2/\sigma^2m\varepsilon$.

Prigogine and coworkers developed an approach, based on the picture of the influence of the zero point energy, to predict the properties of isotopic liquid mixtures.

^{3}He–^{4}He mixtures are less suited for a test of their theory, because also the difference in statistics of the two components is of importance in this case. Since other isotopic mixtures gave too small an effect, it seemed the most promising approach to investigate the thermodynamic properties of the hydrogen isotopic mixtures, i.e. the volume change on mixing and the heat of mixing.

For the volume change on mixing we developed a direct method i.e. we measured the expansion or contraction that occured on mixing (Chapter V). A fortunate coincidence was that Knobler [9]) in his study of the properties of liquid oxygen needed also data on the heat of mixing as is discussed in his thesis. Therefore experience was obtained in this subject and after some changes the calorimeter was suited for liquid hydrogen temperature to measure the heat of mixing of the hydrogen isotopes (Chapter VI). The heat of the mixing results are in good agreement with the afore mentioned theory of Prigogine. It seemed at first that our results on the volume change were in disagreement with the theory, having even the wrong sign. However a more careful analyses of Prigogine's work showed that even the estimation of the effect is outside the possibilities of the theory.

GENERAL REFERENCES

1) Hirschfelder, J. C., Curtiss, C. F. and Bird, R. B., Molecular theory of gases and liquids (John Wiley and Sons, New York, 1954).
2) De Boer, J., Progress in low temperatures physics, edited by Gorter, C. J., Volume I, Chapter XVIII (North Holland Publishing Company, Amsterdam, 1955).
3) Beenakker, J. J. M., Progress in low temperature physics, edited by Gorter, C. J., Volume III, Chapter VI (North Holland Publishing Company, Amsterdam, 1961).
4) Coremans, J. M. J., Thesis Leiden (1960).
5) Rietveld, O. A., Thesis Leiden (1961).
6) Prigogine, I., The molecular theory of solutions (North Holland Publishing Company, Amsterdam, 1957).
7) De Bruyn Ouboter, R., Thesis Leiden (1962).
8) Lünbeck, R. J., Thesis Amsterdam (1951).
9) Knobler, C. M., Thesis Leiden (1961).

CHAPTER I

THE SECOND VIRIAL COEFFICIENTS OF THE HYDROGEN ISOTOPES BETWEEN 20 AND 70°K

Summary

The second virial coefficients of H_2, HD and D_2 are measured at low densities in the temperature region between 20 and 70°K using a differential method. The measurements confirmed the results of the isotherm determinations of Beenakker *e.a.* [1]). At higher temperatures good agreement with the existing data was found.

1. *Introduction.* In this chapter we describe the results of a determination of the temperature dependence of the second virial coefficient B for H_2, HD and D_2 [2]). The second virial coefficient is measured relative to that of He by a differential method. The main advantages of this relative method are: 1° a higher accuracy can be attained, 2° only an approximate knowledge of the volumes of the different parts of the apparatus is required and 3° the method allows a rather rapid determination of B.

A thermostat with a stability of a few thousandths of a degree centrigrade was built for the region between 20 and 70°K.

2. *Experimental method and apparatus.* Fig. 1 gives a schematic diagram of the apparatus which consists mainly of two parts: the reservoirs for the measurement of the second virial coefficient, which are essentially the same as described in [3]) and the thermostat, which is an improved version of a thermostat used by us for the determination of the viscosity of gases between 20 and 80°K [4]). The copper vessels R_1, R_2, R_3 and R_4 are soldered together so as to give good thermal contact. R_1, R_2 and R_3 are connected by narrow stainless steel capillaries to the room temperature section of the apparatus. R_1 is filled to a certain pressure with He, which is always used as reference gas and R_2 with a hydrogen isotope to almost the same pressure P^i at the initial temperature T^i. The

initial pressure difference ΔP^i between the two gases, measured on the differential oil manometer D_1, could be made small by withdrawing from the system if necessary, a certain amount of gas in a volume V, that for this purpose could be cooled. After measuring T^i, P^i and ΔP^i the temperature is changed from T^i to T^f and the pressure difference ΔP^f is measured on the oil manometer D_1. This difference relates the second virial coefficients in the initial state to those in the final situation. After measuring ΔP^f and T^f the temperature is again changed without equalizing the pressure and a measurement is performed at the new temperature. In this way all measurements of a run are related to the same initial situation, so as to avoid an accumulation of errors.

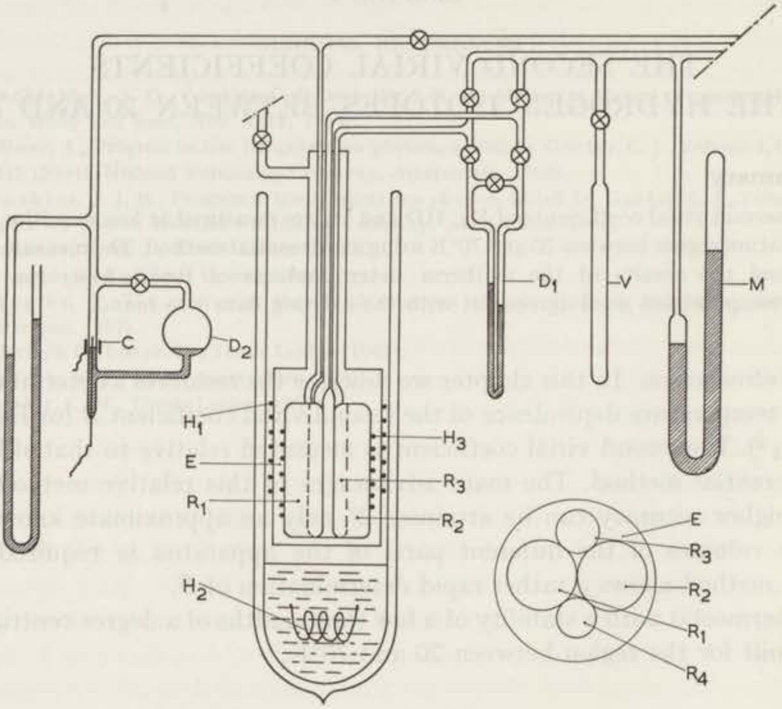

Fig. 1. Schematic diagram of the apparatus.

The H_2 and D_2 used, were always of a high temperature equilibrium ortho-para composition (*i.e.* an ortho para ratio of 3 : 1 for H_2 and 2 : 1 for D_2).

Some precautions were taken to avoid systematic errors. The pressures were always kept well below the saturated vapour pressure to avoid effects of capillary condensation. By changing the volume which is at room temperature slightly, the apparatus was made still more symmetrical *i.e.* no change in oil level resulted from a change in temperature, when both vessels were filled with the same gas.

The vessel R_3 is used as a gas thermometer. A change in pressure in R_3, which is connected to a differential oil manometer D_2 gives rise to a change in oil level. A capacitor C is formed by a ring of foil around one arm of D_2 and a rod inserted in the glass tubing. The change in capacitance, caused by the moving of the oil level operates a Proximity switch, which regulates the current in the heaters H_1 and H_2. Heater H_1 is mounted on a shield enclosing the measuring vessels and the heat is transported by the exchange gas in space E, in this way avoiding temperature gradients along the vessels.

The heater H_2 in the liquid gives the necessary cooling, while heater H_3 is only used to reach a new temperature quickly. The temperature stability is of the order of 0.003°K. The temperature is determined with a platinum thermometer mounted in R_4.

The HD was prepared by equilibrating a 50% mixture of H_2 and D_2 by means of a red hot Ni wire and distillation of the resulting mixture of H_2, HD and D_2. After fractionating the HD (purity higher than 98%) a second time a purity of a few parts in a thousand was reached as could be shown with nuclear relaxation measurements in the liquid HD [5]). The D_2, which was prepared by means of an electrolysis cell, was also fractionated in order to limit the impurities to a few 0.01% O_2 and N_2, so that the partial pressure of O_2 and N_2 was at all temperatures negligible compared to the pressure difference ΔP^{f} on the oil manometer. The H_2 was directly taken from an evaporating hydrogen bath, while the He was purified by passing it over charcoal at liquid He temperatures.

3. *Experimental results.* We use the equation of state in the form

$$P = Ad(1 + Bd)$$

where P is the pressure in normal atmospheres, d the density in amagat units, B the second virial coefficient in amagat units and

$$A = \frac{T}{273.15}(1 + B_0 + C_0 + ..)^{-1}$$

with B_0 and C_0 the second and third virial coefficient at the ice point and T the absolute temperature. For the ratio of the initial pressures in the two reservoirs divided by the ratio of the final pressures one may write, if the values at the initial and final temperature are denoted by "i" and "f":

$$\frac{P_1{}^{\mathrm{i}}P_2{}^{\mathrm{f}}}{P_2{}^{\mathrm{i}}P_1{}^{\mathrm{f}}} = \frac{T_1{}^{\mathrm{i}}T_2{}^{\mathrm{f}}}{T_2{}^{\mathrm{i}}T_1{}^{\mathrm{f}}} \cdot \frac{d_1{}^{\mathrm{i}}d_2{}^{\mathrm{f}}}{d_2{}^{\mathrm{i}}d_1{}^{\mathrm{f}}} \cdot \frac{1 + B_1{}^{\mathrm{i}}d_1{}^{\mathrm{i}}}{1 + B_2{}^{\mathrm{i}}d_2{}^{\mathrm{i}}} \cdot \frac{1 + B_2{}^{\mathrm{f}}d_2{}^{\mathrm{f}}}{1 + B_1{}^{\mathrm{f}}d_1{}^{\mathrm{f}}}$$

Since $T_1{}^{\mathrm{f}} = T_2{}^{\mathrm{f}}$ and $T_1{}^{\mathrm{i}} = T_2{}^{\mathrm{i}}$ and using $P_2 = P_1 + \Delta P$, we obtain

$$1 + \frac{\Delta P^{\mathrm{f}}}{P_1{}^{\mathrm{f}}} = \frac{1 + B_2{}^{\mathrm{f}}d_2{}^{\mathrm{f}}}{1 + B_2{}^{\mathrm{i}}d_2{}^{\mathrm{i}}} \cdot \frac{1 + B_1{}^{\mathrm{i}}d_1{}^{\mathrm{i}}}{1 + B_1{}^{\mathrm{f}}d_1{}^{\mathrm{f}}}\left(1 + \frac{\Delta P^{\mathrm{i}}}{P_1{}^{\mathrm{i}}}\right)\frac{\mathrm{d}_1{}^{\mathrm{i}}d_2{}^{\mathrm{f}}}{d_2{}^{\mathrm{i}}d_1{}^{\mathrm{f}}} \qquad (1)$$

where the term $d_1{}^{\mathrm{i}}d_2{}^{\mathrm{f}}/d_2{}^{\mathrm{i}}d_1{}^{\mathrm{f}} = 1$ apart from a correction due to gas transport from the cold to the warm part of the apparatus that takes place as the temperature is changed from T^i to T^t and a second correction, arising from the change in volume of the room temperature part of the apparatus caused by the oil level difference in D_1.

TABLE I

Constants of the formula $B(T) = B(20.4)\ (20.4/T)^{\alpha}$

	$B(20.4)$ 10^{-3} amagat	α
H_2	-6.78 ± 0.05	1.37
HD	-7.24 ± 0.06	1.54
D_2	-8.06 ± 0.08	1.63

TABLE II

Results of the measurements with H_2

T^i °K	P^i cm Hg	B^i 10^{-3} am	d^i am	P^t cm Hg	T^t °K	ΔP^t cm oil	B^t 10^{-3} am
20.53	38.30	−6.73	7.021	45.44	24.35	6.389	−5.29
				51.94	27.86	11.779	−4.40
				62.41	33.48	19.871	−3.39
				73.14	39.27	27.708	−2.67
39.36	39.50	−2.65	3.642	47.14	47.02	1.474	−1.98
				54.69	54.71	2.863	−1.51
				63.01	63.04	4.273	−1.14
				71.10	71.27	5.542	−0.86
				80.35	80.55	6.821	−0.63
20.58	35.30	−6.70	6.431	40.03	23.24	3.868	−5.61
				48.57	28.35	10.389	−4.27
				58.11	33.92	17.109	−3.31
				67.01	39.15	23.178	−2.65
39.17	38.55	−2.66	3.571	46.28	47.07	1.677	−1.88
				53.58	54.66	3.158	−1.36
				63.00	64.27	4.859	−0.91
				71.00	72.50	6.187	−0.63
				78.18	79.43	7.221	−0.45
20.47	46.11	−6.75	8.567	54.60	24.24	9.275	−5.33
				60.69	26.94	15.461	−4.61
				67.57	30.03	22.295	−3.93
36.21	31.75	−3.00	3.181	40.29	46.09	1.525	−2.00
				48.58	55.68	3.023	−1.37
				57.36	65.94	4.446	−0.94
				66.39	76.56	5.820	−0.61
34.46	36.53^5	−3.23	3.858	48.87	46.23	2.958	−2.02
				55.60	52.71	4.467	−1.59
				62.99	59.83	6.119	−1.20
				70.53	67.13	7.625	−0.92
				78.00	74.39	9.008	−0.70

For the value of the second virial coefficient of He we used Keesom's formula ⁶) $10^3 B = 0.6824 - 17.244/T$, which is valid between 5 and 60°K. The B values for the hydrogen isotopes at the initial temperature (*i.e.* approximately 20.4°K) are calculated using the formula: $B(T) = B\ (20.4)\ (20.4/T)^{\alpha}$, where $B(20.4)$, the second virial coefficient at 20.4°K, and α are taken from ¹) and ³). In table I the values of B (20.4) and α are tabulated. The value of P^f in formula (1) is calculated from the pressure before heating the vessels and was found to consistently agree very well with the pressures observed in the final situation when checked as a control.

The experimental data and the results for B^f are shown in table II, III, and IV for H_2, HD and D_2. In general one initial situation served as a starting point for four individual measurements.

TABLE III

Results of the measurements with HD

T^i °K	P^i cm Hg	B^i 10^{-3} am	d^i am	P^f cm Hg	T^f °K	ΔP^f cm oil	B^f 10^{-3} am
20.55	20.21	−7.16	3.625	25.55	25.99	2.665	−4.93
				33.54	34.12	6.445	−3.00
				42.08	43.02	9.701	−2.06
				52.34	53.67	13.626	−1.25
				73.78	76.14	20.814	−0.36
20.67	28.07	−7.09	5.055	35.47	26.15	5.017	−4.89
				51.09	37.75	14.346	−2.68
				60.44	44.74	19.398	−1.96
				70.06	52.09	24.303	−1.40

TABLE IV

Results of the measurements with D_2

T^i °K	P^i cm Hg	B^i 10^{-3} am	d^i am	P^f cm Hg	T^f °K	ΔP^f cm oil	B^f 10^{-3} am
21.55	16.95	−7.37	2.887	24.13	30.74	2.773	−4.12
				35.61	45.54	6.815	−2.13
				46.09	59.18	10.137	−1.22
				55.76	71.83	13.012	−0.68
20.51	18.21	−7.99	3.274	24.66	27.82	3.448	−4.86
				33.09	37.42	7.170	−3.01
				42.54	48.24	11.034	−2.00
				52.08	59.25	14.653	−1.33
				62.71	71.55	18.313	−0.89

4. *Discussion.* We will divide the discussion into three parts. Firstly the temperature dependence of B will be discussed, as this is the quantity that is directly measured (the absolute value of B enters here only in correction terms). Secondly some conclusions will be drawn as to the absolute value of B and finally the experimental results will be compared with theory.

a) The temperature dependence of *B*. In figure 2 it is shown that the slopes of the log *B versus* log *T* lines for H_2, HD and D_2, which have been derived from our measurements above 20.4°K, agree very well with the slopes of the corresponding straight lines representing the results of Varekamp and Beenakker [3]) below 20.4°K. Up to about 40°K *B* can

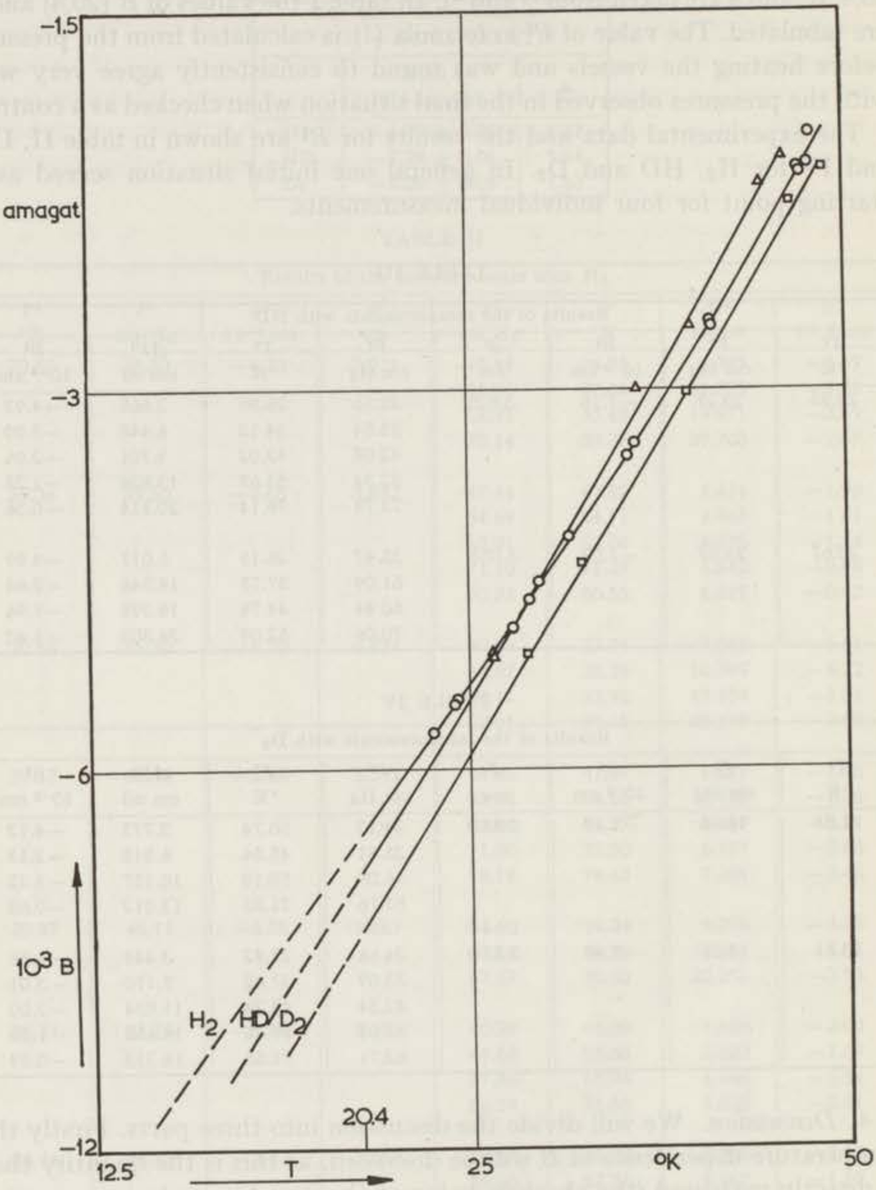

Fig. 2. Experimental results for H_2, HD and D_2.
○ H_2; △ HD; □ D_2
Dotted lines indicate measurements by Varekamp and Beenakker

still be represented by the same formula as used below 20.4°K *i.e.* $B(T) = B(20.4)\,(20.4/T)^{\alpha}$ with B and α differing for each gas. The line for HD intersects that for H_2 as could be expected from the results below 20.4°K. Apart from possible systematic errors, the uncertainty in $\Delta B/\Delta T$ is estimated to be of the order of a few percents.

As a comparison with other measurements the differences between our values for the second virial coefficient of hydrogen and those of Nijhoff and Keesom [7]) and of Johnston and White [8]) are plotted in figure 3. This is a sensible procedure since measurements of B from PV isotherms are often subject to systematic errors. Frequently however, such a systematic error is of the nature of an additive quantity that is only slightly temperature dependent, so that the temperature dependence of B is generally more reliable than its absolute value. It can be seen from figure 3, that over large temperature intervals the data of [7]) and [8]) are simply displaced from our values, confirming the temperature dependence of our results.

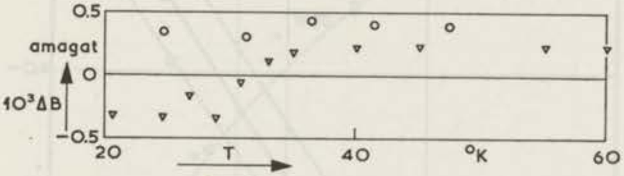

Fig. 3. The deviation from the results of this research for hydrogen.
○ Nijhoff and Keesom △ Johnston and White

b) The absolute value of B. Since these measurements are relative it was necessary to adopt a value for B at some temperature. We chose the value of B at 20.4°K as measured by Beenakker *e.a.* The situation at 20.4°K was discussed in detail in [1]) and [3]), where the authors showed that the only other reliable data at this temperature are the results of Van Agt and Kamerlingh Onnes [9]), which differ by about 0.4×10^{-3} amagat from the data of Beenakker *e.a.* To independently check the isotherm measurements described in [1]) for systematic errors, measurements of the second virial coefficients of mixtures were performed using an alternative method [10]) in which a direct measurement of the excess second virial coefficient E was made (c.f. chapter II). $2x_1x_2E = B_{\mathrm{m}} - x_1B_1 - x_2B_2$, where B_{m} is the B of the mixture and B_1 and B_2 are those of the pure components, x_1 and x_2 are the relative molar concentrations. Comparison of this direct measurement of E with the values calculated from the isotherms indicates that there are no large systematic errors in the absolute measurements reported in [1]).

From figs. 3 and 4 it is clear that there exists a systematic difference between our values, based on the measurements of [1]) at 20.4°K, and those of [7]) and [8]). Nijhoff and Keesom [7]) measured at rather high densities between 15 and 29 amagats and used a platinum thermometer to determine the low density limit of the isotherm. So these data are easily liable to

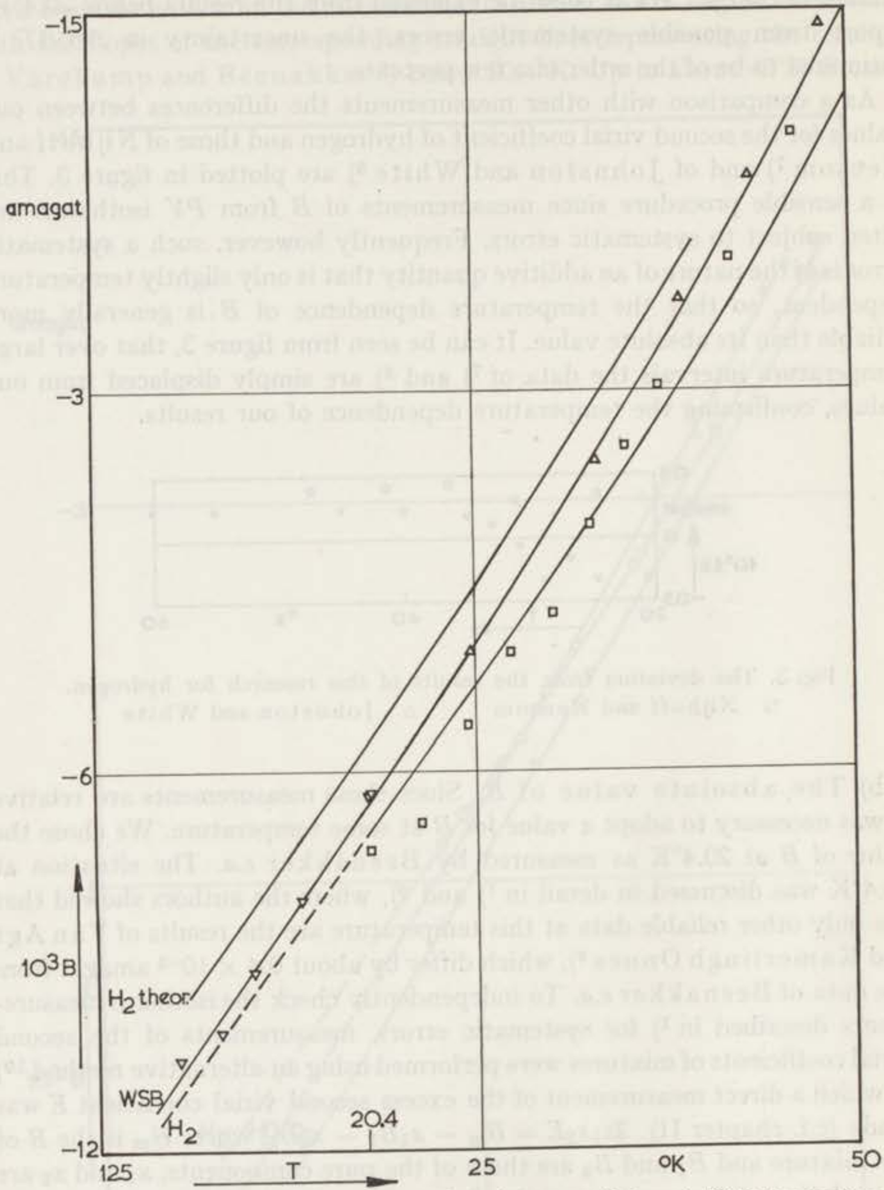

Fig. 4. A comparison with the existing data between 12.5 and 50°K for hydrogen.
—— this research. — — — — — Varekamp and Beenakker.
W.S.B. adopted values by Woolley, Scott and Brickwedde.
▽ Van Agt and Kamerlingh Onnes.
△ Nijhoff and Keesom.
□ Johnston and White.
H_2 theor. calculated by Cohen *e.a.*

systematic errors arising from the large density gap. Beenakker *e.a.* determined the temperature from the extrapolation of their isotherm to zero density. The values of Johnston and White have been calculated from unpublished data and as such no critical evaluation of the errors is as yet available. We have omitted the data of Schäfer [11]) for H_2 in fig. 3, as he was primarily interested in the difference in B between normal and para hydrogen and used a method that gives data which are not independent of those of [7]) and [9]).

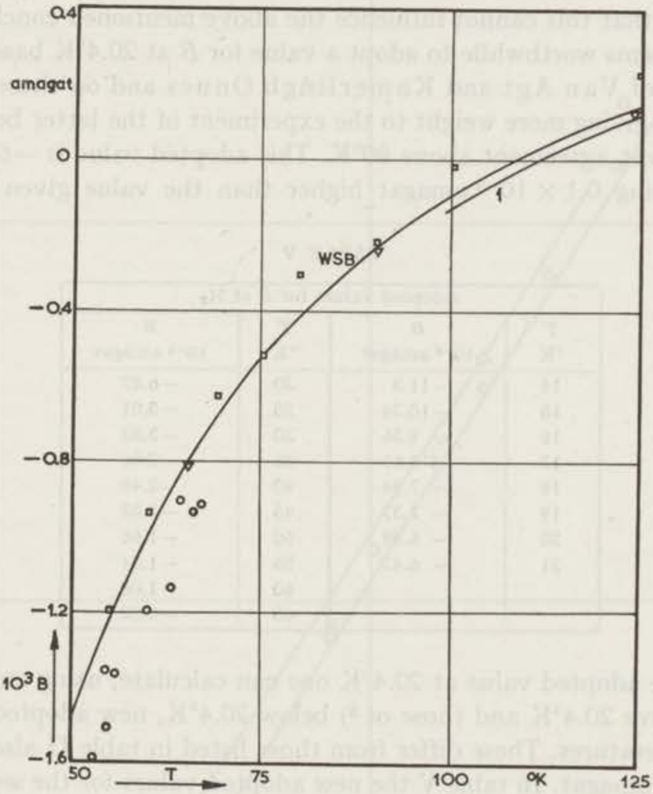

Fig. 5. A comparison with existing data above 50°K for hydrogen.
1 Michels, De Graaff, Wassenaar, Levelt and Louwerse.
□ Johnston and White.
▽ Holborn and Otto.
○ this research.
W.S.B. Woolley, Scott and Brickwedde.

The absolute value of B, found at 70°K is directly linked by the relative measurement technique to the value adopted at 20.4°K. Thus starting with the 0.4×10^{-3} amagat higher value from [9]) one calculates a value of B at 70°K that is also 0.4×10^{-3} amagat higher. However, it can be seen that our values extrapolate rather well to the very accurate data of Michels *e.a.*[12][13]) above 98°K (see fig. 5) and also that the deviations from the values of Holborn and Otto[14]) [15]) [16]) are within the experimental error of $0.1 \times \times 10^{-3}$ amagat. Since we have directly measured the temperature dependence, this agreement with other studies in the easily accessible temperature region around 80°K leads to the conclusion that the work of Beenakker *e.a.* at 20.4°K must be favoured over that of Van Agt and Kamerlingh Onnes. Both groups of authors took no C coefficient into account at 20.4°K, but the correction for this effect would only lower B by 0.03×10^{-3} amagat, so that this cannot influence the above mentioned conclusion.

It now seems worthwhile to adopt a value for B at 20.4°K based both on the results of Van Agt and Kamerlingh Onnes and on those of Beenakker *e.a.*, giving more weight to the experiment of the latter because this gives the best agreement above 80°K. This adopted value is -6.68×10^{-3} amagat, being 0.1×10^{-3} amagat higher than the value given by Beenakker *e.a.*

TABLE V

Adopted values for B of H_2

T °K	B 10^{-3} amagat	T °K	B 10^{-3} amagat
14	−11.3	20	−6.87
15	−10.24	25	−5.01
16	− 9.36	30	−3.83
17	− 8.61	35	−3.06
18	− 7.94	40	−2.48
19	− 7.37	45	−2.02
20	− 6.87	50	−1.66
21	− 6.42	55	−1.34
		60	−1.06
		65	−0.82

From the adopted value at 20.4°K one can calculate, using our values of $\Delta B/\Delta T$ above 20.4°K and those of [3]) below 20.4°K, new adopted values at other temperatures. These differ from those listed in table II also by about 0.1×10^{-3} amagat. In table V the new adopted values for the second virial coefficient of hydrogen are given. The new values of the constant in the formula: $B(T) = B(20.4)(20.4/T)^{\alpha}$ are:

$$B(20.4) = -6.68 \times 10^{-3} \text{ amagat and } \alpha = 1.39.$$

In figs. 4 and 5 a curve is drawn representing the adopted values of Woolley *e.a.*[17]) for H_2.

The B values for D_2 have been plotted in fig. 6 together with the results of Schäfer[11]), whose values for D_2 are directly linked to his B value for H_2. This can account for the small difference between our results and those of Schäfer.

For HD no other data are available.

c) **Comparison with theory.** In fig. 4 we have drawn a curve representing the results of the quantum mechanical calculations of **Cohen** *e.a.* [18]) for H_2, based on a Lennard-Jones 6-12 potential. In fig. 6 a similar curve is drawn for D_2 [19]). The large discrepancy between experiment and the

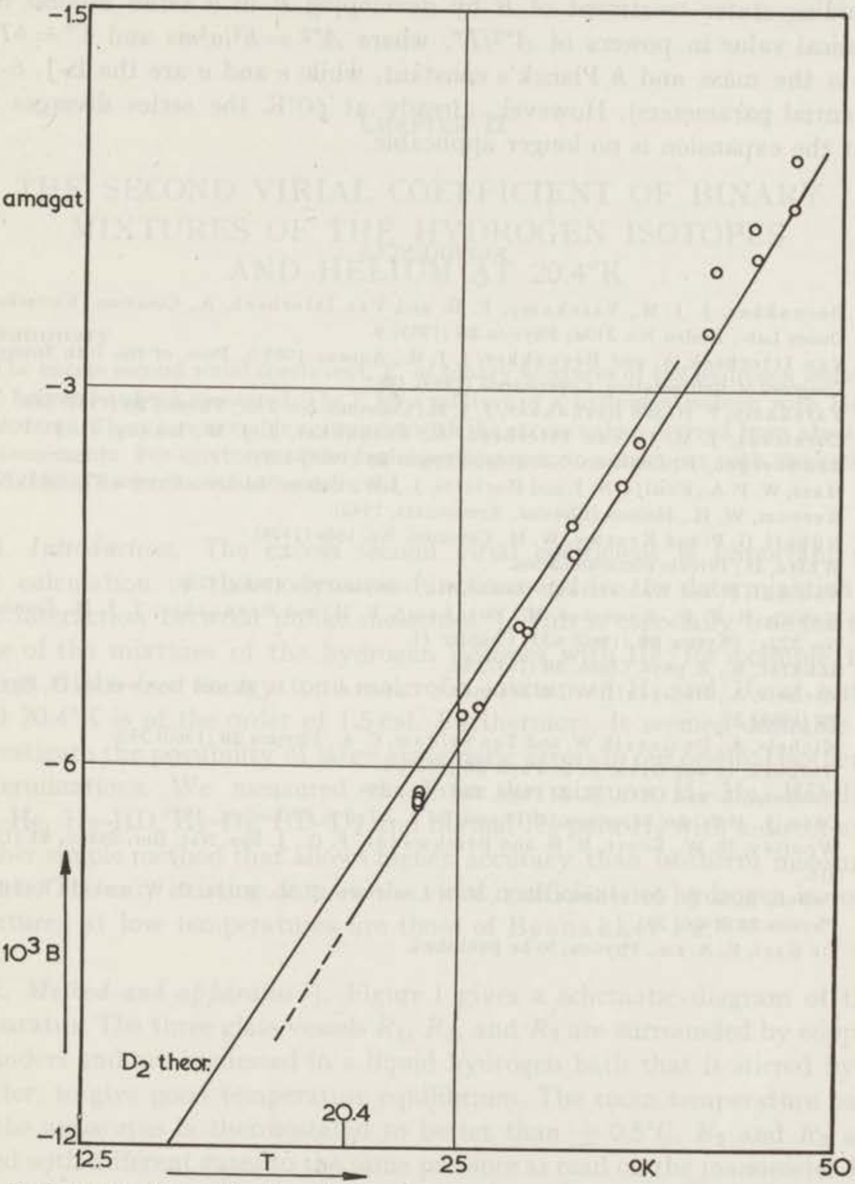

Fig. 6. A comparison with the existing data beween 12.5 and 50°K for deuterium.

———— this research.

– – – – measured by **Varekamp** and **Beenakker**.

D_2 theor. calculated by **De Kerf** *e.a.*

○ **Schäfer**.

results of these calculations for low temperatures arises probably from the influence of the non-spherical part of the intermolecular potential, for which no calculations are available at low temperatures.

At the higher temperatures one is tempted to apply a modified corresponding states treatment of B by developing B in a series around the classical value in powers of Λ^{*2}/T^*, where $\Lambda^{*2} = h^2/\sigma^2 m\varepsilon$ and $T^* = kT/\varepsilon$ (m is the mass and h Planck's constant, while ε and σ are the L-J. 6-12 potential parameters). However, already at 60°K the series diverges so that the expansion is no longer applicable.

REFERENCES

1) Beenakker, J. J. M., Varekamp, F. H. and Van Itterbeek, A., Commun. Kamerlingh Onnes Lab., Leiden No. 313*a*; Physica **25** (1959) 9.
2) Van Itterbeek, A. and Beenakker, J. J. M., Annexe 1959-1, Proc. of the 10th Internat. Congress of Refrigeration, Copenhagen (1959) 146.
3) Varekamp, F. H. and Beenakker, J. J. M., Commun. No. 316*c*; Physica **25** (1959) 889.
4) Coremans, J. M. J., Van Itterbeek, A., Beenakker, J. J. M., Knaap, H. F. P. and Zandbergen, P., Commun. No. 311*a*; Physica **24** (1958) 557.
5) Hass, W. P. A., Poulis, N. J. and Borleffs, J. J.W., Comm. No. 328*c*; Physica **27** (1961) 1037.
6) Keesom, W. H., Helium (Elsevier, Amsterdam, 1942).
7) Nijhoff, G. P. and Keesom, W. H., Commun. No. 188*e* (1928).
8) White, D., Private communication.
9) Van Agt, F. and Kamerlingh Onnes, H., Commun. No. 176*b* (1925).
10) Knaap, H. F. P., Knoester, M., Varekamp, F. H. and Beenakker, J. J. M., Commun. No. 322*a*; Physica **26** (1960) 633; Chapter II.
11) Schäfer, K., Z. phys. Chem. **36** (1937) 85.
12) Michels, A., De Graaff, W., Wassenaar, T., Levelt, J. M. H. and Louwerse, P., Physica **25** (1959) 25.
13) Michels, A., De Graaff, W. and Ten Seldam, C. A., Physica **26** (1960) 393.
14) Holborn, L. and Otto, J., Z. Phys. **33** (1925) 1.
15) Holborn, L. and Otto, J., Z. Phys. **38** (1926) 359.
16) Otto, J., Hdb. der experimental Physik Bd 8, 2.Teil p. 79 Leipzig, 1929.
17) Woolley, H. W., Scott, R. B. and Brickwedde, F. G., J. Res. Nat. Bur. Stand. **41** (1948) 416.
18) Cohen, E. G. D., Offerhaus, M. J., Van Leeuwen, J. M., Roos, B. W. and De Boer, J., Physica **22** (1956) 791.
19) De Kerf, E. A. *e.a.*, Physica, to be published.

Chapter II

THE SECOND VIRIAL COEFFICIENT OF BINARY MIXTURES OF THE HYDROGEN ISOTOPES AND HELIUM AT 20.4°K

Summary

The excess second virial coefficient, E, of binary mixtures of the hydrogen isotopes and helium has been measured. The E for a mixture of a hydrogen isotope with He is quite large. There is reasonable agreement with the excess values derived from absolute measurements. For mixtures of the hydrogen isotopes, in agreement with theoretical predictions, no excess could be detected.

1. *Introduction.* The excess second virial coefficient is important for the calculation of thermodynamic functions and for the determination of the interaction between unlike molecules [1]). This is especially true for the case of the mixtures of the hydrogen isotopes with He; for example, the excess Gibbs free energy for 1 mole of a mixture of H_2 and He at 1 atm and 20.4°K is of the order of 1.5 cal. Furthermore, it seemed desirable to investigate the possibility of large systematic errors in our original isotherm determinations. We measured the E for the mixtures H_2–He, HD–He, D_2–He, H_2–HD, H_2–D_2, HD–D_2 and normal H_2-para H_2 with a direct and rather simple method that allows higher accuracy than isotherm measurements. The only existing data on the virial coefficients of hydrogen isotope mixtures at low temperatures are those of Beenakker *e.a.* [2]).

2. *Method and apparatus* [1]). Figure 1 gives a schematic diagram of the apparatus. The three glass vessels R_1, R_2, and R_3 are surrounded by copper cylinders and are immersed in a liquid hydrogen bath that is stirred by a heater, to give good temperature equilibrium. The room temperature part of the apparatus is thermostated to better than ± 0.5°C. R_2 and R_3 are filled with different gases to the same pressure as read on the manometer M. R_1 serves as a reference and is also filled to the same pressure P^i. By means of Töpler pump T_0, the gas can be forced in and out of the vessels R_2 and R_3. Repeating this procedure ten times the gases are thoroughly mixed and the final pressure is compared with the original pressure in P^i.

The pressure difference that is read on the oil manometer is directly related to the excess value E. E is defined as

$$E = B_{12} - \tfrac{1}{2}(B_{11} + B_{22}) \tag{1}$$

where B_{11} and B_{22} are the second virial coefficients of the pure gases and B_{12} the virial coefficient describing the mixed interaction. We may write the pressure P of a gas as

$$P = Ad(1 + Bd + Cd^2) \tag{2}$$

where d is the density, B and C are the second and third virial coefficients and A is a constant that is linear in temperature and depends on the units used (c.f. chapter I).

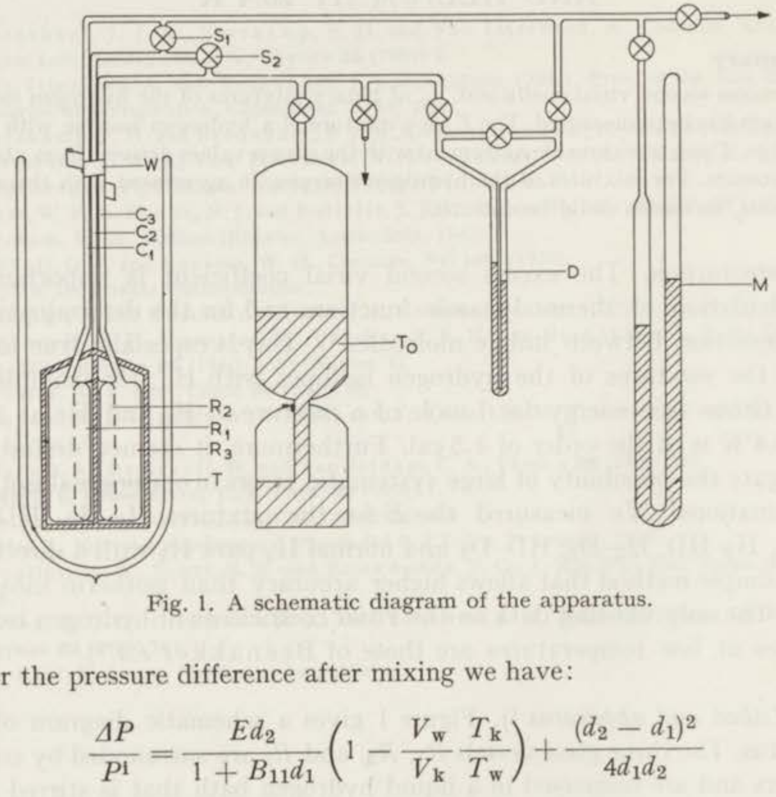

Fig. 1. A schematic diagram of the apparatus.

For the pressure difference after mixing we have:

$$\frac{\Delta P}{P^{\mathrm{i}}} = \frac{Ed_2}{1 + B_{11}d_1}\left(1 - \frac{V_{\mathrm{w}}}{V_{\mathrm{k}}}\frac{T_{\mathrm{k}}}{T_{\mathrm{w}}}\right) + \frac{(d_2 - d_1)^2}{4d_1d_2} \tag{3}$$

where the numbers 1 and 2 refer to the two kinds of molecules. V_{w} and V_{k} are the volumes at the room temperature, T_{w}, and the low temperature, T_{k}, respectively.

The excess for each pair of gases was calculated with equation (3). The densities were calculated by successive approximation using the formula $d = d_0/(1 + Bd)$ where d_0 is the ideal density. The observed pressure difference was corrected for the volume change caused by differences in the oil manometer level. In formula (3) there are still two corrections neglected. First of all the apparatus is slightly asymmetric. This can be taken into account by measuring with the positions of the gases reversed. One can easily show that averaging these measurements corrects for the asymmetry. Furthermore there is a small influence of the third virial coefficient, that can be eliminated by extrapolating the experimental results calculated with (3) to zero pressure. Both these corrections never amounted to more than 1 or 2%. The HD was at least 99% pure as determined by a mass spectrometer.

3. *Results.* In table I the bath temperature, the filling pressure P^i, the observed effect in mm oil, and the uncorrected E are tabulated. Table II gives the excess, E, for the different mixtures together with those from the isotherm measurements 2), reduced to 20.4°K using the value of dE/dT from 3).

TABLE I

Mixture	T °K	P^i cm Hg	ΔP cm oil	E uncorrected 10^{-3} amagat
H_2–He	20.35	65.85	15.77	2.47
	20.38	64.94	15.56	2.51
	20.43	44.83	6.96	2.46
	20.39	35.85	4.32	2.44
	20.39	21.02	1.47	2.48
HD–He	20.43	39.64	6.96	2.66
	20.38	25.02	2.31	2.73
D_2–He	20.38	21.69	1.84	2.89
	20.39	19.91	1.56	2.92

TABLE II

	Excess second virial coefficient E at 20.4°K		
	E 10^{-3} amagat	E cm³/mole	E_{isotherm} 10^{-3} amagat
H_2–He	2.44	54.7	2.75
HD–He	2.70	60.6	2.89
D_2–He	2.90	65.0	3.26

The mixtures H_2–HD, H_2–D_2, HD–D_2 and normal H_2-para H_2 gave an effect that was of the order of 0.2 mm oil, which is too small to be significant since measurements with normal H_2 on both sides of the apparatus gave about 0.2 mm oil as a systematic error. For the mixtures of the isotopes this corresponds to 0.04×10^{-3} amagat or 1 cm³/mole, and for normal H_2-para H_2 it corresponds to 0.004×10^{-3} amagat or 0.1 cm³/mole because of the higher filling pressures.

4. *Conclusions.* As we see from table II there is a small and systematic difference between these values and those derived from our isotherm determinations. The directly measured values are about 0.2 × 10^{-3} amagat smaller.

There can be several causes for this discrepancy. Since for a 50% mixture $E = 2B_m - (B_{11}+B_{22})$ and the error in the absolute determinations is about 0.05×10^{-3} amagat, the probable error in E will be of the order of 0.15×10^{-3} amagat. Furthermore, in the calculations of the second virial coefficient from the isotherm determination the influence of a contribution of the C coefficient was neglected throughout. While this effect was certainly small at the low densities at which the pure isotopes were measured, the influence at the higher densities at which the mixtures were measured, is no longer negligible. Reanalysis of these data showed that this could lead to a correction of, at the most, 0.15×10^{-3} amagat. This was estimated by looking for the largest possible value of C that could still be reconciled within the accuracy of the data. As no information is available on the value of C for the mixtures, the effect is only an estimated one. It would lower the value of the excess by, at the most, 0.15×10^{-3} amagat. Combining these systematic and non-systematic errors a value low by 0.30×10^{-3} amagat is still within the experimental uncertainty of the isotherm determinations. The existing discrepancy is thus acceptable. For the mixtures of hydrogen isotopes the measured effect was smaller than 0.04×10^{-3} amagat in agreement with the theoretical prediction by De Kerf *e.a.* [4]) who found 0.06×10^{-3} amagat for the H_2–D_2 mixture.

In chapter III that deals with the difference in the second virial coefficient between normal and para-hydrogen [5]), we will show that the excess value would give evidence about the dependence of $(B_{\text{mix}} - B_{\text{para}})$ on the concentration. Since E is smaller then 0.004×10^{-3} amagat a linear relation between B_{mix} and concentration seems valid.

REFERENCES

1) Knobler, C. M., Beenakker, J. J. M. and Knaap, H. F. P., Commun. Kamerlingh Onnes Lab., Leiden No. 317*a*; Physica **25** (1959) 909.

2) Beenakker, J. J. M., Varekamp, F. H. and Van Itterbeek, A., Commun. No. 313*a*; Physica **25** (1959) 9.

3) Varekamp, F. H. and Beenakker, J. J. M., Commun. No. 316*c*; Physica **25** (1959) 889.

4) De Kerf, E. A., *e.a.*, Physica, to be published.

5) Beenakker, J. J. M., Varekamp, F. H. and Knaap, H. F. P., Commun., No. 319*a*; Physica **26** (1960) 43; Chapter III.

CHAPTER III

THE SECOND VIRIAL COEFFICIENT OF ORTHO AND PARA HYDROGEN AT LIQUID HYDROGEN TEMPERATURES

Summary

A method is described for measuring the difference between the second virial coefficients of the ortho and para modifications of H_2 and D_2 with a sensitivity of the order of 3×10^{-6} amagat, corresponding to a relative change in the virial coefficient of H_2 of the order of 5×10^{-4}. We found for para and normal H_2 a difference of about 1% in the virial coefficient, the normal hydrogen having the larger absolute value. The change appeared to be linear in the concentration. No measurable effect was found in the case of D_2.

1. *Introduction.* It is well known that hydrogen and deuterium occur in two modifications, depending on the total nuclear spin. The symmetry conditions, imposed on the total wave function of the molecule, give rise to a different set of eigen values for the rotational states of the molecule in accordance with the symmetry properties of the total nuclear spin. Therefore, by combining two spins one half, we get for H_2 a total spin zero with even rotational quantum numbers and a total spin one with the odd values. At the high temperature limit the even and odd rotational states occur in the ratio 1 : 3, according to their statistical weights, the so called normal hydrogen. The most abundant modification at high temperatures is called ortho, the other one para hydrogen. Because of the even rotational quantum numbers which allow zero rotational energy, the para form is the stable one at low temperatures.

For D_2 one gets a similar situation by combining two spins of one; total spin zero and two correspond to even rotational quantum numbers, total spin one to odd values. At high temperatures the ratio of abundance of even to odd is 2 : 1. The most abundant form at high temperatures is again called the ortho modification. In contrast to the case of hydrogen the ortho form is the stable one at low temperatures, because of its possible zero rotational energy.

This difference in rotational states gives rise to large differences in the caloric properties of the ortho and para modifications in certain temperature regions [1]. For the transport properties, with exception of the heat conductivity at intermediate temperatures, the effects appear to be much smaller. Becker *e.a.* found a difference in the viscosity of the order of 1% between normal and para hydrogen [2] at liquid hydrogen temperatures and a similar, though smaller, effect for deuterium [3]. This difference decreases with increasing temperature. Waldmann and Becker [4] could not find a difference in the heat conductivity at 20°K, and at the same temperature the diffusion thermo effect between para and normal H_2 was also negligible. At higher temperatures (80–220°K) Schäfer and Corte [5] found a small separation in a thermal diffusion column filled with normal H_2.

For the equation of state Schäfer [6] and Long and Brown [7] performed some measurements on H_2 above 20°K. Within the reproducibility of their data (1 or 2%) they found no difference in the second virial coefficient.

From the theoretical point of view, reliable calculations are limited to the influence of the symmetry of the wave functions on various properties in the case of H_2. They are given by Cohen *e.a.* [8] for the viscosity and the second virial coefficient, and by Buckingham *e.a.*[9]. for the viscosity only. Starting from a spherically symmetric Lennard-Jones 6–12 potential as was done by the first group of authors or from an exponential-6–8 type in the case of the second group, a small difference in the viscosity arising from symmetry effects is found. This effect is, however, considerably smaller than the experimental values of Becker and Stehl, while the concentration dependence of the difference in viscosity has the wrong curvature. The effect in the second virial coefficient, as calculated by Cohen *e.a.* appears to be smaller than 0.1% at liquid hydrogen temperatures.

From the foregoing it is clear that any experiment on the difference in the second virial coefficient between the two modifications needs a rather high sensitivity. From our experience with isotherm determinations at low temperatures [10] it was clear to us that the sensitivity obtained in this way would be too small. The method described in one of our publications [11] could be of use for determining the temperature dependence of this difference, but for an absolute measurement a new method had to be developed.

The deviation of H_2 from an ideal gas at, for example, 0.5 atm and 20°K is already appreciable because of the large density at these low temperatures. The pressure is 5% lower than would be the case for an ideal gas under the same conditions. Hence, a change in B of 0.1% would cause a pressure change of 0.02 mm Hg, *i.e.* 0.3 mm oil, an easily measurable effect. Thus, if one starts with a reservoir at 20°K filled with normal hydrogen and converts this gas to para hydrogen, the pressure change will allow one to get a rather high sensitivity in the measurement of ΔB. The main difficulty is, however, that the conversion takes place practically infinitely slowly when one does not use a catalyst, the transition being a forbidden one. If one uses a catalyst, the large surface area can easily disturb the measurements by absorption effects. The conclusion is that the conversion has to take place outside the measuring space and at high temperatures. Hence, one has to start with para hydrogen, convert it back to normal hydrogen, and subsequently cool the gas down again and measure the difference in pressure with respect to the initial situation.

2. *Experimental method.* Fig. 1 gives a schematic diagram of our apparatus. Essentially it is the same apparatus that we used for our measurements of the temperature dependence of the second virial coefficient as described previously in more detail [11]). In the present case we filled R_1 with normal hydrogen and R_2 with parahydrogen to the same pressure. Then the temperature of the hydrogen bath was raised and the pressure difference ΔP between the reservoirs was measured with the oil manometer D. This difference is directly related to the change in the difference between the virial coefficients as given by the relation:

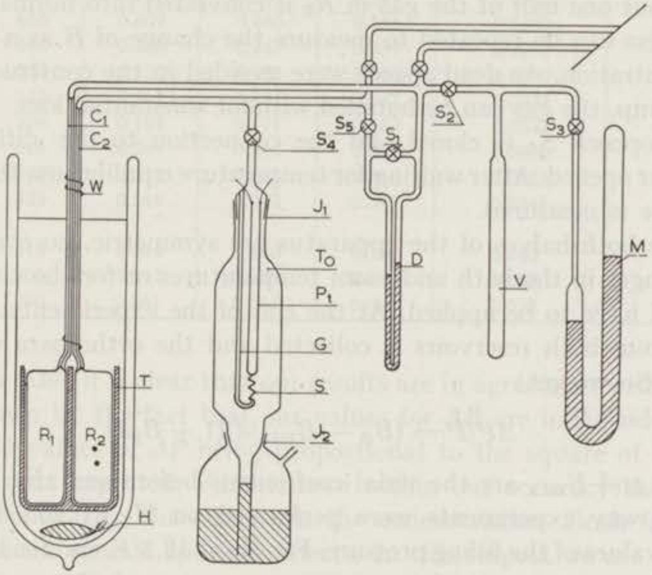

Fig. 1. A schematic diagram of the apparatus.

$$\Delta P/P^{f} = (\Delta B^{f} - \Delta B^{i})\, d \qquad (1)$$

where ΔB^{f} and ΔB^{i} are the differences between the second virial coefficients of the gases in R_1 and R_2 at the initial and final temperatures, d the density and P^{f} the final pressure.

For the determination of the absolute value of the difference in B, we connected R_2 to a Töpler pump T_0 having a volume of about 1000 cm³, with a platinum wire Pt mounted inside.

At the start of an experiment both reservoirs are filled with para hydrogen to the same pressure, which is determined with the manometer M. The stopcocks S_2 and S_5 are closed, S_4 is opened and a part of the gas is let into the Töpler pump. S_4 is then closed again and the platinum wire is heated red hot by passing a current through it. The gas is kept in this situation for about half an hour. In this time a complete conversion from para to normal hydrogen takes place as was shown by analysis of the composition. After the reconversion the gas is allowed to cool and is subsequently brought back into R_2. As the effective volume of R_2 is of the same order of magnitude as T_0, about one half of the gas in R_2 is converted into normal hydrogen. This process can be repeated to measure the change of B as a function of the concentration. As dead spaces were avoided in the construction of the Töpler pump, the gas can be handled without substantial loss.

Now stopcock S_4 is closed and the connection to the differential oil manometer opened. After waiting for temperature equilibrium, the difference in pressure is measured.

Because both halves of the apparatus are symmetric, no corrections for small changes in the bath and room temperatures or for the change in the bath level have to be applied. At the end of the experiments a sample of the gas from both reservoirs is collected and the ortho-para composition analysed. So we get:

$$\Delta P/P = (B_p - B_{mix})d/(1 + B_p d) \qquad (2)$$

where B_p and B_{mix} are the virial coefficients before and after conversion.

In this way experiments were performed on H_2 at 20.5°K for three different values of the filling pressure. For H_2 at 18.3°K and for D_2 at 20.5°K measurements were made for one filling pressure only because of the low saturation pressure.

The apparatus was tested by performing the same experiment with helium gas in both vessels. The results showed a negligible pressure difference as measured on the oil manometer. Thus, it was clear that the Töpler pump was working without loss and that the heating of the platinum wire did not introduce any disturbing effect. Another test run was made with normal hydrogen and it gave the same results.

All gases used were purified by passing them through a long copper capillary at hydrogen temperature. The ortho-para conversion was catalysed by means of Fe_2O_3. The initial and final mole fractions of para x^i and x^f were analysed by means of the standard heat conductivity method and by measuring the vapour pressure with respect to normal hydrogen. The results of the two methods agreed very well with each other.

3. *Experimental results.* Table I gives a survey of our absolute measurements and of the resulting values of ΔB for different values of the change

in concentration, $x^i - x^f$, calculated with eq. (2). A correction has to be applied to ΔP for the volume change caused by the change in oil level. This corrected value is denoted by ΔP_{cor}.

TABLE I

Results of the absolute measurements calculated with eq. (2).

T °K	P mm Hg	ΔP mm Hg	ΔP_{cor} mm Hg	$x^i - x^f$	$10^3(B_p - B_{\mathrm{mix}})$ amagat	$10^3(B_p - B_n)$ amagat
20.5°K	683	0.420	0.463	0.564	0.0476	0.064
	665	0.257	0.282	0.349	0.0307	0.066
	665	0.409	0.450	0.545	0.0490	0.068
	642	0.225	0.247	0.337	0.0290	0.064
	512	0.170	0.183	0.382	0.0350	0.068
	512	0.261	0.281	0.567	0.0538	0.071
	506	0.159	0.171	0.382	0.0335	0.066
	506	0.261	0.281	0.570	0.0550	0.072
	342	0.071	0.075	0.360	0.035^5	0.069
	329	0.068	0.072	0.387	0.034^5	0.067
18.3°K	318	0.084	0.088	0.318	0.040	0.09^5
	300	0.092	0.096	0.330	0.050	0.11^5
	290	0.061	0.063	0.328	0.033	0.07^5

From this table it is clear that our results are in agreement with equation (2) as is shown by the fact that our values for ΔB are independent of the pressure, the values of ΔP being proportional to the square of the filling pressure, as was expected. Furthermore within our accuracy the value of ΔB is proportional to the change in the concentration. Both facts are a strong argument against spurious effects. In this respect we are concerned especially about differential adsorption. Calculations showed, however, that even a differential adsorption of a few molecular layers is smaller then five percent of our measured value. Hence, it can be neglected as our accuracy is at the most of that order.

To obtain the difference between the virial coefficients of normal and para hydrogen or between those of ortho and para hydrogen one may start from the expression for the second virial coefficient of a mixture:

$$B_{\mathrm{mix}} = x^2 B_{\mathrm{pp}} + 2x(1 - x)\, B_{\mathrm{op}} + (1 - x)^2\, B_{\mathrm{oo}} \tag{3}$$

where x is the mole fraction of the para modification and B_{ij} the contribution to B arising from interaction of the molecules of species i and j. This expression reduces to:

$$B_{\mathrm{mix}} = B_{\mathrm{oo}} + x(B_{\mathrm{pp}} - B_{\mathrm{oo}}) \tag{4}$$

if $B_{\mathrm{op}} = \frac{1}{2}(B_{\mathrm{oo}} + B_{\mathrm{pp}})$. As our results are, within our accuracy, linear in the change in concentration, we may assume that this last assumption is valid. Other assumptions, however, are not completely excluded. This is of some importance for a comparison of our data with the theoretical predictions by Cohen *e.a.*[8]).

As we remarked earlier, these calculations take into account the effect of the symmetry properties of the wave functions on the second virial coefficient in the case of a spherical symmetrical intermolecular potential field. Although their results gave a negligible effect on the virial coefficient in this temperature range, this may be fortuitious as can be seen from the following arguments. In this theory there are two main contributions to a difference in B. The first arises from the difference in statistics and is independent of the molecular potential and would also be present in an ideal gas. The second contribution originates from the influence of statistics on the effects of the intermolecular forces. Both contributions are of the order of a few percent of the value of B, but have opposite signs. Hence, a change in the potential constants has only an influence on the second contribution and may cause a non-negligible change in B. The same applies to the choice of the potential model. The dependence on the constants appears, however, to be too small.

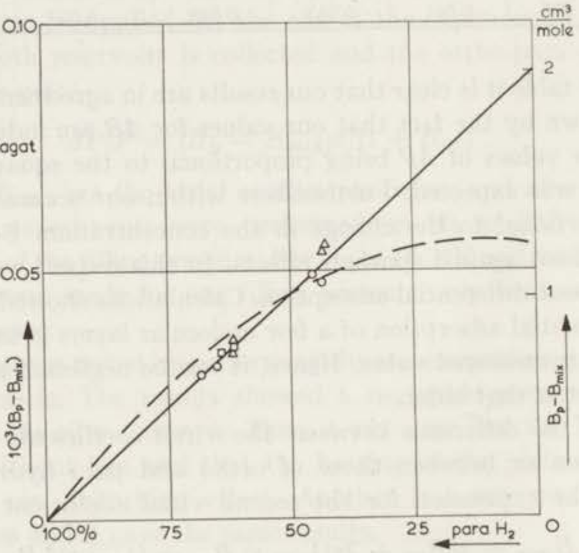

Fig. 2. ΔB as a function of the concentration at 20.5°K.
○ 66 cm Hg △ 51 cm Hg □ 33 cm Hg
--- Curve of Cohen *e.a.* adjusted to our experimental values.

As the form of the theoretical curve representing ΔB as a function of the concentration is independent of the absolute value of the difference, we have calculated a curve based on the theoretical expressions of Cohen *e.a.*, but with the magnitude of the effect adjusted to our experimental values. From fig. 2 we see that our results do not completely exclude such a relation.

Furthermore, one can see that in this case a linear extrapolation to obtain the difference between ortho and para hydrogen would be incorrect. To avoid this type of difficulty we do not extrapolate our data further then strictly necessary, and thus we will give only extrapolated data for the difference between para and normal hydrogen.

The accuracy of ΔB at 20.5°K is about 5%. The value at the lower temperature, 18.3°K, has a much larger uncertainty as the filling pressure is rather low. The accuracy is of the order of 20%. We could obtain a some what higher accuracy by measuring the temperature dependence by the differential method, as in that case we are measuring the full difference between para and normal hydrogen (see table II). The uncertainty in the data measured in this way is of the order of 10% at the lowest temperatures.

TABLE II

Results of the relative measurements calculated with eq. (1).

T^i	20.5	20.5	20.5	°K
T^f	19.1	19.1	19.3	°K
P^f	405	405	423	mm Hg
d	8.1	8.1	8.4	amagat
ΔP	0.039	0.043	0.030	mm Hg
ΔP_{cor}	0.041	0.046	0.032	mm Hg
x_p	0.888	0.888	0.925	
$10^3(\Delta B^f - \Delta B^i)$	0.014	0.016	0.010	amagat
$10^3(B_p - B_n)$	0.081_5	0.083_5	0.077_5	amagat

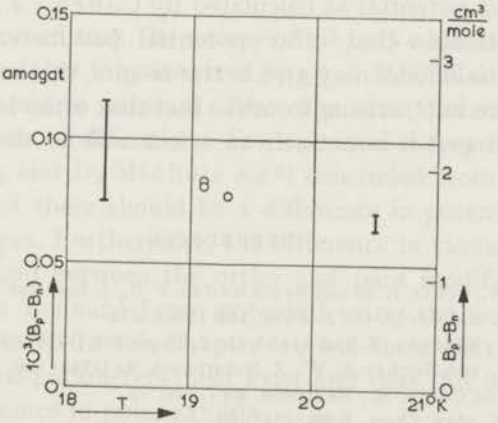

Fig. 3. ΔB as a function of the temperature.

I absolute measurements. ○ relative measurements.

The results of the differential and absolute measurements are given in fig. 3. Both methods agree within the experimental error. Although the methods are not completely independent, (*e.g.* a differential adsorption effect enters in both experiments in the same way) this agreement gives a further argument against systematic errors.

We will now make some remarks on experiments we performed on D_2. There are two reasons that make our apparatus less sensitive for this gas. First of all, the vapour pressure of D_2 at the boiling point of H_2 is already rather small (25.6 cm Hg), resulting in a large decrease in sensitivity with respect to H_2. Furthermore the ortho modification is also the most stable at low temperatures. Thus, while for H_2 we can effect a change in concentration from 25% to 100% para, for D_2 we get only a change from 66.7% to 100% ortho. Hence, the sensitivity of our method is decreased by a factor of 20. As our sensitivity is about 5% of the effect in H_2, it is clear that if the effect in D_2 is not larger than that in H_2, which one does not expect, it will only be possible to determine an order of magnitude.

Within the limits of our accuracy we found, however, no effect at 20.5°K so that we may conclude that the relative change in B between normal and ortho deuterium is smaller than 5×10^{-3}.

The influence of statistics is much smaller for D_2 than for H_2, as in contrast to H_2 both the ortho and the para modifications of D_2 contain symmetric and antisymmetric wave functions. Thus the difference in symmetry properties between the two modifications of D_2 is an order of magnitude smaller than for H_2.

4. *Conclusions.* From the foregoing we may conclude that the experimental results for H_2 are in disagreement with the theoretical predictions for a Lennard-Jones potential as calculated by Cohen *e.a.*. Although it is not absolutely impossible that other potential parameters or that another spherical potential model may give better results, there can be other reasons for the difference in B, arising from the fact that ortho hydrogen is rotating, while para hydrogen is not. Such an effect will be discussed in detail in chapter IV.

REFERENCES

1) Woolley, H. W., Scott, R. B. and Brickwedde, F. G., J. Res. Nat. Bur. Stand. **41** (1948) 379.
2) Becker, E. W. and Stehl, O., Z. Phys. **133** (1952) 615.
3) Becker, E. W., Misenta, R. and Stehl, O., Z. Phys. **136** (1953) 457.
4) Waldmann, L. and Becker, E. W., Z. Naturforsch. **3***a* (1948) 180.
5) Schäfer, K. and Corte, H., Naturwiss. **83** (1946) 92.
6) Schäfer, K., Z. phys. Chem. B **36** (1937) 85.
7) Long, E. A. and Brown, O. L. J., J. amer. chem. Soc. **59**II (1937) 1922.
8) Cohen, E. G. D., Offerhaus, M. J., Van Leeuwen, J. M. J., Roos, B. W. and De Boer, J., Physica **22** (1956) 791.
9) Buckingham, R. A., Davies, A. R. and Gilles, D. C., Proc. phys. Soc. **71** (1958) 457.
10) Beenakker, J. J. M., Varekamp, F. H. and Van Itterbeek, A., Commun. Kamerlingh Onnes Lab., Leiden No. 313*a*; Physica **25** (1959) 9.
11) Varekamp, F. H. and Beenakker, J. J. M., Commun. No. 316*c*; Physica **25** (1959) 889-904.
12) Takayanagi, K. and Ohno, K., Progr. theor. Physics (Japan) **13** (1955) 243.

Chapter IV

THE LENNARD-JONES 6–12 POTENTIAL PARAMETERS OF H_2 AND D_2

Summary

The difference in the Lennard-Jones potential parameters between H_2 and D_2 is calculated. This effect arises mainly from a difference in polarizability. The results are in good agreement with the experimental data of Michels *e.a.*

Similar calculations have been performed on the ortho and para modifications and here the calculated effect can account for the major part of the difference in gaseous and liquid properties between the two species.

1. *Introduction.* In describing the interaction between two hydrogenic molecules one often uses, especially in the gaseous state, the Lennard-Jones potential

$$\varphi(r) = -4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^6 - \left(\frac{\sigma}{r}\right)^{12}\right\}. \tag{1}$$

In general, it is assumed that the values of ε/k and σ are the same for the hydrogen isotopes and that they are given by $\varepsilon/k = 37.00°\mathrm{K}$ and $\sigma = 2.928$ Å [1]) where k is the Boltzmann constant. Also, the same parameters are used for the ortho and para modifications. For a general survey see reference [2]).

In the case of H_2 and D_2 Michels *e.a.*[3]) concluded from their isotherm measurements [4]) that there should be a difference in potential parameters between these isotopes. Furthermore, the difference in viscosity and second virial coefficient found between the ortho and para modifications cannot be described with a Lennard-Jones potential using the same parameters for both modifications [5]). In this chapter we will show that in both cases a difference in potential parameters must exist and that this difference arises mainly from a difference in polarizability.

2. *H_2 and D_2.* Already many years ago Bell [6]) pointed out that there should be a difference in the intermolecular field of H_2 and D_2 caused by a different amplitude of the internuclear vibration due to a difference in zero point motion. Later, De Boer [7]) calculated the influence of this effect on the repulsive field. He found a somewhat stronger repulsion for

a pair of H_2 molecules than for a pair of D_2 molecules, but the influence of this difference on the potential parameters is small and has a sign opposite to that of the effect found by Michels[3]).

However, it can be shown that a difference in the potential parameters arises from the difference in polarizability, α, between H_2 and D_2. α is calculated by Ishiguro *e.a.* [8]) and is also derived by Bell[9]) from the experiments done by Larsen[10]). These authors show that the polarizability of H_2 is about 1.5% larger than that of D_2 and as in a simple model for the London-Van der Waals dispersion forces the strength of the attraction is proportional to α^2, this should lead to a difference in the attractive energy of about 3%. For a 6-12 Lennard-Jones potential, the difference in the attractive energy between hydrogen and deuterium is thus given by:

$$\Delta\varphi_{\text{att}} = -\frac{2\Delta\alpha}{\alpha} \times 4\varepsilon\left(\frac{\sigma}{r}\right)^6 \qquad (2)$$

where $\Delta\alpha$ is the difference in polarizability between the two isotopic modifications. For the difference in the repulsive energy $\Delta\varphi_{\text{rep}}$ we adapt the results of De Boer to a $1/r^{12}$ dependence:

$$\Delta\varphi_{\text{rep}} = A/r^{12}$$

with $A = 6.3 \times 10^{-14}$ erg Å^{12}.
The potential for D_2 is then given by

$$\varphi_{D_2} = -4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^6 - \left(\frac{\sigma}{r}\right)^{12}\right\} + \frac{2\Delta\alpha}{\alpha}\,4\varepsilon\left(\frac{\sigma}{r}\right)^6 - \frac{A}{r^{12}} \qquad (3)$$

where ε and σ are the Lennard-Jones parameters for H_2. At the internuclear distances that are of importance at not too high temperatures the attractive correction term is dominant. One obtains the values of ε and σ for D_2 by adapting (3) to a Lennard-Jones potential.

TABLE I

Values $\frac{\Delta\alpha}{\alpha}$ used	The values of $\frac{\Delta\varepsilon}{\varepsilon}$ and $\frac{\Delta\sigma}{\sigma}$ for H_2 and D_2		
$\frac{\alpha_{H_2} - \alpha_{D_2}}{\alpha_{H_2}}\,100$	$\frac{\varepsilon_{H_2} - \varepsilon_{D_2}}{\varepsilon_{H_2}}\,100$	$\frac{\sigma_{H_2} - \sigma_{D_2}}{\sigma_{H_2}}\,100$	
1.86 [8])	+6.7	−0.5	Calculated in this chapter.
1.3 [9])	+4.5	−0.3	
	+4.3 ± 0.9	+0.2 ± 0.9	Experimental

In table I the differences in parameters calculated for the two different values of $\Delta\alpha/\alpha$ are shown. It is obvious that the value of ε/k is appreciably larger for H_2 than for D_2, while there is nearly no effect on σ, in good agreement with experiment.

In this calculation the dispersion energy has been taken proportional to α^2 but there is some uncertainty in the exact value of the exponent of α. Slater and Kirkwood [11]) found 1.5, while Brandt [12]), from a comparison with experiment, derived the value of 1.86. However, the correctness of the form of the intermolecular potential and the accuracy of this type of calculation makes such a difference irrelevant in our case.

3. *The ortho and para modifications.* The gaseous properties of the ortho and para modifications may differ for three reasons. First of all, there is the statistical symmetry effect as discussed by Cohen *e.a.*[5]) but this is far too small to explain the inequality found in the second virial coefficient, while it is also too small in the case of the viscosity difference. A second effect is due to the non-spherical part of the intermolecular potential, which is not the same for the two modifications and until now, the discrepancy between experiment and theory was attributed to this non-spherical part which has never been treated theoretically.

However, a third effect, namely the difference in the spherical part of the intermolecular potential between the ortho and para varieties, appears to give a large distribution. This arises from a difference in the internuclear distance caused by the different rotational moments. Following the ideas advanced by Babloyantz and Bellemans [13]) in a paper on a crystal model for liquid ortho-para mixtures, one can arrive at the difference in the interaction energies between the two varieties. This can be done by modifying the Lennard-Jones potential for hydrogen and calculating the change in ε/k and σ. (Since only relatively low temperatures will be considered, rotational states with $l > 1$ will not be appreciably populated).

One starts by observing that the internuclear distance of the rotating variety is somewhat larger than that of the molecule in the $l = 0$ state. The shift in the internuclear distance $r_1 - r_0$ can be obtained from:

$$K(r_1 - r_0) = 2\hbar^2/Ir_0 = 4k\theta_{\text{rot}}/r_0, \quad \text{where} \tag{4}$$

K, the restoring constant is 0.57×10^{-11} erg/Å and r_1 and r_0 the equilibrium distances in the molecule with $l = 1$ and $l = 0$ respectively ($r_0 = 0.74$ Å). I is the moment of inertia (4.67×10^{-41}g cm^2) and θ_{rot} the characteristic rotational excitation temperature (θ_{rot} is 85.4°K for H_2 and 42.5°K for D_2); $\hbar$ is Planck's constant and k the Boltzmann constant.

It is now possible to calculate the influence of $r_1 - r_0$ on the repulsive and attractive part of the intermolecular potential. The expression for the repulsive part of the potential given by De Boer [14]) is:

$$\varphi_{\text{rep}} = V\{\mathrm{e}^{-r_{\text{ac}}/\rho} + \mathrm{e}^{-r_{\text{bc}}/\rho} + \mathrm{e}^{-r_{\text{ad}}/\rho} + \mathrm{e}^{-r_{\text{bd}}/\rho}\}$$

where $V = 12 \times 10^{-11}$ erg and $\rho = 0.28$ Å. The significance of the other quantities can be found in figure 1. Nakamura 15) showed that for molecular separations large compared to the internuclear distance r_1 this formula can be rewritten as

$$\varphi_{\text{rep}} = 4V\mathrm{e}^{-r/\rho} \cosh\left(\frac{r_1}{2\rho}\cos\theta_1\right)\cosh\left(\frac{r_1}{2\rho}\cos\theta_2\right)$$

and this can be expanded in spherical harmonics. As it is only the spherical

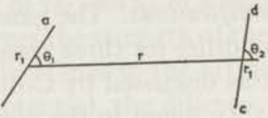

Fig. 1.

part which is of interest we retain only the first term of the expansion, which we denote by

$$\varphi_{\text{spher.rep}} = 4V\mathrm{e}^{-r/\rho}\left\{\frac{\sinh r_1/2\rho}{r_1/2\rho}\right\}^2.$$

After developing this in a series we obtain:

$$\varphi_{\text{spher.rep.}} = 4\,V\mathrm{e}^{-r/\rho}\left\{\frac{\sinh r_0/2\rho}{r_0/2\rho}\right\}^2\left(1 + 0.79\,\frac{r_1 - r_0}{2\rho}\right). \tag{5}$$

From this formula it is clear that molecules with $l = 1$ have the stronger repulsion. In order to calculate the influence on the attractive part we write that the change in polarizability is

$\Delta\alpha = \dfrac{\mathrm{d}\alpha}{\mathrm{d}r}(r_1 - r_0)$ and make use of the $\dfrac{\mathrm{d}\alpha}{\mathrm{d}r}$ as calculated by Ishiguro 8).

We proceed as in the foregoing section and again obtain formula (2)

$$\Delta\varphi_{\text{spher.att}} = -2\frac{\Delta\alpha}{\alpha} \times 4\varepsilon\left(\frac{\sigma}{r}\right)^6. \tag{6}$$

It can be argued that the theoretical potential of Nakamura should be used throughout. However, as the present calculations are not reliable to more than an order of magnitude, the experimental attraction term as given in section 2 is used.

We now adapt a Lennard-Jones potential to the potential for the $l = 1$ molecule using (5) and (6).

$$\varphi = -4\varepsilon\left\{\left(\frac{\sigma_0}{r}\right)^6 - \left(\frac{\sigma_0}{r}\right)^{12}\right\} - 2\frac{\Delta\alpha}{\alpha} \times 4\varepsilon_0\left(\frac{\sigma_0}{r}\right)^6 + {}$$
$$+ 1.35\,\frac{r_1 - r_0}{2\rho} \times 4V\,\mathrm{e}^{-r/\rho}.$$

To do this a $1/r^{12}$ dependence is fitted to the exponential term and ε_1 and

σ_1, the potential parameters of the $l = 1$ molecule are calculated, using (4) to calculate $r_1 - r_0$. In this way we obtain:

$$\frac{\varepsilon_1 - \varepsilon_0}{\varepsilon} = 6 \times 10^{-3}, \quad \frac{\sigma_1 - \sigma_0}{\sigma} = -0.3 \times 10^{-3} \text{ for } \mathrm{H_2}$$

and

$$\frac{\varepsilon_1 - \varepsilon_0}{\varepsilon} = 3 \times 10^{-3}, \quad \frac{\sigma_1 - \sigma_0}{\sigma} = -0.15 \times 10^{-3} \text{ for } \mathrm{D_2}.$$

It should be noted here that notwithstanding the larger internuclear distance of the molecule with $l = 1$, the effective diameter σ is decreased somewhat because of the much larger contribution of the increased attraction, a result that was overlooked by previous investigators [16]).

4. *Calculation of the properties.* In this section we will apply the values $\Delta\varepsilon/\varepsilon$ and $\Delta\sigma/\sigma$ calculated in 3 to some properties of the ortho and para varieties.

a) The second virial coefficient and viscosity. The second virial coefficient B and the viscosity η can be written in a reduced form with ε/k and σ as reduction parameters;

$$B^* = \frac{B}{\frac{2}{3}N\pi\sigma^3}\ ; \ \eta^* = \frac{\eta\sigma^2}{\sqrt{m\varepsilon}}$$

B^* and η^* are functions of $T^* = kT/\varepsilon$, the reduced temperature, and the quantum parameter

$$\Lambda^{*2} = \frac{h^2}{\sigma^2 m\varepsilon}\,,$$

where h is Planck's constant and m the mass, while N is Avogadro's number.

Making an expansion around ε_0, σ_0 we obtain

$$B_1^* - B_0^* = \frac{\partial B^*}{\partial T^*}\frac{\mathrm{d}T^*}{\mathrm{d}\varepsilon} + \frac{\partial B^*}{\partial \Lambda^{*2}}\left\{\frac{\partial \Lambda^{*2}}{\partial \varepsilon}\Delta\varepsilon + \frac{\partial \Lambda^{*2}}{\partial \sigma}\Delta\sigma\right\}$$

$\partial B^*/\partial T^*$ can be calculated from $\mathrm{d}B/\mathrm{d}T$ [17]) and $\partial B^*/\partial \Lambda^{*2}$ is obtained from a comparison of the B's for $\mathrm{H_2}$ and $\mathrm{D_2}$ [17])[18]).

Since

$$B^* = \frac{B}{\frac{2}{3}N\pi\sigma^3}\,,$$

it is clear that when this is expressed in normal units, a contribution from $\Delta\sigma$ remains. The results obtained in this way are shown in table II. The experimental results are taken from [19]). For $\mathrm{H_2}$ the ortho modification has $l = 1$ and the para $l = 0$, while for $\mathrm{D_2}$ the inverse is true *i.e.* para D_2 has $l = 1$ and ortho $\mathrm{D_2}$ $l = 0$ (Table II).

The experiments have always been performed between the high temperature composition *i.e.* the normal composition (for H_2 75% ortho and 25% para and for D_2 66.7% ortho and 33.3% para) and the 20.4°K equilibrium composition (for H_2 0.2% ortho and 99.8% para and for D_2 97.8% ortho and 2.2% para). We found $B_p - B_0$ by extrapolating the experimental data linearly over the entire concentration range, which is a reasonable approximation.

TABLE II

ΔB for the ortho and para modifications of H_2 and D_2					
T in °K	$B_p - B_0$ in 10^{-6} amagat for H_2			$B_0 - B_p$ in 10^{-6} amagat for D_2	
	Calc.	Stat. effect	Exp.	Calc.	Exp.
18	78	<5	130		
20	63	<5	92	39	<120

$B(\text{cm}^3/\text{mole}) = 22.423\ B(\text{amagat units})$.

In the same way using the experimental dependence on Λ^{*2} as found by Coremans *e.a.* [20]) the viscosity difference between the ortho and the para varieties has been calculated and the results are given in table III together with the experimental data of Becker *e.a.* [21])[22]) and the contribution arising from the symmetry effects [5]). The centrifugal effect in the spherical part of the potential accounts for an appreciable part of the experimental values both for the second virial coefficient and for the viscosity.

TABLE III

$\frac{\Delta\eta}{\eta}$ for the ortho and para modifications of H_2 and D_2					
T in °K	$\frac{\eta_p - \eta_0}{\eta_p}\,10^3$ for H_2			$\frac{\eta_p - \eta_0}{\eta_p}\,10^3$ for D_2	
	Calc.	Stat. effect	Exp.	Calc.	Exp.
22	3.1	1.1	7.5	1.4	1.8
37	2.8	—	4.0	1.3	
52	2.0	—	2.8	1.0	

b) Some liquid properties. It seems interesting to see in how far the differences in the liquid properties are due to the centrifugal effect. Again using a modified corresponding states treatment we find the values listed in table IV for the difference in molar volume of the liquid at 20°K, and those listed in table V for the difference in the vapour pressure. The experimental data have been taken from [23])[24]) and were extrapolated to pure ortho and para. As one expects the modification with $l = 1$ has the smaller volume because of the larger attraction, and this also leads, of course, to a lower vapour pressure for this modification. The calculated difference in

TABLE IV

ΔV for the ortho and para modifications of H_2 and D_2				
T in °K	$V_p - V_o$ in cm³/mole		$V_o - V_p$ in cm³/mole	
	Calc.	Exp.	Cal.	Exp.
19	0.119	0.172		
20	0.127	0.181	0.041	0.078

TABLE V

ΔP for the ortho and para modifications of H_2 and D_2				
T in °K	$P_p - P_o$ in cm Hg		$P_o - P_p$ in cm Hg	
	Calc.	Exp.	Calc.	Exp.
19	1.9	2.97	0.4	0.6
20	2.5	3.77	0.5^5	0.9^5

the triple point temperature is 0.14°K while experiment leads to a value of 0.24°K [24]. One could, of course, perform similar calculations for other properties, but we will limit ourselves to those above, our aim being only to show how the difference in the potential parameters can offer an explanation for the experimentally found differences. So it is clear that also in the liquid an appreciable part of the difference between the ortho and para varieties can be accounted for by the centrifugal effect. However, both in the liquid and in the gas the non-spherical part of the potential must also play a role.

REFERENCES

1) Hirschfelder, J. O., Curtiss, C. F. and Bird, R. B., Molecular theory of gases (John Wiley and Sons, New York, 1954).

2) Beenakker, J. J. M., Progress in low temperature physics, edited by Gorter, C. J., Volume III, Chapter VI (North Holland Publishing Company, Amsterdam, 1961).

3) Michels, A., De Graaff, W. and Ten Seldam, C. A., Physica **26** (1960) 393.

4) Michels, A., De Graaff, W., Wassenaar, T., Levelt, J. M. H. and Louwerse, R., Physica **25** (1959) 25.

5) Cohen, E. G. D., Offerhaus, M. J., Van Leeuwen, J. M., Roos, B. W. and De Boer, J., Physica **22** (1956) 791.

6) Bell, R. P., Proc. roy. Soc. **A 174** (1940) 504.

7) De Boer, J., Physica **10** (1943) 357.

8) Ishiguro, E., Arai, T., Kotani, M. and Mizushima, M., Proc. phys. Soc. **65** (1952) 178.

9) Bell, R. P., Trans. Faraday Soc. **38** (1942) 422.

10) Larsen, T., Z. Phys. **100** (1936) 543.

11) Slater, J. C. and Kirkwood, J. G., Phys. Rev. **37** (1931) 682.

12) Brandt, W., J. chem. Phys. **24** (1956) 501.

13) Babloyantz, A. and Bellemans, A., Molecular Phys. **3** (1960) 313.

14) De Boer, J., Physica **9** (1942) 363.

15) Nakamura, T., Progr. theor. Physics (Japan) **14** (1955) 135.

16) Takayanagi, J. and Ohno, K., Progr. theor. Physics (Japan) **13** (1955) 243.

17) Varekamp, F. H. and Beenakker, J. J. M., Commun. Kamerlingh Onnes Lab., Leiden No. 316*c*; Physica **25** (1959) 889.

18) De Kerf, E. A. *e.a.*, Physica, to be published.

19) Beenakker, J. J. M., Varekamp, F. H. and Knaap, H. F. P., Commun. No. 319*a*; Physica **26** (1960) 43; Chapter III.
20) Coremans, J. M. J., Van Itterbeek, A., Beenakker, J. J. M., Knaap, H. F. P. and Zandbergen, P., Commun. No. 311*a*; Physica **24** (1958) 557.
21) Becker, E. W. and Stehl, O., Z. Phys. **133** (1952) 615.
22) Becker, E. W., Misenta, R. and Stehl, O., Z. Phys. **136** (1953) 457.
23) Knaap, H. F. P., Knoester, M. and Beenakker, J. J. M., Commun. No. 325*c*; Physica **27** (1961) 309; Chapter V.
24) Wooley, H. W., Scott, R. B. and Brickwedde, F. C., J. Res. Nat. Bur. Stand. **41** (1948) 379.

CHAPTER V

THE VOLUME CHANGE ON MIXING FOR SEVERAL LIQUID SYSTEMS AND THE DIFFERENCE IN MOLAR VOLUME BETWEEN THE ORTHO AND PARA MODIFICATIONS OF THE HYDROGENIC MOLECULES

Summary

A method is described for measuring the volume change on mixing of liquids at constant pressure in a direct way. Measurements were performed for the systems O_2–N_2, O_2–A, normal H_2-normal D_2, normal H_2-para H_2 and normal D_2-ortho D_2. Furthermore, the difference in molar volume between nH_2 and pH_2 and between nD_2 and oD_2 was determined. The accuracy is of the order of 5 mm^3 per mole.

1. *Introduction.* In recent years considerable interest has been shown in measurements of the properties of mixtures of liquids. This has been stimulated by theoretical calculations [1][2] of the thermodynamic excess functions. Our aim was the investigation of the volume change on mixing, V^E, of liquid mixtures of the hydrogen isotopes and their ortho and para modifications. It was thought that quantum effects might be observed and that especially in the latter systems the effects of deviations from spherical symmetry could play a role.

Since a discrepancy existed between the work of Pool and Staveley [3] and the results of Blagoi and Rudenko [4] on O_2–N_2 and O_2–A mixtures, we decided to start with these systems. Both groups used an absolute method, *i.e.* they determined the density of the mixtures as a function of concentration. These experiments are laborious and one needs an accurate knowledge of the temperature, pressure, volumes and dead spaces, as well as long term temperature stability. We developed a direct and rather fast method for determining the volume change [5]. The apparatus can be used at any concentration without modification.

2. *Experimental method.* Figure 1 gives a schematic diagram of the apparatus. The vessels P_1 and P_2, which are placed in a separate cryostat, were used to purify the liquids. The gases were condensed in these vessels

and then the liquid was distilled from P_1 into the measuring vessel V by passing a current through a heater H_1. After this distillation was completed the separator S was set at the surface of the liquid by means of a permanent magnet M, suspended from 2 metal rods. The rods can be moved up and down from outside the cryostat and two packing boxes ensure their leak-free passage through the cryostat cap. The separator consists of a piece of iron sealed in glass and it fits closely in the glass vessel V so that there is only a narrow slit between it and the wall. The second liquid was condensed from P_2 on top of the separator until V was filled completely.

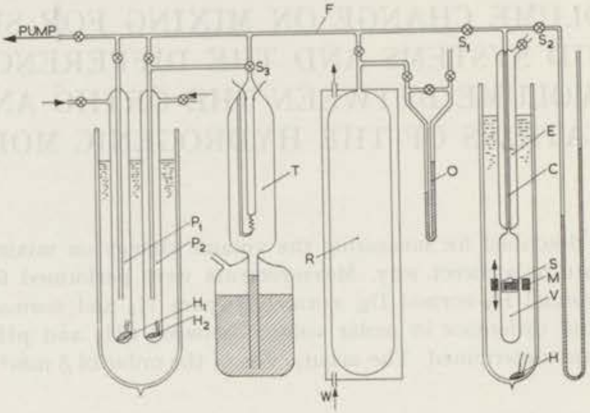

Fig. 1. A schematic diagram of the apparatus.

No condensation occurred in the capillary during the filling because space E was kept evacuated. This vacuum jacket was used because without it, the condensation started high in the capillary, as the capillary was in direct contact with the bath. In this way gas bubbles, formed between drops of liquid, disturbed the measurements, making it impossible to observe the height of the liquid in the capillary. It appeared impossible to get rid of these bubbles even under the application of rather high pressures. In the procedure mentioned above the condensation stopped when the liquid level reached the capillary. By filling the vacuum jacket with exchange gas the capillary was cooled and the gas condensed in the capillary without any vapour bubbles. After waiting for equilibrium the pressure and the height of the liquid level in the capillary with respect to a reference mark were measured. The capillary is 0.25 mm i.d.. After closing the stopcocks S_1 and S_2 the liquid was thoroughly mixed by moving the separator up and down about 15 times.

In the case of a volume contraction, enough pure gas was added so that the liquid again came into the capillary. As we preferred to work at constant pressure so as to avoid large corrections, we continued the condensation until the original pressure was reached. The difference in the amount of liquid between the original and the final situation was always small and could be determined from the level difference in the capillary. The extra gas which was condensed was taken from a thermostated reservoir *R* of known volume, at a pressure of about 1 atmosphere and was forced in by means of Töpler pump *T*. The amount of gas taken from *R* could be determined by measuring the pressure change in *R* on a differential oil manometer against the atmosphere. (In the case of a volume expansion a certain small quantity of gas corresponding to the expected dilatation of liquid in *V* was evaporated into the Töpler pump before mixing to prevent too high pressures after the mixing. Further, the same procedure was followed as in the case of a contraction.) The variation in the barometric pressure during the experiment was measured and the small correction for this effect was always applied. At the end of the experiment all the gas from *V* was evaporated into a large reservoir, from which a sample was taken for analysis of the concentration with a standard heat conductivity method.

We have paid special attention to possible mixing along the separator. To prevent mixing through boiling we always kept the pressure above the liquid higher than the saturation pressure of each component and furthermore, we always had the more dense liquid at the bottom. When no separator was used and the liquids were condensed on each other we could observe, in the case of O_2 and N_2, during more than half an hour a kind of gradually disappearing meniscus between the two liquids, showing even in this case, a very small velocity of mixing. As a further check we also condensed a very thin layer of the lighter liquid on top of the heavier one, the separator again being at the bottom of the vessel. No change in the vapour pressure was observed, showing that there was very little mixing. Since the interface between the liquids, is very much reduced by putting the separator at the surface we concluded that there is no premixing under the experimental conditions which would affect our results.

The apparatus was changed slightly in order to be able to measure the difference in molar volume between nH_2 and pH_2 and between nD_2 and oD_2. The experimental method is quite similar to that used in our previous measurements [6]) with the ortho and para modifications in the gas phase. The 20.4°K equilibrium mixture (for H_2 0.2% ortho and 99.8% para, for D_2 97.8% ortho and 2.2% para.) *) is condensed in P_1 and it is distilled into *V* using heater H_1. Consequently, *E* is filled with exchange gas and the height of the liquid level in the capillary and the pressure are measured. By reducing the temperature of the bath around P_2 the liquid in *V* is distilled to P_2. From P_2 the gas is let into the Töpler system by means of a three way stopcock S_3. *T* is provided with a platinum wire and by electrically heating the platinum wire red hot, the gas was converted to the high temperature equilibrium composition, *i.e.* for H_2 75% ortho and 25% para (normal H_2), and for D_2 66.7% ortho and 33.3% para (normal D_2). Then the gas was again condensed in V by forcing the gas out of the Töpler. After letting new gas into T from P_2, the same procedure was followed. By doing this 6 times all the liquid from P_2 was then brought to room temperature in order to get all the gas back. Subsequently the change in volume was measured in the same way as in the volume excess experiments.

---

*) Here we employ the expression para H_2 instead of 20.4°K equilibrium H_2, since the 20.4°K equilibrium H_2 contains 99.8% para H_2.

It is obvious that our apparatus could also be used to measure the thermal expansion of the liquid by measuring the volume change that occurred after a change in temperature. The separator was now used as a stirrer to get good temperature equilibrium after the temperature change of the surrounding bath.

3. *Calculations and experimental results.* Since the volume of R and the filling line is known, it is possible to calculate the amount of pure gas which was condensed or evaporated, making use of the pressure difference on the oil manometer, the temperature and the pressure of the gas in R. This information together with the known density of the pure liquid enabled us to calculate the change in volume ΔV. Using the volume of V, 5.25 cm³, the excess volume per mole mixture V^E was calculated. V^E is defined as $V^E = V_m - x_1V_1^O - x_2V_2^O$ where V_1^O and V_2^O are the molar volumes of the pure components, V_m the molar volume of the mixture and x_1 and x_2 the molar concentrations. The values of the molar volumes are tabulated in table I.

TABLE I

Molar Volumes							
	O_2	O_2	A	N_2	nH_2	pH_2	nD_2
T °K	90	77	90	77	20.4	20.4	20.4
V cm³/mole	27.96	26.86	29.05	35.24	28.40	28.54	23.63

The values for O_2, A and N_2 were taken from [4]) and those for the hydrogen isotopes from the report of Woolley, Scott and Brickwedde [7]).

In table II, III, IV and V we tabulated the measured quantities and the V^E for the different mixtures. One often finds that V^E depends linearly on

TABLE II

V^E for the mixture O_2–A at 90°K				
x mole fraction O_2	ΔP cm oil	$10^3\,\Delta V$ cm³ liquid	V^E cm³/mole	$V^E/x(1-x)$ cm³/mole
0.211	10.4	13.9	0.073	0.44
0.342	18.8	24.6	0.113	0.50
0.528	19.2	25.0	0.131	0.53
0.711	17.9	25.1	0.121	0.59
0.718	16.4	21.6	0.112	0.56
0.724	13.5	18.0	0.098	0.49

TABLE III

V^E for the mixture O_2–N_2 at 77°K				
x mole fraction O_2	ΔP cm oil	$10^3 \Delta V$ cm^3 liquid	V^E cm^3/mole	$V^E/x(1-x)$ cm^3/mole
0.09	−10.1	−16.4	−0.106	−1.29
0.26	−19.7	−33.2	−0.206	−1.07
0.28	−19.1	−31.4	−0.194	−0.96
0.38	−20.5	−37.6	−0.227	−0.96
0.48	−22.4	−35.4	−0.207	−0.83
0.58	−21.2	−31.7	−0.180	−0.74
0.71	−15.9	−25.9	−0.142	−0.69

TABLE IV

V^E for the mixture nH_2–nD_2 at 20.4°K				
x mole fraction H_2	ΔP cm oil	$10^3 \Delta V$ cm^3 liquid	V^E cm^3/mole	$V^E/x(1-x)$ cm^3/mole
0.210	−12.8	−19.0	−0.089	−0.54
0.264	−17.0	−23.1	−0.109	−0.57
0.420	−20.4	−27.8	−0.135	−0.55
0.434	−21.0	−30.0	−0.147	−0.60
0.471	−20.6	−27.9	−0.138	−0.55
0.687	−17.2	−22.5	−0.115	−0.53
0.698	−17.3	−21.2	−0.109	−0.52

TABLE V

V^E for the mixture nH_2–pH_2 at 20.4°K				
x mole fraction nH_2	ΔP cm oil	$10^3 \Delta V$ cm^3 liquid	V^E cm^3/mole	$V^E/x(1-x)$ cm^3/mole
0.27	2.4	3.2	0.017	0.086
0.28	2.1	2.7	0.014^5	0.072
0.44	2.4	2.9	0.016	0.065
0.50	2.8	3.4	0.018	0.072
0.70	1.3	2.0	0.010^5	0.052
0.70	1.9	2.1	0.011	0.052

the two concentrations, so that the quantity $V^E/x(1-x)$, which we also tabulated, is a constant.

ΔP is the difference in oil level between the beginning and the end of the experiment, ΔV the observed volume change and V^E the volume change per mole.

V^E for normal D_2-ortho D_2 was very small so that we measured only at $x = 0.5$. The effect is of the order of the accuracy of the measurement and is about $+3 \times 10^{-3}$ cm^3/mole. In our experiments the influence of the pressure above the liquid in the capillary on the volume change can be neglected, since the pressures used were not too high.

For the difference in molar volume at constant pressure between normal H_2 and para H_2 0.142 cm^3 per mole was found, while the result for normal D_2 − 20.4°K equilibrium D_2 was 0.024 cm^3 per mole. From the report of Woolley *e.a.* 7) one calculates 0.141 cm^3 per mole for H_2, while for D_2 no data are available. Corrections that have to be applied, for the fact that the molar volumes are given under saturation pressure, are of the order of 0.001 cm^3 per mole.

For 20°K equilibrium D_2 we found nearly the same thermal expansion as that given for normal D_2 by Woolley *e.a.* 7).

With nuclear relaxation measurements 8) it is possible to measure very small amounts of oH_2 in pH_2. A check done with this method showed only a few tenths of a percent ortho H_2 in our para H_2.

4. *Discussion.* *a*) In figure 2 we plotted our results of V^E versus concentration for O_2–N_2 and O_2–A together with those of other authors. For O_2–A we agree very well with Pool and Staveley 3) but the results of Blagoi and Rudenko 4) differ considerably, even when one takes into account that they measured at a different temperature (85°K). Furthermore, their curve has a very irregular shape which makes their results doubtful.

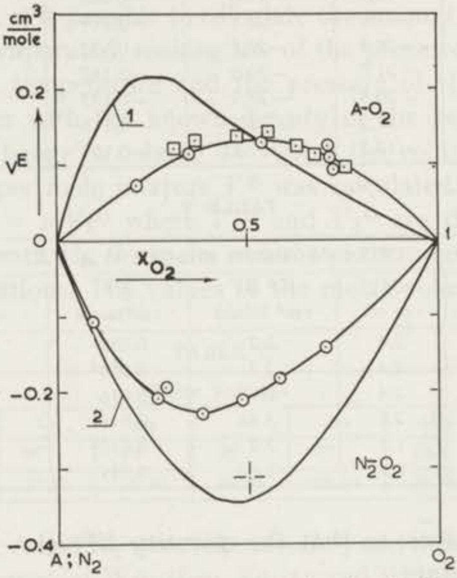

Fig. 2. V^E as a function of concentration for A–O_2 and N_2–O_2.

□ ⊹ Pool and Staveley.
line 1 and 2 Blagoi and Rudenko.
○ Our results.

For the O_2–N_2 mixtures we disagree again with Blagoi and Rudenko while the value of the one reported point measured by Pool and Staveley taken from the survey article by Parsonage and Staveley 9), does not agree either with the other author or us. Our curve for O_2–N_2 is asymmetric, but when one plots the quantity $\Delta V/V$ versus x instead of V^E versus x

one gets, because of the large difference in molar volume of O_2 and N_2, nearly a symmetric curve.

Theoretical calculations have been made for the systems A–O_2 and N_2–O using the theories of Prigogine and coworkers [1]). These theories are based on the law of corresponding states and the excess functions depend on the differences in molecular or critical parameters of the pure components. In a publication of Knobler *e.a.* [10]) the application of this theory on the various excess functions is discussed in more detail. We found that using the theory of Prigogine the results of the calculations depend very much on the set of potential parameters that one chooses for the calculation. The potential parameters were taken from Hirschfelder *e.a.* [11]). Furthermore we also used the critical quantities as in the case of liquids, these seem to be more appropriate than the potential parameters that are derived from measurements with gases. Furthermore, the results of the calculations also depend on the choice of the reference liquid. For O_2–A we calculated an effect ranging from +0.48 cm³ per mole to zero. For O_2–N an effect ranging from +0.9 to −0.15 cm/mole depending on the choice of parameters. Thus it is impossible to get unambiguous results. So one can conclude that in this case the theory cannot be applied.

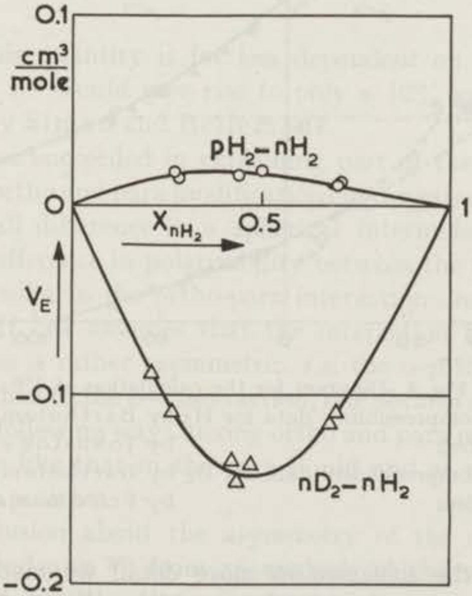

Fig. 3. V^E as a function of concentration for pH_2–nH_2 and nD_2–nH_2
o △ Our results.

b) The results for nH_2–nD_2 and nH_2–pH_2 can be found in fig. 3. For H_2–D_2 a preliminary publication of Lambert [12]) gives results that are in good agreement with our measurements. The small difference might be caused by the fact that we used H_2 and D_2 of the normal composition while they used the low temperature equilibrium modifications. For nH_2–pH_2 they found a smaller effect; however their method seems less accurate than ours.

The effect for pure oH_2–pH_2 and for oD_2–pD_2 would be much greater than for nH_2–pH_2 and for nD_2–oD_2 respectively because of the available concentration range. This is 75% for H_2 and 31% for D_2 so that if the curve of V^E *versus* concentration is a parabola then the effect for oH_2–pH_2 will be nearly twice that for nH_2–pH_2 and for D_2 the effect for oD_2–pD_2 will be nearly 10 times as large as for oD_2–nD_2.

Theoretical investigations for the hydrogen isotopes have been performed by Prigogine 1) and Simon and Bellemans 13). If one assumes that the difference in volume of H_2 and D_2 is only due to the different zero point energy, the two liquids will mix ideally when brought to the same volume. Therefore, in their calculations they effectively compressed D_2 and expanded H_2 to the volume of the final mixture.They calculated in this way a positive volume excess, where as a negative effect was measured.

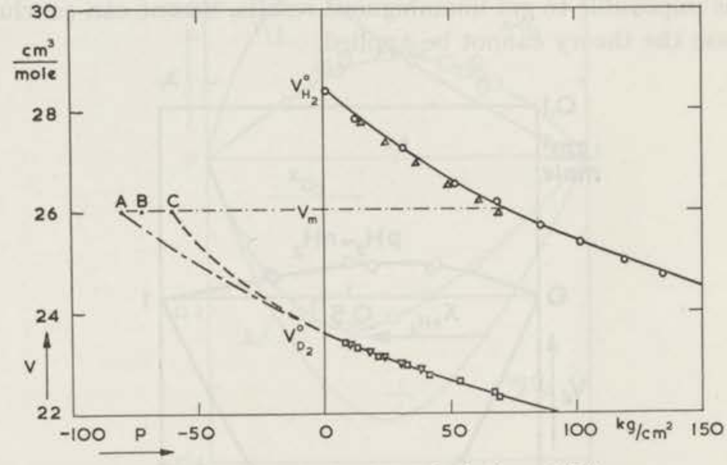

Fig. 4. Diagram for the calculation of V^E.

○ Compressibility data for H_2 by Bartholomé.

△ idem by Johnston *e.a.*

□ Compressibility data for D_2 by Bartholomé.

▽ idem by Friedman *e.a.*

To investigate the situation in more detail we made a graphical representation of the compressibility data of liquid H_2 and D_2 of Bartholomé 14) used by these authors (see fig. 4). We have also plotted the more recent data of Johnston *e.a.* 15) and Friedman *e.a.* 16). To obtain the excess volume, $V^E = V_m - xV_{H_2}{}^0 - (1-x)\,V_{D_2}{}^0$, – where V_m is the volume of the mixture and V^0 is the volume of the pure component at zero pressure – using the method of Simon and Bellemans 13) one has to bring both isotopes to the same molar volume V^{m}. Subsequently, one has to mix such quantities of the two liquids that the total pressure after mixing is zero; *i.e.* $xP_{\mathrm{H}_2} + (1 - x)P_{\mathrm{D}_2} = 0$, where P_{H_2} and P_{D_2} are the pressures to which the isotopes have to be compressed or expanded.

The final result for V^{E} appears to be strongly dependent on the extrapolation of the compressibility data of D_2 to rather large negative pressures. Simon and Bellemans extrapolated according to an empirical relation based on the data of Bartholomé at positive pressures. This corresponds to the line passing through C in fig. 4. From this figure it is clear that such an extrapolation is rather arbitrary. Another extrapolation can easily give a negative value for V^{E}. For this purpose we have drawn the extrapolation that would be required by our measurements (curve through A). For the sake of completeness we also give the value that would correspond to $V^{\mathrm{E}} = 0$ (point B, fig. 4).

From the foregoing it is clear that such a theory does not allow a reliable prediction of the excess volume. However, as the excess free energy is given by the sum of the compression and expansion work, which are both positive:

$$F^{\mathrm{E}} = -x \int_{V^{\circ}_{\mathrm{H}_2}}^{V_{\mathrm{m}}} P\,\mathrm{d}V - (1-x) \int_{V^{\circ}_{\mathrm{D}_2}}^{V_{\mathrm{m}}} P\,\mathrm{d}V$$

it is clear that this quantity is far less dependent on the extrapolation. For example, our V^{E} would give rise to only a 10% greater value of F^{E} than that found by Simon and Bellemans.

In chapter IV we succeeded in explaining part of the differences in the properties of the ortho and para modifications in the gaseous and liquid state in terms of a small difference in a spherical intermolecular potential [17]) arising from the difference in polarisability between the two modifications. Applying these results to the ortho-para interaction one obtains a nearly negligible effect. If one assumes that the interaction between the ortho and para molecules is rather asymmetric, *i.e.* the o–p interaction is much nearer to the p–p then to the o–o interaction, one obtains a positive V^{E}. This can be seen in the following way: mixing ortho and para molecules will make the situation more like that in the para liquid and as this has the larger volume V^{E} will be positive.

The same conclusion about the asymmetry of the o–p interaction is arrived at by Friedman [18]) from an analysis of the vapour pressure of o–p mixtures, and by Woolley, Scott and Brickwedde [7]) from the behaviour of the internal energy of the liquid as a function of the concentration. Furthermore, Becker and Stehl [19]) were led to a similar conclusion from the dependence of the viscosity of o–p mixtures in the gaseous state on the concentration.

The difference between the molar volumes of ortho and normal D_2 is appreciably smaller than in the case of H_2. These differences are discussed in chapter IV.

REFERENCES

1) Prigogine, I., The molecular theory of solutions (North Holland Publishing Company, Amsterdam, 1957).
2) Rowlinson, J. S., Liquids and liquid mixtures (Butterworths, London, 1959).
3) Pool, R. A. H. and Staveley, L. A. K., Nature **180** (1957) 1118.
4) Blagoi, Yu. P. and Rudenko, N. C., Izvestia Vysshikh Ucheb. Zavedenii, Fiz. (1958) 145.
5) Knobler, C. M., Knaap, H. F. P. and Beenakker, J. J. M., Commun. Kamerlingh Onnes Lab., Leiden No. 317*a*; Physica **26** (1960) 142.
6) Beenakker, J. J. M., Varekamp, F. H. and Knaap, H. F. P., Commun. No. 319*a*; Physica **26** (1960) 43.
7) Woolley, H. W., Scott, R. B. and Brickwedde, F. G., J. Res. Nat. Bur. Stand. **41** (1948) 379.
8) Hass, W. P. A., Seidel, G. and Poulis, N. J., Commun. No. 323*b*; Physica **26** (1960) 834.
9) Parsonage, N. G. and Staveley, L. A. K., Quarterly Reviews **13** (1959) 306.
10) Knobler, C. M., Van Heijningen, R. J. J. and Beenakker, J. J. M., Commun. No. 326*b*; Physica **27** (1961) 296.
11) Hirschfelder, J. O., Curtiss, C. F. and Bird, R. B., Molecular theory of gases and liquids (John Wiley, New York, 1954).
12) Lambert, M., Phys. Rev. Letters **4** (1960) 555.
13) Simon, M. and Bellemans, A., Physica **26** (1960) 191.
14) Bartholomé, E., Z. phys. Chemie **B 33** (1936) 387.
15) Johnston, H. L., Keller, W. E. and Friedman, A. S., J. amer. chem. Soc. **76** (1954) 1482.
16) Friedman, A. S., Trezeciak, M. and Johnston, H. Z., J. amer. chem. Soc. **76** (1954) 1552.
17) Knaap, H. F. P. and Beenakker, J. J. M., Commun. Suppl. No. 326*b*; Physica **27** (1961) 523; Chapter IV.
18) Friedman, H. L., J. chem. Phys. **27** (1957) 220.
19) Becker, E. W. and Stehl, O., Z. Phys. **133** (1952) 615.

CHAPTER VI

THE HEAT OF MIXING OF THE LIQUID SYSTEMS H_2–D_2, H_2–HD AND HD–D_2

Summary

The heat of mixing in the liquid state has been measured for the systems nH_2–nD_2, nH_2–HD and HD–nD_2 at 20.4°K over the entire concentration range. In all cases a cooling was found. The results agree rather well with the values predicted by the theory of Prigogine and coworkers [1][2][3]. The solutions are not regular since the excess entropies are different from zero.

1. *Introduction.* The work described in this chapter follows up the research about the heat of mixing of liquid systems by Knobler[4]. We will use the same notation. The subscripts 1 and 2 attached to P (pressure), V (volume), G (Gibbs function), H (enthalpy), F (free energy), S (entropy) and x (molar concentration) indicate components 1 and 2. All quantities are expressed per mole. A superscript o is used to denote quantities of a pure substance, while the subscript m is used for a quantity of the mixture. The superscript E is used to denote thermodynamic excess quantities, which are defined as the difference between a quantity for a real mixture and the corresponding quantity for an ideal mixture.

Using this notation one obtains for a binary mixture per mole

$$H^E(T, P_m, x) = H_m(T, P_m, x) - x_1 H_1{}^o(T, P_1{}^o) - x_2 H_2{}^o(T, P_2{}^o) \quad (1)$$

and

$$G^E(T, P_m, x) = G_m(T, P_m, x) - x_1 G_1{}^o(T, P_1{}^o) - x_2 G_2{}^o(T, P_2{}^o) + \\ - RT(x_1 \ln x_1 + x_2 \ln x_2) \quad (2)$$

in which R is the gas constant.

For quantities not including the entropy the excess is defined analogous to (1) (e.g. V^E) and for quantities including S the excess is analogous to (2), taking into account the entropy of mixing, that is also present in the case of ideal mixing (e.g. F^E and S^E).

In chapter V we described the experiments to determine the volume change on mixing V^E for the system nH_2–nD_2. A volume contraction on mixing was found in contradiction with the predictions of the theory of isotopic mixtures of Prigogine and coworkers[1][2][3]. Looking a little closer, however, we found that the sign of V^E depends on the way in which PV data are extrapolated to negative pressures. Such an extrapolation is of course rather uncertain, making a prediction of V^E impossible.

Since, however, the theory gave an unambiguous result for the thermodynamic functions H^E, G^E and F^E, it seemed important to measure one of these quantities in order to have a more decisive test on the theory. The heat of mixing H^E was determined experimentally, by measuring the heat required to keep the temperature constant during the mixing of the pure components. A calorimeter was constructed similar to the one already used in our laboratory by Knobler[4].

Since the heat of mixing is very small at 20°K, it was necessary to perform the experiment under constant pressure to avoid a heat effect $V\Delta P$ corresponding to a pressure change ΔP.

Furthermore a low temperature valve has been used in the apparatus to avoid a flow of liquid through the calorimeter. Both points will be discussed in more detail. We succeeded in reducing the heat input of the stirring to 1 or 2% of the measured effect by a very careful mixing procedure. For determining the temperature changes a carbon resistance thermometer was used, which has a higher sensitivity at 20°K than a platinum thermometer. The H_2 and D_2 were of normal ortho-para composition.

2. *Apparatus.* In fig. 1 a scheme is given of the calorimeter (volume about 10 cm³). It consists of two brass vessels joined by an indium ring *A* (1 mm wire diameter) that is compressed by six brass bolts to form a vacuum-tight seal. In a recess in the lower chamber an indium ring *B* (0.3 mm) is placed under a 0.02 mm thick aluminium foil *C* that separates the two vessels. When the chambers are bolted together, rings *A* and *B* are compressed, the latter with brass ring *D*, which projects a few tenths of a mm above the lower vessel. The foil can be punctured by the double stirrer *E*, that is soldered to a 0.8 mm stainless steel capillary *F*. This capillary fits closely inside another capillary and is brought out of the calorimeter system through a teflon packing in the top of the cryostat. By changing the volume of the stirrers and by using different lower vessels, which could be done very easily, the volume ratio between upper and lower vessel was varied and measurements could be performed over an extensive concentration range. The temperature changes were measured with a carbon resistance *G* of the De Vroomen type[6], placed on a copper bar, that is soldered with Woods metal into a hole in the upper vessel. The resistance is measured in a Wheatstone bridge with a recorder as zero point instrument. The vessels are enclosed in a vacuum jacket *H*, that is sealed with an indium ring *I*.

The wires of the thermometer and the heating wires J, enter the can from the bath by "Amphenol" seal K. The vessels can be filled through German silver tubes L. These tubes can be closed vacuum-tight by low temperature valves M, which can be operated from outside the cryostat.

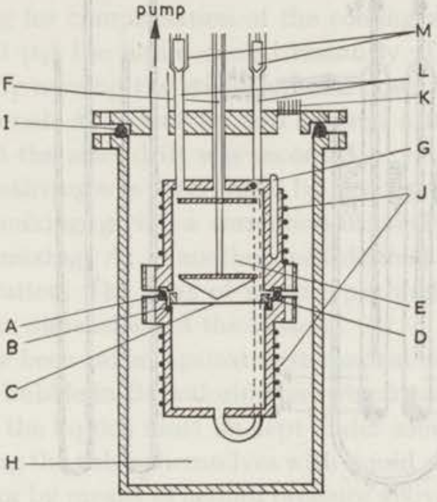

Fig. 1. Heat of mixing calorimeter.

3. *Measuring procedure.* In order to check the tightness of the foil in the calorimeter some gas was admitted to a section of the calorimeter, up to a pressure of a few cm Hg. If the foil between the vessels leaked, the vacuum in the other section was spoiled as could be seen on a vacuum meter. Since a pressure of a few cm Hg gave an appreciable bending of the foil at room temperature, this check was done at low temperature, where no deformation occurred. The gases were condensed in the two purifying vessels P_1 and P_2 placed in a separate cryostat (see fig. 2). From P_1 and P_2 the upper and lower vessels were filled by distillation of the liquids; the upper vessel was always filled with the heavier component in order to promote mixing after the puncturing. The filling pressures were regulated up to about 1.5 atm with heaters H_1 and H_2. When the calorimeter, the vessels and the filling tubes were full, S_1 and S_2 were closed and using S_3 and S_4 helium gas was admitted to the system and both liquids were kept under the same pressure of about 1.5 atm by means of the constant helium pressure.

After waiting some time for equilibrium the exchange gas was pumped out of the vacuum space and the temperature drift was registered on the recorder as can be seen in fig. 3.

Some minutes before the mixing one of the low temperature valves was closed in order to avoid a flow of liquid through the calorimeter caused by a hydrostatic pressure difference after puncturing of the foil. In addition,

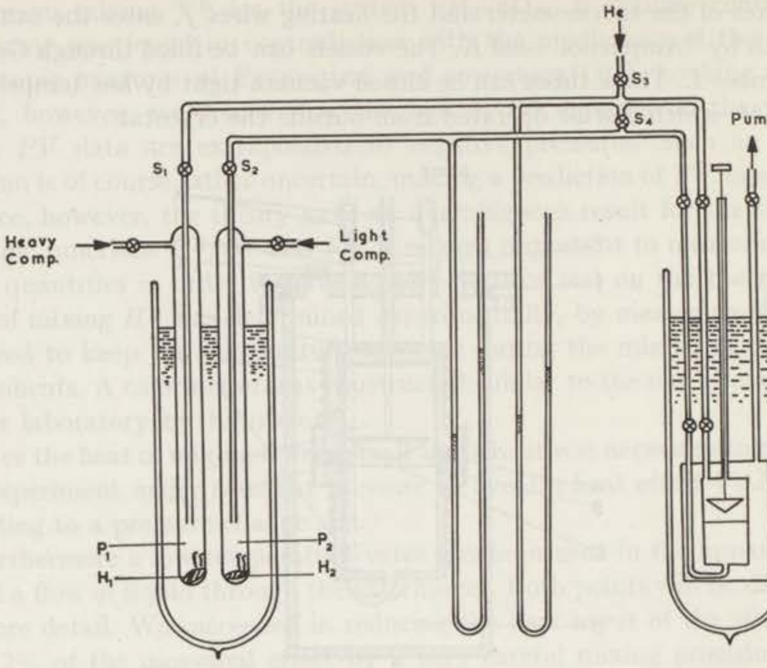
He
S3
S4
Pump
S1
S2
Heavy Comp.
Light Comp.
P1
H1
P2
H2

Fig. 2. Calorimeter filling system.

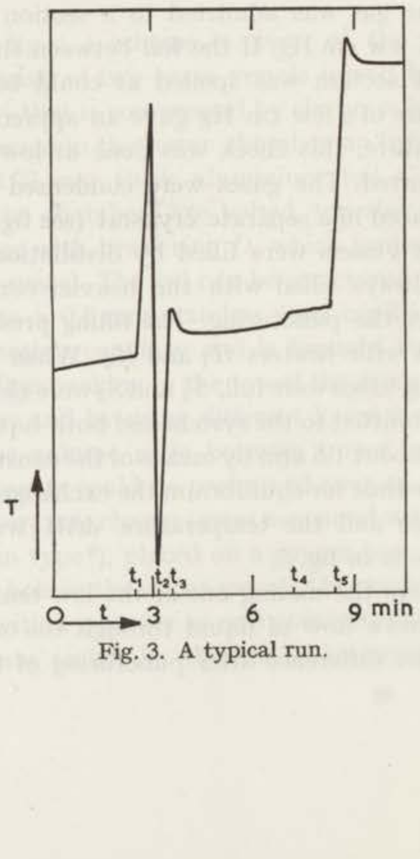

Fig. 3. A typical run.

in this way oscillations of the liquids in the filling lines were prevented. Oscillations between the liquid in the open filling line and the liquid in the stirrer tube were impossible because of the very narrow slit of 0.1 mm between the stirrer and surrounding tube. There was no thermal effect from closing the valve.

At t_1 the heating for compensation of the cooling was started and after puncturing the foil (t_2) the liquid cooled instantly. The liquid was mixed for half a minute by moving the stirrer up and down. The voltage and the current were measured. At t_3, exactly two minutes after t_1, the heat supply was turned off and the after-drift was recorded.

At t_4 the heat of stirring was determined by moving the stirrer in the same way as during the mixing, giving a correction of 1 or 2% in ΔH, the actually measured heat of mixing. At t_5 another well defined amount of heat was supplied for calibration. The heat of mixing per mole of mixture can be calculated using the dimensions of the vessels.

Precautions have been taken against systematical errors. To prevent the formation of a gas bubble in the calorimeter, which can force the liquid out of the calorimeter, the liquids must be kept under some over-pressure. This can be done by filling the tubes themselves with liquid above the level of the surrounding bath, or by means of helium pressure above the liquid. The first solution, however, introduced uncontrollable pressure changes by evaporation of the liquid hydrogen bath. A pressure change ΔP gives a heat effect $V\Delta P$ in the liquid, that is for $\Delta P \approx 10$ cm Hg about 10% of the measured effect. By using a constant pressure these heat effects were avoided. However, we measured in this way a heat of mixing $\mathscr{H}^E$ at constant pressure, while from formula (1) for H^E it is clear that the liquids must be at the saturation pressures $P_1{}^0$ and $P_2{}^0$ before the mixing and at saturation pressure P_m after the mixing. The difference between $\mathscr{H}^E$ and H^E at constant T is small and is given by:

$$\mathscr{H}^E(P, x) - H^E(P_m, x) = H_m(P, x) - H_m(P_m, x) + \\ - x_1\{H_1{}^0(P) - H_1{}^0(P_1{}^0)\} - x_2\{H_2{}^0(P) - H_2{}^0(P_2{}^0)\}. \qquad (3)$$

This can be rewritten with:

$$H_m(P) - H_m(P_m) = \int_{P_m}^{P} dH = \int_{P_m}^{P} \{V - T(\partial V/\partial T)_P\}\, dP$$

and analogous formulae may be given for $H_1{}^0$ and $H_2{}^0$. Evaluating these formulae one gets a difference between the two heats of mixing of a few tenths of a percent which is much smaller than the experimental accuracy. We can therefore identify our experimental results with H^E.

The liquids were under helium pressure only for about 15 minutes. Although some He may dissolve, this will not diffuse into the calorimeter because of the lengths of the filling tubes. The amount of heat generated in puncturing the foil has been determined in measurements with H_2 in both vessels giving a correction of 0.017 cal i.e. 2 or 3% in ΔH. As we found that moving the stirrer up and down along the remnants of the punctured foil could give a large frictional heat input we stirred the lower and upper vessels separately. By this careful mixing with a double stirrer without touching the broken foil the correction for the heat of stirring is at most 1 or 2%.

The pressure in the vacuum can was always kept lower than 10^{-4} mm Hg to make the gaseous heat transport negligible. Heat input by the 0.2 mm copper wires was diminished by making them long; the temperature difference between the calorimeter and the H_2 bath was smaller than 0.5°K during the measurement giving a heat transport less than 5×10^{-4} watt. The heat input by the thermometer current was less than 5×10^{-5} watt.

The D_2 was made by electrolysis of heavy water and the HD was prepared along the lines indicated by Fookson *e.a.* [7]). Both gases were more than 99% pure. We always used H_2 and D_2 of room-temperature ortho-para composition as the difference with respect to pure para H_2 and ortho D_2 is small and furthermore outside the possibilities of the theory we want to test.

4. *Experimental results and discussion.* In table I, II and III, the measured ΔH, the derived H^E and $H^E/4x(1-x)$ are tabulated for the mixtures nH_2–nD_2, nH_2–HD and HD–nD_2. In fig. 4 H^E is plotted vs. x. As can be seen H^E is symmetrical in the components. The quantity $H^E/4x\,(1-x)$ is plotted vs. $x_{\mathrm{H.C.}}$ (concentration heavy component) for the three systems in fig. 5. A factor of 4 is inserted to obtain directly the H^E at $x = 0.5$. As can be seen from this figure the reproducibility of the measurements at one concentration is in general better than the agreement between the results at different concentrations, which is possibly due to small systematical errors. Other experimental results available for H_2–D_2 at 20.4°K, are those of Lambert[8]), who used, however, para H_2 and ortho D_2. A comparison between his value ($H^E/4x(1-x) = 2.95$ cal/mole) and ours shows a good agreement in spite of the different ortho-para compositions.

TABLE I

H^E for the system nH_2–nD_2 at 20.4°K

mole fraction D_2	ΔH cal	H^E cal/mole	$H^E/4\,x\,(1-x)$ cal/mole
0.343	0.988	2.71	3.01
0.343	0.972	2.67	2.96
0.541	1.143	3.09	3.11
0.541	1.024	2.77	2.79
0.541	1.023	2.77	2.78
0.678	0.763	2.59	2.96
0.772	0.507	1.96	2.83
0.784	0.508	1.99	2.94
0.784	0.491	1.93	2.84

TABLE II

H^E for the system nH_2–HD at 20.4°K			
mole fraction HD	ΔH cal	H^E cal/mole	$H^E/4x(1-x)$ cal/mole
0.325	0.368	1.04	1.18
0.325	0.357	1.01	1.15
0.520	0.451	1.27	1.28
0.526	0.444	1.26	1.27
0.526	0.437	1.24	1.25
0.526	0.448	1.27	1.28
0.526	0.444	1.26	1.27
0.659	0.273	0.98	1.09
0.770	0.165	0.69	0.98
0.770	0.191	0.80	1.13

TABLE III

H^E for the system HD–nD_2 at 20.4°K			
mole fraction D_2	ΔH cal	H^E cal/mole	$H^E/4x(1-x)$ cal/mole
0.321	0.269	0.69	0.79
0.321	0.285	0.73	0.84
0.521	0.346	0.90	0.90
0.521	0.363	0.95	0.95
0.766	0.151	0.58	0.81
0.766	0.164	0.63	0.88

From the dew- and boiling point measurements of mixtures of Newman and Jackson⁹) the Gibbs function G^E has been calculated by Bellemans¹⁰) for the system H_2–D_2 at 22°K and the system H_2–HD at 20°K. Using these values in connection with our results for H^E, S^E can be calculated from $TS^E = H^E - G^E$. The experimental data for G^E of the H_2–D_2 mixture were only available at 22°K. Using $S^E = -\partial G^E/\partial T$ we have calculated the value of G^E at 20°K by successive approximation. As can be seen from table IV S^E differs appreciable from zero. This means that these mixtures of isotopes do not form regular solutions (see Guggenheim¹¹)).

The theory for isotopic mixtures has been developed by Prigogine *e.a.*¹)²) and Simon and Bellemans³), based on the idea that the difference in molar volume of isotopic liquids is due to the zero point energy neglecting collective motions. In this model the mixing is considered ideal when the two isotopes are brought to the same volume V_m by applying positive pressure P_1 to compress the lighter component from V_1^0 to V_m and negative pressure P_2 to expand the heavier component from V_2^0 to V_m. (See fig. 6 for the system H_2–D_2).

The excess free energy F^E is equal to the amount of work done in compressing the lighter component and in expanding the heavier one:

$$F^E = -x_1 \int_{V_1^0}^{V_m} P \, dV - x_2 \int_{V_2^0}^{V_m} P \, dV. \qquad (4)$$

Both terms in formula (4) are positive and are indicated by surfaces S_{I} and S_{II} in fig. 6 apart from the factors x_1 and x_2.

For this procedure the compressibilities of both pure components have to be known. However, the extrapolation of the V versus P curve that determines S_{I} is rather arbitrary (of the order of 20% in S_{I} i.e. 10% in F^{E})

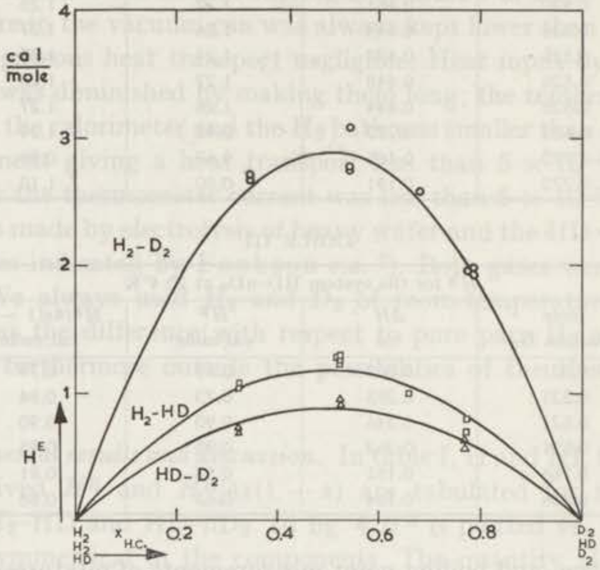

Fig. 4. H^{E} for the systems H_2–D_2, H_2–HD and HD–D_2. $x_{\mathrm{H.C.}}$ is concentration heavy component.

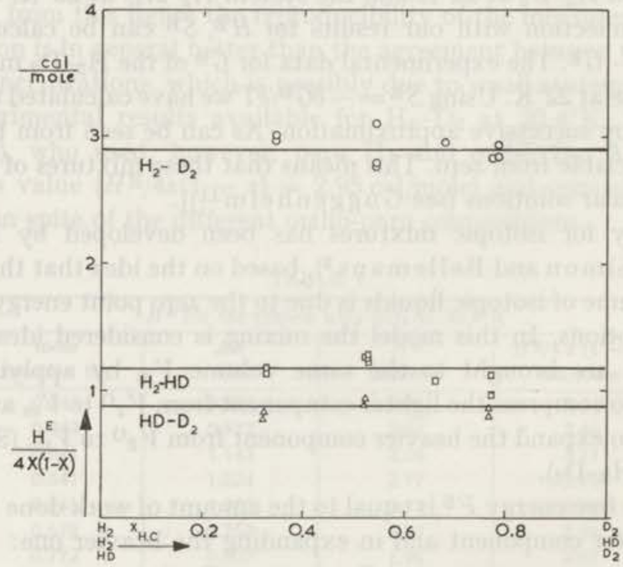

Fig. 5. $H^{\mathrm{E}}/4x(1-x)$ for the systems H_2–D_2, H_2–HD and HD–D_2. $x_{\mathrm{H.C.}}$ is concentration heavy component.

as is already discussed in chapter V[5]). In that chapter V^E is calculated from $V^E = V_m - x_1 V_1^0 - x_2 V_2^0$ in which x_1 and x_2 are determined by the conditions that such relative amounts of the compressed and the expanded liquids must be mixed that the final pressure is zero:

$$x_1 P_1^0 + x_2 P_2^0 = 0. \tag{5}$$

Reversibly using the experimental value of V^E, it is possible to calculate P_2 and to make a better extrapolation for the compressibility. The F^E for the system H_2–D_2 is now calculated from the surfaces indicated in formula (4) in which x_1 and x_2 are again determined by (5).

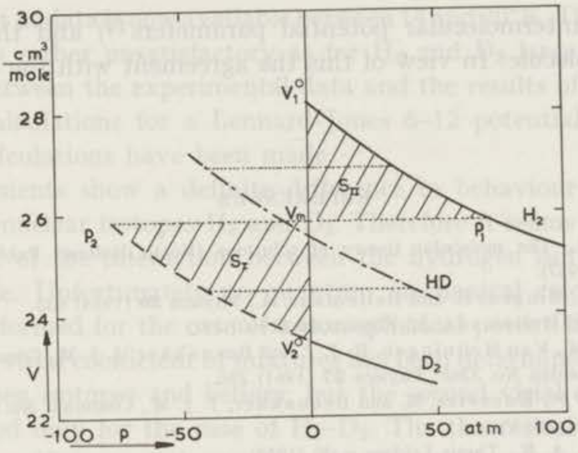

Fig. 6. Diagram for the calculation of F^E.
——— Compressibility for H_2 and D_2 from Friedman and Hilsenrath[12]).
- - - - - - - Extrapolated compressibility for D_2.
·-·-·-·- Estimated compressibility for HD.

Calculation of F^E at different temperatures gives S^E with $S^E = -\partial F^E/\partial T$. One can show that F^E equals G^E in the same way as $\mathscr{H}^E$ equals H^E (eq. (3)). The thermodynamic quantities are then found using $F^E = G^E$ and $H^E = G^E + TS^E$.

For the mixtures with HD the calculations are complicated by the fact that for HD no compressibility data are available. Starting from the known volume at saturation pressure[13]), we have interpolated between the compressibility data of H_2 and D_2 to find the V versus P curve for HD (fig. 6). Using this curve F^E, S^E and H^E have been calculated for H_2–HD and HD–D_2. As can be seen from the surfaces or from table IV the effect for H_2–D_2 is about three times larger than that for H_2–HD, which agrees with the experimental results. The calculated values are collected in table IV. In comparing the experiment with theory, one has to bear in mind the rather crude nature of the theory. One neglects, e.g., collective effects, the

TABLE IV

G^E, H^E and S^E at 20°K for $x = 0.5$

	nH_2–nD_2		nH_2–HD		HD–nD_2	
	exp.	theor.	exp.	theor.	exp.	theor.
G^E cal/mole	1.71	2.13	0.63	0.56	—	0.51
H^E cal/mole	2.90	3.96	1.18	1.33	0.88	0.94
S^E cal/mole °K	0.06	0.09	0.03	0.04	—	0.02

difference in intermolecular potential parameters[14]) and the asymmetry of the HD molecule. In view of this the agreement with the experiment is satisfactory.

REFERENCES

1) **Prigogine, I.**, The molecular theory of solutions (North Holland Publishing Company, Amsterdam, 1957).

2) **Prigogine, I., Bingen, R. and Bellemans, A.**, Physica **20** (1954) 633.

3) **Simon, M. and Bellemans, A.**, Physica **26** (1960) 191.

4) **Knobler, C. M., Van Heijningen, R. J. J. and Beenakker, J. J. M.**, Commun. Kamerlingh Onnes Lab., Leiden No. *326b*; Physica **27** (1961) 296.

5) **Knaap, H. F. P., Knoester, M. and Beenakker, J. J. M.**, Commun. No. *325c*; Physica **27** (1961) 309, Chapter V.

6) **De Vroomen, A. R.**, Thesis Leiden, p. 30 (1959).

7) **Fookson, A., Pomerantz, P. and Rick, E. H.**, Science **112** (1950) 748.

8) **Lambert, M.**, Phys. Rev. Letters **4** (1960) 555.

9) **Newman, R. B. and Jackson, L. C.**, Trans. Faraday Soc. **54** (1958) 1481.

10) **Bellemans, A.**, Bull. Soc. chim. Belg. **68** (1959) 270.

11) **Guggenheim, E. A.**, Mixtures (Clarendon Press, Oxford 1952).

12) **Friedman, A. S. and Hilsenrath, J.**, Nat. Bur. Stand. Rep. 3163.

13) **Woolley, H. W., Scott, R. B. and Brickwedde, F. G.**, J. Res. Nat. Bur. Stand. **41** (1948) 379.

14) **Knaap, H. F. P. and Beenakker, J. J. M.**, Commun. Suppl. No.*119b*; Physica **27** (1961) 523, Chapter IV.

CONCLUSIONS

For the second virial coefficient of the hydrogen isotopes H_2, HD and D_2 a consistent set of data is now available between 14 and 70°K. The comparison with theory is rather unsatisfactory as for H_2 and D_2 large discrepancies were found between the experimental data and the results of the quantum mechanical calculations for a Lennard-Jones 6–12 potential. For HD no theoretical calculations have been made.

Our experiments show a definite difference in behaviour between HD and the homonuclear isotopes H_2 and D_2. Therefore it seems that the non-spherical part of the interaction between the hydrogen isotopes plays an important role. Unfortunately no quantum mechanical calculations have ever been performed for the case of a non-spherical potential.

The second virial coefficient of mixtures has been determined for mixtures of the hydrogen isotopes and helium, but the second virial coefficient has been calculated only for the case of H_2–D_2. The theoretical value for the excess virial coefficient of the system H_2–D_2 agrees rather well with the experimentally found effect. It is hoped that also for the other mixtures theoretical data will become available.

The measured difference in the second virial coefficient between ortho- and para-hydrogen is for the major part explained in terms of a difference in polarizability. Using pure ortho and para deuterium, the latter of which can be prepared by preferential adsorption on Al_2O_3, it would probably be possible also to measure the difference in B coefficient for the case of deuterium.

The data on heat of mixing for the hydrogen isotopes, described in chapter VI, are in very satisfactory agreement with the theory for isotopic mixtures, of Prigogine, e.a. However, it appears that this theory gives only reliable results for the heat effects, while no predictions can be made for the volume change on mixing.

Acknowledgements. We should like to express our sincere thanks to Messrs. H. van Ee, H. van Beek and W. P. A. Hass for analysing the gas mixtures, to Mr. C. le Pair for his never ending stream of liquid hydrogen, to Mr. H. Kuipers and his staff for constructing the glass parts of the apparatus, to Mr. E. Prins and the staff for the construction of the calorimeter, to Mr. L. Neuteboom and Mr. K. I. Mechelse for their assistance and to Dr. C. M. Knobler and Dr. W. Duffy for correcting the English.

The work described in this thesis is a part of the research program of the "Stichting voor Fundamenteel Onderzoek der Materie (F.O.M.)" and has been made possible by financial support from the "Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek (Z.W.O.)"

SAMENVATTING

In dit proefschrift worden enkele onderzoekingen beschreven, die werden verricht aan H_2, HD en D_2 zowel in gasvormige als in vloeibare toestand. Het doel van de experimenten was gegevens te verkrijgen over de invloed van quantummechanische verschijnselen op eenvoudige moleculen; zoals in de inleiding wordt uiteengezet kunnen dergelijke effecten het best bestudeerd worden aan de waterstofisotopen. De proeven vallen in twee groepen uiteen, namelijk onderzoekingen aan de tweede viriaalcoëfficiënt van gassen (1) en onderzoekingen aan thermodynamische eigenschappen van vloeibare mengsels (2).

1. Daar er reeds metingen van de B coëfficiënten tussen 14 en 20°K waren verricht, hebben we onze aandacht voornamelijk op een uitbreiding van het temperatuurgebied tot 70°K gericht. Hiertoe werd een thermostaat geconstrueerd die het mogelijk maakte de B coëfficiënt van H_2, HD en D_2 tussen 20 en 70°K te bepalen. Een en ander wordt besproken in hoofdstuk I. Onze resultaten stemmen goed overeen met gegevens uit aansluitende temperatuurgebieden.

In hoofdstuk II wordt vervolgens de bepaling van de B coëfficiënt van mengsels van de waterstofisotopen onderling en van deze gassen met helium besproken. De resultaten konden tevens worden gebruikt voor een nadere analyse van de eerder verrichte metingen van isothermen bij 20°K.

Bij vergelijking van het totaal van het nu aanwezige experimentele materiaal met de resultaten van de theoretische berekeningen die door Cohen e.a. worden uitgevoerd met behulp van een bolvormige potentiaal (Lennard-Jones 6–12) blijkt er een vrij grote discrepantie tussen theorie en experiment te bestaan. Bovendien blijkt het gedrag van HD af te wijken van dat van H_2 en D_2 hetgeen al bij de bepaling van de viscositeit werd geconstateerd. Wij concluderen dan ook dat het waarschijnlijk is dat het niet-bolvormige deel van de interactie een niet te verwaarlozen bijdrage geeft tot de B coëfficiënt. Tot nu toe ontbreken echter de noodzakelijke quantummechanische berekeningen.

Een apart vraagstuk wierp vervolgens de metingen van het verschil tussen de tweede viriaal coëfficiënt van ortho- en parawaterstof bij 18 en 20°K op. Om dit kleine verschil nauwkeurig genoeg te kunnen bepalen, maakten wij gebruik van een differentiële meettechniek die in hoofdstuk III wordt beschreven. Het verschil blijkt echter tien maal zo groot te zijn als door Cohen e.a. voorspeld werd. Wij menen echter een belangrijk deel van het gevonden "grote" effect te kunnen verklaren, zoals in hoofdstuk IV wordt besproken. Er blijkt namelijk een klein verschil in potentiaal parameter tussen ortho- en parawaterstof te bestaan dat veroorzaakt wordt door een verschil in polariseerbaarheid, afkomstig van het feit, dat orthowaterstof wel en parawaterstof niet roteert. Op analoge wijze gelukte het ons het door Michels e.a. gevonden verschil in potentiaal parameters tussen H_2 en D_2 te verklaren. Hier geeft het verschil in nulpuntsbeweging aanleiding tot een verschil in polariseerbaarheid en dus tot een verschil in potentiaalparameters.

De experimenten, die beschreven worden in de hoofdstukken V en VI zijn voornamelijk verricht om de theorie van Prigogine c.s. voor mengsels van isotopen in vloeibare toestand te toetsen. In hoofdstuk V wordt de meting van de volumeverandering bij menging beschreven, terwijl in hoofdstuk VI de bepaling van de mengwarmte voor de systemen H_2–HD, H_2-D_2 en HD–D_2 wordt besproken. Voor de mengwarmte is de overeenstemming tussen theorie en experiment zeer bevredigend, terwijl wat de volumeverandering bij menging betreft bij nadere bestudering blijkt dat het zelfs niet mogelijk is, in tegenstelling tot de opinie van Prigogine e.a., op grond van de theorie uitspraken te doen over het teken van deze grootheid.

STELLINGEN

I

De berekening van Edwards en Daunt over het gedrag van de phasenscheidingskromme van vloeibare ^3He–^4He mengsels nabij het absolute nulpunt is onjuist.

Edwards, D. O. en Daunt, J. G., Phys. Rev. **124** (1961) 640.

II

Het verloop van het Senftleben-effect in O_2 als functie van de temperatuur kan op eenvoudige wijze worden verklaard.

Senftleben, H. en Pietzner, J., Ann. Phys. **16** (1933) 907.

III

De door Ohtsuka berekende waarde voor de magnetische entropie van $K_3Fe(CN)_6$ bij de Néel-temperatuur is een factor twee te laag.

Ohtsuka, T., J. phys. Soc. Japan **16** (1961) 1549.

IV

De waarde van de reflectie-coëfficiënt van H-atomen aan een oppervlak van vaste waterstof bij 4°K is niet „onverwacht hoog” te noemen; dit in tegenstelling tot de opinie van Brackmann en Fite.

Brackmann, R. T. en Fite, W. L., J. chem. Phys. **34** (1961) 1572.

V

De B coëfficiënt voor een Lennard-Jones 6–12 potentiaal kan in het klassieke geval gegeven worden door de volgende uitdrukking

$$B^*(T^*) = \frac{\pi}{\sqrt{2}}\,\frac{\mathrm{e}^{\frac{1}{2}T^*}}{T^*}\left\{I_{\frac{3}{4}}\left(\frac{1}{2T^*}\right) + I_{-\frac{3}{4}}\left(\frac{1}{2T^*}\right) - I_{\frac{1}{4}}\left(\frac{1}{2T^*}\right) - I_{-\frac{1}{4}}\left(\frac{1}{2T^*}\right)\right\}.$$

In deze vorm zijn B^* en de temperatuur T^* in gereduceerde eenheden uit gedrukt, terwijl de functies I_ν ($\nu = {}^3/_4, -{}^3/_4, {}^1/_4, -{}^1/_4$) hyperbolische Besselfuncties zijn.

VI

Het door Heinzinger, Klemm en Waldmann gevonden verschil in warmtegeleiding tussen ortho- en parawaterstof is in overeenstemming met de resultaten van hoofdstuk IV van dit proefschrift.

Heinzinger, K., Klemm, A. en Waldmann, L., Z. Naturforsch. **16** (1961) 1338.

VII

Het introduceren van nieuwe modellen voor de intermoleculaire potentiaal dient slechts te geschieden indien voldoende physische of mathematische gronden aanwezig zijn.

VIII

De wijze waarop Kropschot en Arp door extrapolatie van metingen aan supergeleidende dunne lagen het critische veld bij stroomsterkte nul bepalen is onjuist.

Kropschot, R. H. en Arp, V., Cryogenics **2** (1961) 1.
Ginsberg, D. M. en Tinkham, M., Bull. amer. phys. Soc. **3** (1958) 338.

IX

Bij het opstellen van de energiebalans voor de vorming van bellen in een bellenvat is door Riepe en Hahn de oppervlakte-energie niet op correcte wijze in aanmerking genomen.

Riepe, G. en Hahn, B., Helv. phys. Act. **34** (1961) 865.

X

Om mechanische redenen verdient bij het roeien in achten en vieren de Italiaanse opstelling de voorkeur boven de traditionele.