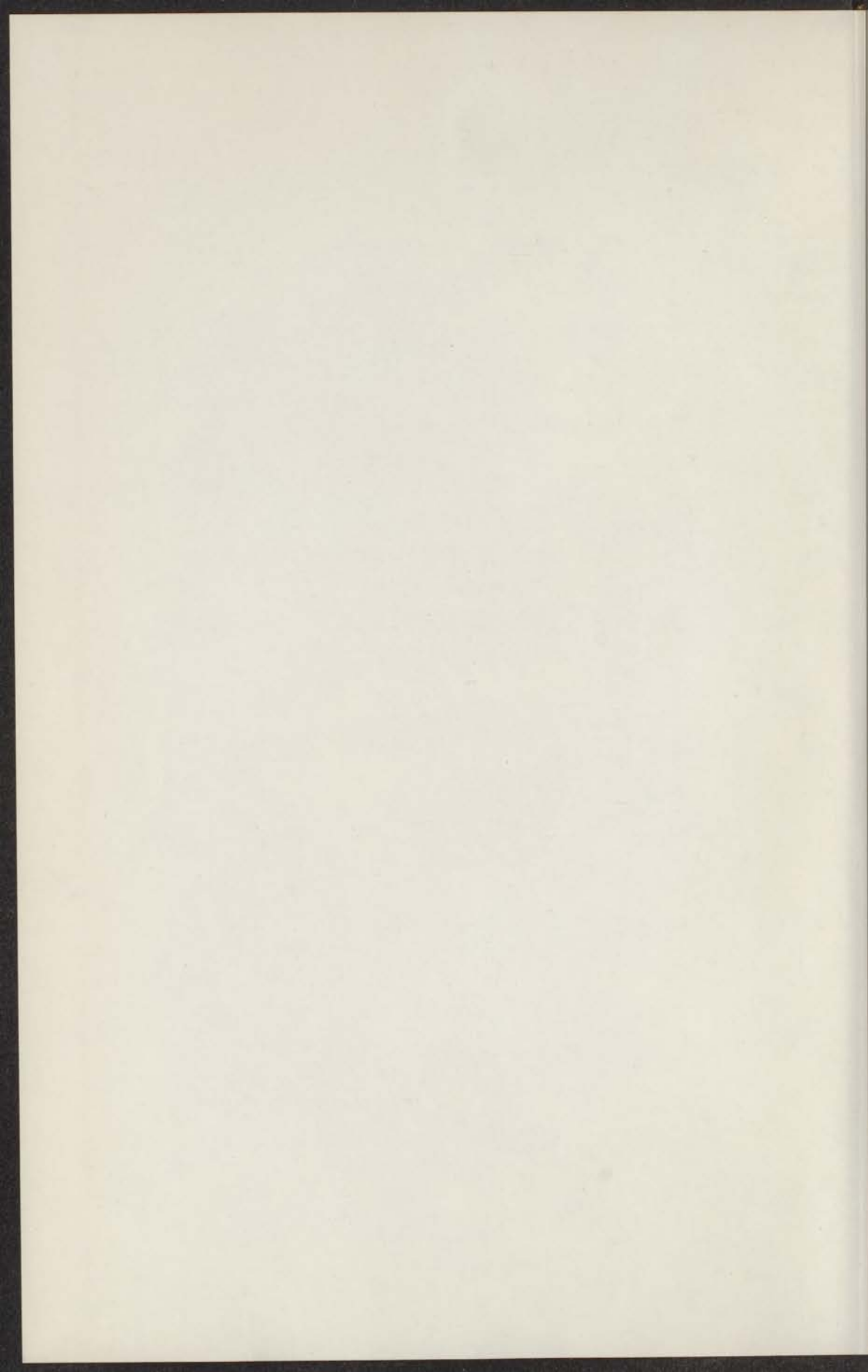


JOHN EXPEDIMENTS WITH LIQUID IN THE WIDENED
IN NARROW SETS



SOME EXPERIMENTS
WITH LIQUID ^3He - ^4He MIXTURES
IN NARROW SLITS

BY FREDERICK B. WOOD

THE UNIVERSITY OF CHICAGO, CHICAGO, ILL.
RECEIVED BY THE EDITOR, APRIL 15, 1954

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CHICAGO, ILL.

WORK EXPERIMENTS WITH LIQUID AIR IN NARROW TUBES
BY H. W. WATSON

SOME EXPERIMENTS
WITH LIQUID ^3He - ^4He MIXTURES
IN NARROW SLITS

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. P. A. H. DE BOER, HOOGLERAAR IN DE
FACULTEIT DER GODGELEERDHEID, TEGEN
DE BEDENKINGEN VAN DE FACULTEIT DER
WIS- EN NATUURKUNDE TE VERDEDIGEN
OP WOENSDAG 19 JUNI 1957 TE 15 UUR

DOOR

DERK HENDRIK NICOLAÛS WANSINK

GEBOREN TE ARNHEM IN 1929

SOME EXPERIMENTS
WITH LIQUID H₂-He MIXTURES
IN NARROW SLITS

PROLOGUE

THE VELOCITY OF SOUND IN LIQUID H₂-He MIXTURES
HAS BEEN MEASURED IN NARROW SLITS
BY THE METHOD OF THE INTERFERENCE OF SOUND WAVES
IN A LIQUID MEDIUM.

Promotor: PROF. DR. K. W. TACONIS

DEPARTMENT OF PHYSICS
UNIVERSITY OF LEIDEN
THE NETHERLANDS

1954

DEPARTMENT OF PHYSICS
UNIVERSITY OF LEIDEN

STELLINGEN

I

Het is noodzakelijk de dichtheid van vloeibare ^3He - ^4He mengsels te meten in verband met de verklaring van verschillende eigenschappen van deze mengsels.

Hoofdstuk IV van dit proefschrift.

J. de Boer and R. J. Lunbeck, *Physica* **14** (1948) 510.

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

II

Uit het verloop van de dampspanning van ^3He - ^4He mengsels als functie van de temperatuur volgt, dat deze mengsels bij het absolute nulpunt ontmengd zijn.

B. Weinstock, D. W. Osborne and B. M. Abraham, *Phys. Rev.* **77** (1950) 400.

H. S. Sommers, *Phys. Rev.* **88** (1952) 113.

B. N. Esel'son and N. G. Berezniak, *J. exp. theor. Phys.* **30** (1956) 628; *Soviet Phys. J.E.T.P.* **3** (1956) 568.

III

De resultaten van Esel'son en Berezniak inzake de dampdruk van ^3He - ^4He mengsels in het gebied van de laagste concentraties zijn onjuist.

B. N. Esel'son and N. G. Berezniak, *J. exp. theor. Phys.* **30** (1956) 628; *Soviet Phys. J.E.T.P.* **3** (1956) 568.

IV

De werking van vloeibare ^3He - ^4He mengsels als warmtegeleidend medium voor adiabatische demagnetisatie berust slechts gedeeltelijk op de warmteweerstand van deze mengsels in de He II-fase.

C. P. Hwang, C. D. Fulton and W. M. Fairbank, *Bull. Am. phys. Soc.* **1** (1956) 217.

J. J. M. Beenakker, K. W. Taconis, E. A. Lynton, Z. Dokoupil and G. van Soest, *Commun. Kamerlingh Onnes Lab., Leiden No. 289a*; *Physica* **18** (1952) 433.

K. G. Walters and W. M. Fairbank, *Phys. Rev.* **103** (1956) 262.

V

Uit het diagram van het evenwicht damp-vaste stof van het ternaire systeem H_2-N_2-CO volgt een bevestiging van het feit, dat de vaste fase uit mengkristallen bestaat.

Z. Dokoupil, G. van Soest and M. D. P. Swenker, Commun. No. 297; Appl. sci. Res. **A 5** (1955) 182.

VI

Het is twijfelachtig of bij het beschrijven van de experimentele resultaten van de toestandsvergelijking van een gas het invoeren van de derde en hogere viriaalcoëfficiënten meer dan een descriptief nut heeft.

VII

Het verdient aanbeveling na te gaan of de temperatuurafhankelijkheid van de viscositeit van vloeibaar argon en neon bij constante dichtheid in sterke mate van de dichtheid afhangt.

N. S. Rudenko und L. W. Schubnikow, Phys. Z. Sowjetunion **6** (1934) 470.
H. H. Tjerckstra, Commun. No. 290a; Physica **18** (1952) 853.
N. F. Zhdanova, J. exp. theor. Phys. **31** (1956) 14;
Soviet Phys. J.E.T.P. **4** (1957) 19.

VIII

Gezien de grootte van de warmtelekken, optredende bij de Leidse demagnetisatie-experimenten, verdient het aanbeveling een systematisch onderzoek naar de oorzaken hiervan in te stellen.

IX

Het is onwaarschijnlijk, dat het door Shimomura, Kojima en Saito beschreven nikkeloxyde de samenstelling $Ni_{15}O_{16}$ heeft.

Y. Shimomura, M. Kojima and S. Saito, J. phys. Soc. Japan **11** (1956) 1136.

X

De veronderstelling, dat met de „single scale”-methode volgens Wood absolute waarden van de zuurstofverzadiging van het bloed bepaald worden, is onjuist.

E. H. Wood and J. E. Geraci, *J. lab. clin. Med.* **34**
(1949) 387.
Waters Corp., Oximeter operating instructions.

XI

Bij een beschrijving van de Nederlandse tabel van de inkomstenbelasting verdient een uitdrukking in I/I_0 , waarbij I het inkomen en I_0 het belastingvrije minimum voorstelt, de voorkeur boven een beschrijving in termen van $(I-I_0)$.

J. C. H. Lisman, *Weekbl. der Belastingen* 4013.

XII

Het is onjuist de vorming van alpinisten te doen aanvangen in oefengebieden als de z.g. Maasrotsen bij Dinant.

The following is a list of the names of the persons who have been elected to the office of Justice of the Peace for the year 1901. The names are given in alphabetical order of their surnames.

VI

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IX

The following is a list of the names of the persons who have been elected to the office of Justice of the Peace for the year 1901. The names are given in alphabetical order of their surnames.

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

Nadat ik in 1947 na mijn eindexamen gymnasium β mijn studie in de wis- en natuurkunde te Leiden was begonnen, legde ik in 1951 het candidaatsexamen A af. Vervolgens behaalde ik in mei 1955 het doctoraal examen experimentele natuurkunde, na hiertoe tentamina te hebben afgelegd bij Dr. J. Korringa *), Dr. N. G. van Kampen **) en Dr. P. Mazur.

Inmiddels was ik sedert september 1951 werkzaam op het Kamerlingh Onnes Laboratorium, waar ik eerst H. C. van Elst assisteerde bij metingen van de elektrische weerstand van metaallegeringen in magnetische velden. Omstreeks Pasen 1952 kwam ik als jongste medewerker bij de ^3He -werkgroep onder leiding van Prof. Dr. K. W. Taconis, waar ik het werken in teamverband heb leren kennen en waarderen. Aanvankelijk assisteerde ik Dr. E. A. Lynton §) en Dr. J. J. M. Beenakker §§), o.a. bij het onderzoek naar de warmtegeleiding van ^3He - ^4He mengsels. Vervolgens heb ik medegewerkt met C. J. N. van den Meijdenberg en Dr. J. J. M. Beenakker aan metingen over het fonteineffect van ^4He , terwijl ik verder met Dr. Z. Dokoupil en G. van Soest †) en later ook Dr. D. G. Kapadnis ††) betrokken was bij metingen van de soortelijke warmte van ^3He - ^4He mengsels. Vanaf eind 1953 hield ik mij inmiddels ook bezig met een aantal onderzoekingen, welke afgezien van een enkel intermezzo de onderwerpen van dit proefschrift betroffen. Bij deze experimenten, welke in het begin van 1956 werden afgesloten, werd ik eerst terzijde gestaan door Dr. J. J. M. Beenakker en C. J. N. van den Meijdenberg, terwijl ik verder geassisteerd werd door o.a. de volgende personen: F. A. Staas (1953-1956), Th. L. Hankins ‡) (1953-1954), J. Reuss (1954-1955), L. J. Bongers (1955-1956) en R. de Bruyn Ouboter (1955-1956). Onontbeerlijke assistentie werd voorts verleend door de leraren-hoofdtechnici H. Kuipers en A. Ouwerkerk en de constructeur L. Neuteboom. De Engelse tekst werd voor mij gecorrigeerd door Dr. W. E. Thompson.

*) thans te Columbus, Ohio, U.S.A.

**) thans te Utrecht.

§) thans te New Brunswick, N.J., U.S.A.

§§) thans werkzaam bij de werkgroep Moleculphysica van de Stichting voor Fundamenteel Onderzoek der Materie, Kam. Onnes Lab., Leiden.

†) thans te Rotterdam.

††) thans te Dhulia, India.

‡) thans te New Haven, Conn., U.S.A.

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10
[The text in this section is also very faint and difficult to read, appearing as a list or a set of notes at the bottom of the page.]

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INTRODUCTION

Kamerlingh Onnes, who in 1908 succeeded in liquefying helium ¹⁾, made the startling observation in 1911 that the density of liquid helium shows a maximum at 2.2°K ²⁾. Although it was found later that liquid helium at this temperature shows more peculiar characteristics ³⁾, it was only in 1928 that Keesom and Wolfke ⁴⁾ supposed a kind of phase transition to take place at this temperature: they introduced the now well-known names "helium I" and "helium II" for the phases above and below the transition temperature. In 1932 Keesom and Miss Keesom ⁵⁾, following a suggestion by Ehrenfest, named this temperature the lambda-point because of the high, lambda-shaped peak in the specific heat ⁶⁾ at this temperature. Then progress in the field was rapid. In the years between 1936 and 1938 it became clear from four successive discoveries that the equations of motion which describe the dynamical properties of customary liquids and also of helium I, do not apply at all to helium II. These four discoveries were: the large, anomalous heat conductivity ⁷⁾; the phenomenon of superfluidity, *i.e.* the unusually large mobility of helium II in narrow slits and capillaries, pointing to an immeasurably small viscosity ⁸⁾; the fountain effect ⁹⁾ which is a flow of He II through a tube as a result of a temperature gradient applied; and finally the liquid He II-film ¹⁰⁾ which covers all surfaces in contact with He II and which shows superfluidity also.

This striking behaviour urged F. London ¹¹⁾ in 1938 to compare He II with a Bose-Einstein gas. Below the degeneracy temperature the bosons start to "condense" in the momentum space into the ground state, the number of condensed particles increasing with decreasing temperature. In this state they are, perforce, unable to exchange momentum or energy: hence the condensed particles have a viscosity zero, accounting in this way for the superfluidity.

From this idea Tisza ¹²⁾ derived his two-fluid model which describes most experiments fairly well. He II is supposed to consist of two interpenetrating fluids: one, the superfluid, lacks both entropy and viscosity and is the equivalent of the condensed Bose-Einstein atoms, the other, the normal fluid, shows all properties of a customary liquid. At the absolute zero-point of temperature only superfluid is postulated to exist, but with increasing

temperature some normal fluid is excited until at reaching the lambda-point all superfluid has been transformed into normal fluid and the He II has become He I.

Actually, natural helium as obtained from wells or from the air consists almost exclusively of the isotope ${}^4\text{He}$ (to which the above-mentioned particulars apply) but it contains also a very slight amount of ${}^3\text{He}$ ¹³⁾, *viz.* in concentrations of the order of 10^{-6} — 10^{-7} ¹⁴⁾. In contrast to ${}^4\text{He}$, the ${}^3\text{He}$ -atom contains an odd number of elementary particles and therefore it obeys Fermi-Dirac statistics instead of Bose-Einstein statistics as ${}^4\text{He}$ does because of its even particle-number. Hence ${}^3\text{He}$ should not show any superfluidity provided that London's interpretation is right. The study of ${}^3\text{He}$ or of ${}^3\text{He}$ — ${}^4\text{He}$ mixtures should therefore yield valuable information on the nature of superfluidity.

The first experiments ¹⁵⁾ in this direction had to be carried out with mixtures of ${}^3\text{He}$ -concentrations of the order of 10^{-4} , obtained from natural helium by means of the "heat flush method" ¹⁶⁾. Only when artificially produced ${}^3\text{He}$ became available could experiments with mixtures of higher concentration and with pure ${}^3\text{He}$ be carried out.

This thesis deals with some properties of ${}^3\text{He}$ — ${}^4\text{He}$ mixtures at concentrations up to about 8% and at temperatures generally below the lambda-point of the mixture. All experiments were performed with very similar apparatus: they all had a very narrow slit as essential part in common.

The thesis can be divided into two main parts: the first half, consisting of three chapters, deals with thermodynamic quantities, the second half, being the fourth chapter, is devoted to dynamical properties of the mixture.

In the first chapter the determination of the vapour-liquid phase equilibrium of mixtures of about 10^{-3} concentration is given. The experiment has been performed in order to extend Sommers' phase equilibrium measurements ¹⁷⁾ to the lower concentration region. A good fit to his data is obtained.

Chapter II gives the measurement of the osmotic pressure of ${}^3\text{He}$ — ${}^4\text{He}$ mixtures of concentrations up to about 4%. A liquid ${}^3\text{He}$ — ${}^4\text{He}$ mixture, when separated from pure ${}^4\text{He}$ by means of a fine capillary, appears to exert an osmotic pressure, quite similar to that of an ordinary solution behind a semi-permeable wall: Van 't Hoff's law applies even in this case. The concentrations are determined from the vapour pressure, known from Sommers' and our experiments.

In chapter III we calculated the chemical potential of mixing of different ${}^3\text{He}$ — ${}^4\text{He}$ mixtures from the vapour pressure data. From them quantities such as the specific heat are derived and compared with the experimentally determined values. In general good agreement is found.

The last chapter deals with the flow of pure ${}^4\text{He}$ and of mixtures of concentrations up to 8% through a slit with a width of about 0.3 micron. At first

sight the mixture flows as pure ^4He , showing the same peculiar dependence on the driving force. Closer examination, however, reveals that its velocity is somewhat smaller and that the ^3He itself most probably shows no superfluidity. Interpretation of the results in terms of a somewhat adapted two-fluid model yields the viscosity and the density of the normal fluid of the mixture. Furthermore, the lowering of the lambda-point with the addition of ^3He is observed. Its value is in good agreement with the now generally accepted value of -0.015 deg per % ^3He added¹⁸).

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CHAPTER I

THE VAPOUR-LIQUID EQUILIBRIUM OF ^3He — ^4He MIXTURES

Summary

Measurements have been made of the ratio of the vapour and the liquid concentration, C_V/C_L , of ^3He — ^4He mixtures of very low concentrations at temperatures between 1.2 and 2°K, forming an addition to the experiments of Sommers. The results are in good agreement with those of Sommers.

1. *Introduction.* Many experiments have been performed on the ratio of the vapour and the liquid concentration, C_V/C_L^* , of ^3He — ^4He mixtures. In 1949 Taconis, Beenakker, Nier and Aldrich¹⁾ published measurements concerning mixtures of about 0.1% concentration at temperatures below the lambda-point down to 1.75°K, from which they concluded that the ^3He is dissolved in the normal fluid fraction of the He II only. Hence the classical formula

$$C_V/C_L = P_3^0/P_4^0 \quad (1)$$

with P_3^0 and P_4^0 denoting the vapour pressures of pure ^3He and ^4He resp., becomes

$$C_V/C_L = (\varrho_4^0 P_3^0)/(\varrho_n P_4^0) \quad (2)$$

where ϱ_4^0 and ϱ_n are the molar densities of pure ^4He and its normal fluid fraction resp. However, since ϱ_n decreases rapidly with decreasing temperature, eq. (2) yields very large values of C_V/C_L at low temperatures, e.g. about 1600 at 1.2°K.

Sommers²⁾ in 1952 at Los Alamos performed experiments on the distribution coefficient with mixtures of concentrations between 0.58% and 13.00%. Extrapolation of his results to low concentrations indicated much lower values of C_V/C_L than those found by Taconis, Beenakker, Nier and Aldrich. But as Sommers' points obtained with the 0.58% mixture lie systematically below the smooth curve that can be drawn through his other points (see fig. 1), this extrapolation is rather

*) In this thesis, C denotes the molar ratio N^3/N^4 , whereas X denotes the molar fraction $N^3/(N^3 + N^4)$.

arbitrary. Thus it is impossible to decide from the two different measurements, mentioned above, how large C_V/C_L is in the limit of zero concentration, especially at lower temperatures where the discrepancy between the two investigators becomes very large. Therefore it seemed useful to take up once more the determination of the distribution ratio in the low concentration region.

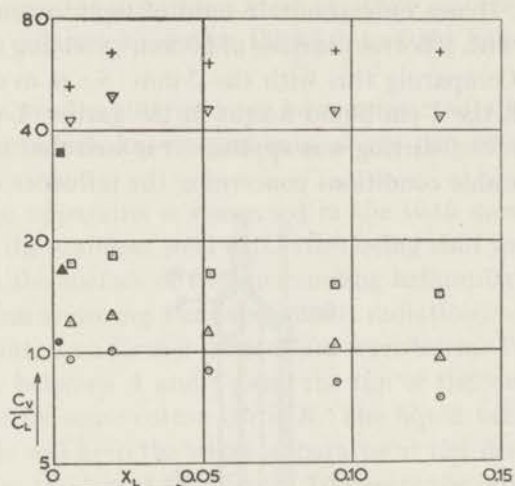


Fig. 1. The distribution coefficient C_V/C_L as a function of the liquid concentration X_L at different temperatures.

Temperature	1.3°K	1.4°K	1.75°K	1.9°K	2.0°K
Sommers	+	∇	□	△	○
Taconis <i>et al.</i>	■	▲	●		

By choosing a different way of determining C_V/C_L we tried to avoid a disturbance which can easily arise in experiments with ^3He - ^4He mixtures at temperatures below the lambda-point. In this case one has to reckon with the existence of heat currents in the mixture, because of heat leaks by film creep or heat conduction along the tubes which connect the apparatus with the outside of the cryostat. These heat currents give rise to a flow of normal fluid in the direction of the heat current, while the superfluid flows in the opposite direction. As the ^3He experiences frictional forces from the normal fluid only, it will move in the same direction as the heat current, yielding in most cases a decrease of the liquid concentration at the surface of the liquid. Calculating C_V/C_L , for example, in such cases from the measured vapour pressure and the known liquid concentration, too low values are obtained, as the vapour is in equilibrium with liquid of lower concentration than is supposed.

As has been shown by Beenakker, Taconis, Lynton, Dokoupil and Van Soest³⁾ in their experiments on the heat conductivity of ^3He - ^4He mixtures, the concentration gradient is proportional to the

heat current density. Therefore one has to reduce the heat leaks as far as possible: the precautions we have taken to ensure this are mentioned in section 2, describing the apparatus. In order to minimize the influence of the heat leaks yet remaining in spite of these precautions, a very thin layer of liquid with a large surface was used in our apparatus, decreasing in this way the difference in concentration between surface and interior of the liquid once more. Hence only about 15 mm^3 of liquid were condensed in a copper container with a bottom surface of 50 mm^2 , yielding a layer thickness of only 0.3 mm . Comparing this with the 3 mm *Sommers* used in his apparatus or with the 1 cm liquid height in the earlier *Leiden* experiment (where, however, stirring was applied), it is seen that we worked under much more favourable conditions concerning the influence of heat leaks.

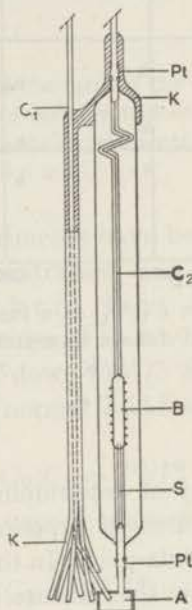


Fig. 2. The apparatus.

2. *Apparatus.* The apparatus is shown in fig. 2. Enclosed in a vacuum space is a glass vessel *B*, connected on one side with a glass capillary C_2 with a cross-section of 0.46 mm^2 and on the other end with a narrow slit *S*, called the "superleak". Around *B* a heating coil has been wound. The superleak consists of two gold wires of 3 cm length and 0.1 mm diameter, fused into a piece of soft glass. Because of the difference between the expansion coefficients of gold and glass an annular slit between the wires and the glass is formed when the apparatus is cooled down. In this way a slit width of about 0.2 micron is obtained at liquid helium temperatures.

The lower end of the superleak is connected with a copper vessel *A* (volume 454 mm^3) by sealing a platinum ring *Pt* into the soft glass and soldering it to

this container. The vessel A , in which the mixture under investigation is condensed, has been connected furthermore with a thin walled stainless steel capillary C_1 by means of a narrow copper tubing. C_1 leads to an oil manometer filled with Octoil-S, on which the vapour pressure difference between the liquid helium in A and the surrounding helium bath can be measured with a cathetometer. In the same way as A , C_2 has been connected with an oil manometer by means of a stainless steel capillary in order to measure the vapour pressure difference between the bath and the helium, condensed in B and C_2 .

Both stainless steel capillaries have been connected also with a Toepler pump system by which known amounts of gas can be condensed in the apparatus.

As long as the apparatus is immersed in the bath completely, the heat leaks are small, the stainless steel capillaries being thin walled and of small diameter. When the surface of the surrounding helium bath falls below the top of the apparatus during the experiment, radiation would increase to a disturbing amount, if no further precautions were taken. To prevent this the copper capillary between A and C_1 and the top of the vacuum space have been surrounded by some cotton cords K . The liquid helium film creeping along these cords will keep the whole apparatus at the desired temperature by evaporating at the top of the cotton. To ensure the latter the cotton has been covered nearly completely with a piece of oiled cloth, only the top being free.

3. *Method.* The ratio C_V/C_L of the mixture in A can be calculated if one knows the partial vapour pressures (which yield C_V) and the number of moles of ^3He in the known amount of liquid (which yield C_L). The partial vapour pressure and the liquid volume can be measured easily, whereas the number of moles of ^3He in the liquid is derived by means of a mass-balance calculation.

According to Sommers' ²⁾ dew-point measurements the following relation between the vapour concentration X_V and the vapour pressure holds:

$$X_V = (\Delta P/P) (1 + F(P, T)) \quad (3)$$

where ΔP is the difference between the vapour pressure of the sample, P , and the vapour pressure of pure ^4He , P_4^0 (which is identical with the bath pressure). If the liquid concentration is less than 0.5% this relation becomes

$$X_V = \Delta P/P \quad (4)$$

with an error less than 0.5%. Hence the molar ratio becomes

$$C_V = \Delta P/P_4^0 \quad (5)$$

By measuring the bath pressure and the pressure difference ΔP on the manometer connected with the vessel A and the bath, C_V is known immediately.

A prime requisite for the calculation of C_L with the aid of the mass-balance is the determination of the total number of moles of ^3He in the vessel A . After condensing a small amount of mixture in A and pure ^4He in B and C_2 until the liquid level becomes visible in the glass capillary, B is heated by means of the heating coil. The resulting fountain pressure draws liquid He II through the superleak S out of the vessel A , at least if the applied fountain pressure is larger than the osmotic pressure exerted by the mixture. Hence the concentration will increase and therefore ΔP also. If the applied fountain pressure is large enough one can draw away all liquid ^4He from A into B , with the exception of the helium film layer staying behind in A . Then all ^3He will be in the vapour phase and neglecting for the time being the influence of second virial coefficients, the total number of moles N_t^3 of it is given by

$$N_t^3 = \Delta P_{\max} V_t / RT \quad (6)$$

where ΔP_{\max} is the pressure difference observed on the oil manometer when A has been emptied, and V_t the total volume of the vessel A (454 mm^3). Perhaps some ^3He has been dissolved in the He II film, but as this amount is negligible compared with the total quantity of ^3He it can be omitted.

By measuring the rise of the liquid level in the capillary C_2 continuously during the emptying process of A , one can calculate the amount of liquid in A , V_L , at any instant as this amount follows immediately from the difference in height of the liquid level at the chosen moment and its final position when A has been emptied completely. This way of determining V_L makes it necessary to keep the temperature of B constant as otherwise evaporation or condensation will take place in C_2 , thereby affecting the height of the liquid level. This is achieved by observing the oil manometer connected with C_2 with a telescope and by regulating the heating current appropriately.

Now the vapour volume V_V in the vessel A is known too, it being the difference between the total and the liquid volume. Combining V_V with the vapour pressure ΔP which is also measured continuously during the emptying process of A , the number of moles of ^3He in the vapour yields

$$N_V^3 = \Delta P V_V / RT. \quad (7)$$

As the total number of moles of ^3He is known too, the mass balance gives

$$N_L^3 = N_t^3 - N_V^3 \quad (8)$$

and from this we obtain

$$C_L = N_L^3 / N_L^4 = (\Delta P_{\max} V_t - \Delta P V_V) / R T \varrho_4^0 V_L. \quad (9)$$

N_L^4 is calculated from

$$N_L^4 = V_L \varrho_4^0 \quad (10)$$

where ϱ_4 , the partial molar density of the ^4He in the liquid, has been put equal to the density of pure ^4He , neglecting the change in density due to the

³He. As C_V has been determined from ΔP directly (eq. (5)) we have finally

$$C_V/C_L = \Delta P R T \varrho_4^0 V_L / P_4^0 (\Delta P_{\max} V_t - \Delta P (V_t - V_L)). \quad (11)$$

Calculating the correction term for C_V/C_L , which is due to the influence of second virial coefficients (these have been neglected so far), we obtain the correction factor

$$\left(1 + \frac{B_m P}{RT}\right) \quad (12)$$

with $B_m = X_V B_{33} + (1 - X_V) B_{44}$, B_{33} and B_{44} being the second virial coefficients of pure ³He and ⁴He. The cross-term B_{34} has been put equal to $\frac{1}{2}(B_{33} + B_{44})$, as has been justified by experiment ⁴⁾ and theory ⁵⁾.

Hence we find as final relations:

$$C_L = \frac{\Delta P_{\max} V_t - \Delta P V_V}{R T \varrho_4^0 V_L} \cdot \frac{1}{1 + B_m P / RT} \quad (13)$$

and

$$\frac{C_V}{C_L} = \frac{\Delta P R T \varrho_4^0 V_L}{P_4^0 (\Delta P_{\max} V_t - \Delta P V_V)} \cdot \left(1 + \frac{B_m P}{RT}\right). \quad (14)$$

In our calculations we used the experimental values of Kistemaker and Keesom ⁶⁾ and of Keller ⁷⁾ ⁸⁾. The correction term $B_m P / RT$ varies between 0.3% at 1.2°K and 3.5% at 2°K.

4. *The measurements and the results.* After switching on the heating current the position of the liquid level in C_2 is measured every half a minute, whereas the vapour pressure ΔP is measured every minute. The results are plotted *versus* time and typical curves are given in fig. 3. From these curves a modified graph is made, containing liquid volume V_L , vapour pressure ΔP and the bath pressure as a function of time from which C_V/C_L and C_L are derived by means of eq. (13) and (14). Usually four points at regular time intervals are chosen for the calculations.

Two different difficulties can arise in this determination of C_V/C_L . In the first place the instants at which ΔP and the liquid level height reach their maximum value do not always coincide exactly, the liquid level reaching its final position a little bit later. This can be caused by the following fact: when the superleak is made by fusing the glass around the gold wires little holes between the glass and the wires remain at some places, as can be seen easily with the naked eye. As it has been shown in flow experiments with the same apparatus ⁹⁾ that the superleak is filled completely with liquid He II by capillary condensation ¹⁰⁾ and not only with a film layer, one has to assume that it is possible to draw liquid out of the holes in the superleak after A has been emptied, this causing the liquid level to reach its equilibrium posi-

tion a little bit later than ΔP . Therefore in the case of no coincidence of the two maxima we corrected the liquid volume *versus* time-curve by subtracting a constant volume in such a way as to get zero volume at the time ΔP reaches its maximum. When this was done the results calculated at the different instants agreed usually rather well with each other, taking into account the changes in bath temperature and concentration.

The other difficulty arose when only a very small quantity of liquid was condensed and the applied heating current was rather large. In this case the emptying process took place in too short a time, making the inaccuracy in the time determination too large. We had to discard these measurements as well as those obtained when the bath pressure had changed too rapidly.

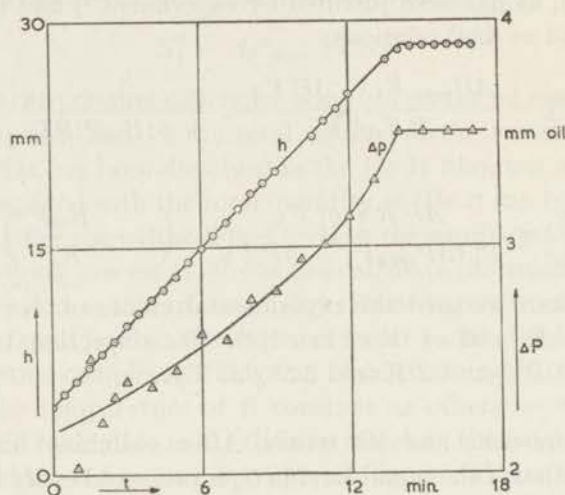


Fig. 3. The height h of the liquid level in the glass capillary C_2 and the vapour pressure difference ΔP as a function of time.

The measured quantities and the values of C_L , C_V/C_L and $\Delta P/X_L$ derived from them are given in table I. The function $\Delta P/X_L$ has been calculated because it is the best one to use when calculating liquid concentrations from vapour pressure measurements. The temperatures are given in the 1948-scale ¹¹). At temperatures above 1.4°K it is possible to compare our results with the values derived from *Sommer's* data. This has been done in fig. 4 where C_V/C_L has been plotted as a function of the liquid concentration X_L at constant temperature. As can be seen from the figure it is not difficult to draw a smooth curve through *Sommer's* and our points if one omits his results with the 0.58% mixture. Usually only one point of a run has been plotted in order to make the figure not too unintelligible; at the temperature of 1.7°K , however, we took three points calculated from the same run in order to show that the deviations between the different points are largely caused by changes in temperature, whereas the two points, drawn at the temper-

TABLE I

The distribution coefficient C_V/C_L											
T deg K	ΔP mm Hg	V_L mm ³	C_L %	C_V/C_L	$\Delta P/X_L$ mm Hg	T deg K	ΔP mm Hg	V_L mm ³	C_L %	C_V/C_L	$\Delta P/X_L$ mm Hg
1.2	1.055	4.02	1.70	103.3	62.0	1.475	0.181	9.15	0.140	40.6	129.3
1.2	1.133	3.04	1.815	104.0	62.5	1.480	0.194	7.15	0.155	38.4	125.2
1.2	1.223	2.08	1.918	106.3	63.8	1.474	0.211	5.20	0.165	40.6	128.0
1.2	1.318	1.21	1.931	113.3	68.2	1.462	0.228	3.50	0.170	44.9	134.0
1.2	1.450	0				1.468	0.270	0			
1.193	0.290	18.00	0.336	145.3	86.3	1.598	0.361	13.65	0.206	31.3	175.3
1.194	0.336	13.32	0.394	142.5	85.4	1.598	0.397	10.19	0.228	31.1	174.0
1.201	0.391	9.20	0.470	131.5	83.2	1.598	0.439	6.96	0.253	31.1	173.3
1.216	0.459	5.72	0.567	115.8	81.0	1.598	0.488	3.97	0.281	31.0	173.8
1.202	0.552	2.65	0.595	146.2	92.8	1.598	0.572	0			
1.182	0.634	0				1.680	0.230	8.95	0.108	27.2	213.0
1.207	0.149	10.13	0.134	168.8	111.2	1.677	0.241	7.40	0.110	28.3	219.0
1.258	0.161	7.68	0.163	101.6	98.8	1.691	0.253	5.77	0.122	25.4	208.4
1.256	0.175	5.25	0.194	98.0	90.2	1.707	0.267	4.17	0.130	23.5	205.4
1.253	0.193	2.88	0.247	86.9	78.2	1.709	0.278	3.10	0.133	23.8	210.0
1.241	0.234	0				1.712	0.311	0			
1.256	0.245	12.48	0.283	94.5	86.7	1.78	0.439	11.50	0.190	20.0	231.0
1.271	0.271	9.07	0.342	78.0	79.2	1.78	0.475	8.52	0.199	20.6	238.7
1.269	0.305	6.05	0.430	71.0	71.0	1.78	0.518	5.50	0.223	20.1	232.4
1.269	0.349	3.50	0.530	65.8	65.9	1.78	0.567	2.81	0.228	21.4	248.5
1.241	0.454	0				1.78	0.618	0			
1.322	0.847	14.97	0.755	81.5	112.1	2.01	0.521	7.34	0.210	10.4	248.7
1.328	0.954	11.53	0.928	71.9	102.8	2.01	0.557	5.25	0.246	9.5	226.4
1.333	1.078	8.55	1.039	70.8	103.9	2.01	0.599	3.22	0.286	8.8	209.5
1.309	1.223	5.36	1.151	83.0	106.3	2.01	0.647	1.26	0.238	11.3	272.0
1.340	1.398	2.76	1.433	63.3	97.5	2.01	0.675	0			
1.313	1.619	0									

ature of 1.598°K (which was perfectly stable during the whole measurement) show the observed concentration dependence. From these curves smoothed values of C_V/C_L as a function of temperature at constant concentration have been evaluated. The results are shown in fig. 5 and table II.

As previously no measurements had been performed at temperatures of 1.2–1.3°K, the larger part of our attention was given to this temperature region. In order to extrapolate these results to zero concentration without having at our disposal other measurements to combine them with, we calculated $(\partial \log C_V/C_L / \partial \Delta P)_{T=\text{const.}}$ in the limit of zero concentration at temperatures above 1.4°K. As this slope appeared to be independent of temperature we used the same value of this slope at lower temperatures in order to obtain C_V/C_L at zero concentration. The results of this procedure are given in fig. 5, from which it is clear that at these low temperatures our results are not any better than those of Sommers. Fortunately, however, the experi-

ments on the osmotic pressure at 1.2°K (see ch. II) yielded us the missing vapour pressure-liquid concentration relation at this temperature, from which C_V/C_L was derived in the way, given in ch. III. The curves and values, given in figs. 5 and 6 and in tables II and III, are obtained by combining

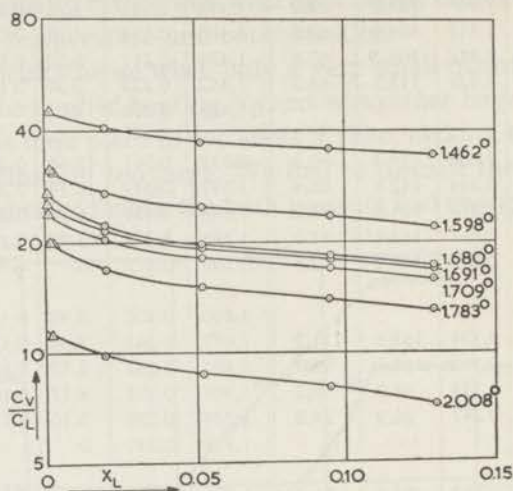


Fig. 4. The distribution coefficient C_V/C_L as a function of the liquid concentration X_L at constant temperature.

○: Sommers, △: Wansink.

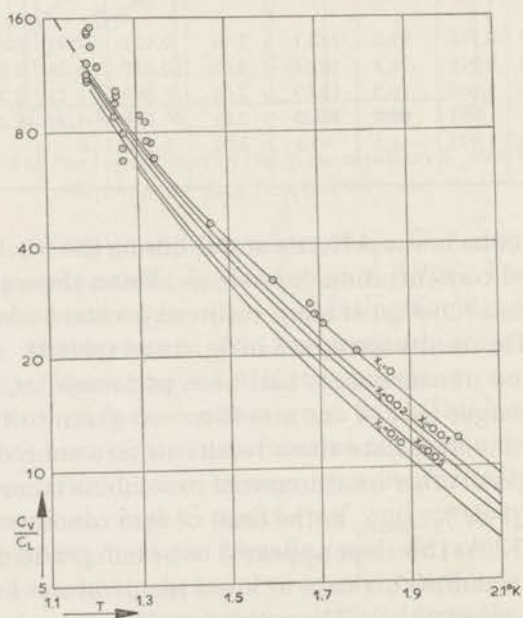


Fig. 5. The distribution coefficient C_V/C_L as a function of temperature at different liquid concentrations X_L .

○: C_V/C_L at zero concentration, obtained by extrapolation of the measured values.

TABLE II

Smoothed values of the distribution coefficient C_V/C_L					
$X_L \backslash T$ deg K	0%	1%	2%	5%	10%
1.2	114.0	111.8	109.9	104.8	
1.3	77.5	74.4	72.2	66.8	
1.4	55.3	51.8	49.3	46.2	44.1
1.5	40.8	38.4	36.0	33.4	31.5
1.6	31.7	29.2	27.2 ^b	24.9	23.0
1.7	24.8	22.6	20.9	18.8 ^b	17.3
1.8	19.5	17.5 ^b	16.2 ^b	14.6	13.3
1.9	15.4	13.7	12.7	11.4	10.4
2.0	12.1	10.7	9.9	9.0	8.1 ^a

these results with the directly measured values of C_V/C_L and $\Delta P/X_L$ at 1.4°K and higher.

The values of $\Delta P/X_L$ at 1.1°K have been obtained by extrapolation. Since obviously both $\Delta P/X_L$ and $\partial(\Delta P/X_L)/\partial T$ are zero at 0°K, the possibilities of drawing the $\Delta P/X_L$ versus T -curve are limited. Because of the relation:

$$(\Delta P/X_L)_{X_L=0} = P_4^0(C_V/C_L)_{X_L=0} \quad (15)$$

this extrapolation yields also the C_V/C_L versus T -curve at zero concentration at this lowest temperature (indicated by a dotted line in fig. 5).

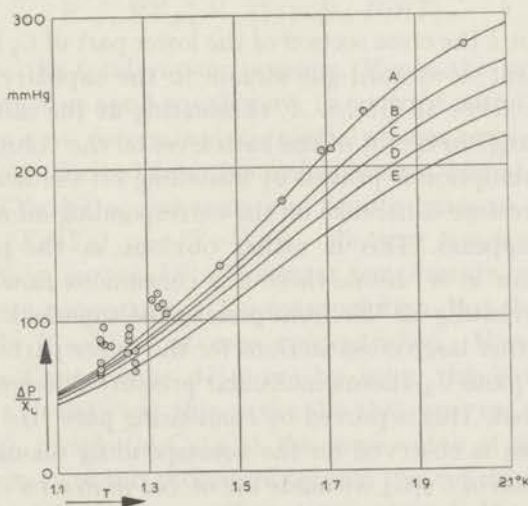


Fig. 6. The ratio $\Delta P/X_L$ as a function of temperature at constant values of ΔP .

○: experimental points at $\Delta P = 0$.

A: $\Delta P = 0$

C: $\Delta P = 2$ mm Hg

B: $\Delta P = 1$ mm Hg

D: $\Delta P = 4$ mm Hg

E: $\Delta P = 8$ mm Hg

TABLE III

Smoothed values of $\Delta P/X_L$					
ΔP mm Hg T deg K	0	1	2	4	8
1.1	54.7	53.0	51.7	49.0	46.0
1.2	74.1	69.4	67.6	64.5	58.8
1.3	94.0	90.0	87.1	82.7	75.0
1.4	119.6	112.8	108.8	102.8	93.6
1.5	147.7	137.3	132.0	125.2	115.0
1.6	178.5	165.3	158.0	148.3	136.3
1.7	210.0	193.3	182.8	171.3	157.3
1.8	238.0	218.5	205.8	192.5	177.6
1.9	260.7	238.0	223.5	209.8	195.0
2.0	279.3	255.5	240.5	225.0	209.7
2.1	294.0	270.5	255.5	239.2	219.8

5. *Discussion.* The following assumptions have been made in our way of determining C_V/C_L :

1) no ^3He leaves the volume A through the capillary C_1 nor does the change in height of the bath level affect the effective volume of A .

2) no ^3He passes through the superleak S .

3) no thermomolecular pressure difference exists along the tubes C_1 and C_2 .

4) the pressure difference ΔP is equal to the partial vapour pressure P_3 .

5) the liquid volume, entering the capillary C_2 is the same as the volume leaving A .

In view of point 1 the cross section of the lower part of C_1 has been chosen small; the constant downward gas stream in the capillary caused by the evaporating film keeps all ^3He in A , eliminating at the same time any influence of the change in height of the bath level on the volume of A .

The second assumption is proved by switching off the heating current in B : the vapour pressure difference on the corresponding oil manometer then immediately disappears. This is rather obvious as the pressure in B is always higher than in A : hence there is a continuous flow of normal fluid from B to A , preventing all ^3He from passing the superleak.

By choosing rather large cross sections for the upper parts of the stainless steel capillaries C_1 and C_2 , thermomolecular pressure differences along these tubes are prevented. This is proved by condensing pure ^4He in A and B : no pressure difference is observed on the corresponding oil manometers.

In our calculation of C_V/C_L we made use of S o m m e r s' relation

$$X_V = (\Delta P/P) (1 + F(P, T)) \quad (3)$$

by showing that the correction term $F(P, T)$ becomes negligible in the region under investigation. But as this function is derived from his experiments with mixtures of rather high concentration, it is not necessary that it

describes the behaviour of the vapour pressure in the right way in the low concentration region. Let us see what happens if the real relation should be of the form

$$P_3 = \Delta P (1 + \delta) \quad (16)$$

where δ is too large to be neglected. Because of the fact that ΔP does not change very much during the whole process of determining C_V/C_L we can assume that δ is a constant for each series of measurements. According to eq. (16) there should be a difference between the value of C_V/C_L , we calculated with the aid of eq. (14), and the real value of the distribution coefficient, calculated by using P_3 . Denoting the latter by $(C_V/C_L)_{P_3}$ and the value, derived from eq. (14) by $(C_V/C_L)_{\Delta P}$, we can derive the relation

$$(C_V/C_L)_{P_3} = (C_V/C_L)_{\Delta P} \cdot (1 - \delta \Delta P/P_4^0)^{-1} \quad (17)$$

by inserting in eq. (14) $\Delta P(1 + \delta)$ instead of ΔP and $P_4^0 - \delta \Delta P$ instead of P_4^0 .

On the other hand we can study the influence of eq. (16) on the distribution coefficient X_V/X_L , which can be calculated in the same way as C_V/C_L . It is easy to see that in the low concentration region the relation becomes

$$\begin{aligned} \left(\frac{X_V}{X_L}\right)_{P_3} &= \frac{P_3}{P} \left/ \frac{P_{3\max} V_t - P_3 V_V}{RT \varrho_4^0 V_L (1 + B_m P/RT)} \right. = \\ &= \frac{\Delta P}{P} \left/ \frac{\Delta P_{\max} V_t - \Delta P V_V}{RT \varrho_4^0 V_L (1 + B_m P/RT)} \right. = \left(\frac{X_V}{X_L}\right)_{\Delta P} \end{aligned} \quad (18)$$

where P denotes the total vapour pressure. Hence the ratio X_V/X_L is insensitive to whether or not δ equals zero, in contrast with C_V/C_L .

Since *Somers* determined the partial vapour pressure P_3 , the distribution coefficients, derived from his measurements have to be denoted by $(C_V/C_L)_{P_3}$ and $(X_V/X_L)_{P_3}$, whereas our results have to be indicated by $(C_V/C_L)_{\Delta P}$ and $(X_V/X_L)_{\Delta P} = (X_V/X_L)_{P_3}$. Plotting *Somers'* and our values of $(X_V/X_L)_{P_3}$ versus ΔP at constant temperature, we can determine $(X_V/X_L)_{P_3}$ at zero concentration by extrapolation. But the latter quantity obviously equals $(C_V/C_L)_{P_3}$ at zero concentration. Hence it is possible to draw the $(C_V/C_L)_{P_3}$ versus ΔP -curve by using this extrapolated value and *Somers'* data on this ratio. In this way we can compare our value of $(C_V/C_L)_{\Delta P}$ with $(C_V/C_L)_{P_3}$ at the same value of ΔP . As far as the inevitable inaccuracy of this procedure permits this conclusion, no difference between the two distribution coefficients was found. Hence assumption 4 ($\Delta P = P_3$) seems to be proved in this way also.

Coming to the last assumption we have to remark that the observed increase of the liquid volume in the glass capillary C_2 during a certain time interval, ΔV , does not correspond exactly to the amount of liquid which has

passed the superleak, since the entering liquid causes condensation of an adequate amount of vapour in this capillary. Hence the number of moles of ${}^4\text{He}$ which have passed the superleak is only $(\rho_4^0 - \rho_v^0) \Delta V$ instead of $\rho_4^0 \Delta V$, where ρ_4^0 and ρ_v^0 denote the molar densities of pure ${}^4\text{He}$ in the liquid and the vapour phase. On the other hand the arrival of this number of moles in the capillary demands a decrease of the liquid volume in A with $\Delta V'$, which obeys the relation

$$(\rho_4 - \rho_v) \Delta V' = (\rho_4^0 - \rho_v^0) \Delta V \quad (19)$$

because of the fact that an appropriate amount of vapour has to be formed in A . ρ_4 and ρ_v denote the partial molar densities of the ${}^4\text{He}$ in A . Since the concentration is very low, we can put $\rho_4 = \rho_4^0$, but as the capillary C_2 has a much higher temperature than the vessel A , we have $\rho_v^0 \neq \rho_v$. Calculating, however, the ratio $(\rho_4 - \rho_v)/(\rho_4^0 - \rho_v^0)$, one finds that it equals unity within the required accuracy, even if the temperature difference is very large (see table IV). Hence we are allowed to put $\Delta V = \Delta V'$ which means that the

TABLE IV

The ratio $(\rho_4 - \rho_v)/(\rho_4^0 - \rho_v^0)$, calculated in the case of a temperature difference, corresponding with a vapour pressure difference of 100 mm Octoil-S			
T (deg K)	1.20	1.46	2.01
$(\rho_4 - \rho_v)/(\rho_4^0 - \rho_v^0)$	1.002	1.0015	1.001

observed change in height in the capillary corresponds exactly to the change in liquid volume in A .

6. *Accuracy.* As can be seen in figure 3 the liquid volume can be determined rather accurately as there is no large scattering in the readings of the liquid level position in the glass capillary. The vapour pressure difference ΔP , on the other hand, is the main cause of the sometimes very large scattering in our results, as is obvious from fig. 3. The deviations of ΔP are mainly due to unobserved changes in the bath pressure; therefore, one has to expect that the scattering becomes larger with lower bath pressure owing to the increasing difficulty in controlling this pressure. This seems to be confirmed by the results (see table I). At 1.598°K the scattering is less than 1%, because of the perfect stability of the bath temperature in this case, whereas at other temperatures the scattering rises to the order of 10%, due either to emptying A too fast (1.47°K) or to lack of control and measurement of the bath pressure (*e.g.* 2.0°K). One has to conclude, however, that it is possible with this method to attain an accuracy of about 1%, if the bath pressure can be kept very constant. On the other hand it seems to be justifiable to put the overall accuracy of our results at 5%, after omitting the obviously wrong results.

7. *Theoretical computations.* We compared our experimental data with a number of theories, viz.:

- 1) the ideal solution (eq. (1)),
- 2) the theory of De Boer and Gorter¹²⁾, which yields eq. (2),
- 3) the classical regular solution-theory of Nanda¹³⁾,
- 4) the "modified Bose-Einstein theory" of Mikura¹⁴⁾.

In fig. 7 the different theoretical values and the experimental result at zero concentration have been drawn, with the exception of the Nanda-curve, which lies even higher than the curve of De Boer and Gorter.

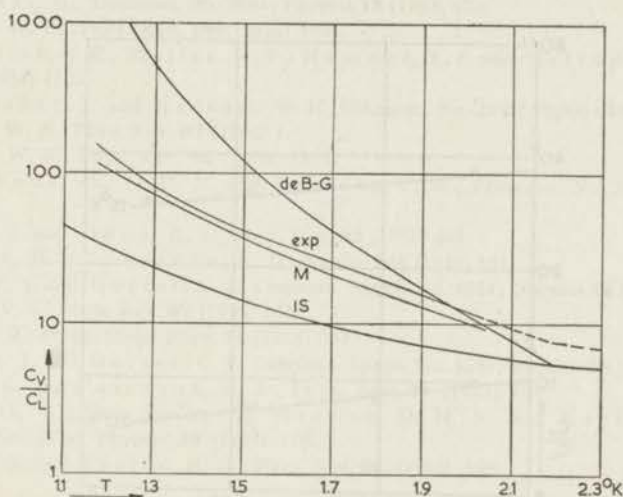


Fig. 7. The distribution ratio C_V/C_L at zero concentration as a function of temperature.

IS: ideal solution-theory.

M: "modified Bose-Einstein theory" of Mikura¹⁴⁾.

exp: experimental result.

de B-G: theory of De Boer and Gorter¹²⁾.

----: extrapolation according to De Boer and Gorter¹⁵⁾.

Mikura gives the best approximation, but his values are somewhat too low. At higher concentrations his results agree much better with experiment (see fig. 8), but this seems to be rather obvious taking into account his adaptations: Mikura introduces an energy gap Δ , equal to $\Delta_0 C_4^{0.4}$, where Δ_0 is the energy gap of pure ^4He and $C_4 = N_4 V_4 / (N_3 V_3 + N_4 V_4)$ with N and V denoting the number of moles and the molar volume in the liquid state of the two components. The exponent 0.4 has been chosen in such a way as to get the right dependence of the lambda-temperature on the concentration. His second adjustment consists of deriving the partial vapour pressure P_3 not from P_3^0 , but from the experimental values of P_3 at a certain liquid concentration (In our case we took the data of the 5.21% mixture of Sommers). Especially the latter adaptation makes his results perhaps rather trivial.

On the other hand one might conclude from fig. 8 that our values are perhaps too high because of a systematical error. This, however, is out of question, as it can be explained only by assuming that A is larger than the calibrated value, as this would give the required larger liquid concentration. But as our error in the calibration should be of the order of 20%, this possibility has to be discarded.

De Boer and Gorter¹⁵⁾ showed as a result of purely thermodynamic reasoning, not based on any particular model, that a discontinuity in the temperature derivative of the distribution ratio has to exist at the lambda-

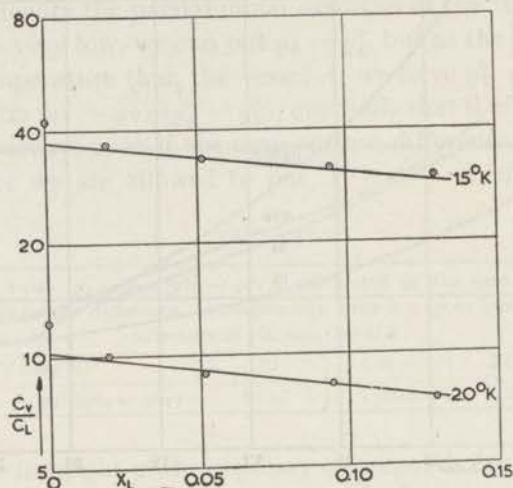


Fig. 8. The distribution coefficient C_V/C_L as a function of the liquid concentration X_L at constant temperature.

The drawn curve denotes Mikura's theoretical value, whereas the circles denote the experimental data of Sommers and the author.

point, if the lambda-transition is assumed to be of the second order. This discontinuity obeys the relation

$$\Delta(\partial \ln (C_V/C_L)/\partial T)_{X_L} = (\Delta C_p/RT^2) \cdot (dT_\lambda/dX_L) \quad (20)$$

where ΔC_p is the jump in the specific heat at the lambda-point and dT_λ/dX_L the change in lambda-temperature as a function of the liquid concentration. In the case of zero concentration $\Delta C_p \approx -4.8 R$, whereas $dT_\lambda/dX_L = -1.49$ deg, according to King and Fairbank¹⁶⁾, to Dokoupil, Van Soest, Wansink and Kapadnis¹⁷⁾ and to Dash and Taylor¹⁸⁾. With these values we find

$$\Delta(\partial \ln (C_V/C_L)/\partial T)_{X_L=0} = 1.5 \text{ deg}^{-1} \quad (21)$$

which yields, combined with the extrapolation of our C_V/C_L versus T -curve, that just above the lambda-point C_V/C_L decreases with increasing temper-

ature somewhat faster than the classical function P_3^0/P_4^0 . This has been indicated in fig. 7 by a dotted line.

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CHAPTER II

THE OSMOTIC PRESSURE OF ^3He — ^4He MIXTURES

Summary

The osmotic pressure of liquid ^3He — ^4He mixtures, condensed in a vessel connected by means of a narrow slit to a similar vessel containing pure ^4He , has been measured by determining the fountain pressure exerted by the pure ^4He , when heated, necessary to obtain equilibrium with the osmotic pressure of the mixture. The osmotic pressure meets Van 't Hoff's law within a few percent up to 4% concentration.

1. *Introduction.* The existence of a kind of osmotic pressure in liquid ^3He — ^4He mixtures at temperatures below the lambda-point was discovered first by Daunt, Probst and Johnston¹⁾ in 1948. Connecting two vessels containing liquid ^3He — ^4He mixtures of different concentration by means of a narrow slit, they observed a liquid level difference to exist between the two containers, the higher liquid level being at the higher concentration side. This osmotic pressure is not very surprising, since one can imagine that the slit acts as a semi-permeable membrane: the ^4He can pass the slit because of its superfluid properties, whereas the ^3He is not able to do so since it lacks superfluidity, as far as is known. It is clear (and it has been confirmed by experiment also²⁾) that at temperatures above the lambda-point no osmotic effect over a narrow slit should exist.

Taconis, Beenakker and Dokoupil³⁾ performed the first quantitative determination of the osmotic pressure. They found, when trying to measure the influence of ^3He on the fountain effect, that it is possible to obtain equilibrium between the osmotic pressure exerted by a mixture in a vessel at one side of a narrow slit, and the fountain pressure exerted by pure ^4He condensed in a vessel at the other end of the slit when it is heated. From these measurements they concluded that the osmotic pressure obeys the relation:

$$f\Delta T = RTX/M_4g \quad (1)$$

where f denotes the fountain constant, expressed in cm He/deg, M_4 the molar

weight of ^4He and g the gravitational acceleration. The concentration X is defined by:

$$X = N_3/(N_3 + N_4), \quad (2)$$

N_3 and N_4 denoting the number of moles of the two isotopes in the liquid. Comparing eq. (1) with Van 't Hoff's law, valid for ideal solutions at zero concentration,

$$\Delta P = RTX/M_4g \quad (3)$$

where the pressure difference with respect to the pure solvent vessel, ΔP , is expressed in cm He also, it is seen that even the osmotic pressure of ^3He - ^4He mixtures obeys this classical relation, when the fountain pressure $f\Delta T$ is identified with the pressure difference ΔP of the isothermal case.

Since this conclusion was based on one series of measurements only, performed at 1.38°K with liquid of about 0.1% ^3He and because the accuracy was rather poor, we extended the measurements of Taconis, Beenakker and Dokoupil to concentrations up to 4% in the temperature region from 1.2 to 1.9°K in order to verify whether the osmotic pressure obeys Van 't Hoff's law at higher concentrations also. Besides being interested in the osmotic pressure itself, we were compelled to measure it also for another reason. Inasmuch as we had the intention of studying the flow properties of ^3He - ^4He mixtures at temperatures below the lambda-point, a better knowledge of the osmotic pressure was indispensable, since one has to expect that it will influence the flow rate in the superfluid region just as the fountain pressure and the hydrostatic pressure influence the flow rate.

From eq. (3) it follows immediately that it is impossible to measure the osmotic pressure of a ^3He - ^4He mixture by balancing it with a hydrostatic pressure ΔP instead of with the fountain effect used. In the case of a 1% mixture the osmotic pressure already becomes of the order of 200-400 cm He, depending on the temperature. Although the necessary pressure can be created easily ^{2) 4)} it is difficult to create it without the introduction of temperature gradients in the mixture, from which intolerable concentration gradients result ⁵⁾ (see also section 2). In the second place the determination of the concentration by means of the vapour pressure becomes impossible and thirdly ^3He will flow to the pure ^4He -vessel as a result of the applied pressure, which eliminates the possibility of measuring the osmotic pressure with respect to pure ^4He . Hence the fountain pressure method is the only one possible.

2. *Apparatus.* The measurements have been performed with two apparatus which differ somewhat from each other in minor details. They are shown in fig. 1. The slit, acting as semi-permeable membrane, is made by fusing a gold wire of 0.1 mm diameter into soft glass. The difference between the dilatation coefficients of gold and glass causes a slit of the

order of 0.2 micron to be formed when this "superleak" *S* is cooled down to liquid helium temperatures. The superleak is connected with two containers *A* and *C*, which in turn are connected, by means of stainless steel tubes, with oil manometers filled with Octoil-S. With these manometers pressure differences with respect to the bath pressure can be measured. The container *C* can be warmed by means of a heating wire. In the case *1a* the vessel *C* therefore always has to be above the bath level, with its successor *1b* this is not necessary because of the vacuum jacket around *C*. The vessels of apparatus *1a* consist of copper, whereas in the case *1b* the vacuum jacket and *B* and *C* have been made of glass. This was an improvement over the apparatus shown in *1a*, for this allowed the liquid level in *C* to be observed, an impossibility in the case *1a*. All metal-glass connections were made by means of platinum-glass seals *Pt*.

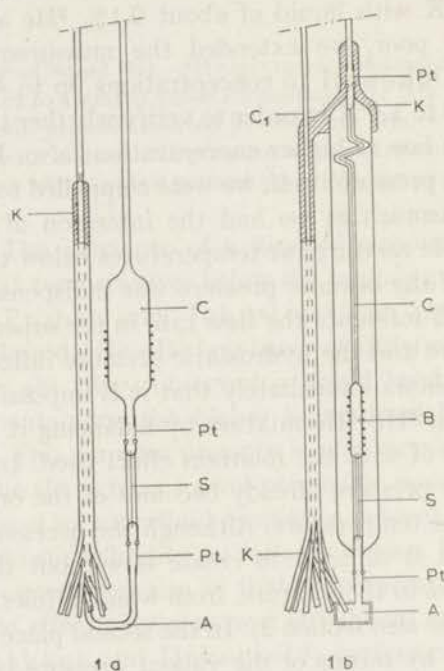


Fig. 1. The apparatus.

As is known from the measurements of Beenakker, Taconis, Lynton, Dokoupil and Van Soest⁵⁾ on the heat conductivity of ^3He - ^4He mixtures, heat leaks give rise to concentration gradients in liquid ^3He - ^4He mixtures at temperatures below the lambda-point. To reduce the heat leaks along the stainless steel tubes, cotton cords *K* have been wound around them. The He II film will creep along these cords and eliminate the heat leaks from above by its evaporation.

Apparatus *1a* was used originally for the indirect measurement of the

fountain effect by Van den Meijdenberg, Tacconis, Beenakker and Wansink⁶⁾, whereas the other apparatus was used also for the determination of the vapour-liquid phase equilibrium of ^3He - ^4He mixtures⁷⁾ and for experiments on the flow of pure ^4He and of ^3He - ^4He mixtures as a function of large fountain pressures²⁾.

3. *Method.* The measurement of the osmotic pressure is preceded by condensing a small amount of mixture in vessel *A*, this container being filled only partially, and by condensing pure ^4He in *C*. The fountain pressure necessary to compensate the osmotic pressure of the mixture in *A* is created by heating *C*; in order to allow calculation of this fountain pressure, it is necessary to have pure ^4He in *C*; if there were a mixture in *C*, it would be impossible to derive the temperature difference between *C* and the bath from the vapour pressure, and furthermore the fountain effect in the case of ^3He - ^4He mixtures is unknown.

Since it is difficult to choose the heating current in such a way that equilibrium between fountain pressure and osmotic pressure is obtained immediately, a flow of He II through the superleak will exist as long as there is no equilibrium between the two forces, the flow direction depending which force is the larger one. By switching off the heating current of *C* it was proved that only ^4He passes the superleak: if any ^3He had passed the slit, a vapour pressure difference with respect to the bath should remain after switching off the heating current, which is not observed in fact. Hence the conditions required for the calculation of the fountain pressure mentioned above are fulfilled during the whole experiment.

The equilibrium between the osmotic pressure and the fountain pressure is reached automatically. When the fountain pressure is chosen larger than the osmotic pressure, ^4He will flow from *A* to *C*, increasing in this way the ^3He -concentration in *A* and hence the osmotic pressure also. The total force across the superleak becomes gradually zero in this way and equilibrium between the two pressures will be reached after waiting a sufficient time, this time depending on the amount of liquid in *A*, on the initial difference between the two pressures and on the transport capacity of the slit.

The change in liquid concentration can be derived from the change of the vapour pressure in *A*: the attaining of the equilibrium is indicated by the vapour pressure of *A* becoming steady.

When using apparatus 1*b* we could also observe the liquid level of *C*: in the equilibrium state this level does not move. Hence this apparatus permitted a double control on whether equilibrium had been reached. As can be seen from the experimental results (see fig. 3) no systematic difference between the data obtained with the two different apparatus exists, indicating that the condition of constant pressure in *A* was a sufficient criterion for the equilibrium.

Once this equilibrium had been reached, the concentration in *A* was calculated from the vapour pressure difference ΔP_A observed on the corresponding oil manometer. The ratio between this excess pressure and the corresponding liquid concentration *X* is known from the measurements of the phase equilibrium of ^3He - ^4He mixtures ⁷⁾. The temperature difference between *C* and the bath is determined from the pressure difference ΔP_C , measured on the corresponding oil manometer. Using the entropy values derived by Kramers, Wasscher and Gorter ⁸⁾ from their measurements of the specific heat of pure ^4He , the temperature difference is transformed into the integrated value of the fountain pressure in dyne/cm², $\int \rho_4^0 S_4^0 dT$, assuming the validity of H. London's equation. S_4^0 and ρ_4^0 stand for the molar entropy and density of pure ^4He .

The fountain pressure $\int \rho_4^0 S_4^0 dT$ has to be corrected for the vapour pressure difference ΔP_C and for the height of the liquid column in *C*. A third small correction results from the fact that *A* is filled with liquid only partially. Hence there exists a free liquid surface at the lower end of the superleak (as is schematically indicated in fig. 2) which exerts a force on the liquid in *C* by means of its surface tension. Calculation of the equilibrium condition of this liquid surface reveals that the exerted surface tension is equal to the pressure exerted by a liquid column reaching from the liquid level in *A* to the liquid surface at the end of the superleak. Combining the influence of this surface and that of the liquid column in *C* we obtain a correction of the order of 5 cm He. The fountain pressure, corrected in this way and expressed in cm He, will be indicated hereafter by *ffdT*.

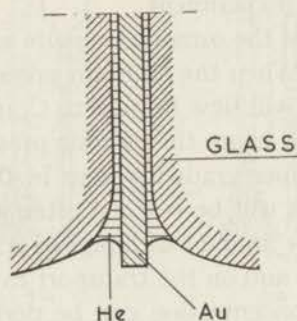


Fig. 2. The liquid surface at the lower end of the superleak.

When the measurement of the osmotic pressure at one equilibrium point had been performed, the heating current was increased. Hence the flow of He II through the superleak started again and equilibrium was reached when the concentration in *A* had increased sufficiently. In this way the larger part of the measurements was performed, the other part being measured in the opposite direction.

The temperature scale used is the 1948-scale ⁹⁾. Since recalculation of the

fountain pressure according to the 1955-scale¹⁰) yielded corrections of a few cm He only in the case of the largest fountain pressures applied, we did not convert the results to this new temperature scale.

4. *Derivation of the osmotic pressure equation.* In order to compare the results with the values of the osmotic pressure to be expected on theoretical grounds or from other experimental data, we shall first derive the equation for the osmotic pressure. Different ways of obtaining the required equation exist.

The first method is based partially on ordinary reversible thermodynamics. As has been pointed out before, the slit is most probably filled with pure ^4He , which implies that the temperature and concentration gradients are separated in space. If furthermore the supposedly very small diffusion of ^3He in the slit is neglected, the conditions for the applicability of reversible thermodynamics seem to be fulfilled. Hence one might be tempted to derive the osmotic pressure equation by putting equal the chemical potentials μ_4 of the ^4He in the two vessels at both sides of the slit. Although this procedure yields the required equation it is doubtful whether it is the correct way of deriving it, since the fact that no special assumptions have to be made, concerning *e.g.* the superfluid character of the ^4He , implies the obtained relation to be of general validity which means that the osmotic pressure of any solution could be compensated by means of a temperature difference. This derivation offers the same difficulties as the one of the fountain effect by means of reversible thermodynamics.

Since the temperature and concentration gradients are separated in space, we can avoid these difficulties by introducing a third, imaginary vessel I , situated somewhere in the lower part of the superleak and filled therefore with pure ^4He . Assuming this vessel to be at bath temperature, we are allowed to apply reversible thermodynamics to the isothermal system, consisting of the two vessels A and I , connected by a part of the superleak. The change of the chemical potential μ_4 of the ^4He -component in A , due to the addition of ^3He , amounts to:

$$\Delta\mu_4^A = RT \ln \{(1 - X) f_4\} \quad (4)$$

where the activity coefficient f_4 ¹¹) accounts for the deviation of the mixture from the ideal solution. In order to obtain equilibrium between A and I , we apply a "negative pressure" ΔP to I , yielding a change of the chemical potential μ_4^I , equal to:

$$\Delta\mu_4^I = V_4^0 \Delta P \quad (5)$$

with V_4^0 denoting the molar liquid volume of pure ^4He . From eqs. (4) and (5) we obtain as equilibrium condition for the system $A - I$:

$$RT \ln \{(1 - X) f_4\} = V_4^0 \Delta P \quad (6)$$

which is equal to Van 't Hoff's law in the case of ideal solution ($f_4 = 1$) and zero concentration.

Let us now consider the system $C - I$, filled with pure ^4He . When heating C from the bath temperature T_A to the temperature T_C , a fountain pressure across the superleak is created which can be compensated by the "negative pressure" ΔP , applied to I . Expressing the fountain constant f in cm He/deg, the equilibrium condition is given by:

$$V_4^0 \Delta P = - M_{4g} \int_{T_A}^{T_C} f dT. \quad (7)$$

Since I is in equilibrium with both A and C , A and C are also in mutual equilibrium. Hence the required equation for the osmotic pressure becomes:

$$\int f dT = - RT \ln \{(1 - X) f_4\} / M_{4g} \quad (8)$$

which stays valid when the volume of I is reduced to zero.

Because eq. (7) can be considered as a purely experimental result, it is not necessary to discuss the theoretical derivation of the fountain pressure. The same is the case with H. London's equation for the fountain effect,

$$M_{4g} \int f dT = \int S_4^0 dT - V_4^0 \Delta P_C. \quad (9)$$

For the present purpose of calculating the fountain pressure from the entropy values of Kramers, Wasscher and Gorter⁸⁾ it is sufficient to know that eq. (9) holds within the experimental accuracy without discussing whether the different derivations of this equation hold.

Instead of the semi-empirical equation (8) we can derive from the eqs. (4), (6), (7) and (9) the equivalent relation:

$$\Delta \mu_4^A = - \int S_4^0 dT + V_4^0 \Delta P_C \quad (10)$$

which will be used later.

Another derivation of the equation of the osmotic pressure is based on the equations of motion of the superfluid and was made first by Gorter^{12) 13)} in 1949, who assumed the normal fluid concentration to be the same on both sides of the slit. On this basis Van 't Hoff's law was found to be valid in the limit of zero concentration, but the validity of this derivation has become somewhat doubtful, since his rather plausible assumption concerning the normal fluid concentration - about which nothing was known at that moment - has not been confirmed by experiment.

Further attempts to derive the osmotic pressure law from the equation of motion of the superfluid have been made by Mazur¹⁴⁾, by Koide and Usui¹⁵⁾ and by Mikura¹⁶⁾. On the basis of irreversible thermodynamics they derived an equation of motion of the superfluid which can be written

in the stationary state as:

$$-x(\partial S_4/\partial x) \text{ grad } T + (M_4/M) V \text{ grad } P = \\ = \{X/(1-X)\} \{(\partial \mu_3/\partial X)_{P,T,x} \text{ grad } X + (\partial \mu_3/\partial x)_{P,T,X} \text{ grad } x\} \quad (11)$$

whereas we can transform eq. (10) with the aid of the Gibbs-Duhem relation:

$$X(\partial \mu_3/\partial X)_{P,T} + (1-X)(\partial \mu_4/\partial X)_{P,T} = 0 \quad (12)$$

into:

$$-x^0(\partial S_4^0/\partial x) dT + V_4^0 dP = \{X/(1-X)\} (\partial \mu_3/\partial X)_{P,T} dX \quad (13)$$

under the assumption that Gorter's relation $S_4^0 = x^0 \partial S_4^0/\partial x$ ¹² holds. In these equations x stands for the normal fluid fraction of the ⁴He, S_4 for the partial molar entropy of ⁴He and M and V for the mean molar weight and volume of the mixture.

Some differences between the two equations (11) and (13) exist, which are mainly due to the fact that in the case of eq. (11) it is supposed that the concentration and the temperature gradient occur at the same place, whereas this was excluded explicitly in the derivation of eq. (13). Furthermore, as a result of the two-fluid model used, the chemical potential μ_3 in eq. (11), besides depending on the temperature, depends also on both the ³He-concentration X and the normal fluid concentration x , whereas the two-fluid concept was not necessary for the derivation of eq. (13). At low concentrations, however, the differences between the two equations disappear, especially if one assumes the concentration and the temperature gradient to be separated in space, since then both the left and the right hand members of eqs. (11) and (13) become identical.

Concerning the derivation of eq. (11) it has to be remarked that, according to Mazur¹⁴, the introduction of the quantity $x \partial S_4/\partial x$ is allowed only when it is supposed that the ³He is dissolved in the normal fluid fraction only. Mikura¹⁶, on the other hand, does not mention this condition explicitly. Furthermore, he replaces $x \partial S_4/\partial x$ by S_4 , assuming that Gorter's relation also holds in the case of dilute mixtures. Under these assumptions Mikura's result can be written formally as:

$$(1-\gamma)f dT = -(RT/M_4g)(1-\delta) \text{ grad } X \quad (14)$$

or

$$f dT = -(RT/M_4g) \{1 + (\gamma - \delta)/(1 - \gamma)\} \text{ grad } X \quad (15)$$

and is the analogue of eq. (8) which can be written as:

$$f f dT = -(RT/M_4g) \{1 + \ln f_4/\ln(1-X)\} \ln(1-X). \quad (8')$$

From eqs. (8') and (15) one sees that the relative deviation of the osmotic pressure from the ideal solution value is given by:

1) $(\gamma - \delta)/(1 - \gamma)$ in the case of the derivation with irreversible thermodynamics with concentration and temperature gradient occurring at the same place,

2) $-\delta$ in the case of the derivation with irreversible thermodynamics with the temperature gradient existing in pure ^4He only ($\gamma = 0$),

3) $\ln f_4/\ln(1 - X)$ in the case of the semi-empirical derivation.

The deviation terms $(\gamma - \delta)/(1 - \gamma)$ and $-\delta$ can be calculated from Mikura's theory, whereas $\ln f_4/\ln(1 - X)$ can be calculated for any given Gibbs-function or derived directly from the vapour pressure of the mixture*), yielding in this way a possibility of comparison with other experimental data.

5. *The experimental results in comparison with the vapour pressure.* The experimental results are given in table I and fig. 3, where the corrected fountain pressure $\int f dT$, divided by the bath temperature T , is plotted versus the liquid concentration X . The observed osmotic pressure shows only small deviations from the ideal solution value of the osmotic pressure, which is rather striking in view of the large deviations from ideality of the distribution coefficient C_V/C_L ⁷). However, calculation of the activity coefficient f_4 from the vapour pressure at 1.6 and 1.9°K and application of it to eq. (8) yields an osmotic pressure which is in perfect accordance with experiment, as can be seen in fig. 3, A and B.

With respect to the results in the temperature region of 1.2°K it has to be remarked that no exactly known values of the vapour pressure were available at this temperature. Hence the calculation of the concentration X from the vapour pressure contained a large error and at the same time it became impossible to calculate the activity coefficient f_4 exactly from the vapour pressure. This difficulty has been overcome in the following way.

Although the vapour pressure was only approximately known, it still permitted the conclusion that the activity coefficient f_4 did not exceed unity by more than half a percent up to concentrations of 5%. On this basis a first approximation of the osmotic pressure as a function of the liquid concentration could be calculated with the aid of eq. (8). Since the measurement of the osmotic pressure gave us the relation between vapour pressure and osmotic pressure of the mixture at this temperature the above mentioned first approximation of the osmotic pressure allowed us to construct the vapour pressure - liquid concentration relation at 1.2°K. Having done this, we recalculated f_4 and the concentrations of the experimental points from the new vapour pressure curve, obtaining in this way the results, given in fig. 3, C. This vapour pressure - liquid concentration relation has been given in chapter I, table III.

*) The calculation of the activity coefficient f_4 and other connected quantities will be dealt with in chapter III ¹⁷).

TABLE I

Observed values of the osmotic pressure						
date	T deg K	ΔP_A mm Hg	ΔP_C mm Hg	$\int S^0_4 dT$ J/g	X %	$\int f dT/T$ cm He/deg
5-11-53	1.226	0.467	1.46	16.72	0.616	124
	1.236	1.227	3.20	36.50	1.617	273
	1.239	0.191	1.07	12.23	0.241	87
	1.214	0.542	2.00	22.81	0.742	173
	1.226	0.540	2.00	22.80	0.714	171
	1.237	0.751	2.67	30.35	0.978	226
	1.234	0.960	3.33	38.03	1.271	286
	1.220	1.179	3.93	45.06	1.622	353
	1.220	2.420	7.67	89.01	3.440	683
	1.220	2.670	8.87	103.47	3.840	795
10-11-53	1.222	1.600	5.33	61.34	2.247	463
	1.222	1.933	6.67	77.09	2.690	584
10-11-53	1.629	0.248	0.02	0.05	0.135	12
	1.629	0.684	1.33	15.72	0.384	89
	1.636	1.358	2.67	31.72	0.790	196
	1.617	2.100	4.07	48.24	1.293	279
	1.630	2.767	5.33	63.60	1.720	363
18-2-54	1.238	0.413	1.33	15.29	0.527	112
	1.194	0.852	2.77	31.62	1.240	245
25-2-54	1.218	0.760	2.67	30.37	1.031	230
	1.195	0.829	3.26	37.20	1.199	292
	1.181	0.858	3.36	38.32	1.289	300
	1.172	0.895	3.40	38.79	1.366	306
	1.175	0.980	3.60	41.15	1.500	325
	1.181	1.032	3.53	40.32	1.565	317
19-3-54	1.214	1.212	4.20	48.20	1.692	368
25-3-54	1.248	0.334	1.57	17.98	0.415	131
	1.246	0.386	1.47	16.76	0.482	122
	1.253	0.402	1.23	14.11	0.495	102
	1.248	0.428	1.33	14.97	0.531	110
13-4-54	1.230	0.596	2.00	22.80	0.780	170
	1.239	0.476	1.47	16.90	0.607	135
6-5-54	1.232	0.229	1.00	11.51	0.296	84
15-7-54	1.239	2.255	6.66	77.00	3.02	580
	1.239	2.970	9.94	116.20	4.08	876
	1.239	2.990	10.00	116.90	4.12	882
	1.239	2.905	9.34	110.20	4.00	828
	1.239	2.763	8.67	101.00	3.80	756
	1.239	2.555	8.07	93.80	3.52	708
	1.239	2.370	7.37	85.80	3.21	644
	1.239	2.770	8.74	101.90	3.80	760
15-7-54	1.494	3.505	7.40	87.35	2.79	548
21-10-54	1.512	1.160	2.53	34.60	0.833	215
21-10-54	1.668	1.540	2.93	34.75	0.860	194
4-11-54	1.476	1.560	3.40	39.60	1.218	247
4-11-54	1.658	2.050	3.80	45.35	1.190	255
4-11-54	1.841	2.600	3.93	50.25	1.250	256

All measurements have been performed with apparatus 1b, except those at 5-11-53 and 10-11-53, where 1a has been employed.

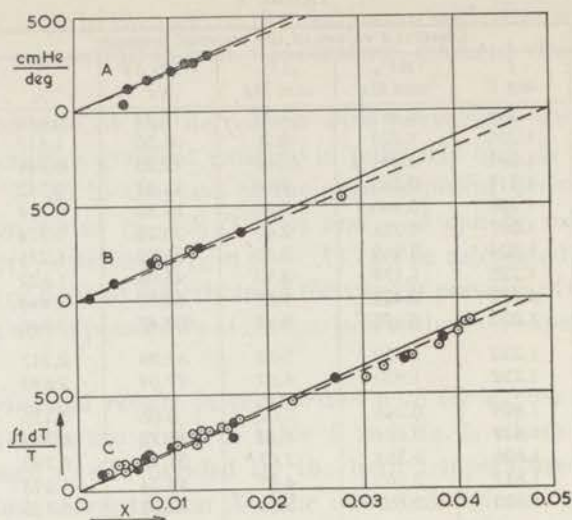


Fig. 3. The corrected fountain pressure $\int f dT$, divided by the bath temperature T , as a function of the liquid concentration X .

- : results, obtained with apparatus 1a. A: $T > 1.8^\circ\text{K}$
- : results, obtained with apparatus 1b. B: $1.4^\circ\text{K} < T < 1.7^\circ\text{K}$
- : ideal solution value. C: $T < 1.3^\circ\text{K}$
- - - : osmotic pressure, calculated according to eq. (8) with the activity coefficient f_4 as determined from the vapour pressure¹⁷⁾.

6. *Comparison with theory.* In order to compare the experimental data with different theories, we calculated the ratio $\ln f_4/\ln(1-X)$ from our results, from the original version of Mikura's theory¹⁶⁾ and from the later modification of his Bose-Einstein model¹⁸⁾ adapted in such a way as to get the right shift of the lambda-point temperature with ^3He -concentration. Furthermore we calculated for both versions the deviation term $-\delta$, whereas the term $(\gamma - \delta)/(1 - \gamma)$ has been calculated for the original version only. The results are given in table II. Only if one assumes $\gamma = 0$, *i.e.* that the temperature gradient exists only in pure ^4He , agreement between Mikura's theories and experiment is found, his original version yielding the closest agreement. The differences between the deviation terms $\ln f_4/\ln(1-X)$ and $-\delta$, calculated both from Mikura's theory are not important. Only in the case of the 5% mixture in his original version this is not the case. Although the reason for this deviation is not clear, it might be connected with the fact that the term $\ln f_4/\ln(1-X)$ has been calculated from the chemical potential μ_4 directly, whereas $-\delta$ is obtained by Mikura himself after a much more complicated calculation, involving his assumption $S_4 = x \partial S_4/\partial x$ and neglecting some terms.

Calculation of $\ln f_4/\ln(1-X)$ from the Gibbs-function as proposed by De Boer and Gorter¹⁹⁾ reveals that the osmotic pressure of a 1% mixture

would be only three quarters of the observed value, whereas the Gibbs-function, quadratic in T , as proposed by De Boer²⁰⁾ yields an osmotic pressure, which is a few times too large.

TABLE II

The relative deviation of the osmotic pressure from the ideal-solution value							
X	T	exper.	Mikura ref. 16)			Mikura ref. 18)	
		$\frac{\ln f_4}{\ln(1-X)}$	$\frac{\ln f_4}{\ln(1-X)}$	$-\delta$	$\frac{\gamma-\delta}{1-\gamma}$	$\frac{\ln f_4}{\ln(1-X)}$	$-\delta$
%	deg K	%	%	%	%	%	%
2	1.3	-2.8	-2.0	-2	-0.3	-1.7	-2
	1.5	-5.0	-2.2	-3	-1.0	-1.8	-2
	1.7	-6.2	-2.5	-4	-2.4	-1.8	-2
	1.9	-6.4	-2.7	-4	-3.0	-1.9	-2
5	1.3	-5.7	-3.2	-6	-0.3	-4.9	-4
	1.5	-7.9	-4.2	-7	-1.4	-5.1	-5
	1.7	-8.6	-5.4	-9	-4.9	-5.5	-5
	1.9	-7.7	-6.6	-11	-7.0	-6.2	-6

Appendix. A remark has to be made on the equilibrium condition used in the experiment. Equilibrium between the fountain pressure and the osmotic pressure was assumed to exist when the total transport through the slit was zero. Now one might suppose, for instance, that equilibrium exists when the velocity of the superfluid in the slit is zero. The influence of the choice of the equilibrium condition can be discussed on the basis of the equations of motion for the normal and the superfluid, given by Gorter and Mellink²¹⁾ and also by Mazur¹⁴⁾. In the case of a mixture they become:

$$0 = -\text{grad } P + \rho_4^0 S_4^0 (1 - \gamma) \text{grad } T + \text{grad } P_{\text{osm}} - A \rho^2 x' (\mathbf{v}_s - \mathbf{v}_n)^m \quad (16)$$

$$0 = -\text{grad } P + \eta_n \Delta \mathbf{v}_n \quad (17)$$

where the term $(1 - \gamma)$ accounts for possible deviations of the fountain force from the pure ^4He -value, where ρ stands for the molar density of the mixture and where x' denotes the normal fluid fraction, the word "normal" bearing upon the combination of ^3He -particles and of the normal fluid of the ^4He . The velocities of the normal and the superfluid are denoted by \mathbf{v}_n and \mathbf{v}_s resp. and the normal fluid viscosity by η_n . The last term of eq. (16) is the Gorter-Mellink mutual friction between the normal fluid and the superfluid.

From eq. (16) it is obvious that equilibrium between the hydrostatic, the fountain and the osmotic pressures requires the relative velocity $\mathbf{v}_r = \mathbf{v}_s - \mathbf{v}_n$ to be zero, whereas we used as equilibrium condition that the total transport $\mathbf{v} = x' \mathbf{v}_n + (1 - x') \mathbf{v}_s$ was zero. Since the pressure difference across the slit is small and the slit is very narrow, negligibly small values of \mathbf{v}_n must be expected. Hence the mutual friction term will be negligible

also in the case of equilibrium, independent of the choice whether \mathbf{v} , \mathbf{v}_T or \mathbf{v}_s should be zero at equilibrium, making the experimental results nearly insensitive to this choice also.

However, if the assumption of Klemens²²⁾ were true that the normal fluid of the He II in the slit adjust its velocity to that of the phonons in the wall of the slit, the choice of the equilibrium condition becomes important. According to his theory, the normal fluid velocity should be increased by a temperature gradient, this increase obeying the relation:

$$\mathbf{v}_n = -cl/T \cdot \text{grad } T \quad (18)$$

where c is the velocity of sound in the material of the wall and l the mean free path of the phonons in the wall. When the total transport is zero, we find for the superfluid velocity:

$$\mathbf{v}_s = -x'\mathbf{v}_n/(1-x') = \{clx'/T(1-x')\} \text{grad } T. \quad (19)$$

Inserting eqs. (18) and (19) into eq. (16), integrating along the slit length L and putting $\gamma = 0$, we obtain as equation for the osmotic pressure in cm He:

$$P_{\text{osm}} = \int f dT - \int_0^L (A \varrho^2 x' / M_4 g \varrho_4^0) \left(\frac{cl}{T(1-x')} \text{grad } T \right)^m dz. \quad (20)$$

In order to calculate the influence of the last term of this equation we used for glass the value of cl , given by Klemens²²⁾; for the gold wire we calculated this product from the lattice heat conductivity which is equal to $\frac{1}{3}clC$ with C denoting the specific heat per cm^3 , using constants from De Nobel and Gerritsen²³⁾. In the case of a 4.12% mixture at a bath temperature of 1.239°K where the equilibrium fountain pressure $\int f dT$ was observed to be 1093 cm He, the last term of eq. (20) appears to be of the order of 10^7 cm He. Both the sign and the magnitude of the osmotic pressure calculated in this way are without sense, as can be proved furthermore from the behaviour of the flow of a mixture under isothermal conditions²⁾. In this case only hydrostatic and osmotic pressure govern the flow: if the theory of Klemens were true, a hydrostatic pressure of 10^7 cm He at the pure ^4He -side of the slit would be necessary in order to prevent the liquid from leaving the mixture vessel, whereas in reality a pressure applied to the mixture is necessary in order to prevent inflow of ^4He into the mixture vessel. Hence we can conclude that the experimental results are in full contradiction with the theory of Klemens. A somewhat less pronounced disproof of this theory was recently given by Broese van Groenou, Poll, Delsing and Gorter²⁴⁾.

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CHAPTER III

CALCULATION OF THERMODYNAMIC QUANTITIES OF ^3He — ^4He MIXTURES FROM THE VAPOUR PRESSURE

Summary

From the vapour pressure of ^3He — ^4He mixtures the change of the Gibbs-function of the mixture with concentration has been calculated in the temperature region between 1.2 and 1.9°K at concentrations up to 7% ^3He . The entropy, enthalpy and specific heat of mixing are given in comparison with experimental data. The phase separation at low temperatures and the mechanocaloric effect of ^3He — ^4He mixtures are calculated.

1. *Introduction.* If Q_m denotes some arbitrary mean molar thermodynamic quantity and X the molar fraction ^3He of a ^3He — ^4He mixture, the partial molar quantities Q_3 and Q_4 are defined by:

$$Q_3 = Q_m + (1 - X) \partial Q_m / \partial X \quad (1)$$

$$Q_4 = Q_m - X \partial Q_m / \partial X \quad (2)$$

from which we obtain:

$$Q_m = XQ_3 + (1 - X)Q_4. \quad (3)$$

On the other hand we can introduce the quantity of mixing ΔQ , defined by:

$$Q_m = XQ_3^0 + (1 - X)Q_4^0 + \Delta Q \quad (4)$$

where Q_3^0 and Q_4^0 denote the molar quantities of the pure components. From eqs. (1), (2) and (4) we find for the partial quantities of mixing, ΔQ_3 and ΔQ_4 , with $\Delta Q_3 = Q_3 - Q_3^0$:

$$\Delta Q_3 = \Delta Q + (1 - X) \partial \Delta Q / \partial X \quad (5)$$

$$\Delta Q_4 = \Delta Q - X \partial \Delta Q / \partial X \quad (6)$$

$$\Delta Q = X \Delta Q_3 + (1 - X) \Delta Q_4. \quad (7)$$

Differentiation with respect to X of eqs. (1) and (2) yields:

$$(1 - X) \partial Q_4 / \partial X + X \partial Q_3 / \partial X = 0. \quad (8)$$

All thermodynamic quantities used in this chapter are defined according to this scheme.

2. *Calculation of the chemical potentials.* Since all thermodynamic quantities can be derived from the chemical potential μ , it is sufficient for the calculation of all quantities ΔQ to know $\Delta\mu_3$ and $\Delta\mu_4$ as a function of temperature and concentration. These mixing potentials can be calculated from the vapour pressure of the mixture, since the mixing potentials of any component in the liquid and the vapour phase are the same and the latter are well known functions of the vapour pressure. For ideal gases we have:

$$\Delta\mu_4 = RT \ln (P_4/P_4^0) \quad (9)$$

which transforms in the case of non-ideal gases into:

$$\Delta\mu_4 = RT \ln (P_4^*/P_4^{0*}) \quad (10)$$

where the fugacities P_4^{*1} are related to the partial pressure P_4 and the total pressure P by:

$$\ln P_4^* = \ln P_4 + B_{44}P/RT \quad (11)$$

$$\ln P_4^{0*} = \ln P_4^0 + B_{44}P_4^0/RT \quad (12)$$

with B_{44} denoting the second virial coefficient of pure ^4He . The partial pressure P_4 is defined by:

$$P_4 = (1 - X_V) P \quad (13)$$

where X_V stands for the vapour concentration. When deriving eq. (11) it has been assumed that $B_m = X_V^2 B_{33} + 2X_V(1 - X_V) B_{34} + (1 - X_V)^2 B_{44}$ can be replaced by $B_m = X_V B_{33} + (1 - X_V) B_{44}$, which implies $2B_{34} = B_{33} + B_{44}$. The latter equality is met within one percent error according to the theoretical calculations of Kilpatrick, Keller, Hammel and Metropolis²⁾. Hence we can calculate $\Delta\mu_3$ and $\Delta\mu_4$ from the two equations:

$$\Delta\mu_3/RT = \ln (P_3/P_3^0) + B_{33}(P - P_3^0)/RT \quad (14)$$

$$\Delta\mu_4/RT = \ln (P_4/P_4^0) + B_{44}(P - P_4^0)/RT \quad (15)$$

supposed that B_{33} , B_{44} , the total pressure and the vapour concentration are known. Because Sommers³⁾ measured both the vapour pressure and concentration as a function of liquid concentration and temperature the calculation of $\Delta\mu_3$ and $\Delta\mu_4$ from his data is possible in principle. Actually, however, this is not the case since the accuracy in the determination of the vapour concentration does not meet the requirements for this calculation:

at higher concentrations and lower temperatures X_V becomes of the order of unity: hence the error in X_V implies an error in P_4 an order of magnitude larger. Furthermore, according to eq. (15) $\Delta\mu_4$ is determined largely by $\ln(P_4/P_4^0) = (P_4 - P_4^0)/P_4^0 - \dots$ and because P_4 and P_4^0 differ only slightly, the error in $\Delta\mu_4$ becomes an order of magnitude larger than that in P_4 . From this argument it is clear that an extremely accurate determination of the vapour concentration is required in order to obtain a reasonably accurate value of $\Delta\mu_4$. Calculating, for instance, the partial fugacities from Sommers' smoothed data, one finds that they do not meet at all the Duhem-Margules relation:

$$(1 - X) \partial \ln P_4^*/\partial X + X \partial \ln P_3^*/\partial X = 0^* \quad (16)$$

which is equivalent to the Gibbs-Duhem relation:

$$(1 - X) \partial \mu_4/\partial X + X \partial \mu_3/\partial X = 0 \quad (17)$$

both being a special form of the general formula (8).

The lack of accuracy of Sommers' data caused us to follow another procedure in calculating the chemical potentials from the vapour pressure. In general we can write for the mixing potential of the liquid:

$$\Delta\mu_3 = RT \ln (X f_3) \quad (18)$$

$$\Delta\mu_4 = RT \ln \{(1 - X) f_4\} \quad (19)$$

where the activity coefficients f_3 and f_4 ¹) account for the deviations of the mixture from the ideal solution. Hence the determination of the activity coefficients is the crucial part of the whole calculation because they are responsible for all deviations from ideality as, for instance, the heat of mixing.

The calculation of f_3 and f_4 was performed in the following way. In zero approximation f_4 is assumed to be equal to unity, yielding $\Delta\mu_4 = RT \ln(1 - X)$. Inserting this value into eq. (15), the partial vapour pressure P_4 is obtained in first approximation, if the total pressure P is known. From P and P_4 the first approximation of P_3 is obtained, insertion of which into eq. (14) yields the same approximation of $\Delta\mu_3$. Eq. (18) then gives the first approximation of f_3 . Now the Gibbs-Duhem relation (17) can be transformed into:

$$(1 - X) \partial \ln f_4/\partial X + X \partial \ln f_3/\partial X = 0 \quad (20)$$

from which we obtain:

$$\ln f_4 = - \int_0^X \{X/(1 - X)\} d \ln f_3. \quad (21)$$

By graphical integration of the curve $\ln f_3$ versus $X/(1 - X)$ the first approximation of $\ln f_4$ is obtained. Once this first approximation is cal-

*) The liquid concentration is indicated by X : only when confusion with the vapour concentration X_V might occur is the symbol X_L used.

culated, the whole procedure using eqs. (19), (15), (14), (18) and (21) is repeated. Since the first and second order approximation of $\ln f_3$ differ only slightly the same is the case with the two approximations of $\ln f_4$. Hence it was sufficient to perform the calculation of the activity coefficients only twice.

The vapour pressure data used in the high temperature region were obtained from the measurements of Sommers³⁾ and of ourselves, given in ch. I⁴⁾ and concerning the phase equilibrium of ^3He - ^4He mixtures. Because these measurements lacked the required accuracy at low temperatures, we used in this temperature region the vapour pressure as calculated from the osmotic pressure of ^3He - ^4He mixtures at 1.2°K⁵⁾. The second virial coefficients used were those calculated by Kilpatrick, Keller and Hammel⁶⁾.

The values of $\ln f_4$ and $\ln f_3$ obtained in this way are given in table I as a function of temperature and concentration. In fig. 1 $\ln f_3$ is shown as a function of $X/(1 - X)$ at different temperatures.

TABLE I

		The activity coefficients f_3 and f_4									
T deg K	X %	$\ln f_3$					$10^3 \ln f_4$				
		0	1.0	2.5	5.0	7.1 ³	0	1.0	2.5	5.0	7.1 ³
1.2		1.33	1.31	1.29	1.25	1.22	0	0.06	0.46	1.93	4.06
1.3		1.27	1.23	1.19	1.14	1.11	0	0.18	0.83	2.82	5.29
1.4		1.21	1.16	1.11	1.05	1.01	0	0.27	1.14	3.57	6.25
1.5		1.16	1.08	1.03	0.96	0.91	0	0.36	1.38	4.04	6.89
1.6		1.10	1.01	0.95	0.87	0.83	0	0.42	1.57	4.32	7.24
1.7		1.04	0.93	0.86	0.78	0.74	0	0.47	1.68	4.39	7.19
1.8		0.96	0.84	0.76	0.70	0.66	0	0.51	1.73	4.24	6.60
1.9		0.86	0.74	0.66	0.60	0.56	0	0.52	1.72	3.97	6.00

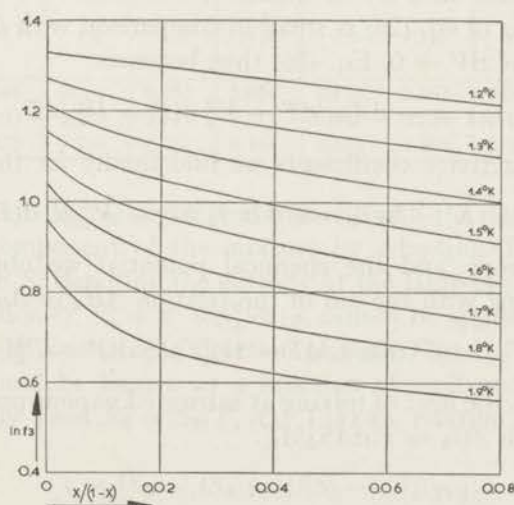


Fig. 1. The activity coefficient f_3 as a function of $X/(1 - X)$ at different temperatures.

3. *The derivation of the different thermodynamic quantities.* Once $\ln f_3$ and $\ln f_4$ are known we can calculate various thermodynamic quantities such as entropy of mixing. In general one has for the change of the chemical potential μ with temperature and pressure:

$$d\mu = -S dT + V dP \quad (22)$$

where S and V stand for the molar entropy and volume. In the case of pure ^4He eq. (22) becomes:

$$d\mu_4^0 = -S_4^0 dT + V_4^0 (dP_4^0/dT) dT \quad (23)$$

and in the case of a mixture:

$$d\mu_4 = -S_4 dT + V_4 (\partial P/\partial T)_X dT. \quad (24)$$

Subtraction of eqs. (23) and (24) yields the change of the mixing potential $\Delta\mu_4$ with temperature:

$$d\Delta\mu_4 = (-\Delta S_4 + V_4 (\partial P/\partial T)_X - V_4^0 dP_4^0/dT) dT \quad (25)$$

from which the partial entropy of mixing is found to be:

$$\Delta S_4 = -(\partial\Delta\mu_4/\partial T)_{P,X} = -d\Delta\mu_4/dT + V_4 dP/dT - V_4^0 dP_4^0/dT \quad (26)$$

with all differentiations to be performed at constant concentration.

From eqs. (3), (4) and (7) it is seen that:

$$V_4 = V_4^0 + \Delta V_4 \quad (27)$$

with

$$\Delta V_4 = \Delta V - X\partial\Delta V/\partial X. \quad (28)$$

No experimental data concerning ΔV exist, but from theoretical arguments⁷ one has to conclude that ΔV is negative, but small. Because the sum of the last two terms of eq. (26) is small in comparison with $d\Delta\mu_4/dT$, we are allowed to assume $\Delta V = 0$. Eq. (26) thus becomes:

$$\Delta S_4 = -d\Delta\mu_4/dT + V_4^0 d(P - P_4^0)/dT. \quad (29)$$

Introducing the activity coefficients we find finally for the entropy:

$$\Delta S_4/R = -\ln(1-X) - \ln f_4 - T d \ln f_4/dT + (V_4^0/R) d(P - P_4^0)/dT. \quad (30)$$

From the entropy and the chemical potential we obtain the partial enthalpy of mixing with the aid of the relation $\Delta H_4 = \Delta\mu_4 + T\Delta S_4$:

$$\Delta H_4/R = -T^2 d \ln f_4/dT + (V_4^0 T/R) d(P - P_4^0)/dT. \quad (31)$$

The partial specific heat of mixing at saturated vapour pressure is derived from eq. (30) with $\Delta C_4 = T d\Delta S_4/dT$:

$$\begin{aligned} \Delta C_4/R = \\ = -2T d \ln f_4/dT - T^2 d^2 \ln f_4/dT^2 + (T/R) d\{V_4^0 d(P - P_4^0)/dT\}/dT. \end{aligned} \quad (32)$$

Since the enthalpy and the specific heat at constant pressure are related by the relation $C_P = \partial H/\partial T$ we obtain from eqs. (31) and (32), neglecting as usual¹⁾ the difference between C_P and the specific heat at saturated vapour pressure:

$$\Delta H_4/R = \int_0^T (\Delta C_4/R) dT + \int_0^T (V_4^0/R) d(P - P_4^0) + (\Delta H_4/R)_{T=0} \quad (33)$$

which is equal to:

$$\Delta H_4/R = \int_0^T (\Delta C_4/R) dT + V_4^0 (P - P_4^0)/R + (\Delta H_4/R)_{T=0} \quad (34)$$

when the change of V_4^0 with temperature is neglected. Because ΔC_4 can be calculated in the temperature interval from 1.2 to 1.9°K and on the other hand has to be zero at 0°K, ΔC_4 can be found in the temperature region from 0 to 1.2°K by interpolation, allowing in this way the evaluation of the integral in eq. (34). Hence the enthalpy of mixing at 0°K is known too. In a similar way the entropy of mixing at the absolute zero point of temperature can be calculated.

All partial ³He-quantities are calculated in an analogous way. Combination of the partial quantities according to eq. (7) yields the total quantity of mixing.

4. *The entropy of mixing.* The entropy of mixing calculated with the aid of eq. (30) is given in table II and fig. 2. At low temperatures the entropy of mixing appears to be smaller than the ideal value $-R[X \ln X + (1 - X) \ln (1 - X)]$, becoming larger than this value with increasing temperature. No direct experimental data concerning this quantity are available.

TABLE II
The entropy of mixing $\Delta S/R$

T deg K X	0	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9
0.010	0.048	0.052	0.053	0.054	0.055	0.057	0.060	0.064	0.070
0.025	0.100	0.109	0.111	0.114	0.118	0.124	0.131	0.139	0.149
0.071 ³	0.233	0.256	0.261	0.268	0.278	0.289	0.303	0.321	0.342

The partial entropy S_4 might be compared with the normal fluid fraction x of the ⁴He-component of the mixture by adapting Tisza's relation⁸⁾ $x^0 = S_4^0/S_\lambda^0$ with S_λ^0 denoting the entropy at the lambda-point temperature. Gorter's equation⁹⁾, $S_4^0 = x^0 (\partial S_4^0/\partial x)_T$, cannot be applied since it requires the entropy to be known as a function of both T and x^0 . In the case of a mixture S_4 should be known as a function of x , T and X , whereas our calculations only yield $S_4 = S_4(T, X)$. Tisza's relation is modified easily by writing:

$$x = \{S_4 - (S_4)_{T=0}\} / \{S_\lambda - (S_4)_{T=0}\} \quad (35)$$

where $(S_4)_{T=0}$ has been introduced in order to get $x = 0$ at 0°K, since, in

contrast with pure ^4He , the partial entropy at the absolute zero point, as obtained by extrapolation, is not equal to zero.

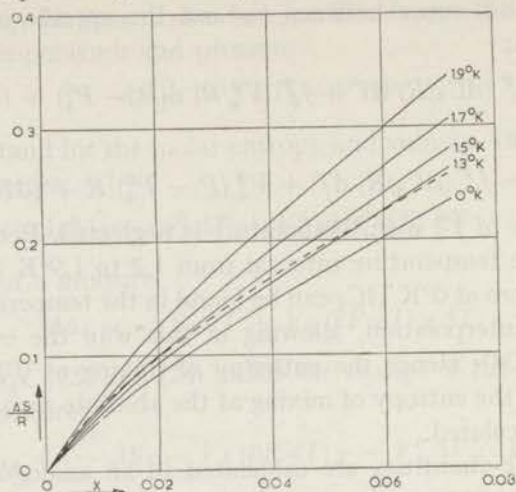


Fig. 2. The entropy of mixing ΔS as a function of the concentration X at different temperatures. ---: ideal solution value.

The normal fluid fraction can be derived from flow experiments with mixtures through narrow slits¹⁰⁾, from second sound measurements^{11) 12) 13)} and from experiments with oscillating disks¹⁴⁾. In fig. 3 values of $\ln \{S_4 - (S_4)_{T=0}\}/R$, calculated from the vapour pressure with the aid of the entropy values of pure ^4He , derived from the specific heat measurements by Kramers, Wasscher and Gorter¹⁵⁾, are given together with values of $\ln x$, calculated from the flow experiments. Reasonable parallelity between the two sets of curves exists which is the more striking since not only Tisza's assumption has been involved in this comparison, but also a special, although plausible supposition concerning the flow properties of the mixtures was necessary in order to obtain the normal fluid fraction.

From the second sound measurement by King and Fairbank¹²⁾ with a 4.3% mixture, we calculated the normal fluid fraction with the aid of the Pomeranchuk-type formula of Price¹⁶⁾ under the assumption that the ^3He moves entirely with the normal fluid. The increase of the normal fluid fraction at low temperature is much larger than according to the flow experiments, as can be seen in fig. 3. This is caused by the fact that the second sound velocity reaches its maximum at a much lower temperature than in the pure ^4He -case. On the other hand, one might ask whether the fact that the ^3He -component is not any more a small impurity with respect to the normal fluid fraction at these low temperatures, might disturb the validity of the assumption that the ^3He -velocity and the normal fluid velocity are the same, and therefore also the calculation of the normal fluid fraction. However, the experiment by Pellam¹⁴⁾ with oscillating

disks also yields a large increase of the normal fluid fraction at low temperatures, but at 1.9 — 2.0°K his increase of the normal fluid fraction is negligible and the shift of the lambda-point temperature with concentration is too small. The discrepancies between the various determinations of x make it impossible to draw a definite conclusion concerning Tisza's relation.

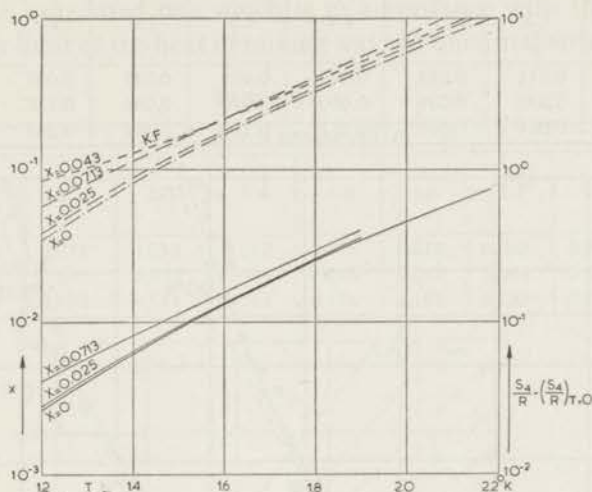


Fig. 3. The normal fluid fraction x and the partial entropy S_4 as a function of the temperature for different concentrations.

- : the partial entropy $\{S_4 - (S_4)_{T=0}\}/R$.
- - - - -: the normal fluid fraction of pure ^4He .
- - - - -: the normal fluid fraction according to the flow experiments¹⁰⁾.
- - - - -: the normal fluid fraction according to the second sound measurements of King and Fairbank¹²⁾.

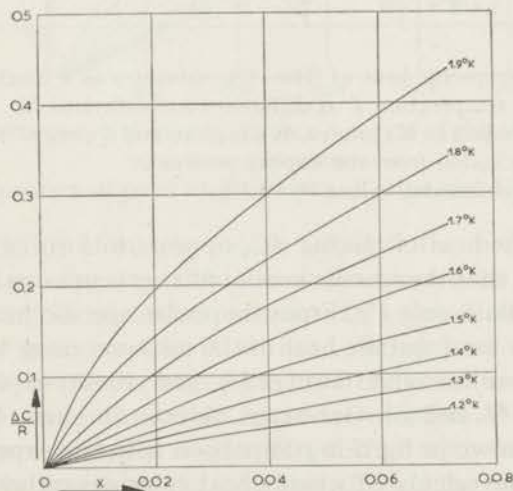


Fig. 4. The specific heat of mixing ΔC as a function of the concentration X at different temperatures.

5. *The specific heat of mixing.* The specific heat of mixing is calculated with the aid of eq. (32). In fig. 4 and table III the results are shown. Since

TABLE III
The specific heat of mixing $\Delta C/R$

T deg K X	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9
0.010	0.011	0.014	0.019	0.025	0.037	0.057	0.089	0.122
0.025	0.028	0.038	0.050	0.070	0.094	0.125	0.166	0.223
0.071 ³	0.064	0.088	0.117	0.154	0.200	0.263	0.339	0.434

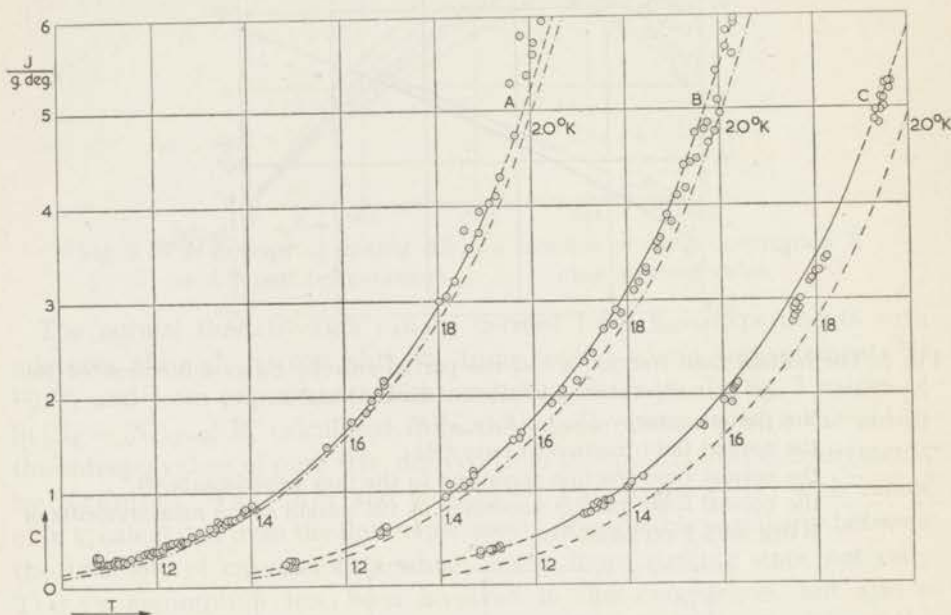


Fig. 5. The specific heat of $^3\text{He}-^4\text{He}$ mixtures as a function of the temperature T at different concentrations X .

- - - - : C_4^0 , according to Kramers, Wasscher and Gorter¹⁵⁾. A: $X = 0.010$
 ——— : C_m , calculated from the vapour pressure. B: $X = 0.025$
 ○ : C_m , experimental values^{20) 21) 22)}. C: $X = 0.071^3$

the partial specific heat of mixing ΔC_4 appears to form only a minor part of ΔC it indicates that the specific heat of mixing is not due to the excitation of extra normal fluid only¹⁷⁾. From the molar specific heat of mixing ΔC we calculated the total specific heat of the mixture, using the data of C_4^0 of Kramers, Wasscher and Gorter¹⁵⁾ and those of C_3^0 of Roberts and Sydoriak¹⁸⁾ and of Osborne, Abraham and Weinstock¹⁹⁾. The results are shown in fig. 5 in comparison with the experimental Leiden data^{20) 21) 22)}. The calculated specific heat coincides rather well at low and high temperatures, but in between it is slightly too large, especially in the case of the 7.13% mixture.

6. *The enthalpy of mixing.* The enthalpy of mixing has been calculated with the aid of eqs. (31) and (34). The results are given in table IV and fig. 6, where the only existing experimental point of the heat of mixing (which is identical with the enthalpy of mixing) measured by Sommers, Keller and Dash²³) at 1.02°K has been entered too. The experimental value is smaller than the calculated one which is in accordance with their remark that only a lower limit of the heat of mixing was obtained in their experiment.

TABLE IV
The enthalpy of mixing $\Delta H/R$

T deg K X	0	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9
0.010	0.006	0.011	0.012	0.013	0.015	0.018	0.023	0.030	0.041
0.025	0.021	0.030	0.032	0.036	0.043	0.052	0.064	0.078	0.097
0.071 ³	0.087	0.107	0.114	0.124	0.138	0.157	0.183	0.210	0.250

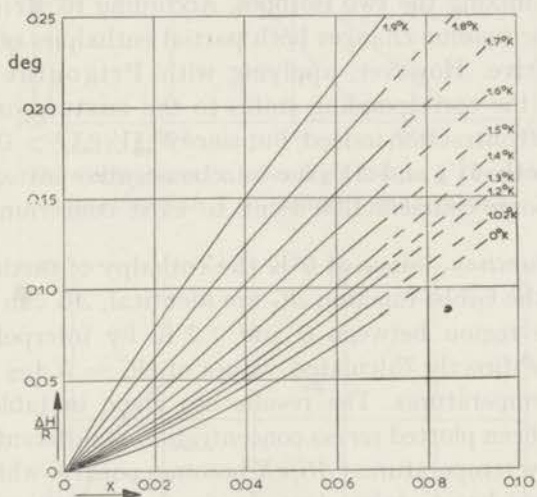


Fig. 6. The enthalpy of mixing ΔH as a function of the concentration X at different temperatures.

●: experimental point of Sommers, Keller and Dash²³).

From the enthalpy of mixing we can calculate the mechanocaloric effect for a mixture. Assuming reversible thermodynamics to be valid we can perform the following imaginary experiment. In a vessel containing one mole of a mixture of concentration X with an enthalpy of mixing $(\Delta H)_X$ we create a phase separation in such a way that the vessel contains y mole pure ^4He and $(1 - y)$ mole of mixture of a concentration $X' = X/(1 - y)$ and a total enthalpy of mixing $(1 - y)(\Delta H)_{X'}$. After removing the y mole pure ^4He by means of a superleak, the total heat effect of the experiment amounts to:

$$\Delta Q = (\Delta H)_X - (1 - y)(\Delta H)_{X'} + yTS_4^0 \quad (36)$$

where yTS_4^0 stands for the mechanocaloric effect of pure ^4He . The deviation of the mechanocaloric effect of the mixture from the pure ^4He -value, $\Delta Q - \Delta Q_0$, approximately obeys the relation:

$$(\Delta Q - \Delta Q_0)/\Delta Q_0 = X^2(36 - 875/T^6). \quad (37)$$

Hence the deviation is expected to be positive at temperatures above 1.7°K whereas it becomes negative at lower temperatures, which is in accordance with the change of the curvature of the ΔH versus X curve. For a 5% mixture the deviation varies between +4% at 1.9°K and about -60% at 1.2°K. These values indicate only the order of magnitude of the effect because the deviation depends somewhat on the amount of liquid removed from the vessel, since X' increases with increasing y . Therefore the deviation does the same.

Since the partial enthalpies at 0°K appear to have opposite sign, one might conclude perhaps that the partial volume V_4 increases and that V_3 decreases, when mixing the two isotopes. According to Prigogine⁷⁾ who assumes the same volume changes both partial enthalpies of mixing should have to be positive. However, applying with Prigogine the theory of De Boer²⁴⁾ of the corresponding states to the mixtures of ^3He and ^4He we find a volume contraction indeed, but since $\partial^2\Delta V/\partial X^2 > 0$ for $0 < X < 1$ it is clear that both ΔV_3 and ΔV_4 have to be negative instead of the latter being positive. Some contradiction seems to exist concerning this subject.

7. *The Gibbs-function.* Since at 0°K the enthalpy of mixing ΔH and the mixing term of the Gibbs-function ΔG are identical, ΔG can be obtained in the temperature region between 0 and 1.2°K by interpolation between $(\Delta H)_{T=0}$ and the directly calculated values of $\Delta G = X\Delta\mu_3 + (1 - X)\Delta\mu_4$ at the higher temperatures. The results are given in table V and fig. 7 where $\Delta G/R$ has been plotted versus concentration at different temperatures. At sufficiently low temperatures $\partial\Delta G/\partial X$ becomes positive which implies that a phase separation has to take place. In fig. 8 the temperature at which

TABLE V

The Gibbs-function of mixing $\Delta G/R$							
$T \backslash X$ deg K	0.010	0.025	0.071 ³	$T \backslash X$ deg K	0.010	0.025	0.071 ³
0	+0.006	+0.021	+0.087	1.0	-0.041	-0.080	-0.149
0.1	+0.002	+0.012	+0.065	1.1	-0.046	-0.090	-0.174
0.2	-0.003	+0.002	+0.041	1.2	-0.051	-0.101	-0.200
0.3	-0.007	-0.008	+0.019	1.3	-0.056	-0.112	-0.226
0.4	-0.012	-0.018	-0.004	1.4	-0.062	-0.123	-0.252
0.5	-0.016	-0.028	-0.028	1.5	-0.067	-0.134	-0.278
0.6	-0.021	-0.038	-0.052	1.6	-0.072	-0.146	-0.306
0.7	-0.026	-0.048	-0.076	1.7	-0.078	-0.159	-0.336
0.8	-0.031	-0.058	-0.100	1.8	-0.084	-0.173	-0.368
0.9	-0.036	-0.069	-0.125	1.9	-0.091	-0.187	-0.402

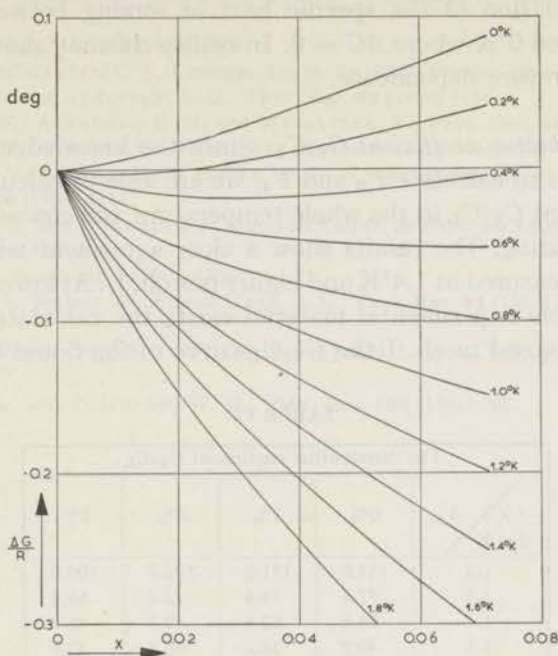


Fig. 7. The Gibbs-function of mixing ΔG as a function of the concentration X at different temperatures.

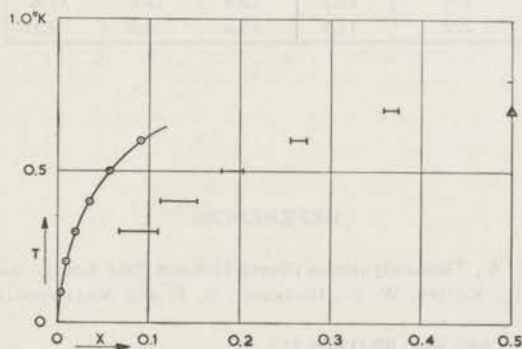


Fig. 8. The phase separation temperature T as a function of the concentration X .

- : calculated from the vapour pressure.
- △ : calculated by Prigogine⁷⁾.
- |— : experimental values of Walters and Fairbank²⁵⁾.

the phase separation occurs is shown as a function of the liquid concentration. The value, used at 0.6°K , has been obtained by extrapolation, whereas the point at $X = 0.5$ has been calculated by Prigogine⁷⁾ theoretically. Furthermore the experimental data obtained very recently by Walters and Fairbank²⁵⁾ are shown. Qualitative agreement exists and much better agreement cannot be expected since our calculations are based on a

smooth interpolation of the specific heat of mixing between the higher temperatures and 0°K where $\Delta C = 0$. In reality ΔC may show a more complicated temperature dependence.

8. *The distribution coefficient C_V/C_L .* Since the knowledge of $\ln f_3$, $\ln f_4$ and P allows us to calculate P_3 and P_4 , we are able to calculate the distribution coefficient C_V/C_L in the whole temperature and concentration region under consideration. The results show a close agreement with the experimental data, measured at 1.4°K and higher (see ch. I). At lower temperatures where no reliable experimental material exists the calculated values have been used to extend in ch. I the C_V/C_L -curve of fig. 5 and table II.

TABLE VI

The distribution coefficient C_V/C_L				
$T \backslash X_L$ deg K	0%	1%	2%	5%
1.2	114.0	111.8	109.9	104.8
1.3	77.5	74.4	72.2	66.8
1.4	55.6	52.6	49.7	46.7
1.5	40.7	38.2	36.8	33.6
1.6	31.7	28.8	27.7	25.0
1.7	24.7	22.1	21.0	19.0
1.8	19.3	17.2	16.1	14.7
1.9	15.1	13.4	12.6	11.6
2.0	11.9	10.6	9.9	9.15

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CHAPTER IV

THE FLOW PROPERTIES OF PURE ${}^4\text{He}$ AND OF ${}^3\text{He}$ — ${}^4\text{He}$ MIXTURES

Summary

The flow of pure ${}^4\text{He}$ and of ${}^3\text{He}$ — ${}^4\text{He}$ mixtures at temperatures below the lambda-point through a slit with a width of 0.3 micron as a function of hydrostatic pressure heads up to 7000 cm He and fountain pressure differences up to 2500 cm He has been studied. It is concluded that the flow resistance is proportional to the slit length. Values of the normal fluid viscosity, of the normal fluid fraction and of the lambda-point temperature as a function of the ${}^3\text{He}$ -concentration are given. The volume contraction on mixing the two isotopes is estimated.

1. *Introduction.* Many experiments have been made on the flow properties of He II in narrow slits as a function of the applied hydrostatic pressure head or fountain force. For a review of these experiments we may refer to the relevant chapter in *Progress in Low Temperature Physics, II* ¹⁾. When discussing the flow properties on the basis of the two-fluid model one assumes the normal fluid to obey Poiseuille's law, whereas the superfluid flows without friction. However, as soon as the superfluid velocity surpasses a critical value which depends on the slit diameter, a friction between the two fluids arises determining the superfluid velocity. At these supercritical velocities of the superfluid nearly all experiments can be described by the equations of motion proposed originally by Gorter and Mellink ²⁾ to account for the strange behaviour of the heat conductivity of He II and which are not inconsistent with the equations derived *e.g.* by Mazur ³⁾ on the basis of irreversible thermodynamics. At saturated vapour pressure they become for the superfluid and the normal fluid resp.:

$$(1 - x^0)M_4\rho_4^0 d\mathbf{v}_s/dt = - (1 - x^0) \text{grad } P + x^0(1 - x^0)\rho_4^0 S^* \text{grad } T - A^0 x^0(1 - x^0)(\rho_4^0)^2(\mathbf{v}_s - \mathbf{v}_n)^{m^0} \quad (1)$$

$$x^0 M_4 \rho_4^0 d\mathbf{v}_n/dt = - x^0 \text{grad } P - x^0(1 - x^0)\rho_4^0 S^* \text{grad } T + A^0 x^0(1 - x^0)(\rho_4^0)^2(\mathbf{v}_s - \mathbf{v}_n)^{m^0} + \eta_n^0(A\mathbf{v}_n + \frac{1}{3} \text{grad div } \mathbf{v}_n)^* \quad (2)$$

* In general the term $(\mathbf{v}_s - \mathbf{v}_n)^{m^0}$ has not the required dimension of a vector (times a scalar). As a matter of fact it stands for the exact form $|\mathbf{v}_s - \mathbf{v}_n|^{(m^0-1)}(\mathbf{v}_s - \mathbf{v}_n)$ and is used only for the simplicity of the equations. All similar quantities have to be interpreted in the same way.

where v_s and v_n denote the velocity of the superfluid and the normal fluid resp., ρ_4^0 the molar liquid density, M_4 the molar weight of ^4He , and x^0 and η_n^0 the normal fluid fraction and viscosity of pure ^4He . S^* is a quantity with dimensions entropy/mol and A^0 and m^0 are two parameters which depend on experimental circumstances. A^0 is usually of the order of 1000 cgs units and m^0 of the order of three. The first term on the left hand side accounts for the acceleration of the fluid, the first one on the right hand side gives the influence of the applied pressure gradient and the second one the influence of the temperature gradient, which gives rise to a gradient in the normal fluid concentration x^0 and hence to a diffusion force between the two fluids. In a narrow slit this diffusion force causes in the stationary state the well-known fountain effect; therefore we shall denote it by fountain force. The third term accounts for the mutual friction between the two fluids and the last term in eq. (2) stands for the viscous friction of the normal fluid, supposed to be essentially absent in the case of the superfluid.

The eqs. (1) and (2) can be simplified since the acceleration terms are always relatively very small and because the compressibility term $\text{grad div } \mathbf{v}_n$ is negligible. Using the experimentally verified relation of H. London⁴⁾, we substitute S_4^0 , the molar entropy of pure ^4He , for $x^0 S^*$ in the expression for the diffusion force; and finally obtain as momentum balance in the stationary state:

$$\text{grad } P - \rho_4^0 S_4^0 \text{ grad } T = - A^0 x^0 (\rho_4^0)^2 (\mathbf{v}_s - \mathbf{v}_n) m^0 \quad (3)$$

$$\text{grad } P = \eta_n^0 \Delta \mathbf{v}_n. \quad (4)$$

Because these equations were verified in the case of rather small temperature or pressure gradients only, we were interested to know whether any further complications in the flow would occur if the applied forces were chosen much larger. This became especially important when Swim and Rohrschach⁵⁾, who used pressure heads up to 20 cm He, the largest ones ever employed, reported that the flow rate seemed to reach a saturation value at these high pressure heads.

On the other hand we wanted to investigate the influence of small amounts of ^3He , added to ^4He , on the flow properties through narrow slits. Only two experiments connected with the influence of ^3He on the flow had been made before. Osborne, Weinstock and Abraham⁶⁾ studied the flow of pure ^3He , and Hammel and Schuch⁷⁾ made an experiment with a 3.9% ^3He - ^4He mixture. In both cases liquid was condensed in a vessel at one side of a narrow slit whereas the container at the other end had been evacuated. From the pressure increase in the latter vessel some information on the flow rate through the slit was obtained: Osborne, Weinstock and Abraham concluded that ^3He shows no superfluidity, whereas Hammel and Schuch believed the opposite to be the case. It has to be remarked, however, that it is very well possible that only gas flow through the slit was observed in

the latter case, since the liquid was not in direct contact with the slit but by means of liquid film and gas. In any case no numerical results were obtained and hence it remained interesting to see what happens when a truly liquid mixture flows through the slit.

From our osmotic pressure measurements⁸⁾ it has been concluded in accordance with the result of Osborne, Weinstock and Abraham that ^3He does not take part in the motion of the superfluid. Experiments on the heat conductivity of ^3He - ^4He mixtures⁹⁾ have shown that the ^3He is dragged along with the normal fluid of the ^4He -component. Therefore we are free to assume that the ^3He -particles and the normal fluid of the ^4He -component of the mixture move together as one homogeneous liquid, to be treated as a new kind of normal fluid.

Since the main part of the transport is provided by the superfluid ^4He , the mixture at one side of the slit is diluted by the entering ^4He and *vice versa*. The resulting concentration gradient gives rise to an osmotic volume force which enters in the equations of motion in the same way as the diffusion force. In the stationary state in a narrow slit this osmotic volume force causes the osmotic pressure: hence we shall denote it by grad P_{osm} . For the mixture we obtain as analogue of the eqs. (3) and (4):

$$\text{grad } P - \rho_4^0 S_4^0 (1 - \gamma) \text{ grad } T - \text{grad } P_{\text{osm}} = -Ax' \rho^2 (\mathbf{v}_s - \mathbf{v}_n)^m \quad (5)$$

$$\text{grad } P = \eta_n \Delta \mathbf{v}_n \quad (6)$$

where γ accounts for possible deviations of the fountain force from the pure ^4He -value. The molar liquid density is denoted by ρ , the normal fluid fraction, as defined above, by x' and the normal fluid viscosity by η_n . The parameters A and m possibly depend on the ^3He -concentration. The osmotic pressure is given in the isothermal case by the experimentally verified relation⁸⁾:

$$P_{\text{osm}} = -\rho_4^0 RT \ln[(1 - X)/f_4] \quad (7)$$

where X denotes the molar ^3He -fraction of the mixture. The activity coefficient f_4 ^{10) 11)} accounts for the deviations from the ideal solution. In the limit of zero concentration f_4 equals unity, yielding Van 't Hoff's law:

$$P_{\text{osm}} = \rho_4^0 RTX. \quad (8)$$

Equations of the type of eqs. (5) and (6) have been derived on the basis of irreversible thermodynamics by Mazur³⁾, by Koide and Usui¹²⁾ and by Mikura¹³⁾. The eqs. (3), (4), (5) and (6) will be modified further when dealing with the different experiments.

2. *The apparatus.* The flow experiments can be divided into two groups, one concerning the flow as a function of the hydrostatic pressure head (to be indicated hereafter as isothermal flow) and one dealing with the flow as a

result of the applied fountain force, which have been performed with apparatus 1a and 1b resp. (see fig. 1).

a. *Apparatus 1a.* Of this apparatus the essential part consists of a narrow slit or superleak *S* made by fusing a gold wire of 0.1 mm diameter into a piece of soft glass. Because of the difference between the dilatation coefficients of gold and glass an annular slit of 0.33 micron is formed when this combination is cooled down to liquid helium temperatures. At its upper end the superleak is connected with a glass capillary *C* and at the lower end with the glass vessel *A*.

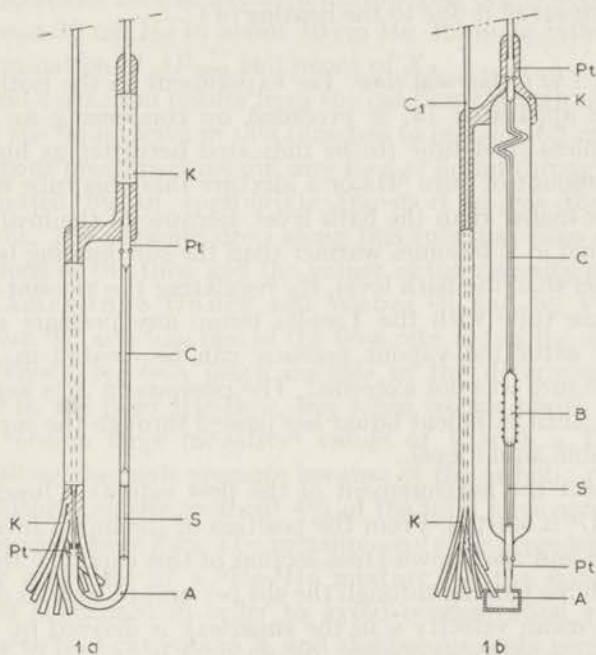


Fig. 1. The apparatus.

By means of a thin-walled stainless steel tube the capillary *C* is connected with an oil manometer filled with Octoil-S, on which pressure differences with respect to the bath pressure can be measured. The vessel *A* is connected in the same way with a mercury-filled Toepler pump system outside the cryostat with which pressures up to one atmosphere can be attained. Both *A* and *C* are surrounded partially with some cotton cords *K* for the following reason: when the bath level falls below the top of the apparatus, the heat leaks along the stainless steel tubes might disturb the experiments, especially in the case of mixtures where a temperature gradient gives rise to a concentration gradient ⁹⁾. The cotton cords allow the He II-film to creep upwards, and since they have been covered nearly completely with oiled cloth, only their top being free, the film will evaporate at the top of these cords,

eliminating in this way nearly all heat leaks into *A* and *C*. All metal-glass connections are made with the aid of platinum-glass seals *Pt*.

b. Apparatus 1b. This apparatus differs in some details from apparatus 1*a*. Firstly the superleak contains two gold wires and has an estimated slit width of 0.2 micron. Secondly, *C* is surrounded by a vacuum jacket and can be heated by means of a heating wire around *B*. Because the fountain force created in this way acts as the driving force, the connection of *A* with the Toepler system is superfluous and is replaced by a differential oil manometer. Finally, *A* is made of copper instead of glass to avoid any temperature increase of it due to the heating of *C*.

3. *Method. a. The isothermal flow.* The experiment on the isothermal flow performed with apparatus 1*a*, is preceded by condensing in *A* and the connecting stainless steel tube (to be indicated hereafter as high pressure tube) such an amount of pure ^4He or a mixture that this tube is filled to a level equal to or higher than the bath level. Because of the heat leak along the tube the liquid in it becomes warmer than the surrounding bath as soon as it stands higher than the bath level. By regulating the amount of liquid in the high pressure tube with the Toepler pump any pressure equal to or larger than the saturated vapour pressure can be created in *A*. Usually atmospheric pressure was not exceeded. The pressure in *A* is kept at about one atmosphere until sufficient liquid has passed through the superleak into *C* to form a visible liquid level.

At this moment the measurement of the flow rate as a function of the pressure head ΔP is started. From the position of the liquid level in *C* as a function of time and the known cross-section of this capillary the flow rate \dot{V} , being the volume passing through the slit per unit of time, is determined, from which the mean velocity \hat{v} in the superleak is derived by dividing \dot{V} by the cross-section of the superleak. Readings of the liquid level are taken every fifteen seconds with a cathetometer during a period depending on the flow rate and varying between two minutes at 1.2°K and eight minutes at temperatures near the lambda-point.

The pressure difference across the slit, ΔP , is given mainly by the difference in vapour pressure between the high pressure tube and the capillary *C*. The former pressure is measured in the Toepler system on a mercury manometer, the latter is derived from the pressure difference measured on the oil manometer and the bath pressure. Two small corrections, to be dealt with later, have to be applied to this pressure difference.

When working with mixtures, the osmotic pressure difference ΔP_{osm} across the slit has to be known. It is determined by measuring the pressure difference ΔP for which zero flow rate is attained. From it the concentration difference ΔX across the slit is calculated with the aid of eq. (7). Together with the concentration X_C , derived from the vapour pressure difference δ^{14}

on the oil manometer of *C*, it yields the concentration X_A in the high pressure vessel.

Of the two corrections mentioned above, one consists of the hydrostatic pressure exerted by the liquid columns in *A* and *C*. The height of the latter, determined visually, is only a few cm, the one in *A* depends on the bath level height in a somewhat complicated way because the height of the liquid column which is above the bath level is determined by the heat leak along the high pressure tube, which depends in turn on the bath level height. The correction decreases very slowly with the lowering of the bath from an initial value of about 30 cm He to about 10 cm He. Its main influence lies in the exact determination of ΔP_{osm} and hence of X_A .

The second correction results from the gas flow through the high pressure tube. Since the liquid level in this tube has to remain stationary in order to keep its vapour pressure constant, any flow of liquid through the slit has to be compensated by an appropriate transport of gas through the high pressure tube. The pressure drop along this tube has been calculated from the dimensions of the tube and the values of the viscosity of He-gas, measured by Kamerlingh Onnes and Weber¹⁵⁾ and by Van Itterbeek and Keesom¹⁶⁾, as a function of the flow rate \dot{V} and the mean pressure in the tube. This correction plays no role in the determination of ΔP_{osm} ($\dot{V} = 0$) nor in the pure ^4He -flow, but when working with a mixture it is possible to obtain large (negative) values of \dot{V} with a Toepler pressure nearly equalling the bath pressure because of the osmotic pressure. In this way its influence can rise to about 4% of the total force acting.

b. The fountain force flow. The measurements are preceded by condensing in *A* either pure ^4He or a ^3He - ^4He mixture. Of the latter only a small amount was condensed in order to avoid concentration gradients in the liquid owing to heat currents in it, and also because only very small amounts of mixture were available at the time of the experiment. Both *B* and *C* are filled with liquid ^4He until a liquid level becomes visible in the glass capillary. By means of the heating current a fountain force is created drawing the liquid out of *A* into *C*, at least as long as the fountain force is larger than the osmotic pressure of the mixture in *A*.

Apart from a rare exception the vapour pressure in *C* is always higher than that in *A*. The normal fluid flow of ^4He from *C* into *A* prevents the ^3He from passing or even entering the slit which is proved by switching off the heating current of *B*: no vapour pressure difference with respect to the bath pressure is observed then. Therefore the slit will be filled with pure ^4He only and the fountain force will have its pure ^4He -value (*i.e.* $\gamma = 0$ in eq. (5)). From the vapour pressure in *C* the created temperature difference is derived, from which in combination with the entropy values of Kramers, Wasscher and Gorter¹⁷⁾ the applied fountain force is calculated. The temperature scale used is the 1948-scale¹⁸⁾. Recalculation of the fountain force in the

1955-scale¹⁹⁾ yielded corrections of less than 0.5%. Furthermore, the accuracy of the obtained results, as *e.g.* the normal fluid concentration and viscosity, is not such that the error in the temperature caused by the use of the 1948-scale is of any importance.

The osmotic pressure of the mixture in *A* is either determined directly by measuring the fountain force for which zero velocity is attained or by calculating it by means of eq. (7) from the concentration X_A , derived from the vapour pressure difference^{8) 14)} on the differential oil manometer of *A*.

Because of the partial filling of *A* only the first one of the two pressure corrections, mentioned in section 3*a*, remains. This hydrostatic correction contains the pressure of the liquid column in *C* and the surface tension exerted by the liquid at the entrance of the slit in *A*, equal to the height of this entrance above the liquid level in *A*⁸⁾. The total correction is of the order of 5 cm He and is nearly constant throughout the experiment.

4. *The determination of the cross-section of the capillary C and the superleak S.* The cross-section of *C* has been determined by filling it with mercury. It appeared to be 0.46 mm² with a variation along the length of the capillary of less than 2%, which is unimportant in connection with the accuracy of the determination of the flow rate. This value of the cross-section applies to both apparatus since the capillary was used first in apparatus 1*b* and in 1*a* afterwards.

The determination of the width of the superleak caused much trouble because it had to be performed at low temperatures. He-gas flow experiments at liquid hydrogen temperatures appeared to be a complete failure because the amount of gas passing through the slit could not be measured owing to the change of the effective volume of the vessels in consequence of the lowering of the bath level during the experiment.

Finally the slit width was determined from flow experiments with He I, performed analogously to the isothermal He II-flow. Many precautions and a good deal of routine proved to be necessary before we were able to obtain reliable results. Since the flow rates were very small, *viz.* of the order of 10⁻⁶ cm³/sec, a change in the bath temperature affected the observed flow rate seriously because of the evaporation or condensation in the capillary *C* accompanying the change in bath temperature. Hence it took more than an hour before sufficient stability was obtained.

Assuming the He I-viscosity above 2.5°K to be 28 μ P, we found the slit width of apparatus 1*a* to be 0.33 (\pm 0.01) micron, yielding a cross-section of 1.04×10^{-6} cm². The slit width of apparatus 1*b* was estimated at 0.2 micron from comparison with the other apparatus.

5. *The isothermal flow of pure ⁴He. a. The momentum balance.* In order to compare our experimental results with the Gorter-Mellink equations (3)

and (4) we shall write these equations in an appropriate form. The observed flow rate \dot{V} , the volume passing through the slit per unit of time, is connected with the mean normal fluid and superfluid velocities \hat{v}_n and \hat{v}_s by the relation:

$$\dot{V} = O[(1-x)\hat{v}_s + x\hat{v}_n] \quad (9)$$

where O denotes the cross-section of the superleak and x the normal fluid fraction. The relative velocity v_r therefore can be written as:

$$v_r = v_s - v_n = \hat{v}_s - \hat{v}_n = (\dot{V} - O\hat{v}_n)/[O(1-x)]. \quad (10)$$

In the isothermal case we can integrate the eqs. (3) and (4) over the slit length L and the slit width A . Introducing the relative flow rate $\dot{V} - O\hat{v}_n$ and expressing the pressure in cm He, we obtain as momentum balance in the isothermal case:

$$\Delta P = (A^0 x^0 L \rho_4^0 / g) v_r^{m^0} = B^0 (\dot{V} - O\hat{v}_n)^{m^0} \quad (11)$$

$$B^0 = (A^0 x^0 L \rho_4^0 / g) / [O(1-x^0)]^{m^0} \quad (11')$$

$$\Delta P = (12L / \rho_4^0 g A^2) \eta_n^0 \hat{v}_n = C \eta_n^0 \hat{v}_n \quad (12)$$

where g denotes the gravitational acceleration. The normal fluid fraction at saturated vapour pressure, x^0 , is given by:

$$x^0 = (T/T_\lambda)^{5.6} \quad (13)$$

which describes the experimental results of Andronikashvili^{20, 21} fairly well.

The values of the normal fluid viscosity η_n^0 , obtained with the oscillating disk^{22, 23, 24}) and with the rotating viscometer²⁵), show a ten per cent difference above 1.8°K but at 1.2°K they differ by about a factor two. Fortunately the ratio $O\hat{v}_n/\dot{V}$ is of the order of 0.01 at this latter temperature, increasing gradually with temperature and reaching unity at the lambda-point. Therefore the uncertainty in the value of η_n^0 always forms a correction of about one per cent only, excluding temperatures very near the lambda-point. In fact we used the mean value of both η_n^0 -determinations.

b. The experimental results at temperatures below 2°K. As has been mentioned already in section 1 Swim and Rohrschach⁵) suggested the possible existence of a saturation velocity at high pressure heads (20 cm He). In contradiction to them no such limit was observed in our experiments (see fig. 2) although pressure heads up to 7000 cm He were employed, yielding pressure gradients a factor fifteen higher than those of Swim and Rohrschach.

The validity of eq. (11) is verified by plotting $\dot{V} - O\hat{v}_n$ versus ΔP on a logarithmic scale (see fig. 3), taking the validity of eq. (12) for granted. At temperatures below 2°K eq. (11) is obeyed throughout the whole pressure

region under discussion, m^0 being equal to 3.45, which is in good agreement with the values, found by Winkel, Delsing and Görtner²⁶⁾ for similar slit widths. The factor B^0 appears to be proportional to $(1 - x^0)^{-3.45}$, implying the temperature independence of Ax^0 (see eq. (11')). Hence the relative velocity v_r is independent of temperature also (see table I) and a function

TABLE I

The flow rate of pure ^4He at $\Delta P = 1000$ cm He			
T deg K	\dot{V} 10^{-6} cm ³ /sec	$\dot{V} - O\hat{v}_n$ 10^{-6} cm ³ /sec	v_r cm/sec
2.14	3.53	3.24	27.3
2.08	7.15	6.75	27.3
2.00	11.2	10.8	27.3
1.79	20.2	19.0	27.2
1.70	22.4	21.4	27.2
1.55	24.8	24.3	27.3

of the pressure gradient only. At all temperatures below 2°K v_r is found to obey the relation:

$$\text{grad } P = -\alpha^0 v_r^{m^0} \quad (14)$$

with $\alpha^0 = A^0 x^0 \rho_4^0 / g = 5.6 \times 10^{-3}$ (cm He/cm)/(cm/sec) $^{m^0}$ and $m^0 = 3.45$.

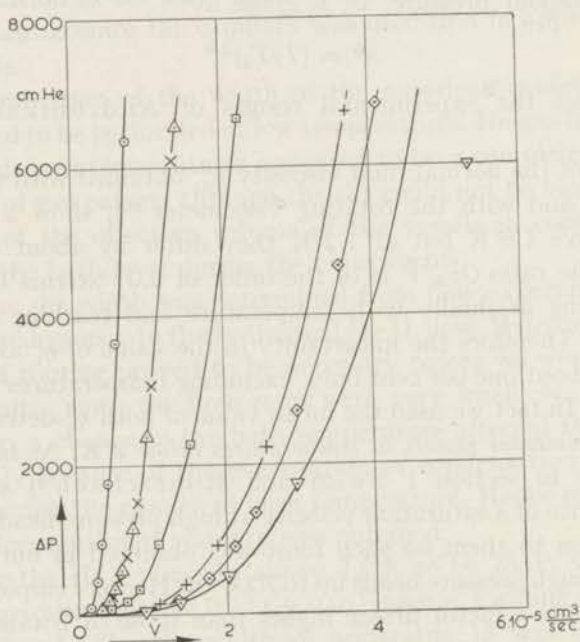


Fig. 2. The flow rate \dot{V} of pure ^4He as a function of the pressure head ΔP at different temperatures.

○ : 2.14°K □ : 2.00°K ◇ : 1.70°K
 △, × : 2.08°K + : 1.79°K ▽ : 1.55°K

An equal result was arrived at by Swim and Rohrschach⁵⁾ in their experiments with slits of 2.4 and 4.3 micron. It has to be remarked, however, that this temperature independence of v_r seems to be a property of these particular slits only. Winkel, Delsing and Gorter²⁶⁾ employing similar slit widths as Swim and Rohrschach, found v_r to be a function of temperature ($dAx^0/dT > 0$), although this dependence became weaker with decreasing slit width (down to 0.8 micron). Furthermore, the experiments with apparatus 1b (although being somewhat less accurate than those performed with apparatus 1a) yielded at a slit width of 0.2 micron a similar temperature dependence of v_r as observed by Winkel, Delsing and Gorter in their slit of 0.8 micron. However, it might still be possible that these discrepancies are only due to the particular properties of the different slits (as e.g. inhomogeneities) and that the temperature dependence of v_r is actually ruled by the slit width only. More experimental material is to be known before this can be concluded definitely.

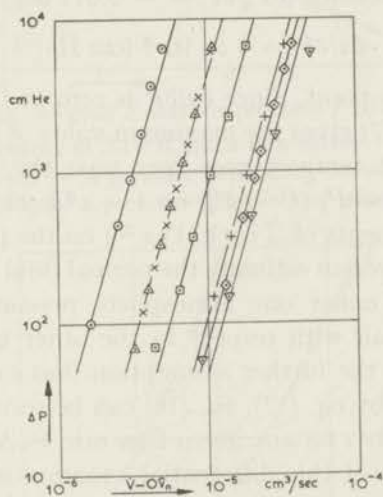


Fig. 3. The relative flow rate $\dot{V} - \hat{O}\hat{v}_n$ of pure ^4He as a function of the pressure head ΔP at different temperatures.

\odot : 2.14°K \square : 2.00°K \diamond : 1.70°K
 \triangle, \times : 2.08°K $+$: 1.79°K ∇ : 1.55°K

c. *The experimental results at temperatures above 2°K.* At these temperatures no m-th power relation between the relative flow rate $\dot{V} - \hat{O}\hat{v}_n$ and the pressure head ΔP is found: the plot of $\log(\dot{V} - \hat{O}\hat{v}_n)$ versus $\log \Delta P$ becomes a curve instead of a straight line, the curvature increasing with increasing temperature. The invalidity of eq. (11) at these temperatures is not in contradiction with eq. (14), found to be valid at lower temperatures, as will be shown.

From the shift of the lambda-point with pressure it is clear that the

superfluid fraction is a function of the pressure. Therefore the superfluid concentration in the slit will differ from point to point. Because \dot{V} is a constant throughout the slit, v_r and hence $\text{grad } P$ will be a function of the length coordinate z of the slit, and we are not allowed to integrate eqs. (3) and (4) into eqs. (11) and (12) by writing $\partial P/\partial z = -\Delta P/L$, unless the pressure dependence of the superfluid fraction can be neglected. The normal fluid fraction x at a pressure P can be written as:

$$x = x^0 + (\partial x/\partial P) (P - P_4^0) \quad (15)$$

where P_4^0 is the saturated vapour pressure and x^0 is given by eq. (13). Supposing eq. (14) to be valid at all temperatures, we obtain from eqs. (10), (12), (14) and (15):

$$\dot{V}/O = -(L/C\eta_n) (\partial P/\partial z) + [1 - x^0 - (\partial x/\partial P) (P - P_4^0)] [-(\partial P/\partial z)/\alpha^0]^{1/m^0}. \quad (16)$$

From the data of Keesom and Miss Keesom²⁷⁾ on the shift of the lambda-point with pressure ($\partial T_\lambda/\partial P = -0.011 \text{ deg/atm}$) one finds that

$$\partial x/\partial P = 4 \times 10^{-6} (\text{cm He})^{-1} \quad (17)$$

at the normal lambda-point. Since $\partial x/\partial P$ is zero at the absolute zero point of temperature, eq. (17) gives the maximum value of $\partial x/\partial P$. Because $1 - x^0$ is only very small at temperatures very near the lambda-point, the influence of the term $(\partial x/\partial P) (P - P_4^0)$ on $1 - x^0$ is of importance only here.

From the measurements of Tjerkstra²⁸⁾ on the pressure dependence of the viscosity of He I we can estimate the normal fluid viscosity at $T \approx T_\lambda$ to increase about 10% under one atmosphere pressure. Because the term $(L/C\eta_n) (\partial P/\partial z)$ is small with respect to the other two we are allowed to write $\eta_n = \eta_n^0$. Under the further assumption that $\partial x/\partial P$ is independent of pressure and is given by eq. (17), eq. (16) can be solved for P as a function of the length coordinate z for any given flow rate \dot{V} . A typical result is given in fig. 4. The solution of this differential equation is rather laborious and therefore we looked for an approximational method, found in the calculation of \dot{V} or $\dot{V} - O\hat{v}_n$ from the usual (somewhat rewritten) momentum balance:

$$\dot{V} - O\hat{v}_n = O(1 - x) (\Delta P/\alpha^0 L)^{1/m^0} \quad (11)$$

$$\Delta P = C\eta_n^0 \hat{v}_n \quad (12)$$

where the normal fluid fraction x is taken equal to the mean value \hat{x} in the slit:

$$\hat{x} = x^0 + (\partial x/\partial P) (\Delta P/2). \quad (18)$$

In this way the relation between ΔP and the (relative) flow rate in the high temperature region is obtained easily. In fig. 5 the results of these calculations are given in comparison with the experimental values of the relative flow rate. The good agreement between the calculated and the observed curve

allows the conclusion that at all temperatures below the lambda-point in the slit under consideration the relative velocity v_r is a function of the pressure gradient only and is independent of the temperature.

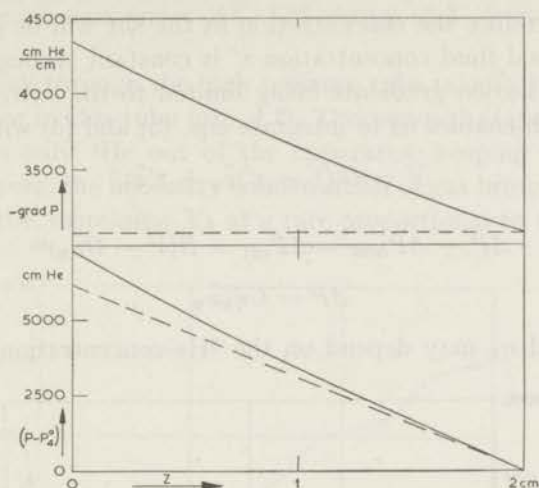


Fig. 4. The pressure gradient $\text{grad } P$ and the pressure P in the superleak as a function of the length coordinate z at 2.14°K and a flow rate $\dot{V} = 7.8 \times 10^{-6} \text{ cm}^3/\text{sec}$.
 ———: values for a pressure-dependent normal fluid fraction.
 - - - -: values for a pressure-independent normal fluid fraction.

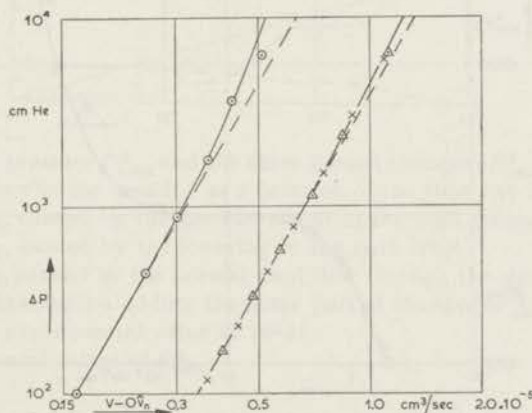


Fig. 5. The relative flow rate $\dot{V} - O \hat{v}_n$ of pure ^4He as a function of the pressure head ΔP at different temperatures.
 ———: calculated for a pressure-dependent normal fluid fraction.
 - - - -: calculated for a pressure-independent normal fluid fraction.
 ○ : experimental results at 2.14°K .
 △, × : experimental results at 2.08°K .

6. The isothermal flow of ^3He - ^4He mixtures. a. The momentum balance and the calculation of the osmotic pressure difference. Excluding temperatures

close to the lambda-point, we find the flow rate to depend only on the concentration X_A and not on X_C , allowing the conclusion that the slit is filled with the same mixture as the high pressure vessel A . This is plausible: the normal fluid containing the ^3He always flows from the high pressure side A to C and therefore the concentration in the slit will be governed by A . Hence the normal fluid concentration x' is constant throughout the whole slit, the concentration gradients being limited to the extreme ends of the superleak, which enables us to integrate eqs. (5) and (6) with the aid of:

$$\dot{V} = O[(1 - x')\hat{v}_s + x'\hat{v}_n] \quad (19)$$

into

$$\Delta P - \Delta P_{\text{osm}} = \Delta P_{\text{eff}} = B(\dot{V} - O\hat{v}_n)^m \quad (20)$$

$$\Delta P = C\eta_n\hat{v}_n \quad (21)$$

where B , m and η_n may depend on the ^3He -concentration.

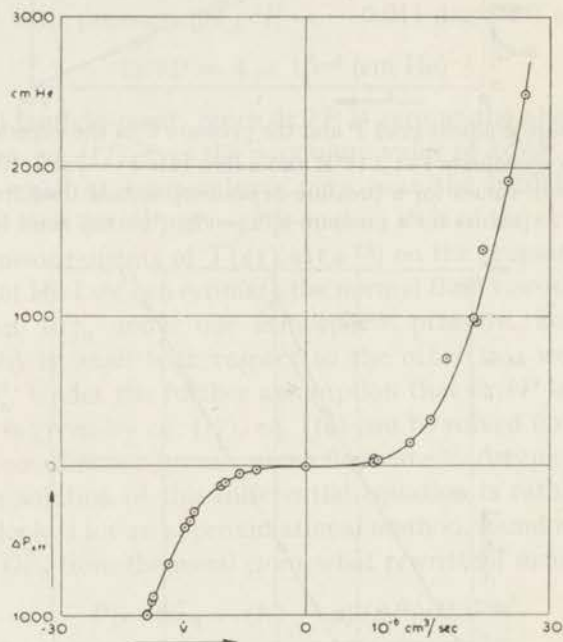


Fig. 6. The flow rate \dot{V} of a 4.1% ^3He - ^4He mixture as a function of the effective pressure head ΔP_{eff} at 1.70°K.

From fig. 6 it is seen that the flow rate \dot{V} (which is nearly equal to the relative flow rate $\dot{V} - O\hat{v}_n$) and ΔP_{eff} always have the same sign, in agreement with eq. (20). Furthermore, we see that it is unimportant whether ΔP_{osm} is taken equal to the value of ΔP , at which \dot{V} is zero (as we actually did) or to that, at which $\dot{V} - O\hat{v}_n$ is zero (as is the condition of eq. (20)), since $\partial\Delta P_{\text{eff}}/\partial\dot{V}$ is negligible in this velocity region.

Unfortunately ΔP_{osm} is a function of time because X_A and X_C change continuously during the experiment. Therefore ΔP_{osm} is measured at regular intervals and its value during these periods is calculated from X_A and X_C with eq. (7). X_C is known continuously by observing the vapour pressure difference on the oil manometer of C . The change of X_A is governed by three factors:

1) the heat leak through the high pressure tube takes all ^3He away from the liquid surface in this tube into A ⁹). The removal of gas from this tube therefore brings only ^4He out of the apparatus, keeping X_A unchanged. At $\dot{V} > 0$, however, the necessary condensation of gas brings a new amount of ^3He in the tube, increasing X_A at a rate proportional to \dot{V} .

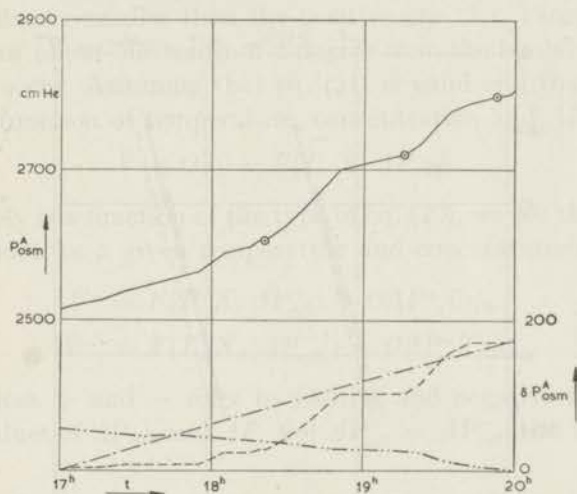


Fig. 7. The osmotic pressure P_{osm}^A and the three partial changes δP_{osm}^A of a 6.2% ^3He - ^4He mixture in the vessel A as a function of the time t at 2.02°K .

- : $(\delta P_{\text{osm}}^A)_1$, caused by the gas movement in the high pressure tube.
- - - - -: $(\delta P_{\text{osm}}^A)_2$, caused by the lowering of the bath level.
-: $(\delta P_{\text{osm}}^A)_3$, caused by the normal fluid flow through the slit.
- : P_{osm}^A , obtained by adding the three partial changes δP_{osm}^A and by fitting it to the experimental value at $18^{\text{h}}21$.
- : experimental values of P_{osm}^A .

2) the decrease in height of the liquid column in the high pressure tube, caused by the lowering of the bath level during the experiment, reduces the liquid volume available for the ^3He and causes a nearly constant increase of X_A with time.

3) ^3He leaves A with the normal fluid flow through the superleak at a rate proportional to ΔP (see eq. (21)), decreasing X_A and increasing at the same time X_C . Estimations of η_n show that this effect is small in comparison with 1) and 2). It is fairly constant in time because the larger part of

the measurements is performed at pressure differences ΔP of the order of ΔP_{osm} .

In fig. 7 the osmotic pressure in A , P_{osm}^A , as a function of time is shown in comparison with the experimental data. The variation with time is obtained by adding the three variations δP_{osm}^A , corresponding to 1), 2) and 3) and calculated from known gas concentrations, flow rates, etc. The variation of P_{osm}^A appears to be described fairly well by two slopes, the steep one corresponding to positive and the flat one to negative flow rate. For practical purposes it is therefore sufficient to calculate the variations $(\delta P_{\text{osm}}^A)_2$ and $(\delta P_{\text{osm}}^A)_3$ for an average ΔP and estimated η_n , yielding the increase of P_{osm}^A for negative flow rate, and to give $(\delta P_{\text{osm}}^A)_1$ such a value as to get the required coincidence with the experimentally determined P_{osm}^A .

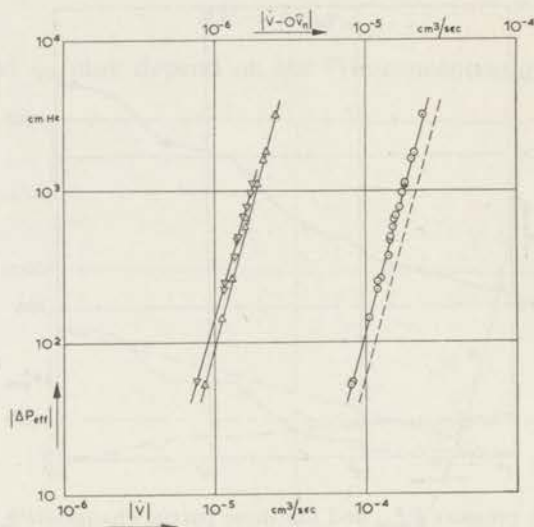


Fig. 8. The flow rate \dot{V} and the relative flow rate $\dot{V} - \hat{O}v_n$ of a 7.9% ^3He - ^4He mixture as a function of the effective pressure head ΔP_{eff} at 1.70°K.

$$\Delta: \dot{V} > 0$$

$$\nabla: \dot{V} < 0$$

$$\circ: \dot{V} - \hat{O}v_n$$

$$-----: \dot{V} - \hat{O}v_n \text{ of pure } ^4\text{He}.$$

b. The determination of the normal fluid viscosity η_n . The number of moles of ^3He in the capillary C and connected volumes can be calculated from the known vapour and liquid volumes and concentrations, the latter being derived from the vapour pressure^{8) 14)}. The increase of this number should be proportional to ΔP , since the ^3He forms a part of the normal fluid, and, in combination with the ^3He -concentration in the slit (X_A), it should yield the normal fluid velocity \hat{v}_n from which η_n is easily obtained (see eq. (21)). We did not succeed completely in this test of eq. (21) and the calculation of η_n , which may be caused by the facts that 1) the value of the effective vapour volume of C , in connection with the oil manometer, is very uncertain,

and that 2) it is not certain at all that a uniform distribution of the ^3He over this large vapour volume is attained immediately when the liquid concentration in C changes, although the vapour pressure follows this change without delay. Hence the calculation of the number of moles of ^3He in the vapour phase is very unreliable. Nevertheless, it can be stated that during the experiment the number of moles of ^3He in C increases gradually and that the general trend of X_C is in agreement with eq. (21), excluding any superfluidity of ^3He .

Although the lack of accuracy of the mass-balance calculation prevented us from deriving η_n from it, fortunately another possibility for the determination of η_n remained. The plot of $\log |\dot{V}|$ versus $\log |\Delta P_{\text{eff}}|$, shown in fig. 8, reveals that for the same value of $|\Delta P_{\text{eff}}|$ the modulus of the negative flow rate, $|\dot{V}^-|$, is always smaller than the positive one, \dot{V}^+ , except at temperatures less than about one tenth of a degree from the lambda-point where complications occur. Assuming that eq. (21) is valid and that the relative flow rate is a function of temperature, concentration and ΔP_{eff} only:

$$\dot{V} - O\hat{v}_n = F(T, X, \Delta P_{\text{eff}}) \quad (22)$$

where F possibly is a function of the type of eq. (20), we see that the following relations hold for a given temperature and concentration:

$$\dot{V}^+ = F(T, X, \Delta P_{\text{eff}}^+) + O\Delta P^+/C\eta_n \quad (23)$$

$$|\dot{V}^-| = F(T, X, |\Delta P_{\text{eff}}^-|) - O\Delta P^-/C\eta_n \quad (24)$$

where the indices $+$ and $-$ refer to positive and negative flow rates and appropriate values of ΔP_{eff} and ΔP . For $\Delta P_{\text{eff}}^+ = |\Delta P_{\text{eff}}^-|$ the two equations reduce to:

$$\Delta\dot{V} = \dot{V}^+ - |\dot{V}^-| = O(\Delta P^+ + \Delta P^-)/C\eta_n = 2O\Delta P_{\text{osm}}/C\eta_n. \quad (25)$$

Determination of $\Delta\dot{V}$ from graphs of the type of fig. 8 reveals that it is a constant indeed throughout the pressure region under consideration to the same accuracy with which ΔP_{osm} stays constant during the experiment. The results obtained in this way are shown in table II and fig. 9, where the ratio of the normal fluid viscosity of the mixture, η_n , to that of pure ^4He , η_n^0 , is given as a function of the ^3He -concentration. From this graph the smoothed values given in table III and fig. 10 have been derived. Good agreement exists with the single available η_n -value, obtained by Pellam²⁹⁾ for a 4.2% mixture with an oscillating disk.

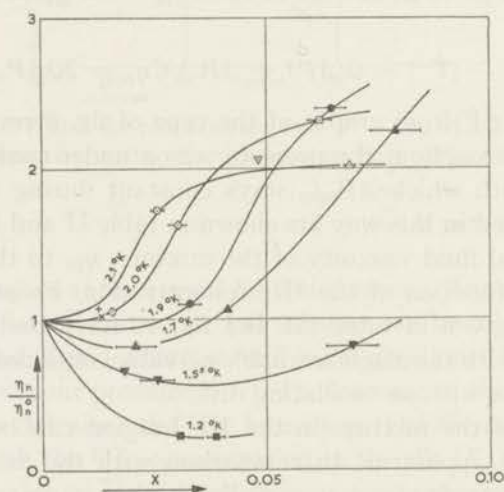
The viscosity of the mixture in the He I-region can be determined in principle with our apparatus. In comparison with the measurement with pure ^4He (see section 4) one more complication occurs since it is impossible to determine the concentration from the osmotic pressure which is confined essentially to the superfluid region. One can only determine X_A at a temperature just below the lambda-point and assume that it stays nearly the same

TABLE II

The relative flow rate of ^3He - ^4He mixtures at $\Delta P_{\text{eff}} = 1000 \text{ cm He}$, and derived quantities.				
T deg K	$\dot{V} - \hat{O}v_n$ $10^{-6} \text{ cm}^3/\text{sec}$	X %	η_n μP	Δx %
1.20	27.3	3.1	4.3	
1.22	25.6	3.7-4.1	4.2	1.5-1.0
1.54	22.5	2.2-3.0	8	3.6-2.7
1.56	20.3	6.4-7.5	11	7.1-5.7
1.56	23.5	1.8-1.9	7	0
1.70	20.7	1.7-2.6	10	1.3-0.5
1.70	19.7	4.1-4.2	13	2.6-2.5
1.70	17.5	7.3-8.5	27	7.5-6.4
1.90	13.7	3.1-3.6	13	4.5-4.4
1.98	11.2	1.5-1.6	14	1.9-1.8
1.98	10.1	2.8-3.3	21	5.4
2.02	4.55	6.0-6.5	31	19.1-19.0
2.05	4.45	4.8	29	13.2
2.07	6.50	1.3-1.4	15	3.2
2.08	6.11	1.3-1.4	17	2.2
2.087	1.32	5.3-5.5	1)	17.8
2.089	4.03	2.5-2.7	26	6.8
2.089	3.66	2.9-3.1	50	8.9
2.11	2)	6.8-7.0	32.2	2)
2.14	2)	6	31.2	2)
2.21	0	7	31.6	3)
2.29	0	6	32.2	3)
2.29	0	6	31.6	3)
2.52	0	6	31.6	3)

1) nearly intermediate temperature.

2) intermediate temperature.

3) $T > T_{\lambda}^0$ Fig. 9. The ratio of the normal fluid viscosity η_n of a ^3He - ^4He mixture to that of pure ^4He , η_n^0 , as a function of the concentration X at different temperatures.

Δ : 2.11°K $+$: 2.08°K \square : 2.02°K \bullet : 1.90°K ∇ : 1.54-1.56°K
 \circ : 2.09°K \times : 2.07°K \diamond : 1.98°K \blacktriangle : 1.70°K \blacksquare : 1.20-1.22°K

when the temperature is increased to above the lambda-point. This is rather questionable since at $T > T_\lambda$ there is no heat flush effect tending to increase X_A . One has to expect that X_A will decrease gradually because of the diffusion of ^3He into the high pressure tube. Nevertheless, the results obtained with a "6%" mixture show a good fit to the η_n -curve for the same concentration at $T < T_\lambda$.

TABLE III

Smoothed values of η_n			
X T deg K	0.02	0.04	0.06
1.2	6.3	4.3	5.6
1.3	6.8	4.9	6.2
1.4	7.5	5.7	7.1
1.5	8.1	6.9	8.6
1.6	8.8	8.6	11.5
1.7	9.6	10.8	17.4
1.8	10.6	14.0	24.4
1.9	12.1	20.3	28.2
2.0	14.9	26.2	30.2
2.1	21.2	28.7	31.1

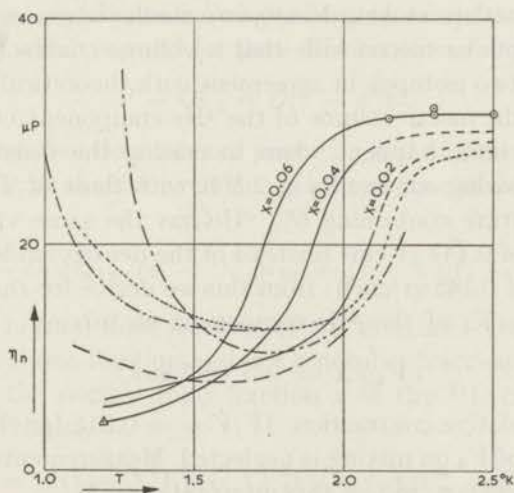


Fig. 10. The normal fluid viscosity η_n as a function of the temperature T .

- : η_n^0 , determined with the rotating viscometer ²⁵).
- - - - -: η_n^0 , derived from heat conductivity measurements ³¹).
-: η_n^0 , determined with oscillating disks ²² ²³ ²⁴).
- · - · - ·: η_n^0 , derived from the attenuation of second sound ³⁰).
- : η_n , derived from fig. 9 at three different concentrations X .
- : η of a 6% ^3He - ^4He mixture, measured at $T > T_\lambda$.
- △ : η_n of a 4.2% ^3He - ^4He mixture, determined by Pellam ²⁹).

At low temperatures η_n is much smaller than η_n^0 , which is derived from experiments with oscillating disks ²²⁾ ²³⁾ ²⁴⁾, with the rotating viscometer ²⁵⁾ and from the attenuation of second sound ³⁰⁾. The difference between η_n and the η_n^0 -curve derived from heat conductivity experiments ³¹⁾ is much smaller, which perhaps has to be attributed to the fact that the latter experiment is substantially a flow experiment, similar to ours, while in the oscillating disk experiment *e.g.* no steady state of the flow is attained.

The behaviour of the viscosity cannot be explained, as for a gas, by adding the viscosities of pure ³He and ⁴He. The viscosity of pure ³He varies between 22 μ P at 2.8°K and 30 μ P at 1.05°K ³²⁾, showing the normal temperature dependence of the viscosity of a liquid. At temperatures above the lambda-point it is smaller than the ⁴He-viscosity but at lower temperatures it is much larger: therefore one would expect a similar behaviour for the normal fluid viscosity of the mixture, in contrast with experiment.

From the high-pressure viscosity measurements by Brewer and Edwards ³³⁾ we know that below about 1.5°K the normal fluid viscosity of ⁴He decreases slightly with increasing density, whereas a strong increase of the viscosity is observed at temperatures between 1.5°K and the lambda-point, obviously caused by the shift of the lambda-point with pressure. From the experiments of Tjerkstra ²⁸⁾ we know that above the lambda-point the increase of the viscosity with density is much smaller. Hence the ⁴He-viscosity changes with increasing density in a similar way as with the addition of ³He. This tempts us to conclude that a volume contraction takes place when mixing the two isotopes, in agreement with theoretical predictions ³⁴⁾. For, in this case, the molar volume of the ⁴He-component of the mixture is reduced and the same happens when increasing the density of the pure component. Comparing our results at 2.5°K with those of Tjerkstra, it is found that a mixture containing 6% ³He has the same viscosity as pure ⁴He of a density of 0.147 gr/cm³ (instead of the density under the saturated vapour pressure of 0.145 gr/cm³): from this we derive for the contraction of the molar volume V_4 of the ⁴He-component on mixing:

$$\partial V_4 / \partial X = -7 \text{ cm}^3 / \text{mol}, \quad (26)$$

yielding a total relative contraction $\Delta V / V = -0.015$ for this 6% mixture, when the change of V_3 on mixing is neglected. Measurements of the mixture density will be necessary to test this interpretation *).

c. The relative flow rate and the normal fluid fraction. For the determination of η_n it was sufficient to assume that eqs. (21) and (22) represented the momentum balance of the mixture, without discussing the particular form of the function F in eq. (22). However, by transforming \dot{V} into $\dot{V} - O\hat{v}_n$ with the aid of eq. (21) and using the η_n -values, given above, we find also in

*) Since no numerical values of η_n^0 as a function of the density ³³⁾ were at our disposal, we could not estimate the contraction at $T < T_\lambda$.

the case of a mixture a m -th power relation between ΔP_{eff} and $\dot{V} - O\hat{v}_n$ to exist, confirming our supposition in eq. (20). The exponent $m = 3.45$ is equal to m^0 , the pure ^4He -exponent, but the mutual friction factor B is larger than B^0 and increases with concentration. Writing for the relative velocity the relation:

$$\text{grad } P_{\text{eff}} = -\alpha \mathbf{v}_r^m \quad (m = m^0) \quad (27)$$

where α may depend on temperature and concentration, we can write for the mutual friction term B of the mixture, employing eqs. (19), (20) and (27):

$$B = \alpha L / [O(1 - x')]^m \quad (m = m^0) \quad (28)$$

whereas we obtain from eqs. (14) and (11') for pure ^4He :

$$B^0 = \alpha^0 L / [O(1 - x^0)]^{m^0}. \quad (29)$$

Thus the observed increase of B with concentration depends either on the difference between α and α^0 or on that between x' and x^0 or on both. Unfortunately no directly measured data of x' (with the exception of a single measurement by Pellam²⁹) exist, preventing the decision from which term the difference between B and B^0 originates. However, since $m = m^0$, we were tempted to try the supposition that $\alpha = \alpha^0$ (see eq. (27)), *i.e.* that the relative velocity of the mixture is still given by eq. (14) when ΔP is replaced by ΔP_{eff} , and hence is independent of temperature and concentration. Eq. (10) which is valid for pure ^4He becomes for a mixture:

$$\dot{V} - O\hat{v}_n = O(1 - x')v_r. \quad (30)$$

Comparing the relative flow rates of pure ^4He and of a mixture at the same value of ΔP_{eff} , *i.e.* at the same relative velocity v_r , we can determine x' from the relation:

$$(\dot{V} - O\hat{v}_n)_{\text{mixt}} / (\dot{V} - O\hat{v}_n)_{^4\text{He}} = (1 - x') / (1 - x^0). \quad (31)$$

Because x' , the normal fluid fraction of the mixture, ^3He -atoms included, is essentially a volume fraction and not a number fraction (*cf.* eq. (19)) it is connected with the normal fluid fraction x of the ^4He -component of the mixture by the relation:

$$x' = [x(1 - X)V_4^0 + XV_3^0] / [(1 - X)V_4^0 + XV_3^0] \quad (32)$$

where V_3^0 and V_4^0 denote the molar volumes of the pure components. The contraction on mixing is neglected, since no experimental data are available and our estimated value of the contraction is so small that it has only negligible influence on eq. (32).

In fig. 11 the relative flow rate is shown as a function of the concentration at constant temperature and $|\Delta P_{\text{eff}}| = 1000 \text{ cm He}$. From the ratio $(1 - x') / (1 - x^0)$, derived from it with eq. (31), x' was obtained and trans-

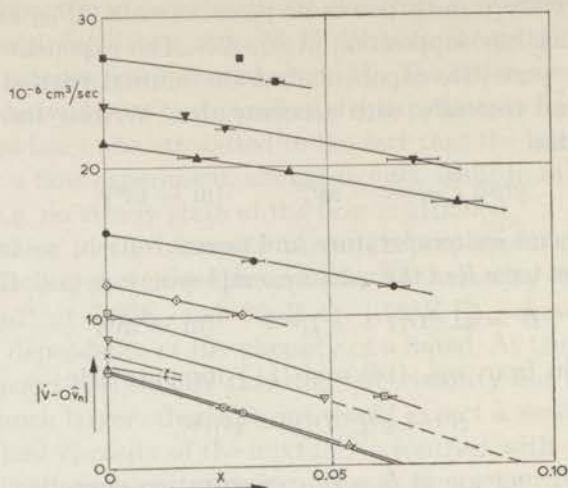


Fig. 11. The relative flow rate $|\dot{V} - O\hat{v}_n|$ at $|\Delta P_{\text{eff}}| = 1000$ cm He as a function of the concentration X at different temperatures.

- | | | |
|-------------------------|-----------|----------------|
| ○: 2.08 ₉ °K | ▽: 2.05°K | ▲: 1.70°K |
| △: 2.08 ₇ °K | □: 2.02°K | ▼: 1.54-1.56°K |
| + : 2.08°K | ◇: 1.98°K | ■: 1.20-1.22°K |
| × : 2.07°K | ●: 1.90°K | |

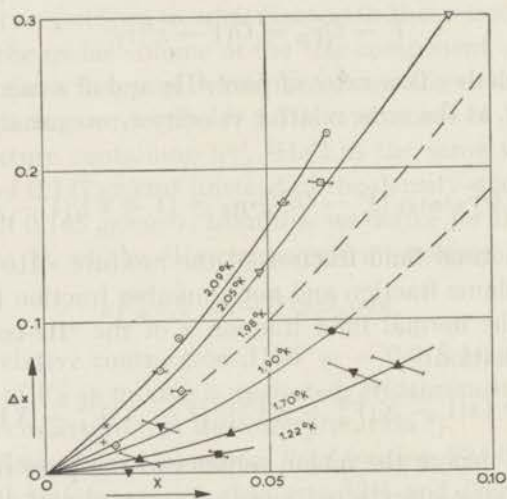


Fig. 12. The increase Δx of the normal fluid fraction of the ^4He -component of a ^3He - ^4He mixture as a function of the concentration X at different temperatures.

- | | | |
|-------------------------|-----------|----------------|
| ○: 2.08 ₉ °K | ▽: 2.05°K | ▲: 1.70°K |
| △: 2.08 ₇ °K | □: 2.02°K | ▼: 1.54-1.56°K |
| + : 2.08°K | ◇: 1.98°K | ■: 1.20-1.22°K |
| × : 2.07°K | ●: 1.90°K | |

formed into x , inserting in eq. (32) $V_3^0/V_4^0 = 1.35$. In table II and fig. 12 $\Delta x = x - x^0$ is plotted *versus* concentration at constant temperature, while table IV and fig. 13 give Δx as a function of the temperature at constant X . The sharp increase of Δx near the lambda-point is remarkable. Good correspondence exists with the increase of the normal fluid fraction as calculated

TABLE IV

Smoothed values of Δx in %			
$T \backslash X$ deg K	0.02	0.04	0.06
1.2	0.5	1.3	2.3
1.3	0.5	1.4	2.5
1.4	0.6	1.5	2.7
1.5	0.7	1.7	3.1
1.6	0.8	1.9	3.6
1.7	1.0	2.5	4.5
1.8	1.4	3.3	6.0
1.9	2.0	4.8	8.7
2.0	3.2	7.9	14.2
2.1	5.5	13.0	20.0

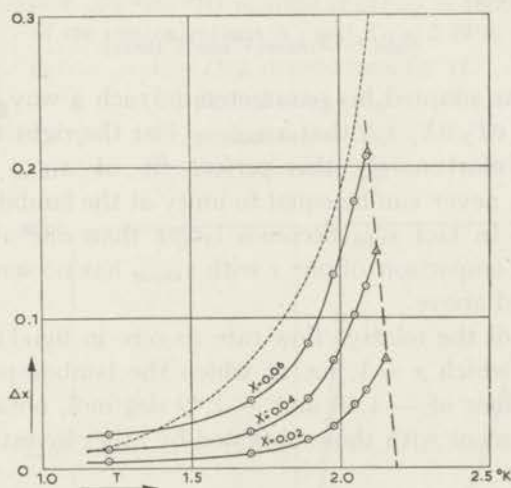


Fig. 13. The increase Δx of the normal fluid fraction of the ^4He -component of a ^3He - ^4He mixture as a function of the temperature T at different concentrations.

○ : Δx , derived from fig. 12.

△ : Δx , calculated from the shift of the lambda-point with concentration ^{35) 36) 37).}

— — — : T_λ as a function of the concentration X .

- - - - - : Δx_{obs} for $X = 0.06$, according to Mikura's theory ^{40).}

from the shift of the lambda-point with concentration ^{35) 36) 37).} Although it is questionable whether our assumption concerning the mutual friction in the mixture, *viz.* that the ^3He -atoms behave mechanically as normal

^4He -particles, is correct, one still can expect Δx to have a temperature dependence as shown, because the influence of the ^3He on the relative flow rate is the largest at the higher temperatures. Only assumptions of strongly temperature dependent effective ^3He -masses *e.g.* would yield other temperature dependencies of Δx . Calculation of Δx from second sound in mixtures³⁸⁾ by means of a Pomeranchuk-type formula³⁹⁾ or from the oscillating disk experiment by Pellam²⁹⁾ gives much larger values at low temperatures¹¹⁾ than we obtained with our assumptions. However, the calculation of Δx from second sound also involves a large number of assumptions, whereas the direct method of Pellam, which should give more reliable values, unfortunately yields a shift of the lambda-point of -0.86 deg/mol instead of the now generally accepted value of about -1.5 deg/mol. More experiments with the oscillating disk will be necessary before the discrepancies between the different results can be understood and final discussion of Δx is possible.

Mikura^{13) 40)} has derived theoretical values of the normal fluid fraction for pure ^4He and for mixtures, but since his x^0_{theor} does not fit the observed data, x^0_{obs} , he does not expect x_{theor} of the mixture to behave better. Actually he supposes both theoretical values to suffer from the same error and therefore writes:

$$x_{\text{obs}} = x_{\text{theor}}[x^0_{\text{obs}}/x^0_{\text{theor}}]. \quad (33)$$

Now Mikura has adapted his parameters in such a way as to obtain the correct value of $\partial T_\lambda/\partial X$, *i.e.* that $x_{\text{theor}} = 1$ at the right temperature and concentration. Unfortunately this perfect fit of x_{theor} to experiment implies that x_{obs} never can be equal to unity at the lambda-point, because $x^0_{\text{obs}}/x^0_{\text{theor}} \neq 1$. In fact x_{obs} becomes larger than one at T_λ , as can be seen in fig. 13. Comparison of our x with x_{theor} has no sense either for the reasons mentioned above.

Extrapolation of the relative flow rate to zero in fig. 11 yields the concentration X at which $x = 1$, *i.e.* at which the lambda-point is attained. The observed values of -1.48 and -1.49 deg/mol, obtained at 2.09°K , are in good agreement with those obtained by other investigators^{35) 36) 37)} (see fig. 16).

d. The flow rate as a function of X_A and X_C . In order to test our statement that the flow rate depends on the concentration of the liquid in the high pressure vessel only, we measured the positive and negative flow rates, \dot{V}^+ and \dot{V}^- , at 2.09°K for eleven hours: during this time X_A changed only from 3.1 to 3.8%, but X_C changed much more, *viz.* from 0.4 to 2.4%. If X_C had any influence on the flow rate, the effect would have been detected in this experiment because of the relatively large change of X_C . Actually the flow rates appeared to decrease only when X_A increased and not when X_C changed. In fig. 14 we plotted \dot{V}^+ and \dot{V}^- as a function of X_A and of X_C . We can obtain the right values of the pure ^4He flow rate and the right

lambda-point concentration X_λ by extrapolating the curves depending on X_A . Extrapolation of \dot{V}^- as a function of X_C yields absurd values of both $(\dot{V})_{X=0}$ and X_λ . Furthermore the quantity $\Delta\dot{V}$ (see eq. (25)) was fairly well proportional to ΔP_{osm} during the whole experiment which is also in agreement with our assumptions. Hence our statement concerning the concentration dependence of the flow rate seems to be confirmed, if we exclude once more the temperature region very near the lambda-point.

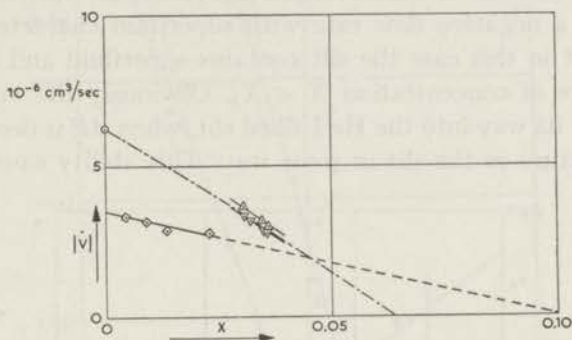


Fig. 14. The flow rate \dot{V} of a ^3He - ^4He mixture at $|\Delta P_{\text{eff}}| = 1000$ cm He as a function of the concentrations X_A and X_C at 2.09°K .

- — — — : $\dot{V} - \hat{O}\hat{v}_{n_1}$, derived from fig. 11.
- △ : \dot{V}^+ , plotted versus X_A .
- ▽ : \dot{V}^- , plotted versus X_A .
- ◇ : \dot{V}^- , plotted versus X_C .

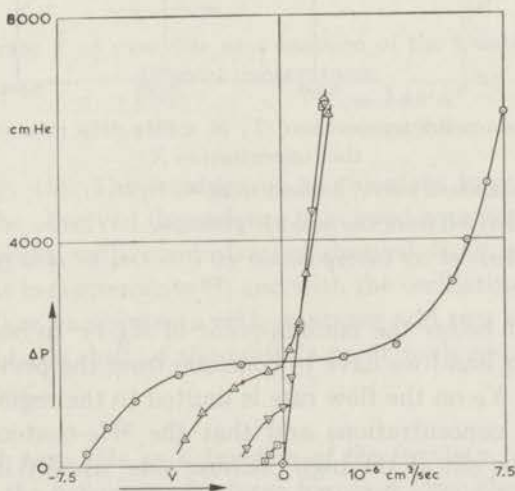


Fig. 15. The flow rate \dot{V} of a 4.6% ^3He - ^4He mixture as a function of the pressure head ΔP at different temperatures.

- : 2.05°K
- △ : 2.10°K
- ▽ : 2.12°K
- : 2.14°K
- ◇ : 2.15°K

e. *The flow at temperatures very near the lambda-point.* When increasing the bath temperature gradually to about 0.05 deg from the lambda-point of the mixture in *A*, and higher, the first deviation from the normal behaviour we observe is that the negative flow rate \dot{V}^- becomes larger than \dot{V}^+ (see fig. 15). When the temperature is increased further, the lambda-point of X_A is passed, whereas the mixture in *C* remains still superfluid. At these intermediate temperatures \dot{V}^+ is a normal Poiseuille flow and the whole slit will be filled with a mixture of concentration X_A . However, when ΔP is decreased below ΔP_{osm} , a negative flow rate with superfluid character is observed, indicating that in this case the slit contains superfluid and hence is filled with a mixture of concentration $X < X_\lambda$. Obviously the superfluid in *C* is able to force its way into the He I-filled slit, when ΔP is decreased, and to dilute the mixture in the slit in some way. This ability causes at temper-

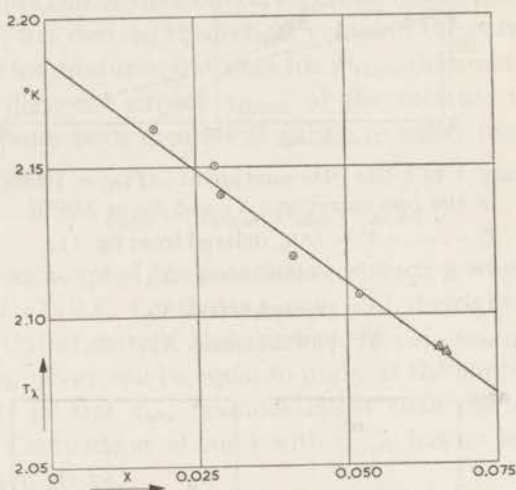


Fig. 16. The lambda-point temperature T_λ of a ^3He - ^4He mixture as a function of the concentration X .

— : standard curve, derived from ³⁵⁾ ³⁶⁾ ³⁷⁾.

○ : derived from the osmotic pressure.

△ : derived by extrapolation of $\dot{V} - \hat{O}\hat{v}_n$ to zero (see fig. 11).

atures somewhat below the lambda-point of X_A \dot{V}^- to become larger than \dot{V}^+ . On the other hand we have to conclude from the previous section that this influence of X_C on the flow rate is limited to the region of very low (or zero) superfluid concentrations and that the ^3He -content of the normal fluid, entering the slit at the high pressure side, usually is the all-deciding factor. A detailed study of the flow in this intermediate temperature region will be necessary in order to understand the obviously complicated mechanism by which X_C influences the flow.

From the arguments given above it is clear that near the end of the

superleak the concentration jumps from a value smaller than X_λ to X_λ . Hence somewhere the concentration X_λ is passed. Now the osmotic pressure of ^3He - ^4He mixtures is a typical He II-effect and hence we have to expect that at intermediate temperatures ΔP_{osm} is given by $RT(X_\lambda - X_C)/M_{4g}$ in first approximation instead of by $RT(X_\lambda - X_C)/M_{4g}$ (see eq. (8)) and that it therefore decreases rapidly with increasing temperature, which is actually

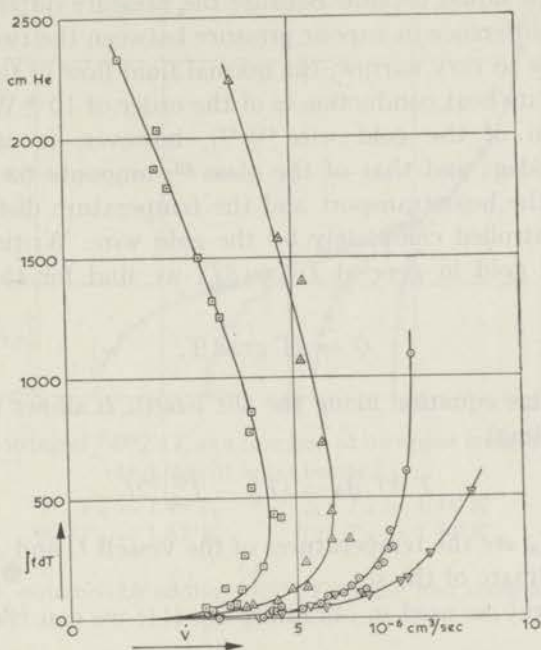


Fig. 17. The flow rate \dot{V} of pure ^4He as a function of the fountain force $\int f dT$ at different temperatures.

- | | |
|-----------|-----------|
| □: 1.97°K | ○: 1.67°K |
| △: 1.84°K | ▽: 1.49°K |

observed (see fig. 15). This enables us to calculate from ΔP_{osm} X_λ as a function of T . The observed dependence is in good agreement with the shift of the lambda-point with concentration derived from second sound ³⁵, from specific heat measurements ³⁶ and with the oscillating disk ³⁷ (see fig. 16). Hence the flow experiments with mixtures add two new, independent determinations of the shift of the lambda-point with concentration to the three existing ones.

7. *The flow of pure ^4He as a function of the fountain force.* The flow of pure ^4He under the influence of a large fountain force shows a dependence on this driving force remarkably different from the isothermal flow (see fig. 17): it passes through a maximum value instead of increasing continuously (cf. fig. 2). Nevertheless, this strange behaviour is in agreement with

the results of the isothermal flow experiments with the same apparatus. Because of the large temperature gradients employed we have to integrate over the slit length not only the fountain force, but also the flow resistance B^0 , since it depends strongly on the temperature.

To perform this integration, the temperature distribution in the slit has to be known. It is governed by the heat conduction through the gold wire, the glass and the liquid helium. Because the pressure difference across the slit is only the difference in vapour pressure between the two vessels A and C , and the slit is so very narrow, the normal fluid flow of the liquid helium is so small that its heat conduction is of the order of 10^{-8} W/deg only. The heat conduction of the gold wire^{41) 42)}, however, is of the order of $1.5 \times 10^{-4} T$ W/deg; and that of the glass⁴³⁾ amounts to about $10^{-5} T^{1.3}$ W/deg. Hence the heat transport and the temperature distribution in the superleak is controlled completely by the gold wire. Writing for the heat conductivity of gold in general $\lambda_{Au} = \beta T$, we find for the heat current density:

$$\dot{Q} = \beta T \text{ grad } T. \quad (34)$$

Integration of this equation along the slit length L allows the elimination of \dot{Q} and β , yielding:

$$T \, dT/dz = (T_C^2 - T_A^2)/2L \quad (35)$$

where T_C and T_A are the temperatures of the vessels C and A resp. and z is the length coordinate of the slit.

In a similar way as used in obtaining eq. (11) we can transform eq. (3) into:

$$(S_4^0/g)dT - dP = (B^0/L) (\dot{V} - \hat{O}\hat{v}_n)m^0 dz \quad (36)$$

where the pressures are expressed in cm He. For the reasons mentioned above $\hat{O}\hat{v}_n/\dot{V} < 0.01$, which allows us to write for eq. (36):

$$f dT = (B^0/L) \dot{V} m^0 dz \quad (37)$$

where f is the fountain constant in cm He/deg, corrected for the vapour pressure difference. Because $d\dot{V}/dz$ is zero, we obtain from eqs. (35) and (37):

$$\int_{T_A}^{T_C} f dT = \frac{\dot{V} m^0}{L} \int_{T_A}^{T_C} B^0 \frac{dz}{dT} dT = \frac{2\dot{V} m^0}{(T_C^2 - T_A^2)} \int_{T_A}^{T_C} B^0 T dT. \quad (38)$$

Because \dot{V} is measured as a function of T_A and T_C , and m^0 is known from isothermal flow experiments*) with the same apparatus, the integral $\int B^0 T dT$ can be derived directly from experiment. It can be compared with B^0 ,

*) As has been mentioned already in section 5b, the relative velocity v_r in these experiments is a function of both pressure head and temperature, in contrast to the results obtained with apparatus 1a.

determined isothermally with the same apparatus as a function of T , either by integrating the latter over the temperature region $T_A - T_C$ or by differentiating the integral $\int B^0 T dT$ with respect to its upper limit T_C , yielding $B^0 T_C$. The latter way has been followed. In fig. 18 $\int B^0 T dT$ is

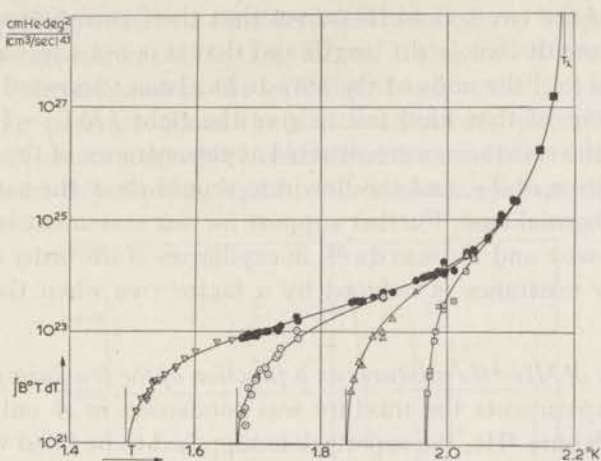


Fig. 18. The integral $\int B^0 T dT$ as a function of its upper integration limit T_C at different lower limits T_A .

∇ : $T_A = 1.49^\circ\text{K}$ \triangle : $T_A = 1.84^\circ\text{K}$
 \odot : $T_A = 1.67^\circ\text{K}$ \square : $T_A = 1.97^\circ\text{K}$

\bullet : $\int_{1.49}^{T_C} B^0 T dT$, obtained by adding $\int_{1.49}^{T_A} B^0 T dT$ to the four integrals $\int_{T_A}^{T_C} B^0 T dT$.

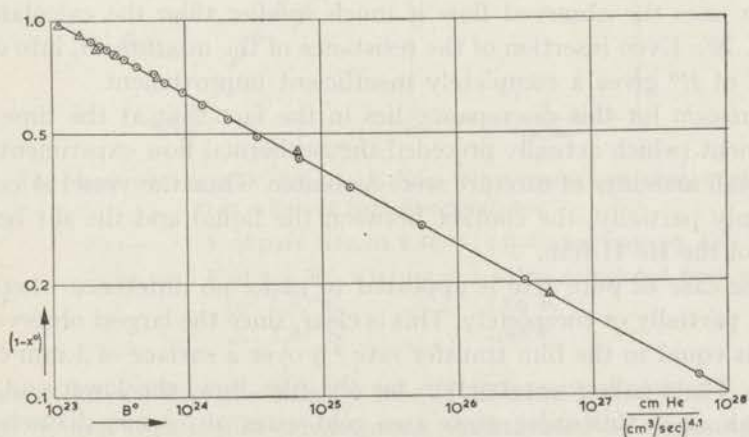


Fig. 19. The resistance factor B^0 of pure ^4He as a function of the superfluid fraction $1 - x^0$.

\triangle : obtained from isothermal flow experiments.
 \odot : obtained by differentiating $\int B^0 T dT$.

plotted *versus* T_C for four different bath temperatures T_A . By a simple process of addition these four curves are converted into a single one, being $\int B^0 T dT$ with $T_A = 1.49^\circ\text{K}$ and T_C varying between 1.49 and 2.17°K , from which B^0 is derived by differentiation. In fig. 19 the results are shown, together with the isothermal values of the flow resistance. The perfect coincidence of the two sets of B^0 proves that the flow resistance is actually distributed over the whole slit length and that it is not concentrated at one or two points (*e.g.* the ends of the slit) as has been suggested occasionally. All assumptions of that kind fail to give the right $\int f dT - \dot{V}$ relation. If, for instance, the resistance were situated at the entrance of the slit, it should not be a function of T_C , and the flow rate should show the same behaviour as in the isothermal case. Further support for our statement is found in the result of Brewer and Edwards³²⁾ in capillaries of the order of 100 micron that the flow resistance is reduced by a factor two when the capillary is bisected.

8. *The flow of ^3He - ^4He mixtures as a function of the fountain force.* Since in these flow experiments the mixture was condensed in A only, whereas C was filled with pure ^4He , the superleak is supposed to be filled with pure ^4He only, as has been argued before (see section 3*b*). Hence the only difference with respect to eq. (38) of the previous section to be expected is the introduction of the osmotic pressure difference across the slit, yielding:

$$\int_{T_A}^{T_C} f dT - \Delta P_{\text{osm}} = \left(\int f dT \right)_{\text{eff}} = \frac{2\dot{V}_{\text{m}^0}}{(T_C^2 - T_A^2)} \int_{T_A}^{T_C} B^0 T dT. \quad (39)$$

Comparing, however, the experimental data with the curve calculated from eq. (39), we find a good agreement for the negative flow rates, but for positive ones the observed flow is much smaller than the calculated one (see fig. 20). Even insertion of the resistance of the mixture, B , into eq. (39) instead of B^0 gives a completely insufficient improvement.

The reason for this discrepancy lies in the fact that at the time of the experiment (which actually preceded the isothermal flow experiments) only very small amounts of mixture were available. Thus the vessel A could be filled only partially, the contact between the liquid and the slit being by means of the He II-film.

In the case of pure ^4He it appeared to make no difference whether we filled A partially or completely. This is clear, since the largest observed flow rate was equal to the film transfer rate⁴⁴⁾ over a surface of 1 mm circumference. The smallest constriction for the film flow, the lower end of the superleak, is of this order, since two gold wires of 0.1 mm diameter were used in this superleak and a small drop of liquid is present around these wires at the entrance of the superleak because of the surface tension. On the other hand, this equilibrium is seen to be rather critical: if the film transport had been somewhat smaller, we would not have measured the properties of

the bulk liquid flow in the slit, but rather the film flow in the vessel *A*.

At the time of the experiments with the mixture, however, we thought that the film transport would be sufficient for the mixture also. From the observed discrepancy with respect to eq. (39) it is clear that this is not so and that our positive flow rates are connected with film flow rather than with bulk liquid flow. Let us consider what might have happened with the film. From the measurements by Inghram, Long and Meyer⁴⁵⁾ we know that the ³He-concentration in the bulk liquid and in the film is the same for a given vapour pressure. Since the slit contains only pure ⁴He, a concentration jump *X* exists somewhere near the entrance of the slit, exposing the film at this point to a tension, equal to the osmotic pressure of the mixture.

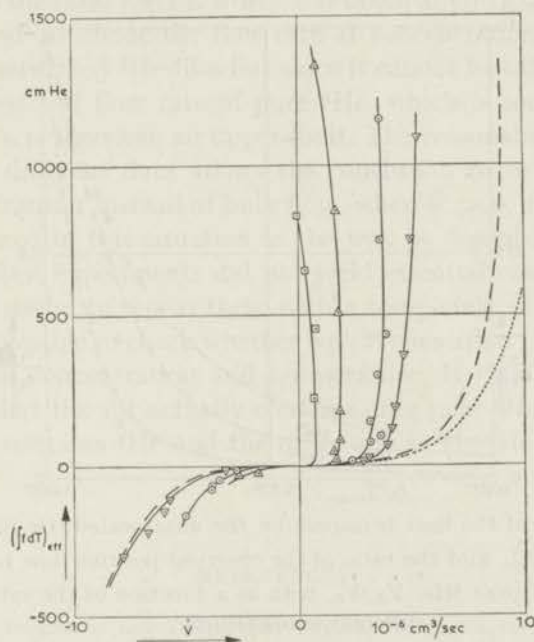


Fig. 20. The observed flow rate \dot{V} of a 1.3% ³He-⁴He mixture as a function of $(f d T)_{\text{eff}}$ at different bath temperatures.

- : \dot{V} of pure ⁴He, at 1.48°K, calculated from eq. (38).
 - - - : \dot{V} of a 1.3% mixture at 1.48°K, calculated from eq. (39).
 □: 1.97°K ○: 1.66°K
 △: 1.84°K ▽: 1.48°K

It is well-known that the transfer rate of an unsaturated film is strongly reduced⁴⁶⁾ and that a film can be made unsaturated by exposing it to a tension. This has been shown in the indirect measurement of the fountain effect⁴⁷⁾ where the vessel *A* of an apparatus, similar to our apparatus 1*b*, contained such a small amount of ⁴He that only film was present in it. By heating *C* which contained some bulk liquid, a fountain force $f d T$ was

created which exerted a tension on the film in A . As a result of this tension the film appeared to become unsaturated reducing its vapour pressure by an amount ΔP equal to:

$$\Delta P = (\rho_v/\rho_4^0)\pi \quad (40)$$

where π is the exerted tension equal to $\int f dT$, and where ρ_v and ρ_4^0 denote the molar vapour and liquid density resp. If we now take this tension π equal to the osmotic pressure of a mixture of concentration X , we have, employing cgs-units (cf. eq. (7)):

$$\Delta P = -\rho_v RT \ln [(1-X)f_4] = -(P_4^0 - \Delta P) \ln [(1-X)f_4] \quad (41)$$

where the activity coefficient f_4 ¹⁰ accounting for the non-ideality of the

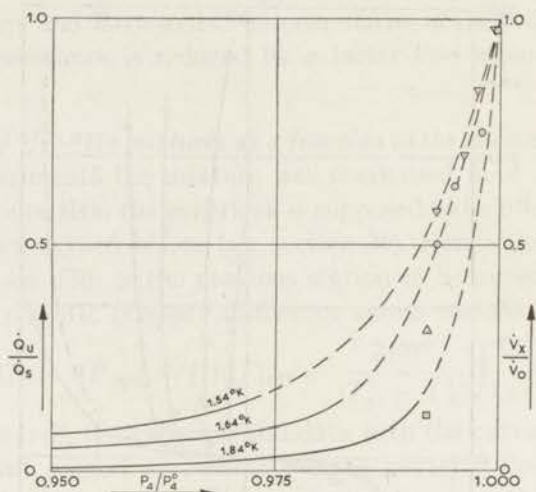


Fig. 21. The ratio of the heat transport by the unsaturated ^4He -film to that of the saturated film, \dot{Q}_u/\dot{Q}_s , and the ratio of the observed positive flow rate of a ^3He - ^4He mixture to that of pure ^4He , \dot{V}_x/\dot{V}_0 , both as a function of the saturation P_4/P_4^0 at different temperatures.

- : \dot{Q}_u/\dot{Q}_s , measured by Bowers, Brewer and Mendelssohn⁴⁶.
 - - - -: \dot{Q}_u/\dot{Q}_s , interpolated curve.
 ∇ : \dot{V}_x/\dot{V}_0 at 1.49°K. \triangle : \dot{V}_x/\dot{V}_0 at 1.84°K.
 \circ : \dot{V}_x/\dot{V}_0 at 1.66°K. \square : \dot{V}_x/\dot{V}_0 at 1.97°K.

mixture obeys the inequality $0 < f_4 - 1 \ll 1$. Second virial coefficients are neglected. The vapour pressure of the film thus becomes:

$$P_4^0 - \Delta P = P_4^0 \{1 - \ln [(1-X)f_4]\} = P_4^0(1-X)f_4 \quad (42)$$

with a relative error of the order of X^2 . The partial vapour pressure P_4 of a mixture of concentration X , on the other hand, is given by¹⁰:

$$P_4 = P_4^0(1-X)f_4 \quad (43)$$

which is equal to the result of eq. (42). Hence the ^4He -film under a tension equal to the osmotic pressure of a given mixture has a vapour pressure equal to the partial ^4He -pressure of this mixture, and its transfer rate will be that of a film at saturation P_4/P_4^0 .

Now it is reasonable to suppose that in our case the film, being under the same tension, will flow also as a ^4He -film at a saturation P_4/P_4^0 . In order to verify this and to see whether the positive flow rates are film transfer rates indeed, we compared our flow rates as a function of P_4/P_4^0 , calculated from the liquid concentration ¹¹⁾, with the directly measured transfer rate of the unsaturated film ⁴⁶⁾. In fig. 21 we plotted *versus* the saturation P_4/P_4^0 both the ratio of the heat transport of the unsaturated and the saturated ^4He -film, \dot{Q}_u/\dot{Q}_s , and the ratio \dot{V}_X/\dot{V}_0 , where \dot{V} is taken at $(\int/dT)_{\text{eff}} = 300 \text{ cm He}$. Actually we had to divide the flow rate at concentration X , \dot{V}_X , by the transfer of the saturated ^4He -film but since it cannot be calculated exactly, we took the observed flow rate of pure ^4He , which is somewhat smaller. The ratio \dot{V}_X/\dot{V}_0 is therefore an upper limit. The reasonable agreement between the two different data allows the conclusion to be drawn that we measured film transfer instead of bulk flow, when $\dot{V} > 0$, and that the film transfer is reduced in this situation in the way as described above.

Hence these last experiments did not yield essential results on the bulk flow. It will be useful to repeat them with a completely filled lower vessel, since then it is possible to check whether eq. (39) describes the flow correctly as a function of concentration and temperature. If this is so, the exact proof is given that the slit actually contains only pure ^4He , when the high pressure vessel contains ^4He and the other one a ^3He - ^4He mixture.

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SAMENVATTING

In dit proefschrift worden enige eigenschappen van ^3He — ^4He mengsels bij temperaturen beneden het lambda-punt van het mengsel besproken.

De onderzoeken zijn uitgevoerd met behulp van toestellen, welke in hoofdzaak bestaan uit twee vaten, verbonden door een nauwe spleet. Een van de vaten kan eventueel worden verwarmd. De spleet wordt gevormd door een of twee gouddraden van 0.1 mm diameter in te smelten in een stuk zacht glas. Door het verschil in uitzettingscoëfficiënt tussen beide materialen ontstaat er bij afkoeling een spleet, die bij He-temperaturen van de orde van 0.2–0.3 micron is.

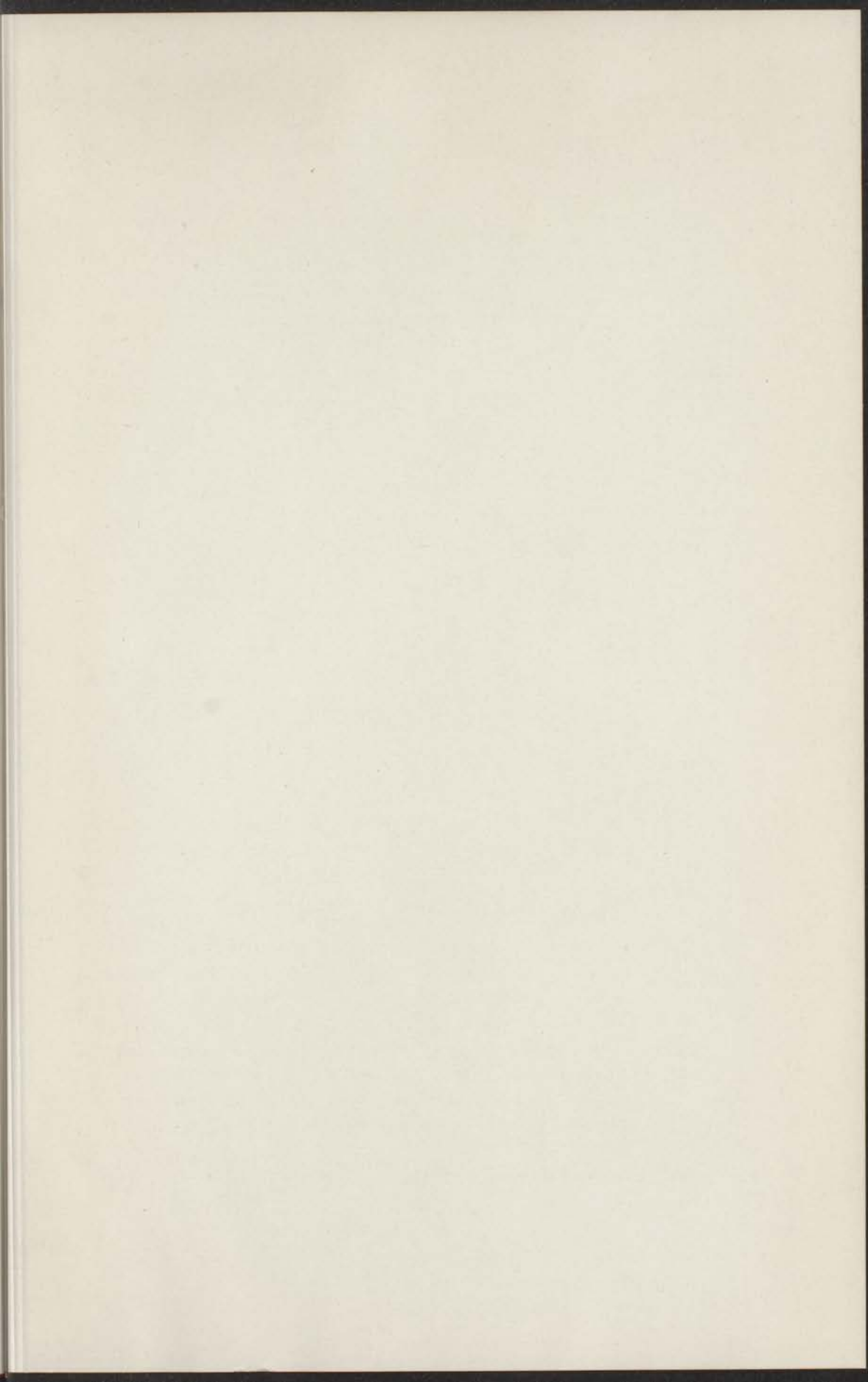
In het eerste hoofdstuk worden metingen over het fase-evenwicht tussen damp en vloeistof van ^3He — ^4He mengsels bij vloeistofconcentraties van de orde van 10^{-3} beschreven. Zij zijn uitgevoerd met zeer kleine hoeveelheden vloeistof ter vermindering van concentratiegradienten in de vloeistof. Een redelijke aansluiting aan de resultaten van Sommers bij hogere concentraties is gevonden.

Het tweede hoofdstuk is gewijd aan de osmotische druk, die door een ^3He — ^4He mengsel wordt uitgeoefend ten opzichte van zuiver ^4He , als beiden door een nauwe spleet van elkaar gescheiden zijn. De gemeten osmotische drukken blijken aan de klassieke thermodynamische relaties te voldoen in het hele onderzochte gebied.

In hoofdstuk III zijn uit de dampdrukgegevens de chemische mengpotentialen voor mengsels tot 7% concentratie berekend. Door differentiatie e.d. zijn hieruit mengentropie, mengenthalpie en meng-soortelijke warmte afgeleid. Voorts wordt de temperatuur geschat, waarbij een fasescheiding in het mengsel zal kunnen optreden. Over het algemeen blijkt er een redelijke tot goede overeenstemming met de bestaande experimentele gegevens te bestaan.

In het laatste hoofdstuk komen de verschijnselen ter sprake, die optreden bij de stroming van een ^3He — ^4He mengsel door een nauwe spleet. Deze stroming is in eerste benadering analoog aan die van zuiver ^4He en vertoont dezelfde merkwaardige afhankelijkheid van de drijvende kracht, zij het dat de stroomsnelheid afneemt met toenemende concentratie. Uit de resultaten wordt met behulp van een enigszins aangepast twee-fluida

model de viscositeit van het conglomeraat, gevormd door het ^3He en het normale fluidum van het ^4He , afgeleid, terwijl tevens onder bepaalde veronderstellingen de toename van de hoeveelheid normaal fluidum van het ^4He t.g.v. de toevoeging van ^3He wordt geschat. Bovendien leveren de metingen een waarde voor de verschuiving van het lambda-punt met de ^3He -concentratie op, welke in overeenstemming is met de thans algemeen aanvaarde waarde van -0.015°K per procent ^3He . Door bij temperaturen boven het lambda-punt de viscositeit van het mengsel te vergelijken met die van zuiver ^4He onder druk wordt een schatting van de volumecontractie bij menging verkregen.



The first part of the book is devoted to a general introduction to the subject of the history of the English language. The author discusses the various influences that have shaped the language over time, including the contributions of Old English, Middle English, and Modern English. He also touches upon the role of literature and the standardization of the language.

