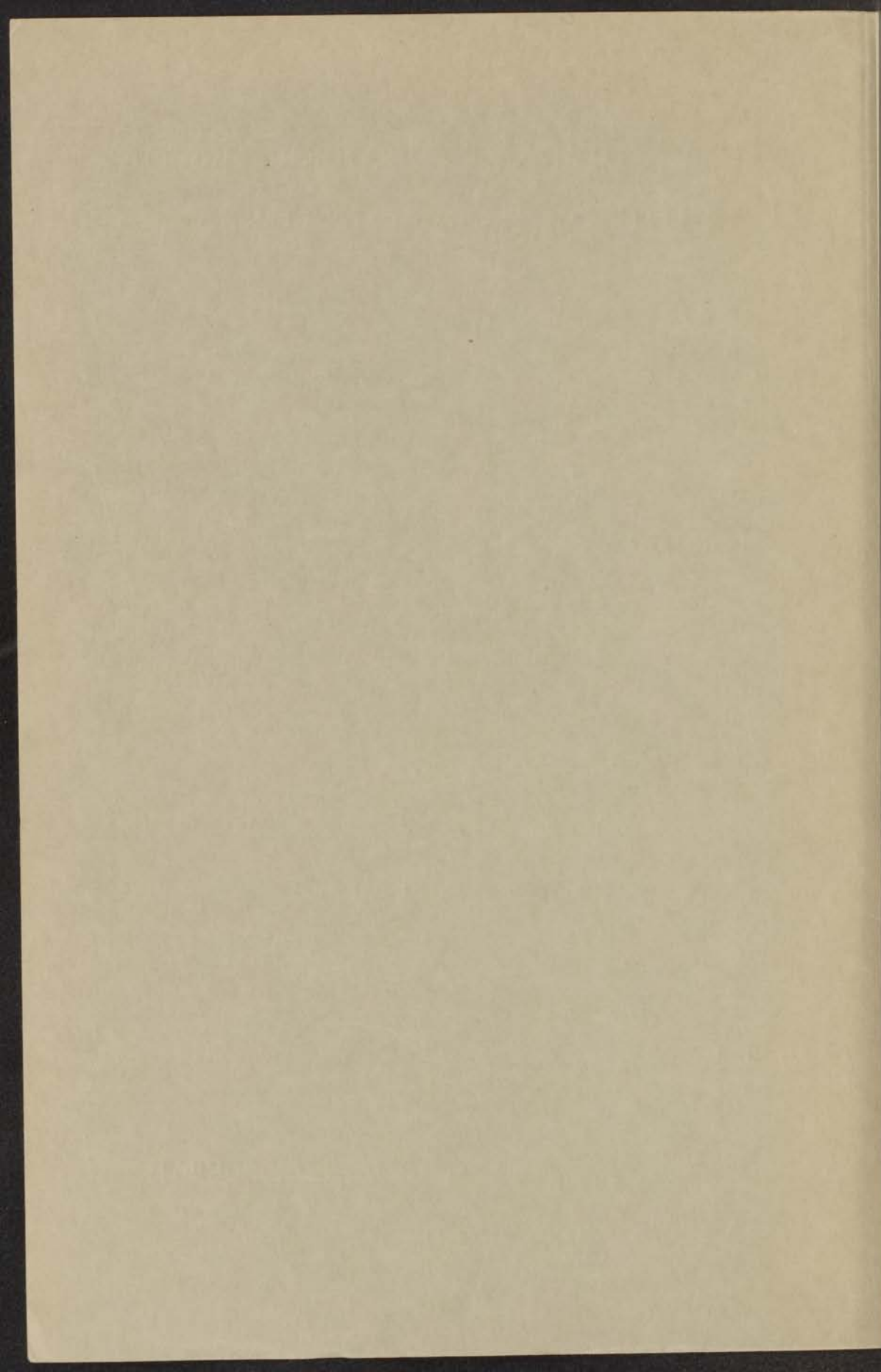


THERMODYNAMIC PROPERTIES OF
LIQUID ^3He - ^4He MIXTURES

R. DE BRUYN OUBOTER



STELLINGEN

I. Een op de mengvertoefen van vier twee ^3He - ^4He mengels verkende toestand kan waarschijnlijk goede diepten bereiken voor uitdrukkingen in het temperatuurbereik van 0,1°K.

II.

Het is twijfelachtig of het gebrek van een experimentele test als basis van THERMODYNAMIC PROPERTIES OF LIQUID ^3He - ^4He MIXTURES

III.

Ten onrechte wordt voor eenvoudige vloeistoffen aan de theorie van de continue menging een grote quantitative betekenis toegekend.

Hasse, G. G., N. 45, and Staveland, L. A. R., *Quart. Revs.*, (London) 11 (1957) 26.

IV.

De veronderstelling van Joy en Libby, dat de verandering van het molal volume bij isotopische substitutie is niet gegeven door de derde macht van de atoommassa variatie van de uitgangsstoffen, kan een heel belangrijk punt zijn. Eigenaardig niet wondermeer aanvaardbaar.

Joy, H. W. and Libby, W. F., *Journ. Chem. Phys.* 25 (1957) 1276.

V.

Het verdient aanbeveling de aangevoerde warmte metingen van nitrofol, welke door Keesom en Pearlman verricht zijn, uit te breiden tot beneden 1°K.

Keesom, P. M. and Pearlman, N., *Phys. Rev.* 112 (1958) 593.

THE UNIVERSITY OF CHICAGO PRESS

STELLINGEN

I

Een op de mengwarmte van vloeibare ^3He - ^4He mengsels werkende koelmachine kan waarschijnlijk goede diensten bewijzen voor onderzoeken in het temperatuurgebied van 0.1°K .

II

Het is twijfelachtig of het gebruik van een supersonische jet als bron van molecuulstralen van hoge intensiteit praktische voordelen biedt.

III

Ten onrechte wordt voor eenvoudige vloeistoffen aan de theorie van de conforme mengsels een grote quantitative betekenis toegekend.

Parsonage, N. G. and Staveley, L. A. K., *Quart. Rev.* (Londen) **13** (1959) 306.

IV

De onderstelling van Joy en Libby, dat de verandering van het molair volume bij isotopische substitutie wordt gegeven door de derde macht van de amplitudo variatie van de nulpuntstrillingen binnen het molecuul, is in zijn algemeenheid niet zonder meer aanvaardbaar.

Joy, H. W. and Libby, W. F., *Journ. Chem. Phys.* **33** (1960) 1276.

V

Het verdient aanbeveling de soortelijke warmte metingen van rutiel, welke door Keesom en Pearlman verricht zijn, uit te breiden tot beneden 1°K .

Keesom, P. H. and Pearlman, N., *Phys. Rev.* **112** (1958) 800.

VI

Vergelijking van de entropie-bepaling van vloeibaar ^3He , berekend uit de soortelijke warmte gemeten door Brewer, Daunt en Sreedhar en uit de verdampingswarmte gemeten door Weinstock, Abraham en Osborne, toont een verschil aan groter dan de opgegeven meetnauwkeurigheid. Dit verdient nader onderzoek.

Brewer, D. F., Daunt, J. G. and Sreedhar, A. K., Phys. Rev. **115** (1959) 836, 843.

Weinstock, B., Abraham, B. M. and Osborne, D. W., Nuovo Cimento [N. 1 del Supplemento al Vol. **9**, Serie X] (1958) 310.

VII

De wijze, waarop Sandiford en Fairbank uit hun metingen van de snelheid van „second sound” in verdunde ^3He - ^4He mengsels de effectieve massa van het ^3He atoom berekenen, is aanvechtbaar.

Sandiford, D. J. and Fairbank, H. A., Sec. symp. on liquid and solid ^3He , Ohio State University, Columbus, 1960, p. 154.

VIII

De, door Bendt gegeven, herleiding van de gas-diffusie coëfficiënt van ortho-para waterstof tot de gas-diffusie coëfficiënt van een waterstof-deuterium mengsel is onjuist.

Bendt, P. J., Phys. Rev. **110** (1958) 85.

IX

De stollingskromme van ^3He - ^4He mengsels dient, indien vloeistof en vaste stof van samenstelling verschillen, een knik te vertonen in het punt waar deze de λ -lijn snijdt; deze knik wordt bepaald door de betrekking:

$$\Delta \left(\frac{dP}{dT} \right)_{X_L} = \frac{V_L \left(\frac{dP}{dT} \right)_{X_L} \Delta\beta - \frac{\Delta C_P}{T}}{\frac{\partial V_L}{\partial X_L} - \frac{V_L - V_S}{X_L - X_S} - V_L \left(\frac{dT}{dX} \right)_\lambda \Delta\beta} \left(\frac{dT}{dX} \right)_\lambda.$$

Voor $\Delta(dX_L/dT)_P$ geldt een analoge uitdrukking als gegeven in dit proefschrift (pag. 56, vergl. 10).

THERMODYNAMIC X PROPERTIES OF

De verbetering, welke Roberts en Swartz geven van de relatie van de Boer en Gorter met betrekking tot de knik in de dampspannings kromme van vloeibare ^3He - ^4He mengsels in het punt waar deze de λ -lijn snijdt, is onvolledig en is bovendien omslachtig afgeleid.

Roberts, T. R. and Swartz, B. K., Sec. symp. on liquid and solid ^3He , Ohio State University, Columbus, 1960, p. 162.

XI

Het verdient aanbeveling te onderzoeken, of voor het ijken van manometers in het gebied van ultra-hoge vacua gebruik kan worden gemaakt van de bekende dampspanning van vaste waterstof in het temperatuurgebied van vloeibaar helium.

RUDOLF DE BEUN'S OUBOTER

GEBOREN TE BLOKBERGDALE IN 1921

De analyse van de vloeistof is als volgt uitgevoerd: 1. De vloeistof wordt eerst gedroogd op 100°C. 2. De gedroogde vloeistof wordt vervolgens in een nauwkeurig afgemeten volume opgelost in een bekende hoeveelheid water. 3. De oplossing wordt vervolgens geanalyseerd op de aanwezigheid van de betreffende componenten.

De analyse is uitgevoerd door de heer J. J. van der Vliet, die hiervoor de nodige opleiding heeft gevolgd. De analyse is uitgevoerd op 15 maart 1964.

Het resultaat van de analyse is onderstaand te vinden. Het blijkt dat de vloeistof bestaat uit een mengsel van water en een onbekende vloeistof. De vloeistof is waarschijnlijk een oplosmiddel.

De vloeistof is geanalyseerd op de aanwezigheid van water en op de aanwezigheid van een onbekende vloeistof. Het resultaat van de analyse is onderstaand te vinden.

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IX

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$$\left(\frac{\partial P}{\partial T}\right)_{x_k} = \frac{V_k \left(\frac{\partial P}{\partial T}\right)_{x_k} - \frac{R T}{V} \left(\frac{\partial P}{\partial T}\right)_k}{\frac{\partial V_k}{\partial x_k} - \frac{V_k - V_f}{x_k - x_f} - V_k \left(\frac{\partial V}{\partial x}\right)_k}$$

Voor $\left(\frac{\partial V}{\partial x}\right)_k$ geldt een analoge uitdrukking als gegeven in dit geval. Zie pag. 26, vergl. 10.

THERMODYNAMIC PROPERTIES OF LIQUID ^3He - ^4He MIXTURES

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN
DOCTOR IN DE WIS- EN NATUURKUNDE
AAN DE RIJKSUNIVERSITEIT TE LEIDEN,
OP GEZAG VAN DE RECTOR MAGNIFICUS
MR J. V. RIJPPERDA WIERDSMA, HOOG-
LERAAR IN DE FACULTEIT DER RECHTS-
GELEERDHEID, TEGEN DE BEDENKINGEN
VAN DE FACULTEIT DER WIS- EN NATUUR-
KUNDE TE VERDEDIGEN OP WOENSDAG
26 APRIL 1961 TE 15 UUR

DOOR

RUDOLF DE BRUYN OUBOTER

GEBOREN TE BLOEMENDAAL IN 1933

2

THE THERMODYNAMIC PROPERTIES OF
LIQUID He^3 - He^4 MIXTURES

PROEFSCHRIFT

TER VERRIJGING VAN DE GRAAD VAN
DOCTOR IN DE WIS EN NATUURKUNDE
VAN DE RIJKSUNIVERSITEIT TE LEIDEN,
OP GEAAG VAN DE RECTOR MAGNIFICUS
MR. J. RIJFFERDA WIRDSMA, HOOG-
LERaar IN DE FACULTEIT DER RECHT-
GELEERDEN

Promotor: PROF. DR. K. W. TACONIS

WAN DE FACULTEIT DER WIS EN NATUUR-
KUNDE TE VERDIENEN OP WOENSDAG

28 APRIL 1961 TE 10 UUR

NOOR

DE DOLZ DE BRUYN QUOTER

GEBOREN TE ROTTERDAM IN 1935

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

Nadat ik in 1951, na mijn eindexamen H.B.S.B aan het Kennemer Lyceum te Overveen te hebben afgelegd, mijn studie in de natuurkunde te Leiden was begonnen, legde ik in 1955 het candidaatsexamen C af. Vervolgens deed ik in januari 1959 het doctoraal examen experimentele natuurkunde, na hiertoe de vereiste tentamina in de mechanica en de theoretische natuurkunde te hebben afgelegd.

Inmiddels was ik sedert november 1955 werkzaam op het Kamerlingh Onnes Laboratorium als medewerker bij de helium-werkgroep onder leiding van Prof. Dr K. W. Taconis. Aanvankelijk assisteerde ik Dr D. H. N. Wansink *) bij metingen en berekeningen over thermodynamische en hydrodynamische eigenschappen van ^3He - ^4He mengsels. Vervolgens heb ik gewerkt met de heer C. J. N. van den Meijdenberg aan metingen over het fontein-effect van ^4He onder druk en met de Heer F. A. Staas aan metingen over de kritische snelheid van ^4He . Sinds 1957 hield ik mij inmiddels ook bezig met een aantal onderzoekingen, welke de thermodynamische eigenschappen van vloeibaar ^3He - ^4He mengsels betroffen. In het begin van 1959 begon ik met het verrichten van soortelijke warmte metingen van vloeibaar ^3He - ^4He mengsels met behulp van een ^3He cryostaat, welke in dit proefschrift beschreven zijn. Deze metingen werden verricht in samenwerking met de heer C. le Pair. De discussie van de resultaten vond plaats in samenwerking met Dr J. J. M. Beenakker.

Sinds 1957 heb ik geassisteerd op het practicum voor prae-candidaten en in september 1960 werd ik tot wetenschappelijk ambtenaar benoemd.

* Thans werkzaam bij Kon. Shell Lab. te Amsterdam.

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INTRODUCTION

The isotopes ^3He and ^4He are the only two stable substances which can remain liquid down to absolute zero, in contradiction to the predictions of classical statistics that all substances ought to be solid at absolute zero. This is a consequence of the weakness of the interatomic attractive forces (London-Van der Waals forces) and the large zero-point energy of the atoms in the liquid, which is equivalent to an extra repulsive force between the atoms. At equal distances the interatomic attractive potentials are almost the same for ^3He and ^4He , but the zero-point energy varies inversely proportional to the atomic mass. Owing to this difference in zero-point energy pure liquid ^3He has a larger molar volume V and the absolute value of the internal energy U is smaller than in pure liquid ^4He .

This thesis deals with the thermodynamic properties of liquid ^3He - ^4He mixtures.

The vapour pressures of ^3He - ^4He mixtures show strong positive deviations from an ideal liquid mixture. An analysis of the existing vapour-liquid equilibrium data and a calculation of the excess chemical potentials from the known boiling point measurements show that in the neighbourhood of 0.9°K the excess Gibbs function G^E can reasonably be expressed by means of the expression $G^E = X(1 - X)W$, in which $W/R \approx 1.54^\circ\text{K}$, indicating an almost regular behaviour of the solution. These strong deviations from an ideal liquid mixture are not too surprising since there exists a large difference in the molar volumes of the pure isotopes. Such a mixture becomes unstable below a critical temperature $T_{\text{crit}} = W/2R \approx 0.8^\circ\text{K}$ and below this temperature the mixture separates in two phases of different composition as has been observed. At the phase separation curve the specific heat shows a discontinuity, since below the phase separation curve there is an additional contribution to the specific heat due to the large heat of mixing and to the changes in amount and composition of both phases.

Another phenomenon which plays an important role in the thermodynamic properties of liquid ^3He - ^4He mixtures is the λ -transition. The specific heat of pure liquid ^4He shows a sharp peak at 2.17°K , which corresponds to a transition from the superfluid state, He II, to the normal state, He I, and is called, on account of its shape, the λ -point.

The superfluid properties of liquid ^4He have been ascribed to the peculiarities of Bose-Einstein statistics, since the ^4He atom contains an even number of fundamental particles. However, the ^3He atom contains an odd number of fundamental particles and obeys Fermi-Dirac statistics. Pure liquid ^3He shows no sign of superfluidity (or λ -transition) down to 0.08°K . Near absolute zero liquid ^3He has an abundance of low energy excitations in contrast to liquid ^4He . Addition of ^3He to liquid ^4He lowers its λ -temperature and the peak in the specific heat at its λ -temperature falls rapidly with increasing concentration.

The specific heat of dilute mixtures of ^3He in liquid ^4He shows below 1°K an almost constant contribution by the ^3He of close to $3/2 RX$ to the specific heat. The ^3He atoms can be treated as free particles which move through the superfluid and the specific heat is that of an ideal monatomic gas.

In the specific heat measurements, described in this thesis, use has been made of a new technique, developed during the last years, to reach temperatures below 1°K . A small ^3He -cryostat was built into the calorimeter, which could be cooled to a temperature of about 0.35°K by evaporation of the ^3He .

CHAPTER I

THE VAPOUR-LIQUID EQUILIBRIUM OF ^3He - ^4He MIXTURES. A CALCULATION OF THE EXCESS CHEMICAL POTENTIALS

Summary

The existing vapour-liquid equilibrium data on ^3He - ^4He mixtures are analysed. From the vapour pressure measurements of Roberts and Sydoriak the change of the excess chemical potentials with concentration has been calculated in the temperature region between 0.6°K and 2°K . Below 1°K the mixture seems to behave as a regular solution.

1. *Introduction.* The first one to interpret with success the vapour-liquid equilibrium data on ^3He - ^4He mixtures by means of classical solution theories was Sommers.¹²⁾ At that time, however, data were still rather scarce.

Some years ago Wansink¹⁾ gave a calculation of the thermodynamic quantities of ^3He - ^4He mixtures from the vapour pressure and the osmotic pressure at concentrations up to 7% ^3He in the temperature region between 1.2°K and 2°K . At the moment vapour pressure measurements for the complete concentration range are available from experiments by Esel'son and Berezniak²⁾ and by Roberts and Sydoriak³⁾. From these new experimental data it is possible to calculate the partial Gibbs functions for all concentrations in the temperature region between 0.6°K and 2°K .

In this thesis the following notation is used:

- N = number of moles
- X = mole fraction (^3He of a ^3He - ^4He mixture)
- C = molar ratio ($C = X/(1 - X)$)
- S = entropy
- H = enthalpy
- G = Gibbs function
- μ = partial chemical potential
- c_p = heat capacity at constant pressure
- T = absolute temperature
- T_{crit} = critical temperature of mixing

- V = molar volume
 p = pressure
 B_{ij} = second virial coefficient arising from the interactions between molecules of species i and j .

All quantities will be expressed per mole.

Subscripts 3 and 4 refer to the component ^3He and ^4He respectively, e.g. p_i is the partial vapour pressure of the i^{th} component. The subscript L refers to the liquid phase and the subscript V to the vapour phase. The superscript $^\circ$ is used to denote quantities referring to a pure substance.

The superscript E is used to denote the excess functions.

An asterisk distinguishes the partial fugacity p_i^* from the partial vapour pressure p_i .

$\Delta A = A_{\text{I}} - A_{\text{II}}$ is the difference between values of the quantity A at both sides of the lambda-transition curve.

2. *Thermodynamic formulae.* a) Vapour-liquid equilibrium, general. We can define the thermodynamic properties of a liquid binary mixture by means of the excess functions $^{\text{E}}$, the partial chemical potential being equal to

$$\mu_{i\text{L}} = \mu_{i\text{L}}^\circ + RT \ln X_{i\text{L}} + \mu_{i\text{L}}^{\text{E}} \quad (1)$$

where the excess chemical potential μ_i^{E} accounts for the deviation of the mixture from the ideal solution.

It is useful to define the activity coefficient f_i by means of the relation $\mu_{i\text{L}}^{\text{E}} = RT \ln f_i$ ⁴.

From the equilibrium condition between the liquid and vapour phase

$$\mu_{i\text{L}} = \mu_{i\text{V}} \quad (2)$$

it follows that the excess chemical potential μ_i^{E} can be determined from the chemical potential of the vapour, which is equal to

$$\mu_{i\text{V}} = \mu_{i\text{V}}^\circ + RT \ln X_{i\text{V}} + RT \ln (p_{\text{tot}}/p_i^\circ) + (p_{\text{tot}} - p_i^\circ)B_{ii}. \quad (3)$$

We now define the partial pressure p_i by

$$p_i = X_{i\text{V}} p_{\text{tot}} \quad (4)$$

and the partial fugacities p_i^* by

$$\ln p_i^* = \ln p_i + B_{ii} p_{\text{tot}}/RT. \quad (5)$$

and

$$\ln p_i^{\circ*} = \ln p_i^\circ + B_{ii} p_i^\circ/RT. \quad (6)$$

Hence equation (3) becomes:

$$\mu_{i\text{V}} = \mu_{i\text{V}}^\circ + RT \ln (p_i^*/p_i^{\circ*}). \quad (7)$$

In deriving (3) we assume that

$$B_m = X_{\text{V}}^2 B_{33} + 2X_{\text{V}}(1 - X_{\text{V}})B_{34} + (1 - X_{\text{V}})^2 B_{44} = X_{\text{V}}B_{33} + (1 - X_{\text{V}})B_{44}$$

which implies that

$$2B_{34} = B_{33} + B_{44}.$$

The latter equality is justified by the theoretical calculations of Kilpatrick, Keller, Hammel and Metropolis⁵⁾ and the measurements of Keller⁶⁾.

Substituting (1) and (7) in (2) we get

$$\mu_{iL}^E = \mu_{iV}^E = \mu_i^E = RT \ln (p_i^*/X_{iL}p_i^{\circ*}). \quad (8)$$

Hence it is in principle possible to calculate μ_i^E if one knows the total pressure as a function of the liquid concentration (boiling-curve) and the concentration of the vapour in equilibrium with this liquid (dew-curve).

We can write the Gibbs-Duhem equation

$$-S dT + V dp = \sum_i X_i d\mu_i \quad (9)$$

in the following form adapting our notation to the case of a ${}^3\text{He}$ - ${}^4\text{He}$ mixture:

$$X_L \frac{d\mu_3^E}{dX_L} + (1 - X_L) \frac{d\mu_4^E}{dX_L} = 0 \quad (\text{const. } T, p_{\text{tot}}). \quad (10)$$

Formula (10) may be rewritten in the integral form

$$\mu_4^E = - \int_0^{X_L} \frac{X_L}{1 - X_L} d\mu_3^E \quad (\text{const. } T, p_{\text{tot}}). \quad (11)$$

Even when p is not strictly constant the term $V dp$ on the left hand side of (9) is usually negligible compared with any one term on the right hand side, this being true in our case. Consequently (10) and (11) are still effectively valid.

Formula (11) enables us to compute the excess chemical potential μ_4^E at a concentration X_L provided we know the excess chemical potential μ_3^E at all compositions intermediate between zero concentration and the concentration X_L .

Partial integration of (10) over the whole concentration range gives us the following expression:

$$\int_0^1 \mu_3^E dX_L = \int_0^1 \mu_4^E dX_L \quad (\text{const. } T, p_{\text{tot}}). \quad (12)$$

Satisfaction of this equation may therefore be considered a necessary but not sufficient test of the thermodynamic consistency of experimental data. Extending the method of Redlich and Kister⁴⁾⁷⁾ it is possible to write eq. (12) in a somewhat different form:

$$\begin{aligned} \int_0^1 \ln \frac{C_V}{C_L} dX_L = & \ln \frac{p_3^\circ}{p_4^\circ} + \frac{(B_{33} + B_{44} - V_3^\circ - V_4^\circ)(p_3^\circ - p_4^\circ)}{2 RT} - \\ & - \frac{(B_{33} - B_{44}) - (V_3^\circ - V_4^\circ)}{RT} \int_0^1 p^E dX_L - \\ & - \frac{(p_3^\circ - p_4^\circ)}{RT} \int_0^1 V^E dX_L - \frac{1}{RT} \int_0^1 V^E dp^E. \end{aligned} \quad (13)$$

Here we have also considered the case when ϕ is not constant. We used (13) as a test for the consistency of the phase diagram of ^3He - ^4He mixtures at different temperatures.

b) Regular solutions. We will now define the properties of a class of mixtures, which are called regular solutions⁴⁾⁸⁾. For convenience we write down the expressions for ^3He - ^4He mixtures:

$$\mu_3^E = W(1 - X_L)^2 \quad (14)$$

$$\mu_4^E = WX_L^2 \quad (15)$$

where W is a constant independent of the temperature and the composition. The main idea of a regular solution is that, although there exists a difference in the interaction energy between the like and unlike pairs of atoms which results in a heat of mixing, $H^E = X_L(1 - X_L)W$, there is still a complete random mixing of the different atoms resulting in an excess entropy equal to zero and hence a zero specific heat of mixing. Thus we have the following equations in the case of a regular solution:

$$S^E = 0 \quad (16)$$

$$G^E = H^E = X_L(1 - X_L)W. \quad (17)$$

From (8) and (14, 15) it follows that the partial fugacities are given by:

$$\phi_3^* = X_L \phi_3^{\circ*} e^{(1-X_L)^2 W/RT} \quad (18)$$

$$\phi_4^* = (1 - X_L) \phi_4^{\circ*} e^{X_L^2 W/RT}. \quad (19)$$

The critical point of mixing is determined by the following simultaneous equations:

$$X_L = \frac{1}{2} \quad (20)$$

$$W/RT_{\text{crit}} = 2, \quad (21)$$

and the phase separation curve is given by:

$$T_{\text{P.S.}} = \frac{W}{R} (1 - 2X) \ln \left(\frac{X}{1 - X} \right).$$

In the case of a regular solution the distribution coefficient C_V/C_L is given by

$$\frac{C_V}{C_L} = \frac{\phi_3^{\circ*}}{\phi_4^{\circ*}} e^{(W/RT)(1-2X_L)} \quad (22)$$

if we assume the vapour phase to be ideal, and we can obtain an osmotic pressure between the liquid mixture and pure ^4He which is equal to

$$\phi_{\text{osm}} V_4 = -RT \ln (1 - X_L) - WX_L^2. \quad (23)$$

c) The discontinuity in the temperature derivative of the

vapour pressure at the lambda point. We make the assumption of a transition of the second order from the helium I phase into the helium II phase. De Boer and Gorter⁹⁾ extended the Keesom¹⁰⁾-Ehrenfest¹¹⁾ relation to the case of a mixture and showed that the change at the lambda point in the specific heat at constant pressure is connected to the change in the slope of the vapour pressure curve in the following way:

$$\Delta \left(\frac{\partial p}{\partial T} \right)_{X_L} = [(1 - X_L)X_V - X_L(1 - X_V)] \frac{p \Delta c_p}{RT^2} \frac{dT_\lambda}{dX_L} \quad (24)$$

assuming that the vapour behaves as a mixture of two ideal gases.

3. *Review of the experimental data.* Many boiling point measurements have been performed by Sommers¹²⁾, at concentrations up to 13% and at temperatures between 1.2 and 2.0°K, by Esel'son and Berezniak²⁾, at many concentrations and at temperatures between 1.4 and 2.6°K, and by Roberts and Sydoriak³⁾, at many concentrations and at temperatures between 0.6 and 2.0°K²⁰⁾. Dew point measurements have been performed by

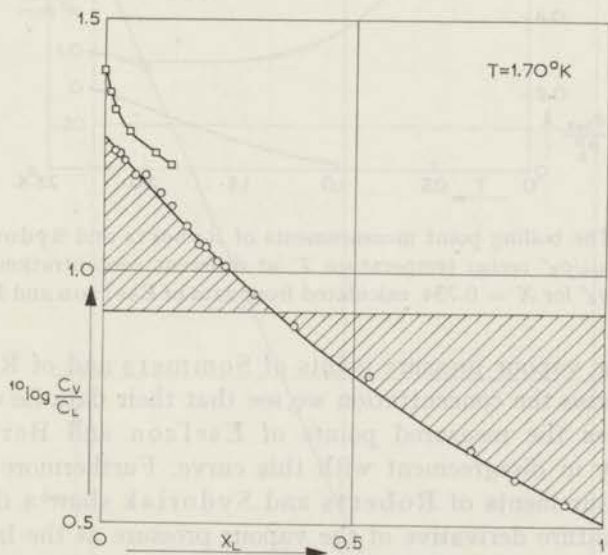


Fig. 1. Redlich and Kister test at 1.7°K cf. eq. (13).

Horizontal solid line: an ideal mixture.

□ Sommers and Wansink

○ Esel'son and Berezniak

Sommers¹²⁾ and by Esel'son and Berezniak²⁾. Furthermore we have measurements on very dilute mixtures by Wansink, Taconis and Staas¹³⁾ of the distribution coefficient C_V/C_L at temperatures between 1.2 and 2.0°K and measurements of the osmotic pressure¹⁾.

We used the method of Redlich and Kister to test the phase diagram of Esel'son and Berezniak by means of eq. (13). The last three terms on the right side of eq. (13) appear to be very small compared to the first two terms. Their data are not consistent, as we can see for example in fig. 1.

In the same figure we also see the discrepancy between the C_V/C_L determinations of Esel'son and Berezniak and those of Wansink¹³⁾ and of Sommers at low concentrations. Moreover, there are large disagreements at the high concentration values of the boiling point measurements with the very accurate determinations of Roberts and Sydoriak³⁾, as one can see in fig. 2.

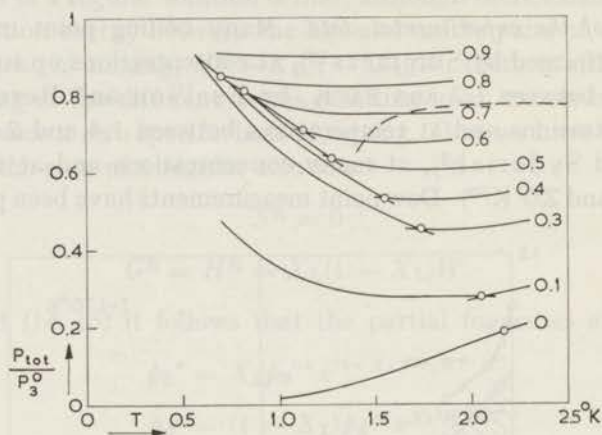


Fig. 2. The boiling point measurements of Roberts and Sydoriak³⁾.

p_{tot}/p_3^0 versus temperature T , at different concentrations.

--- p_{tot}/p_3^0 for $X = 0.734$, calculated from data of Esel'son and Berezniak²⁾.

Plotting the vapour pressure points of Sommers and of Roberts and Sydoriak versus the concentration we see that their data lie on a smooth curve, whereas the measured points of Esel'son and Berezniak are systematically in disagreement with this curve. Furthermore the vapour pressure measurements of Roberts and Sydoriak show a discontinuity in the temperature derivative of the vapour pressure at the lambda point of the mixture as one should expect. From the measured discontinuity in the temperature derivative of the vapour pressure at the lambda point, they calculated the change in the specific heat at constant pressure with the aid of eq. (24) (cf. fig. 3). Their results are in reasonable agreement with the specific heat measurements of mixtures by Dokoupil¹⁴⁾ containing 21.1% and 41.7% of ^3He (cf. fig. 4).

Hence in our thermodynamic considerations we prefer to base our calculations mainly on the measurements of Sommers¹²⁾ as analysed by Wansink¹⁾ and of Roberts and Sydoriak³⁾ and we have used the

dew point measurements of Esel'son and Berezniak only in a zero approximation.

4. *Calculation of the excess chemical potentials.* In section 2 we have seen that we can calculate the excess chemical potentials from the boiling- and dew point measurements. Actually, however, this is not the case, since the dew point measurements do not meet the requirements for a thermodynamic calculation: at higher concentrations X_V becomes of the order of unity, hence an error in X_V implies an error of an order of a magnitude larger in p_4 . Furthermore according to eq. (8) μ_4^E is determined largely by

$$\ln(p_4/(1 - X_L)p_4^\circ),$$

so the error in μ_4^E becomes too large.

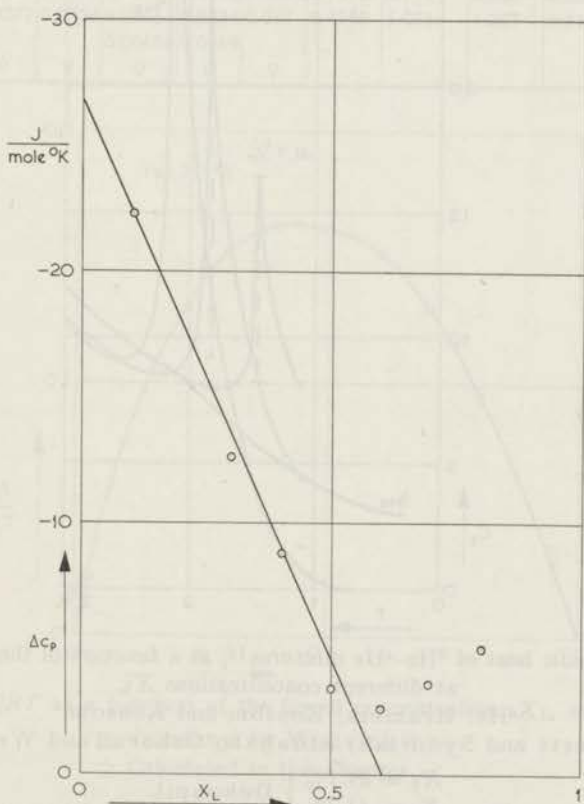


Fig. 3. The discontinuity in the specific heat, Δc_p , at the lambda point of a mixture as a function of the liquid concentration, X_L .

○ Calculated by Roberts and Sydoriak³⁾ from their measurements with eq. (24).

We follow another procedure in calculating the chemical potentials from the vapour pressure. As a zero approximation we use the dew point measure-

ments by Esel'son and Berezniak, from which we can calculate the partial vapour pressure $p_3 = X_V p_{tot}$, as the total pressure p_{tot} is known from the boiling point measurements made by Sommers and by Roberts and Sydoriak. With the second virial coefficients calculated by Kilpatrick, Keller and Hammel¹⁵⁾ we determine the partial fugacity p_3^* . Hence $\mu_3^E = RT \ln (p_3^*/X_L p_3^{0*})$ is known to a zero approximation at different concentrations. Now it is possible to determine μ_4^E to a first approximation by graphical integration of eq. (11). From μ_4^E we derive the partial pressure

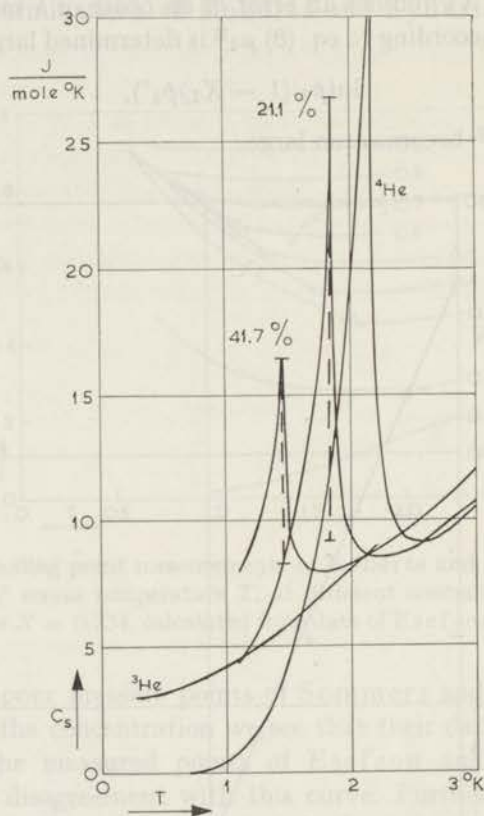


Fig. 4. The specific heat of ^3He - ^4He mixtures¹⁴⁾ as a function of the temperature T at different concentrations X_L .

^4He : Kramers; Keesom and Keesom.

^3He : Roberts and Sydoriak; Abraham, Osborne and Weinstock.

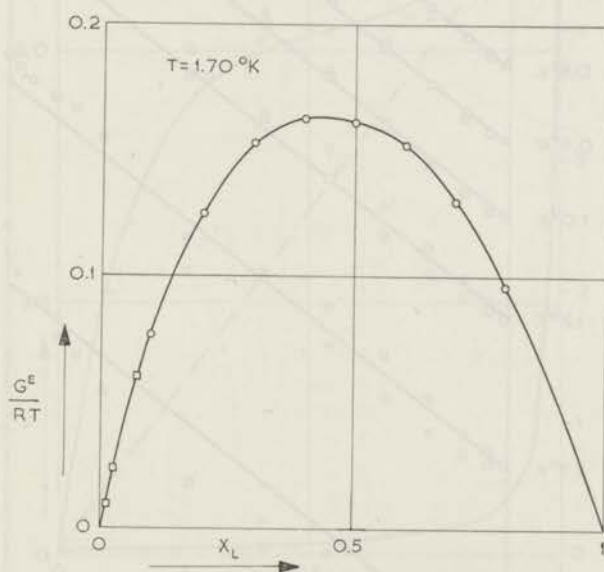
$X_L = 21.1\%$ } Dokoupil.
 $X_L = 41.7\%$ }

$\int \Delta c_p$ calculated by Roberts and Sydoriak³⁾ from their measurements (see fig. 3).

p_4 and now we have $X_V = 1 - (p_4/p_{tot})$ in a first approximation. Once the first approximation is calculated, the whole procedure is repeated. Since the second and third order approximations of the excess chemical potential differ only slightly, it was sufficient to repeat the process only three times.

TABLE I

The excess chemical potentials μ_3^E/R and μ_4^E/R												
X	μ_3^E/R ($^{\circ}\text{K}$)						μ_4^E/R ($^{\circ}\text{K}$)					
	0.8	0.9	1.0	1.2	1.3	1.7	0.8	0.9	1.0	1.2	1.3	1.7
0				1.597	1.651	1.77	0	0	0	0	0	0
0.01	1.337	1.357	1.362	1.572	1.599	1.58	0.00032	0.00036		0.00007	0.000234	0.0008
0.025				1.549	1.547	1.462				0.00055	0.001079	0.00286
0.05	1.280	1.327	1.325	1.50	1.482	1.325	0.00184	0.00135		0.00232	0.003666	0.00747
0.0713				1.463	1.443	1.257				0.00487	0.00688	0.01222
0.1	1.165	1.206	1.196	1.413	1.324	1.108	0.01175	0.011505	0.00865	0.00746	0.01500	0.0207
0.2	0.880		1.022	1.076	0.789	0.75	0.06025		0.04155	0.0565	0.0711	0.0782
0.3	0.696	0.761	0.783	0.800	0.761	0.487	0.1201	0.1258	0.11385	0.134	0.1595	0.1615
0.4	0.556	0.565	0.577	0.549	0.502	0.314	0.1983	0.231	0.229	0.244	0.2817	0.251
0.5	0.392	0.394	0.385	0.332	0.280	0.193	0.3308	0.372	0.388	0.373	0.454	0.354
0.6	0.246	0.231	0.216	0.171	0.1443	0.119	0.5090	0.5745	0.597	0.562	0.639	0.468
0.7	0.1222	0.106	0.0999	0.089	0.0696	0.0595	0.7410	0.711	0.808	0.6885	0.784	0.595
0.8	0.0421	0.0377	0.0334	0.0366	0.0234	0.017	0.9750	1.055	1.007	0.8105	0.915	0.748
0.9	0.0024			0.00658	0.0169							
1.0	0	0	0	0	0	0						

Fig. 5. G^E/RT as a function of the liquid concentration, X_L , at 1.70 $^{\circ}$ K.

□ Calculated by Wansink¹⁾

○ Calculated in this chapter

Since we only have dew point measurements above 1.4 $^{\circ}$ K we used the calculated dew points of the next higher temperature at lower temperatures in the zero approximation. The values of μ_3^E and μ_4^E obtained in this way are given in table I as a function of temperature and concentration. We have also calculated the dew-point curve from the boiling point curve; the results are shown in the figures 7 and 8.

5. *Analysis of the character of the solution.* We can calculate the excess Gibbs function $G^E = X_L \mu_3^E + (1 - X_L) \mu_4^E$ at different temperatures and concentrations. (See for example fig. 5).

To analyse the character of the solution we plot μ_3^E/R versus $(1 - X_L)^2$ and μ_4^E/R versus X_L^2 , as is shown in fig. 6. We see that below about 1.1°K all points lie on one straight line, as one should expect if the mixture

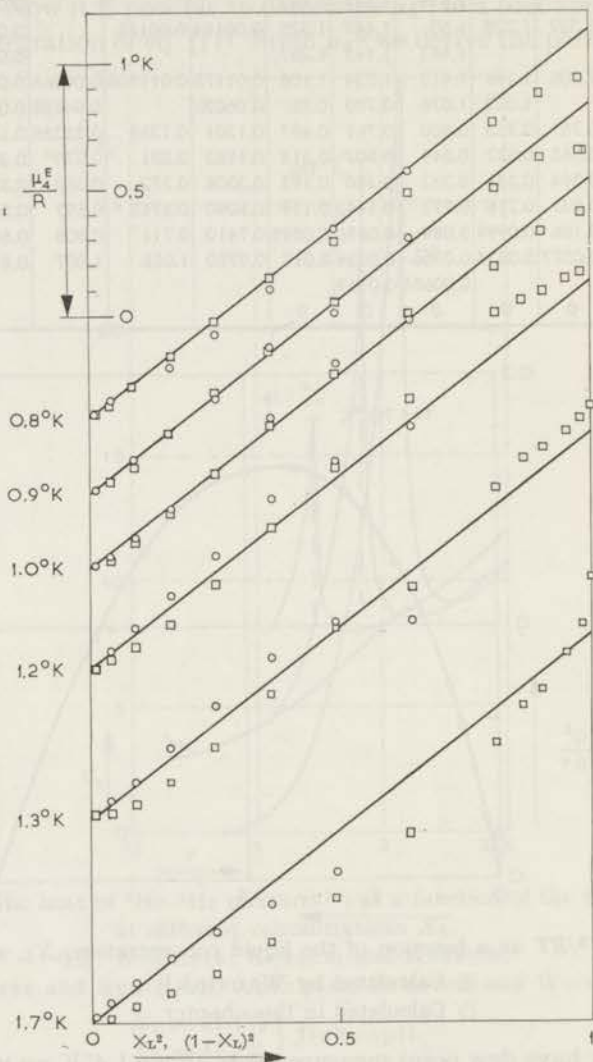


Fig. 6. The regular solution behaviour at different temperatures.

Vertical scale: μ_3^E/R , \square , and μ_4^E/R , \circ .

The scale is shifted for the different temperatures.

Horizontal scale: $(1 - X_L)^2$ and X_L^2 for ^3He and ^4He respectively.

$$\begin{cases} \mu_3^E/R = 1.54 (1 - X_L)^2 \\ \mu_4^E/R = 1.54 X_L^2 \end{cases}$$

behaves as a regular solution in accordance with eqs. (14) and (15). From the slope the heat of mixing, W , can be determined and is found to be $W/R \approx 1.54^\circ\text{K}$; which gives a critical temperature of mixing which is, according to eq. (21), equal to 0.77°K . This is in reasonable agreement with the experimental value which can be derived from the phase separation diagram (cf. fig. 9¹⁴ 16) 18) 19)).

There exists only one heat of mixing point measured by Sommers, Keller and Dash¹⁷). The experimental value gives $W/R \approx 1.1^\circ\text{K}$, which is smaller than the calculated one in accordance with their remark that only a lower limit of the heat of mixing was obtained in their experiment.

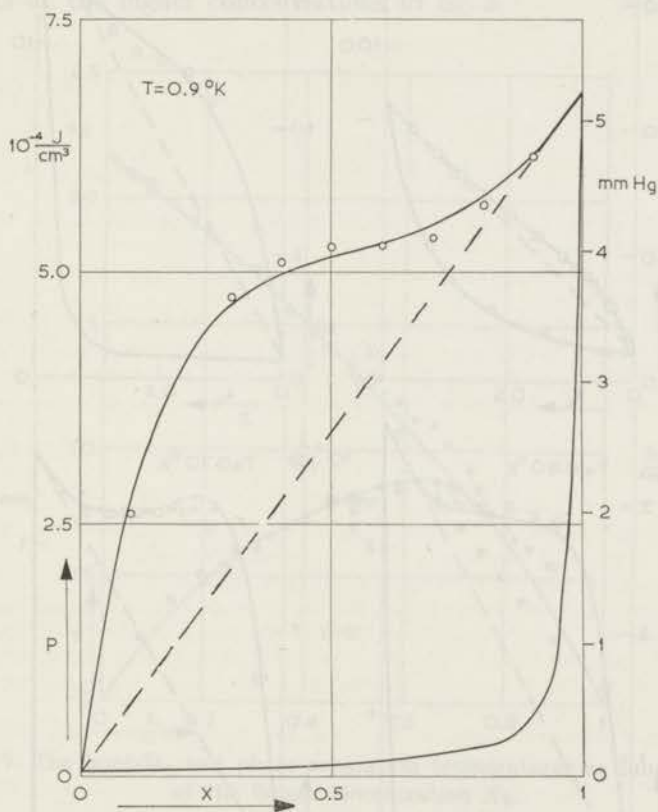


Fig. 7. Vapour-liquid equilibrium diagram at 0.9°K .

Solid lines calculated for a regular solution ($W/R = 1.54^\circ\text{K}$) taking into account the nonideality of the vapour phase. The broken line is the ideal solution boiling curve.

○ Roberts and Sydorciak³⁾

It is now also possible to invert the calculation, which is a more satisfying method, and from the calculated value of $W/R \approx 1.54^\circ\text{K}$ we can predict the partial fugacities by means of eqs. (18) and (19). Together with the knowledge of the second virial coefficients the partial and total vapour pressures can

now be computed and hence the boiling- and dew-point curve can be calculated. The results satisfy the experimentally determined vapour pressures (cf. figs. 7 and 8).

The rapid fall of the change of the specific heat Δc_p at the lambda point with the concentration indicates that the second order transition becomes thermodynamically of minor importance at lower temperatures. Hence the

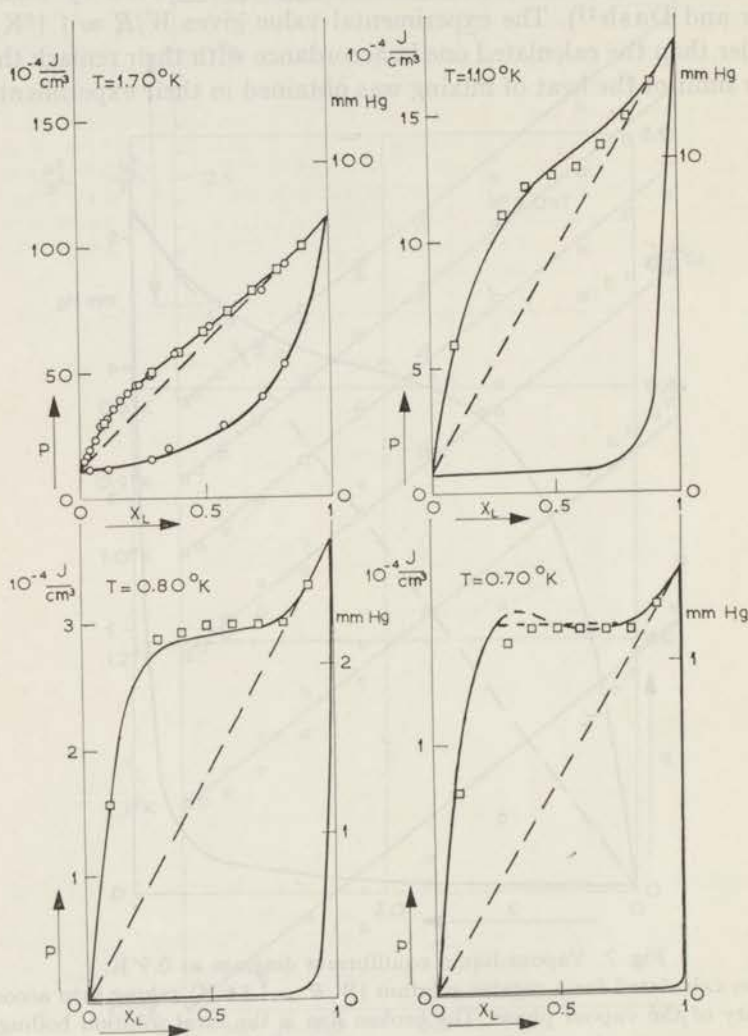


Fig. 8. Vapour liquid equilibrium diagrams at $T = 0.7^\circ\text{K}$, $T = 0.8^\circ\text{K}$, $T = 1.1^\circ\text{K}$ and $T = 1.7^\circ\text{K}$.

At $T = 0.7, 0.8, 1.1^\circ\text{K}$ the solid lines are calculated for a regular solution ($W/R = 1.54^\circ\text{K}$). At $T = 1.7^\circ\text{K}$ the solid lines are the experimental curves.

- Esel'son and Berezniak²⁾
- Roberts and Sydoriak³⁾

regular solution character can become more dominant at these temperatures. It is interesting to compare our results at these temperatures with the predictions of Prigogine, Bingen and Bellemans¹⁸). These authors proposed a model based on the difference in the molar volumes of the pure isotopes, neglecting the lambda phenomenon. They found a value for W/R between 1 and 2°K in reasonable agreement with our results.

Finally we would like to remark that in analysing the discontinuity of dp/dT as was done by Roberts and Sydoriak³) (cf. fig. 3) one has also to take into account a contribution arising from the phase separation if the lambda transition and the phase separation coincide. This effects the points at the higher concentrations in fig. 3.

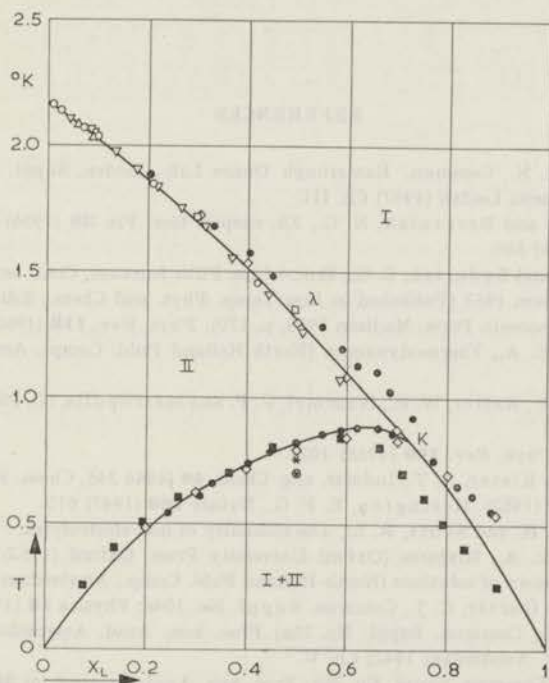


Fig. 9. The lambda- and phase separation temperatures as functions of the liquid concentration X_L .

- | | |
|---|--|
| ○ Dokoupil ¹⁴) | ▽ Elliott and Fairbank ¹⁶) |
| △ Dash and Taylor ²¹) | ● Peshkov ¹⁶) |
| □ Kerr ¹⁶) | ■ Walters and Fairbank ¹⁸) |
| ◇ Roberts and Sydoriak ¹⁹) | ⊗ Prigogine ¹⁸) |
| * This publication, $T_{crit} = \frac{1}{2} \times 1.54 = 0.77^\circ\text{K}$ | |

From fig. 6 it is clear that from 1.2°K upwards the behaviour of the mixture starts to differ considerably from that of a regular solution. As we pointed out earlier this is presumably due to the lambda phenomenon. The

accuracy of the vapour liquid equilibrium data does not allow a further quantitative analysis of the influence of the lambda transition.

Of course the conclusions derived from the vapour liquid equilibrium data are only approximate and a slight temperature and concentration dependence of W cannot be excluded. In this respect we point to the fact that the phase separation curve is not symmetrical as should be expected for a regular solution.

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CHAPTER II

THERMODYNAMIC PROPERTIES OF LIQUID ^3He - ^4He MIXTURES DERIVED FROM SPECIFIC HEAT MEASUREMENTS BETWEEN 0.4°K AND 2°K OVER THE COMPLETE CONCENTRATION RANGE

Summary

Heat capacities of ^3He - ^4He mixtures over the complete concentration range have been measured using a calorimeter that can be cooled down to 0.4°K by means of evaporation of ^3He . Special attention has been given to the additional contribution to the specific heat due to the heat of mixing which is observed when stratification takes place below the phase separation temperature and to the discontinuity in the specific heat at the corresponding lambda temperature. The heat of mixing can be derived from the specific heat measurements inside and outside the phase separation region. The excess entropy has been calculated. For dilute mixtures of ^3He in liquid ^4He at temperatures below 1°K the energy spectrum of Pomeranchuk seems to be satisfied.

PART I: SPECIFIC HEAT OF LIQUID ^3He - ^4He MIXTURES BETWEEN 0.4°K AND 2°K OVER THE COMPLETE CONCENTRATION RANGE.

1. *Introduction.* The first measurements of the specific heat of liquid ^3He - ^4He mixtures by Dokoupil¹⁾ *et al.* were restricted to the temperature region attainable in the usual ^4He bath (above 1.1°K). In the experiments described here we were able to extend the measurements to lower temperatures. The availability of reasonable amounts of ^3He made it possible to use ^3He cryostats and since the vapour pressure of ^3He is about 70 times greater than that of ^4He at 1°K and 1700 times greater at 0.6°K , it is a real advantage to use ^3He instead of ^4He in obtaining low temperatures by pumping off the vapour. Since ^3He does not show superfluidity a ^3He cryostat is very favourable in comparison with a ^4He cryostat, as the superfluid helium film of ^4He usually introduces appreciable heat input into the bath and makes it difficult to obtain very low pressures by pumping. One can find details on ^3He cryostats in the review article by

Taconis²⁾. The rare isotope ^3He in our experiments was supplied by the U.S.A. Atomic Energy Commission.

In (2) the construction of the calorimeter and the way in which the experiments are performed is described. (3) gives the results obtained and in (4) the results are qualitatively discussed. The discussion is divided into the following concentration regions: (A) the dilute mixtures of ^3He in liquid ^4He , (B) the intermediate region (phase separation region), and (C) the dilute mixtures of ^4He in liquid ^3He . In part II the heat of mixing and the excess entropy are calculated from the specific heat measurements and a theoretical quantitative discussion of the thermodynamic properties is given.

2. *The calorimeter (construction, method and measurements).* The calorimeter is shown in fig. 1. Enclosed in a vacuum jacket J is a copper block with two chambers, one for the mixture M and the other for the cooling ^3He bath. The ^3He chamber is connected to a relatively wide stainless steel tube C_2 10 cm long with a 2 mm inner diameter, and a 0.1 mm thick wall.

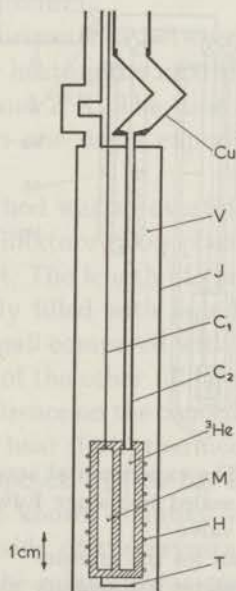


Fig. 1. The calorimeter.

The chamber M is connected to a stainless steel capillary C_1 with a 0.2 mm inside diameter, so that its volume is very small compared with the volume of chamber M of 0.535 cc. A heating coil H ($\approx 550 \Omega$) is wound around the the copper block and a carbon thermometer T , of the De Vroomen type³⁾, deposited on an insulated copper bar, is soldered to it.

After pumping the exchange gas out of the vacuum space V at 4°K the

stopcock S_2 (see fig. 2) is closed, and the ^4He bath is reduced to a temperature of about 1.2°K. Next the condensation of the ^3He in its chamber starts. In fact, the condensation takes place in the copper radiation trap Cu and the condensed liquid drops through tube C_2 into the relatively hot ^3He chamber, evaporates there, and recondenses in the radiation trap Cu and so on. In this way after a short time the calorimeter is cooled to the ^4He bath temperature of 1.2°K. Subsequently the mixture is condensed in the chamber M , and the calorimeter is cooled to a temperature of about 0.35°K by reducing the pressure of the ^3He bath with a specially sealed two stage rotary pump of 20 L/min capacity. At certain intervals during the cooling period the inlet valve R of the pump (see fig. 2) is closed for a short time and as soon as pressure equilibrium above the ^3He bath is reached the carbon thermometer is calibrated against the vapour pressure of the ^3He bath. The vapour pressure is measured with a mercury manometer, an oil manometer filled with octoil-S and a MacLeod gauge depending on the magnitude of the pressure. Thermomolecular pressure corrections can be neglected, since the German-silver tube which connects the calorimeter with the ^3He pump

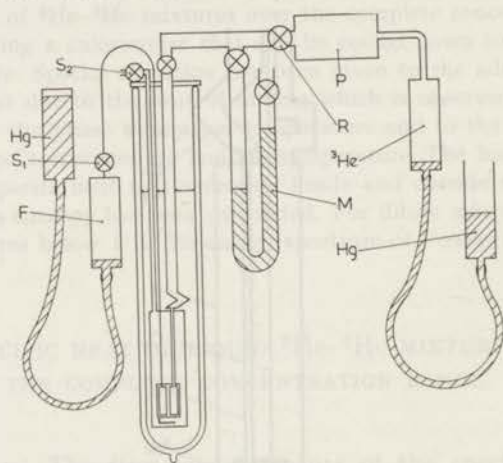


Fig. 2. The experimental arrangement

- P = specially sealed two stage Edwards rotary pump 2 S 20
- R = reducing valve
- F = storage can for the mixture
- M = Oil manometer (or mercury manometer)

has a 14 mm inner diameter⁴). For the determination of the temperature we employed the scale of Sydoriak and Roberts⁴). The resistance of the carbon thermometer and the heater is measured in a Wheatstone bridge circuit with an electronic D.C. voltmeter as a zero point instrument.

Now the contact with the ^3He bath is broken by completely evaporating it at the lowest temperature. The quantity of condensed ^3He is chosen in such a way that just after the lowest obtainable temperature is reached the

^3He bath is nearly empty. If not, the heater is carefully applied to empty it completely, which may be observed from the temperature rise on the carbon thermometer. From this moment on the heat capacity of the mixture can be determined.

For measuring the heat capacity standard calorimetric technique was used. First the temperature drift was measured (foredrift), then a small amount of heat was supplied by the heater for ten seconds, and then the drift of the temperature was again followed (afterdrift; see fig. 3). The quantity of heat applied can be calculated from the measured current and resistance of the heater.

The temperatures were measured with the above mentioned carbon thermometer. The fore- and afterdrifts were determined by balancing the resistance of the thermometer in a Wheatstone bridge circuit. In such a way one obtains the value of the resistance of the thermometer as a function of the time at which the bridge is balanced. The contribution to the total heat capacity due to the copper block is about 1% (derived from the specific heat determinations by Kok and Keesom⁵). A correction for this is always taken into account.

The heat leak in this calorimeter is between 10 and 30 erg/s. In one run of measurements, each time heating the mixture about 0.015°K fifty points are measured between 0.4 and 2°K . The time for such a run is two hours. Two runs are performed in one day's experiment using the same liquid ^3He - ^4He concentration.

Most essential in this method was an overfilled calorimeter, to make sure that no evaporation of the mixture takes place somewhere in the capillary C_1 inside the vacuum jacket. The length of the capillary C_1 is about 80 cm and the capillary is partially filled with liquid. The inside diameter is 0.2 mm, so that its volume is small compared with the volume of chamber M of 0.535 cc. Also, the volumes of the other filling tubes at higher temperatures are negligible so that the influence on the concentration inside the calorimeter of effects due to film creep, heat flush, thermodiffusion *etc.* is avoided, and for the same reason the stopcock S_1 (see fig. 2) in the filling tube (C_1) was closed immediately after the known quantity of the mixture was condensed from a storage balloon outside of the cryostat into the chamber M (see fig. 2). Every time before the mixture was condensed, it was cleaned in a liquid helium cooled impurity trap.

It seems to us that this calorimeter has a much wider applicability since the method is very convenient.

The ^3He pump was a revised two stage Edwards rotary pump type 2S20. To prevent the loss of the rather expensive gas the rotor axis was double sealed with an oil filled space between the two seals. A small oil bath with an oil level indicator was mounted between these two seals. All flanges were

provided with "O" ring seals. The pump had almost no dead space and the total quantity of oil in the pump was reduced to 5 cm³.

The oil which is pushed out of the outlet valve is slowly sucked back into the pump again through a narrow channel connected to the bronze bearing of the pump and there it takes care of the tightness of the pump and its lubrication.

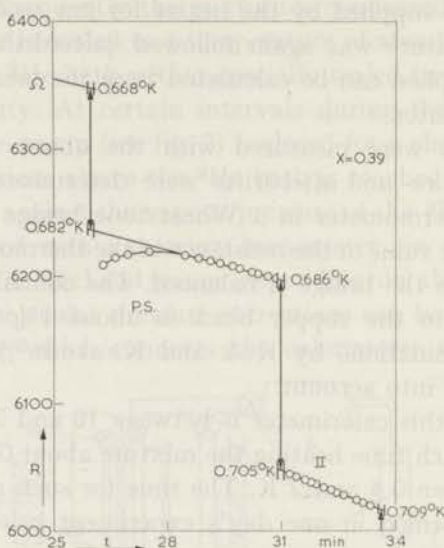


Fig. 3. Overheating curve during the afterdrift for a 39% mixture. The resistance R of the carbon thermometer is plotted against the time t . During the heating period the phase separation curve P.S. is passed at the 31st minute.

After the heating period in the phase separation region, there was overheating during the afterdrift at the 26th minute.

After the heating period in the He II region no overheating was observed during the afterdrift at the 31st minute.

3. *Results.* Specific heat measurements have been performed between 0.4°K and 2°K for the following concentrations: $X = 0.0466, 0.094, 0.15, 0.291, 0.39, 0.478, 0.575, 0.638, 0.70, 0.75, 0.805, 0.847, 0.894, 0.954, 1.00$ ($X =$ mole fraction ^3He of a ^3He - ^4He mixture). The results are tabulated in tables I and II and are shown in the figs. 4, 5, 6, 7, 8, 9 and 10. As a check we measured the specific heat of pure liquid ^3He ; the results are in agreement with the data of Brewer, Daunt and Sreedhar⁶); Roberts and Sydoriak⁸) and Abraham, Osborne and Weinstock⁷) (see fig. 4).

4. *Qualitative discussion of the results.* We can divide the discussion in terms of the phase diagram into the following concentration regions as will be clear afterwards (see fig. 11):

A) $0 < X \leq 0.15$. Dilute mixtures of ^3He in liquid ^4He

TABLE I

The measured values of the specific heat C							
T	C	T	C	T	C	T	C
$^{\circ}\text{K}$	$\text{J/mole } ^{\circ}\text{K}$	$^{\circ}\text{K}$	$\text{J/mole } ^{\circ}\text{K}$	$^{\circ}\text{K}$	$\text{J/mole } ^{\circ}\text{K}$	$^{\circ}\text{K}$	$\text{J/mole } ^{\circ}\text{K}$
$X = 0.0466$		1.529	6.23	1.283	3.418	1.062	1.783
0.500	0.504	1.568	7.65	1.314	3.70	1.105	1.972
0.55	0.499	1.606	8.87	1.353	4.23	1.143	2.241
0.635	0.524	1.632	9.64	1.388	4.76	1.177	2.408
0.677	0.535	1.671	10.35	1.419	5.26	1.203	2.605
0.724	0.525	1.700	11.25	1.458	6.01	1.229	2.85
0.763	0.582	1.740	12.49	1.500	7.02	1.251 ^s	3.063
0.799	0.613	1.793	14.92	1.536	7.82	1.275 ^s	3.29 ^s
0.861	0.692	1.840	16.48	1.572	8.83	1.296	3.50
0.891	0.741	1.880	18.90	1.602 ^s	9.93	1.315	3.80 ^s
0.923	0.810	1.912	20.57	1.636	10.55	1.332	3.94 ^s
0.949	0.842	1.942	22.90	1.664	11.65	1.360	4.35
0.974	0.905	1.972	24.90	1.698	12.50	1.392	4.81 ^s
0.997	0.966	1.996	28.90	1.735	14.10	1.423	5.44
1.020	1.053	2.020	31.10	1.768	15.39	1.451	5.92
1.041	1.117	2.042	32.20	1.806	17.32	1.478	6.42
1.061	1.195	2.062	38.10	1.846	19.33	1.500	6.96
1.079	1.257	2.082	37.78	1.880	21.64	1.523	7.41
1.096	1.320	2.111	17.50	1.905	23.30	1.541	8.05
1.132	1.531	2.158	12.66	1.938	26.03	1.565	8.57
1.177	1.750			1.963	26.50	1.602	9.94
1.215	2.03	$X = 0.094$		1.993	32.30	1.633	10.44
1.248	2.31	0.415	0.859	2.041	21.73	1.663	11.23
1.277	2.54	0.445	0.916	2.120	11.79	1.689	12.34
1.302	2.835	0.470	0.907	0.343	0.874	1.714	12.81
1.326	3.005	0.493	0.922	0.365	0.979	1.749	14.42
1.346	3.39	0.515	0.942	0.395	0.937	1.798	16.66
1.365	3.64	0.539	0.948	0.420	0.911	1.838	18.51
1.379	3.83	0.565	0.961	0.446	0.900	1.872	20.55
1.395	4.11 ^s	0.583	1.004	0.466	0.974	1.905	22.45
1.408	4.28	0.616	0.982	0.491	0.977	1.932	24.30
1.448	4.98	0.642	1.009	0.513	0.972	1.958	27.75
1.498	6.00	0.6655	1.012	0.536	0.954	1.980	31.25
1.540	6.81	0.695	1.012	0.559	0.967	2.000	34.2
1.580	7.83	0.717	1.004	0.585	0.974	2.027	27.2
1.616	9.16	0.741	1.037	0.609	0.977	2.062	14.40
1.649	9.66	0.766	1.037	0.633	1.004	2.114	11.93
1.680	10.68	0.784	1.107	0.658	1.007	2.160	10.13
1.708	11.71	0.803	1.128	0.684	1.014		
1.734	12.11	0.825	1.144	0.710	1.011		
1.772	13.39	0.847	1.180	0.734	1.054	$X = 0.15$	
1.822	15.71	0.863	1.286	0.755	1.077	0.546	1.336
1.861	17.80	0.906	1.297	0.776	1.095	0.603	1.368
1.897	20.70	0.968	1.466	0.815	1.159	0.644	1.400
1.926	22.41	1.022	1.619	0.834	1.194	0.666	1.438
2.044	36.2	1.069	1.820	0.853	1.206	0.681	1.428
2.069	35.5	1.116	2.044	0.871	1.238	0.697	1.443
2.117	18.70	1.154	2.235	0.889	1.248	0.712	1.485
2.162	12.10	1.181	2.476	0.899	1.320	0.727	1.495
2.186	11.15	1.212	2.666	0.923	1.338	0.744	1.518
1.434	4.80	1.238	2.886	0.961	1.454	0.787	1.529
1.487	5.79	1.261	3.095	1.018	1.646		

TABLE I (continued)

<i>T</i> °K	<i>C</i> J/mole °K	<i>T</i> °K	<i>C</i> J/mole °K	<i>T</i> °K	<i>C</i> J/mole °K	<i>T</i> °K	<i>C</i> J/mole °K
0.803	1.565	1.127	2.743	0.956	3.96	0.836	3.57
0.817	1.609	1.154	2.91	0.979	4.20	0.852	3.55
0.833	1.564	1.180	3.11	1.001	4.20	0.868	3.68 ⁵
0.866	1.698	1.236	3.715	1.037	4.35	0.882	3.75
0.914	1.784	1.314	4.57	1.077	4.55	0.897	3.86 ⁵
0.959	1.923	1.425	6.35 ⁵	1.116	4.84 ⁵	0.912	3.83
0.997	2.067	1.469	7.13	1.153	5.09	0.926	3.83
1.036	2.103	1.590	11.15	1.187	5.39	0.941	3.87 ⁵
1.070	2.366	1.642	13.20	1.219	5.81 ⁵	0.956	3.92
1.104	2.570	1.678	13.43	1.248	6.09	0.971	4.06
1.134	2.820	1.724	16.38	1.276	6.46	0.991	4.26
1.160	3.205	1.764	18.06	1.301	6.86	1.012	4.16
1.185	3.14	1.800	21.1	1.325	6.99	1.032	4.24
1.242	3.71 ⁵	1.830	22.2	1.347	7.93	1.050	4.34
1.320	4.63	1.868	26.2	1.367	8.05	1.068	4.46
1.383	5.47	1.914	31.25	1.385	8.41	1.086	4.64
1.432	6.43	1.956	17.45	1.404	8.88	1.121	4.88
1.508	8.30	2.014	10.05	1.428	9.20	1.137	5.30
1.541	9.34	2.060	10.24	1.454	10.72	1.164	5.26
1.574	10.09	2.144	9.49	1.480	11.23	1.197	5.47
1.618	12.13	0.398	1.292	1.511	12.15	1.228	5.87
1.672	14.08	0.415	1.255	1.535	12.85	1.257	6.18
1.720	16.16	0.430	1.340	1.559	13.35	1.283	6.58
1.764	18.95	0.455	1.305	1.596	15.74	1.308	7.03
1.796	20.93	0.470	1.340	1.642	17.05	1.331	7.30
1.842	24.50			1.683	19.73	1.353	7.67
1.884	29.23	<i>X</i> = 0.291		1.723	17.37	1.373	8.19
1.940	26.00	0.430	3.545	1.777	12.00	1.391	8.80
0.475	1.324	0.455	3.763	1.828	9.76	1.409	8.99
0.518	1.256	0.478	3.975	1.862	9.45	1.433	9.67
0.532	1.225	0.494	3.925	1.899	8.83	1.460	10.6
0.553	1.315	0.507	3.942	1.934	8.25 ⁵	1.491	11.47
0.571	1.345	0.519	3.942	1.972	8.15	1.516	12.45
0.591	1.363	0.531 ⁵	4.18	2.013	8.05	1.540	13.00
0.607	1.373	0.546	4.07	2.053	7.97	1.564	13.69
0.646	1.394	0.559	3.99	0.506	4.07 ⁵	1.588	14.96
0.661	1.421	0.572 ⁵	4.01	0.519 ⁵	4.10	1.621	16.55
0.676	1.439	0.590	3.57	0.532 ⁵	4.12	1.663	18.97
0.692	1.442	0.604	3.05	0.545 ⁵	4.13	1.704	19.49
0.707	1.495	0.621	3.08	0.558 ⁵	3.87	1.750	13.18
0.723	1.501	0.639	3.09	0.590	3.34	1.831	9.72
0.739	1.528	0.655	3.14	0.604	3.02	1.865	9.40
0.758	1.545	0.693	3.13	0.621	3.02		
0.776	1.555	0.711	3.14	0.639	3.05	<i>X</i> = 0.39	
0.793	1.545	0.728	3.24	0.658	3.11	0.556	5.14
0.809	1.586	0.745	3.26 ⁵	0.676	3.09 ⁵	0.574	5.25
0.824	1.608	0.760	3.33	0.695	3.12	0.591	5.48
0.857	1.661	0.781	3.41	0.714	3.11 ⁵	0.609	5.41
0.903	1.758	0.806	3.42 ⁵	0.730	3.21	0.625	5.50
0.950	1.919	0.829	3.53	0.753	3.24	0.642	5.50
0.991	1.999	0.854	3.58	0.773	3.32 ⁵	0.658	5.85
1.031	2.187	0.878	3.75	0.789	3.36 ⁵	0.675	5.69
1.096	2.539	0.932	3.88 ⁵	0.820	3.46	0.696	4.00

TABLE I (continued)

<i>T</i> °K	<i>C</i> J/mole °K	<i>T</i> °K	<i>C</i> J/mole °K	<i>T</i> °K	<i>C</i> J/mole °K	<i>T</i> °K	<i>C</i> J/mole °K
0.719	4.02	0.927	5.80	0.656	7.24	0.497	5.83
0.743	4.12	0.943	6.00	0.671	7.27	0.513	6.09
0.766	4.16	0.959	6.28	0.684	7.38	0.529	6.27
0.790	4.38	0.973	6.45	0.698	7.29	0.545	6.48
0.817	4.52	0.988	6.48	0.712	7.50	0.560	6.64
0.850	4.54	1.002	6.51	0.724	7.41	0.575	6.81
0.919	5.18	1.021	6.73	0.740	6.95	0.590	6.91
1.026	6.17	1.049	6.91	0.758	6.90	0.605	6.93
1.112	7.18	1.075	7.22	0.768	6.81	0.618	7.16
1.171	7.90	1.101	7.67	0.782	6.34	0.632	7.32
1.210	8.90	1.127	7.83	0.795	7.43	0.645	7.28
1.242	8.80	1.150	8.16	0.808	6.25	0.660	7.59
1.362	11.98	1.173	8.56	0.814	6.54	0.674	7.51 ^s
1.424	12.83	1.195	8.84	0.827	6.81	0.689	7.77
1.453	13.17	1.217	9.36	0.853	6.35	0.704	7.57
1.483	14.63	1.237	10.05	0.867	6.40	0.719	7.85
1.502	15.65	1.255	9.89	0.881	6.50	0.733	7.86
1.517	16.69	1.266	10.27	0.896	6.50	0.746	7.77
1.533	17.99	1.296	10.77	0.918	6.94	0.760	7.71
1.542	17.51	1.314	11.10	0.948	7.20	0.773	7.72
1.559	16.22	1.331	11.51	0.976	7.24	0.786	8.08
1.607	12.21	1.346	12.61	1.004	7.35	0.799 ^s	7.84 ^s
		1.367	12.44	1.031	8.44	0.813	7.58 ^s
<i>X</i> = 0.478		1.395	10.90	1.055	8.50	0.827	7.36 ^s
0.425	3.98	1.430	9.45	1.078	8.77	0.840	7.56
0.465	4.54	1.467	8.51	1.099	8.99	0.854 ^s	7.29
0.500	4.48	1.506	8.02	1.120	9.19	0.869	6.86
0.513	5.84	1.546	7.91	1.145	9.52	0.882	7.54
0.531	5.25 ^s	1.592	7.42	1.160	9.50	0.896	7.36
0.548	5.49 ^s	1.640	6.89	1.186	8.89	0.908	7.27
0.565	5.60	1.684	7.41	1.205	6.82	0.920	7.62
0.580	5.78	1.729	6.93	1.234	6.78	0.932	7.57
0.595	5.99	1.772	7.06	1.261	7.18	0.944	7.49
0.609	6.16	1.816	7.00	1.290	7.17	0.956	7.75
0.624	6.23	1.888	7.14	1.325	6.66	0.968	7.38
0.641	6.18	1.930	6.89	1.353	7.02	0.980	7.34
0.655	6.45	1.960	7.14	1.376	6.66	0.993	6.98
0.669	6.37	2.030	7.28	1.410	6.61	1.007	6.93
0.684	6.53	2.080	7.21	1.444	6.07	1.02	6.84
0.699	6.17	2.140	7.11	1.470	6.23	1.034	6.51
0.714	6.29			1.505	6.54	1.075	6.53
0.728	6.02	<i>X</i> = 0.575		1.564	6.14	1.089	6.51
0.742	5.94	0.490	5.17	1.606	6.35	1.104	6.20
0.757	5.39	0.512	5.58	1.653	6.45	1.118	6.31
0.775	4.91	0.524	5.84	1.710	6.26	1.147	5.99
0.793	5.02	0.538	6.02	1.756	6.63	1.162	6.10
0.812 ^s	5.13	0.552	6.25			1.218	5.80
0.829	5.25	0.568	6.29	<i>X</i> = 0.638		1.281	5.66
0.846	5.33	0.583	6.53	0.395	4.90	1.312	5.74
0.863	5.41	0.598	6.70	0.420	4.84 ^s	0.587	6.88
0.872	5.76	0.612	7.16	0.442	5.14 ^s	0.602	7.04
0.894	5.64	0.627	7.02	0.461	5.67	0.616	7.22
0.910	5.75	0.642	7.27	0.479	5.61	0.629	7.28

TABLE I (continued)

<i>T</i> °K	<i>C</i> J/mole °K	<i>T</i> °K	<i>C</i> J/mole °K	<i>T</i> °K	<i>C</i> J/mole °K	<i>T</i> °K	<i>C</i> J/mole °K
0.643	7.25	0.652	7.90	0.690	7.61	1.063	4.92
0.657	7.43	0.666	8.00	0.707	7.31	1.081	4.87
0.671	7.50	0.680	8.11	0.741	6.91	1.100	4.76
0.684	7.55	0.695	8.04	0.760	5.82	1.119	5.14
0.701	7.48	0.708	7.99	0.780	5.78	1.156	4.90
0.715	7.60	0.721	8.18	0.799	5.69	1.174	5.05
0.730	7.63	0.735	7.99	0.819	5.44	1.192	4.98
0.743	7.54	0.748	8.04	0.885	5.34	1.210	5.03
0.756	7.59	0.759	8.08	0.910	5.24	1.227	5.00
0.768	7.59	0.771	7.81	0.934	5.20	1.244	4.95
0.781	7.63	0.785	8.16	0.959	5.17	1.262	4.92 ^s
0.792	7.74	0.798	8.76	0.988	4.82	1.280	5.01
0.805	7.51	0.809	8.06	1.063	4.88	1.297	4.73
0.817	7.41	0.823	7.75	1.081	4.79	1.324	4.93
0.831	6.89	0.835	7.80	1.101	4.76	1.361	5.21 ^s
0.843	6.99	0.849	7.77	1.119	4.87	1.395	5.28
0.855	6.97	0.863	7.57	1.300	5.20	1.427	5.34
0.868	6.91	0.877	7.55	1.336	5.07		
0.880	7.04	0.891	7.30	1.371	5.16	<i>X</i> = 0.805	
0.893	7.03	0.905	7.09	1.439	5.30	0.410	4.68
0.905	7.33	0.927	6.92	1.471	5.40 ^s	0.433	4.40
0.917	7.51	0.959	6.65	0.445	5.64	0.449	5.28
0.928	7.58	0.992	6.33	0.470	5.79	0.465	5.63
0.940	7.52	1.024	6.42	0.484	5.95	0.480	5.99
0.952	7.47	1.058	6.43	0.501	6.20 ^s	0.497	6.24
0.963	7.44	1.093	5.90	0.517	6.44	0.516	6.50
0.976	7.23	1.128	5.78	0.533	6.60 ^s	0.530	6.57
0.989	7.02	1.162	5.44	0.548	7.07	0.543	6.89
1.002	6.82	1.185	5.67	0.564	7.02	0.557	7.23
1.015	6.92	1.22	5.73	0.579	7.09	0.571	7.38
1.042	6.53	1.29	5.55	0.594	7.47	0.586	7.60
1.055	6.52	1.34	5.53	0.608	7.62	0.600	7.76
1.068	6.49	1.37	5.65	0.623	7.73	0.613	8.31
1.220	5.75	1.40	5.58	0.652	7.89	0.626	8.29
1.253	5.81	1.44	5.54	0.667	7.97	0.642	8.43
1.316	5.56	1.47	5.73	0.683	7.56	0.658	5.88
1.348	5.73	1.50	5.72	0.698	7.99	0.685	5.24
		1.55	5.83	0.714	7.57	0.711	5.02
<i>X</i> = 0.70		1.59	5.79	0.729	7.64	0.731	5.12
0.437	4.93	1.63	5.63	0.746	6.31	0.752	5.04
0.455	5.27	1.66	5.90	0.764	5.94	0.774	4.97
0.474	5.58	1.71	5.93	0.783 ^s	5.86	0.795	4.93
0.500	5.55	1.77	6.10	0.802	5.73	0.887	4.88
0.508	5.92	1.83	6.13	0.819	5.58	0.908	4.74
0.523	6.14	1.87	6.33	0.837	5.39 ^s	0.932	4.72
0.538	6.44	1.95	6.47	0.856	5.27	0.955	4.76
0.550	6.67			0.875	5.15	0.977	4.82
0.566	6.80			0.896	5.00	1.000	4.84
0.580	6.92	<i>X</i> = 0.75		0.916	4.99	1.037	4.67
0.593	7.16	0.626	7.68	0.937	4.80	1.083	4.73 ^s
0.607	7.43	0.642	7.63	0.959	4.78	1.132	4.56
0.621	7.56	0.658	7.80 ^s	0.980	4.87 ^s	1.178	4.66
0.637	7.67	0.674	7.87	1.045	5.24	1.225	4.72

TABLE I (continued)

<i>T</i> °K	<i>C</i> J/mole °K	<i>T</i> °K	<i>C</i> J/mole °K	<i>T</i> °K	<i>C</i> J/mole °K	<i>T</i> °K	<i>C</i> J/mole °K
1.454	5.13	0.528	7.15 ^s	1.042	4.16	0.879	4.20
1.493	5.20	0.545	7.35	1.067	4.07	0.903	4.36
1.530	5.33	0.563	7.68	1.089	4.29	0.927	4.29
1.566	5.40	0.582	7.71	1.111	4.29	0.951	4.30
1.599	5.48	0.601	6.33	1.133	4.39	0.975	4.17
1.632	5.66	0.623	4.98	1.154	4.51	0.997	4.03
1.663	5.84	0.650	4.77	1.175	4.58	1.020	4.38
1.696	5.90	0.682	4.59	1.196	4.49	1.042	4.29
1.728	5.99	0.715	4.38	1.216	4.58	1.062	4.33
1.760	6.13	0.747	4.38	1.236	4.71	1.083	4.31
1.793	6.08	0.777	4.41	1.256	4.58	1.104	4.39
1.825	6.25	0.806	4.53	1.275	4.78	1.125	4.46
1.855	6.26	0.835	4.46	1.293	4.75	1.145	4.46
1.886	6.65	0.863	4.43	1.312	4.85	1.165	4.36
		0.891	4.47 ^s	1.330	4.81	1.186	4.52
		0.921	4.41	1.343	5.09	1.206	4.63
		0.952	4.47	1.360	4.98	1.238	4.60
<i>X</i> = 0.847		0.981	4.63	1.376	5.13	1.280	4.79
0.430	5.77	1.013	4.58	1.393	5.14	1.322	4.88
0.450	6.23	1.043	4.57	1.411	5.08	1.361	4.91
0.469	6.33	1.075	4.50	1.431	5.25	1.398	5.14
0.488	6.72	1.102	4.45	1.455	5.34	1.433	5.20
0.505	6.92	1.129	4.42	1.565	5.52	1.467	5.41
0.520	7.23	1.157	4.55	1.604	5.62	1.506	5.49
0.536	7.30 ^s	1.219	4.89	1.719	5.91	1.545	5.52
0.553	7.57	1.299	5.03	1.755	5.94	1.579	5.58
0.571	7.37	1.369	5.23	1.793	6.16	1.619	5.72
0.587	7.27	1.444	5.42	1.830	6.10	1.656	5.95
0.605	5.11 ^s	1.512	5.67	1.865	6.24	1.687	5.87
0.631	4.85	1.583	6.03 ^s	0.37	4.85	1.730	5.97
0.660	4.86			0.39	5.20	1.765	6.19
0.693	4.48			0.410	5.24	1.805	6.17
0.727	4.31			0.427	5.60	1.839	6.28
0.758	4.43	<i>X</i> = 0.894		0.445	5.63	1.882	6.46
0.786	4.43	0.495	4.13	0.460	5.96	0.380	5.21
0.815	4.47	0.520	4.14	0.473	6.31	0.400	5.40
0.844	4.33	0.541	3.94	0.488	6.46	0.415	5.70
0.872	4.46	0.567	3.93	0.502	6.86	0.435	6.17
0.902	4.32	0.592	3.85	0.518	4.25	0.455	6.50
0.931	4.43	0.649	3.78	0.539	3.99	0.466	6.44
0.962	4.51	0.680	3.84	0.562	4.00	0.482	6.61
0.993	4.64	0.710	3.86	0.586	3.88	0.499	4.91 ^s
1.055	4.62	0.736	4.15	0.609	4.10	0.519 ^s	3.81
1.085	4.62	0.761	4.03	0.635	3.94	0.543	3.95
1.116	4.61	0.785	4.10	0.660	3.97	0.567	3.97
1.123	4.97	0.810	4.18	0.686	3.93	0.592	3.99
1.171	4.95 ^s	0.834	4.08	0.712	3.97	0.619	3.85
1.207	4.91	0.859	4.09	0.737	4.13	0.644	3.76
1.276	4.91	0.885	4.13	0.761	4.09	0.672	3.93
1.351	5.12 ^s	0.911	4.12	0.785	4.13	0.700	3.89
1.426	5.35	0.936	4.18	0.808	4.17	0.727	3.92
0.473	6.51	0.963	4.29	0.832	4.17	0.752	3.98
0.492	6.70	0.988	4.22	0.856	4.18	0.776	4.02
0.510 ^s	7.00	1.016	4.12				

TABLE I (continued)

<i>T</i> °K	<i>C</i> J/mole °K	<i>T</i> °K	<i>C</i> J/mole °K	<i>T</i> °K	<i>C</i> J/mole °K	<i>T</i> °K	<i>C</i> J/mole °K
0.847	4.15	1.067	4.24	0.832	3.89	0.780	3.75
0.872	4.22	1.091	4.31	0.862	3.94	0.809	3.96
0.909	4.12	1.115	4.45	0.895	4.03	0.836	3.90
0.922	4.27	1.139	4.47	0.923	4.14	0.890	3.99
0.947	4.33	1.157	4.52	0.960	4.15	0.918	4.05
0.972	4.06	1.180	4.49	0.991	4.23	0.944	4.10
0.995	4.06	1.201	4.73	1.021	4.27	0.994	4.26
1.018	4.19	1.222	4.63	1.050	4.13	1.020	4.36
1.042	4.16	1.242	4.63	1.075	4.10	1.092	4.52
1.063	4.38	1.262	4.78	1.101	4.02	1.114	4.61
1.084	4.33	1.282	4.92	1.124	4.41	1.138	4.48
1.105	4.28	1.300	4.79	1.147	4.24	1.183	4.63
1.127	4.41	1.320	4.95	1.169	4.41	1.236	4.85
1.147	4.53	1.338	5.08	1.189	4.46	1.400	5.30
1.167	4.50	1.356	4.93	1.211	4.44	1.491	5.60
1.187	4.50	1.374	5.07	1.232	4.45	1.563	5.96
1.207	4.53	1.392	5.06	1.252	4.65	1.638	6.11
1.226	4.56	1.410	5.07	1.272	4.69	1.762	6.65
1.236	4.67	1.428	5.08	1.292	4.65	1.820	6.92
1.280	4.62	1.456	5.05	1.312	4.79	1.878	7.14
1.293	4.84	1.523	5.29	1.330	4.88	0.410	3.14
1.314	4.68	1.532	5.32	1.360	4.90	0.440	3.11
		1.570	5.79	1.402	5.04	0.467	3.21
<i>X</i> = 0.954		1.609	5.95	1.442	5.19	0.523	3.34
0.397	3.97	1.647	5.90	1.481	5.37	0.555	3.37
0.410	3.47	1.686	6.01	1.517	5.51	0.586	3.45
0.425	3.40 ^s	1.724	6.01	1.555	5.51	0.614	3.54
0.437 ^s	3.33 ^s	1.761	6.34	1.595	5.81	0.644	3.54
0.449	3.40	1.801	6.08	1.635	5.75	0.674	3.56
0.461	3.37	1.838	6.49	1.674	5.83	0.704	3.59
0.474	3.37	1.874	6.45	1.713	6.07	0.738	3.69
0.487	3.40	1.907	6.58	1.750	6.13	0.768	3.75
0.501	3.43	1.941	6.78	1.787	6.32	0.798	3.81
0.514	3.38	0.457	3.34	1.828	6.05	0.825	3.86
0.528	3.49 ^s	0.497	3.39 ^s	1.864	6.49	0.854	3.92
0.540	3.57	0.509	3.41	1.898	6.45	0.882	3.99
0.563	3.54	0.523	3.35	1.931	6.62	0.912	4.01
0.598	3.60	0.536	3.42	1.964	6.59	0.938	4.01
0.634	3.61	0.552	3.48	1.998	6.59	0.962	4.15
0.668	3.63	0.565	3.39	2.042	7.06	0.990	4.20
0.712	3.66 ^s	0.580	3.58			1.014	4.30
0.748	3.75	0.595	3.54	<i>X</i> = 1.00		1.038	4.35
0.777	3.81	0.611	3.48	0.425	3.25	1.063	4.34
0.805	3.90	0.628	3.55	0.460	3.21	1.088	4.30
0.834	3.97 ^s	0.642	3.55	0.512	3.38	1.144	4.40
0.876	4.03	0.656	3.53	0.573	3.46	1.233	4.84
0.922	4.10	0.670	3.59	0.629	3.60	1.320	5.08
0.955	4.16	0.695	3.66	0.659	3.61	1.398	5.25
0.984	4.27	0.731	3.68	0.689	3.65	1.475	5.57
1.014	4.23	0.766	3.74	0.720	3.66	1.547	5.85
1.042	4.20	0.801	3.82	0.751	3.72		

TABLE II

The lambda- and phase separation-temperatures T_λ = lambda temperature, $T_{P.S}$ = phase separation temperature, N_L = amount of liquid condensed in the calorimeter			
X_L	$T_\lambda(^{\circ}\text{K})$	$T_{P.S}(^{\circ}\text{K})$	$N_L(\text{mole})$
0.0466	2.105		$19.26 \cdot 10^{-3}$
0.094	2.03		$19.00 \cdot 10^{-3}$
0.15	1.94	(0.398)	$18.73 \cdot 10^{-3}$
0.291	1.715	0.590	$18.03 \cdot 10^{-3}$
0.39	1.535	0.695	$17.52 \cdot 10^{-3}$
0.47 ⁸	1.35	0.775	$17.00 \cdot 10^{-3}$
0.57 ⁵	1.15	0.84	$16.49 \cdot 10^{-3}$
0.63 ⁸	0.95 ⁵	0.87	$16.3 \cdot 10^{-3}$
0.70	0.84	0.825	$15.97 \cdot 10^{-3}$
0.75		0.76	$15.73 \cdot 10^{-3}$
0.80 ⁵		0.67	$15.45 \cdot 10^{-3}$
0.84 ⁷		0.60	$15.23 \cdot 10^{-3}$
0.89 ⁴		0.50	$15.0 \cdot 10^{-3}$
0.95 ⁴		0.385	$14.48 \cdot 10^{-3}$
1.00			$14.38 \cdot 10^{-3}$

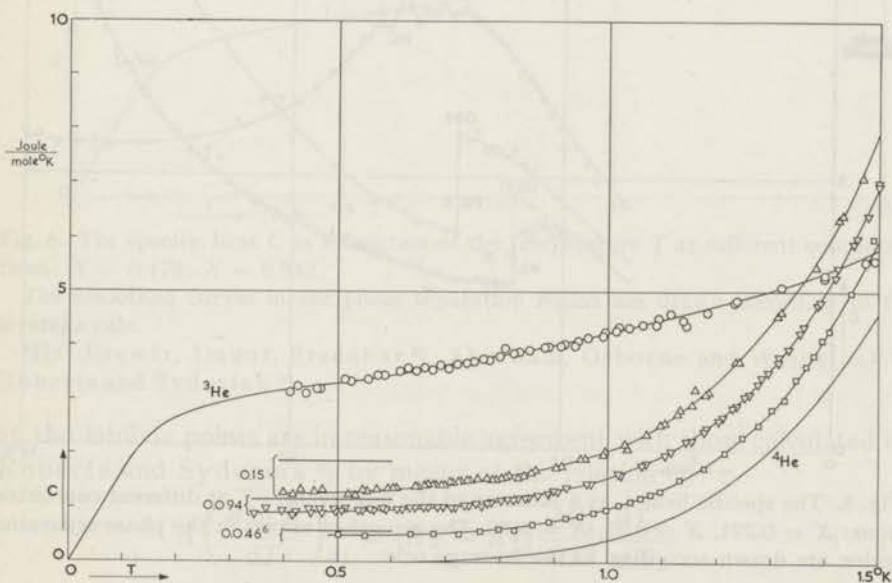


Fig. 4. The specific heat C of ^3He - ^4He mixtures as a function of the temperature T at different concentrations: $X = 1.00$, $X = 0.15$, $X = 0.094$, $X = 0.0466$. The smoothed line drawn through the experimental ^3He points is taken from the values of Brewer, Daunt and Sreedhar⁶⁾; Abraham, Osborne and Weinstock⁷⁾; and Roberts and Sydoriak⁸⁾. ^4He : Kramers¹⁴⁾, Keesom and Keesom¹⁵⁾.

The horizontal lines at low temperatures just above the curves for $X = 0.0466$, $X = 0.094$ and $X = 0.15$ are the theoretical values according to the theory of Pomeranchuk¹⁶⁾ ($C_3 = \frac{3}{2}RX$).

B) $0.15 < X < 0.954$. The intermediate region (phase separation region)

B1) $0.15 < X < 0.51$

B2) $0.51 < X < 0.73$

B3) $0.73 < X < 0.954$

C) $0.954 \leq X \leq 1$. Dilute mixtures of ^4He in liquid ^3He .

A) $0 < X \leq 0.15$ (dilute mixtures of ^3He in liquid ^4He , $X = 0.0466$, 0.094 , 0.15 , see the figs. 4 and 10).

Here we have a discontinuity in the specific heat ΔC_λ at the corresponding lambda temperature T_λ . Below 1°K the specific heat measurements show the ^3He to give an almost constant contribution of very nearly $\frac{3}{2}RX$ to the specific heat. This behaviour can be explained by means of the theory of Pomeranchuk¹⁶⁾ (see later II, 4A). In this concentration region we do not reach the phase separation curve PS. The lambda temperatures can be determined rather accurately from our measurements.

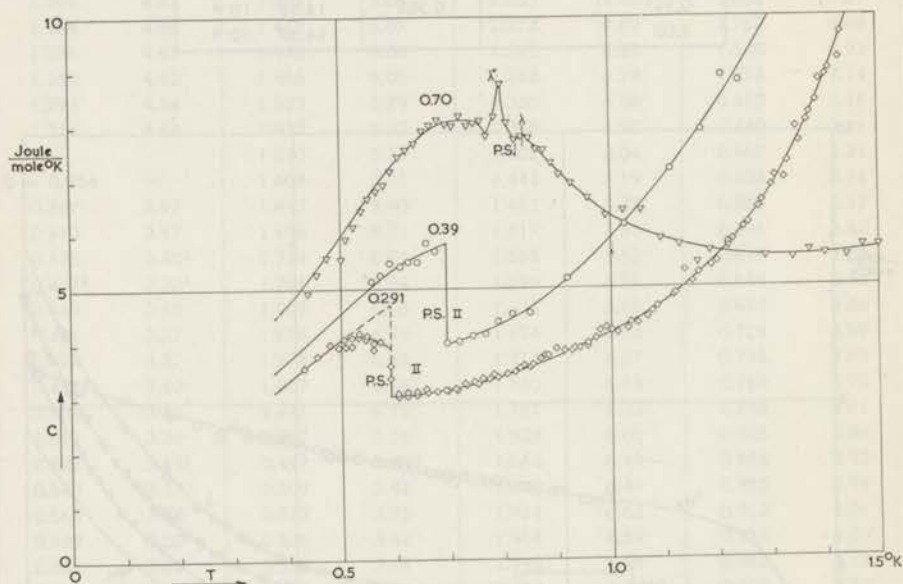


Fig. 5. The specific heat C as a function of the temperature T at different concentrations: $X = 0.291$, $X = 0.39$, $X = 0.70$. The smoothed curves in the phase separation region are drawn according to the leverage rule.

B) $0.15 < X < 0.954$. The intermediate region (phase separation region, see the figs. 5, 6, 7, 8 and 9).

Below the phase separation temperature we have an additional contribution to the specific heat due to the heat of mixing which is the result of the mixing of the isotopic liquids when the temperature rises.

B1) $0.15 < X < 0.51$ ($X = 0.291$, 0.39 , 0.478 , see the figs. 5 and 6).

A discontinuity in the specific heat ΔC_{PS} is found at the phase separation curve, since it is only below the phase separation curve that there is an additional contribution due to the heat of mixing, and a discontinuity in the specific heat ΔC_λ is found at the corresponding lambda temperature. The temperatures at which the discontinuity ΔC_{PS} and ΔC_λ occur can be determined with a reasonable accuracy. The values of the lambda temperatures are in agreement with the lambda line of Roberts and Sydoriak^{9) 19)} (see fig. 11). The magnitudes of the discontinuities in the specific heat ΔC_λ

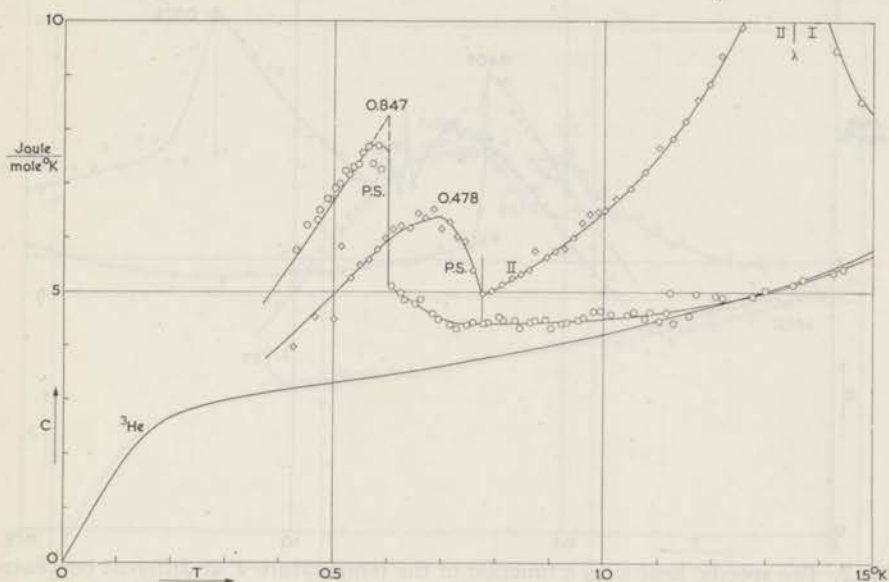


Fig. 6. The specific heat C as a function of the temperature T at different concentrations: $X = 0.478$; $X = 0.847$.

The smoothed curves in the phase separation region are drawn according to the leverage rule.

³He: Brewer, Daunt, Sreedhar⁶⁾, Abraham, Osborne and Weinstock⁷⁾, Roberts and Sydoriak⁸⁾.

at the lambda points are in reasonable agreement with those calculated by Roberts and Sydoriak⁹⁾ by means of the relation²⁰⁾:

$$\Delta \left(\frac{d \ln P}{dT} \right)_{X_L} = (X_V - X_L) \frac{\Delta C_\lambda}{RT^2} \frac{dT_\lambda}{dX_L} \quad (1)$$

from the measured change in the slope of the vapour pressure curves measured by them and are drawn in the figs. 7 and 10. It is remarkable that the magnitude of the discontinuity in the specific heat at the lambda point ΔC_λ falls rapidly with the increasing concentration X ²⁰⁾. There is no short range ordering observed just above the phase separation curve.

In the He I and in the phase separation region there was overheating during the afterdrift, but not in the He II region. See, for example, fig. 3 in

which the afterdrift for a temperature just below and just above the phase separation curve is shown for a 39% mixture. During the heating period at the 31st minute the phase separation curve PS was passed. After the heating period at the 26th minute in the phase separation region there was overheating during the afterdrift. After the heating period at the 31st minute in the He II region no overheating was observed during the afterdrift, showing the entry into the superfluid region.

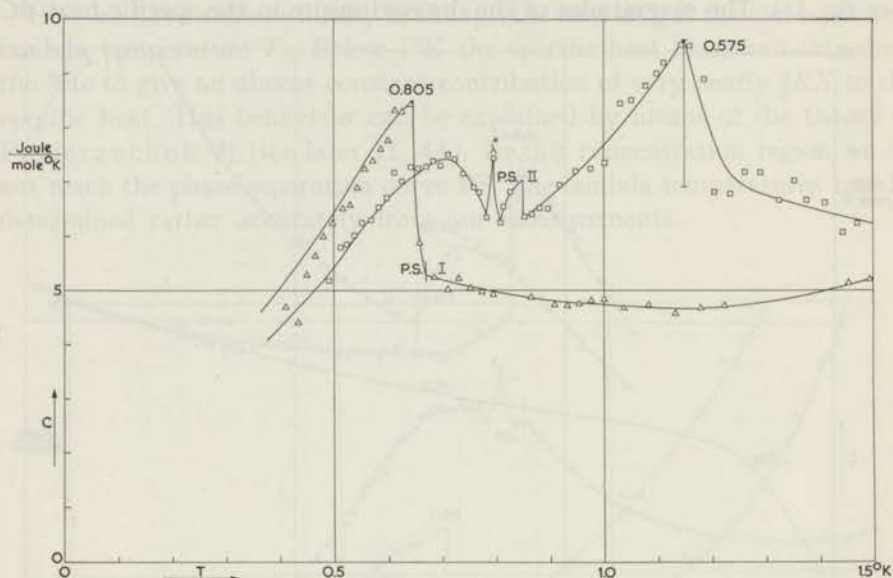


Fig. 7. The specific heat C as a function of the temperature T at different concentrations: $X = 0.575$, $X = 0.805$.

The smoothed curves in the phase separation region are drawn according to the leverage rule.

$\bar{\Delta}C_p$: ΔC_p calculated by Roberts and Sydoriak from their vapour pressure measurements⁹).

B2) $0.51 < X < 0.73$ ($X = 0.575, 0.638, 0.70$, see the figs. 5, 7 and 8). We see that the discontinuity ΔC_{PS} in the neighbourhood of the top of the phase separation curve and the discontinuity ΔC_λ at the corresponding lambda temperature becomes less pronounced. Hence from our measurements the location of the phase separation and lambda curve cannot be determined very accurately.

At λ^* (see fig. 11), the lambda line λ meets the phase separation curve PS *). Above this temperature the upper ^3He rich phase is superfluid, while below this temperature it is normal, as found by Zinov'eva and Peshkov¹⁰) by visual observation, while the lower ^4He rich phase always remains superfluid. A very small discontinuity in the specific heat was found for the concentrations: $X = 0.575, 0.638, 0.70$ (see

*) See chap. III.

figs. 5, 7 and 8), at the same temperature $T_{\lambda}^* \approx 0.8^\circ\text{K}$ and $X^* \approx 0.73$ (in the concentration range $0.51 < X < 0.73$), indicating a lambda transition in the upper phase. The values of Zinov'eva and Peshkov¹⁰⁾ are $T_{\lambda}^* = 0.67^\circ\text{K}$ and $X^* = 0.82$ and were found for a 63.1% mixture by visually observing that the upper phase was vigorously boiling around a small heating coil at temperatures below T_{λ}^* , while the lower phase remained immobile. As the temperature was raised, there came a moment ($T \geq T_{\lambda}^*$) at which the boiling of the upper phase ceased instantaneously,

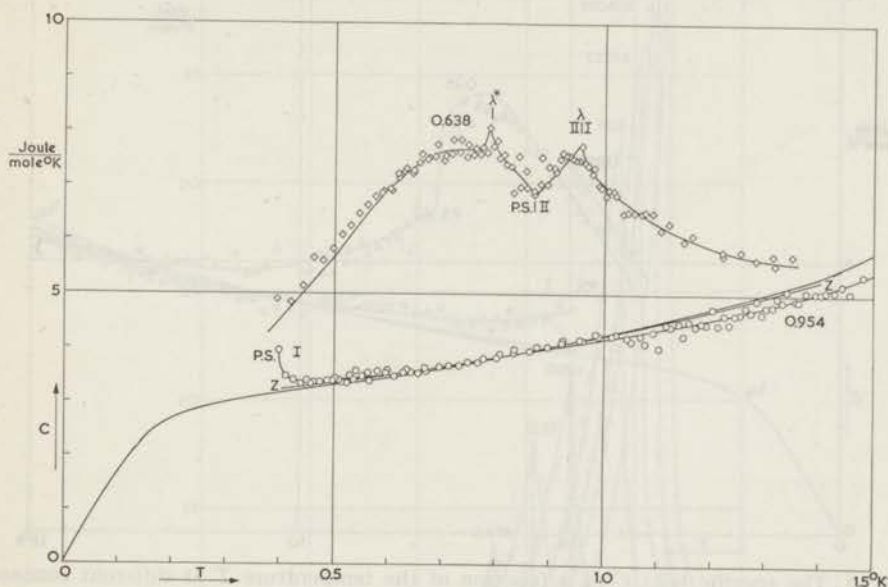


Fig. 8. The specific heat C as a function of the temperature T at different concentrations: $X = 0.638$, $X = 0.954$.

The smoothed curves in the phase separation region are drawn according to the leverage rule.

³He: Brewer, Daunt, Sreedhar⁶⁾, Abraham, Osborne and Weinstock⁷⁾, Roberts and Sydoriak⁸⁾. Z: theoretical value according to the theory of Zharkov and Silin¹⁷⁾ for $X = 0.954$.

becoming just as quiet as the lower phase. Here we like to remark that the Zinov'eva and Peshkov experiment is in first place a qualitative one, giving direct evidence of superfluidity. However it may be that the heat input used for making the vapour bubbles, disturbs the absolute determination of the lambda temperature and concentration.

B3) $0.73 < X < 0.954$ ($X = 0.75, 0.805, 0.847, 0.894$, see the figs. 6, 7 and 9).

Here we have no lambda point contribution. At the phase separation temperature there is a discontinuity ΔC_{PS} . Here again the phase separation curve can be reasonably localised. The increase in the specific heat just

above the phase separation curve is presumably due to a short range ordering occurring above the lambda transition, although this transition has now disappeared because of the phase separation.

At higher concentrations this short range ordering becomes less pronounced because the extrapolated lambda line is then most probably further away from the phase separation curve.

Finally we remark that in the whole phase separation region the total

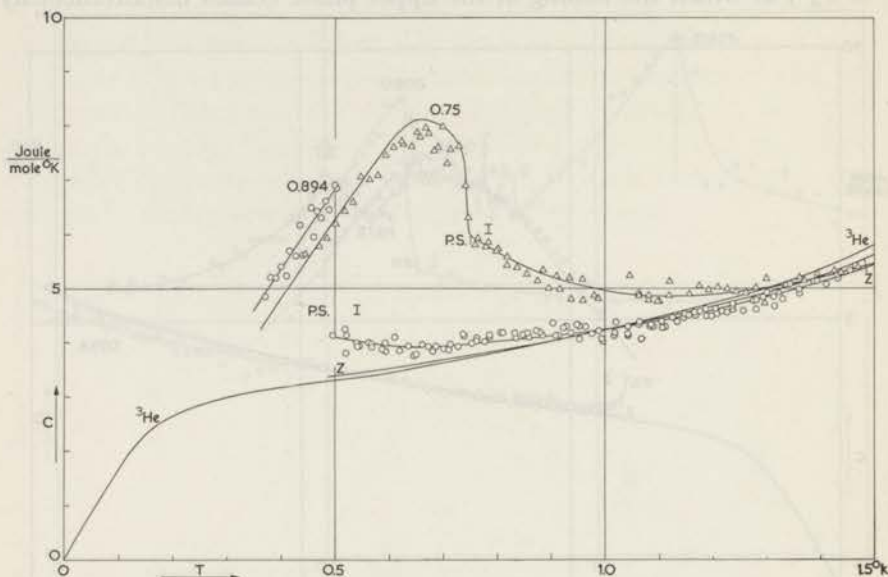


Fig. 9. The specific heat C as a function of the temperature T at different concentrations: $X = 0.75$ $X = 0.894$.

The smoothed curves in the phase separation region are drawn according to the leverage rule.

³He: Brewer, Daunt, Sreedhar ⁶⁾, Abraham, Osborne and Weinstock ⁷⁾, Roberts and Sydoriak ⁸⁾.

molar enthalpy H is, according to the leverage rule, equal to:

$$H = \frac{X_u - \bar{X}}{X_u - X_l} H_l(T, X_l) + \frac{\bar{X} - X_l}{X_u - X_l} H_u(T, X_u) \quad (2)$$

(see fig. 11). The subscripts u and l refer to the upper ³He rich phase and the lower ⁴He rich phase. Hence the specific heat C , according to the leverage rule, must be equal to:

$$C_{\bar{X}} = \left(\frac{dH}{dT} \right)_{\bar{X}} = \frac{d}{dT} \left(\frac{H_u(T, X_u) - H_l(T, X_l)}{X_u - X_l} \right) \bar{X} + \frac{d}{dT} \left(\frac{X_u H_l(T, X_l) - X_l H_u(T, X_u)}{X_u - X_l} \right) \quad (3)$$

and is found to be linearly proportional to the average concentration \bar{X} of the condensed mixture. In fig. 12 the specific heat C in the phase separation region is plotted against the total condensed concentration for different temperatures. The lines drawn through the measured specific heat points in the phase separation region in the figs. 5, 6, 7, 8 and 9 are smoothed according to the leverage rule.

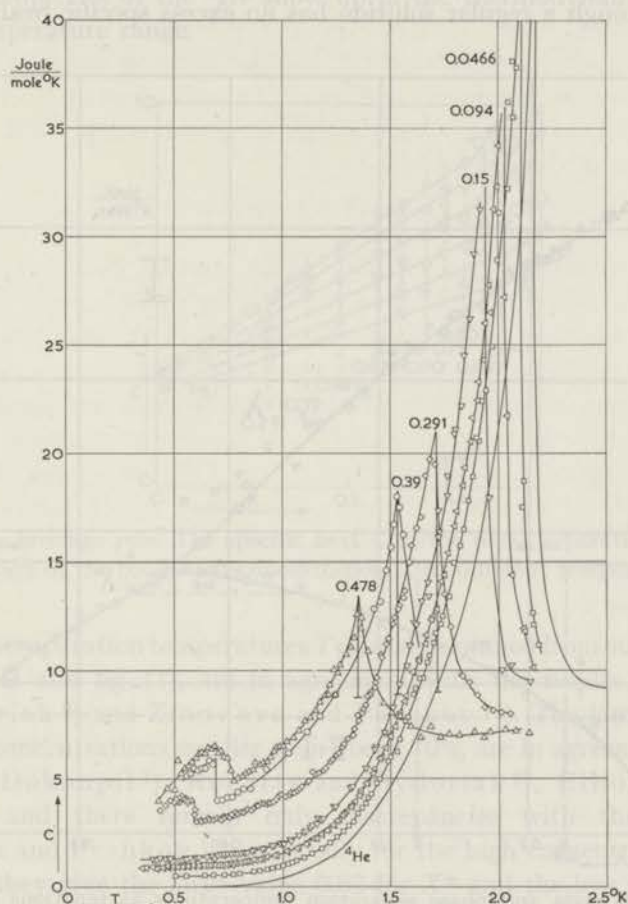


Fig. 10. The specific heat C as a function of the temperature T between 0.4°K and 2°K at different concentrations:

- $X = 0.0466$
- ◁ $X = 0.094$
- ▽ $X = 0.15$
- ◇ $X = 0.291$
- $X = 0.39$
- △ $X = 0.478$

ΔC_p calculated by Roberts and Sydoriak from their vapour pressure measurements⁹).

It is perhaps interesting to remark that a regular solution, where the heat of mixing H^E is equal to $X(1 - X)W^{20}$ (as will be explained in part II) would give the following expression for the specific heat in the phase separation region:

$$C = XC_3^0 + (1 - X)C_4^0 + W(1 - 2X_{PS})\left(\frac{dX}{dT}\right)_{PS}. \quad (4)$$

Thus, although a regular solution has no excess specific heat C^E , it has

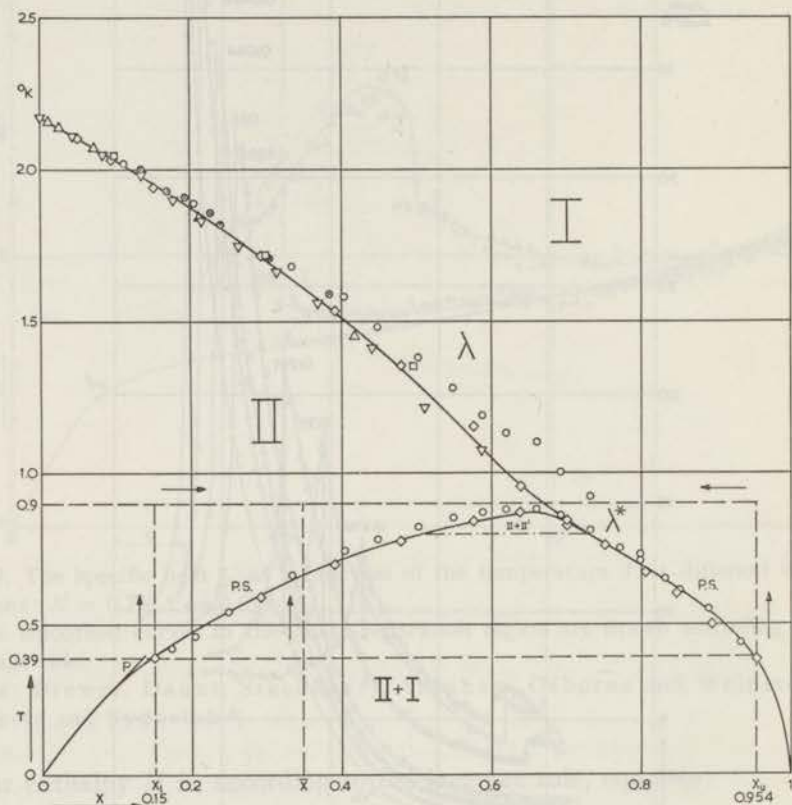


Fig. 11. The lambda and phase separation temperatures as functions of the liquid concentration. The smoothed line denotes the values of Roberts and Sydoriak^{9,19}.

- △ Dokoupil¹⁾
- Zinov'eva and Peshkov¹⁰⁾
- Kerr¹¹⁾
- ▽ Elliot and Fairbank¹²⁾
- ⊗ Esel'son, Beręzniak and Kaganov¹³⁾
- ◇ Our experiments

P. Theoretical value theory Pomeranchuk

x_u = concentration of the ^3He rich upper phase

x_l = concentration of the ^4He rich lower phase

\bar{x} = average concentration of the condensed mixture.

of course just as well an extra contribution in the phase separation region due to the heat of mixing (see II, section 2).

C) $0.954 \leq X \leq 1$ (Dilute mixtures of ^4He in liquid ^3He $X = 0.954$, $X = 1$, see the figs. 4, 8). No lambda and phase separation points.

We can compare the results for $X = 0.954$ with the theory of Zharkov and Silin¹⁷⁾ (see later II, 4C). There are no indications that the nuclear magnetic properties of the ^3He show up in the thermodynamic properties in this temperature range.

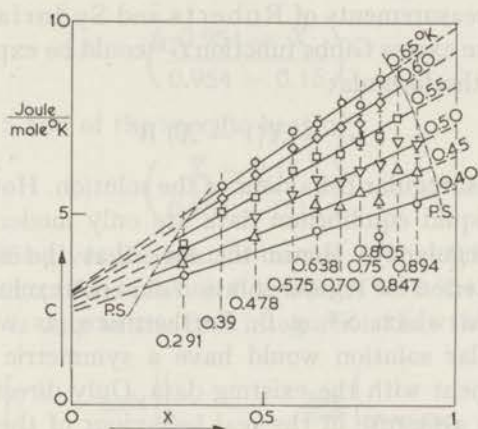


Fig. 12. The leverage rule. The specific heat C in the phase separation region as a function of the condensed concentration X at different temperatures.

The phase separation temperatures T_{PS} , as determined from our experiment (see table II and fig. 11), are in agreement with the results of Roberts and Sydoriak⁹⁾ and Zinov'eva and Peshkov¹⁰⁾. The lambda temperatures for concentrations smaller than about 70% are in agreement with the results of Dokoupil¹⁾, Roberts and Sydoriak⁹⁾, Elliot and Fairbank¹²⁾, and there remain only discrepancies with the results of Zinov'eva and Peshkov¹⁰⁾, especially for the high concentration values, for which they give the large value 0.82 for X^* and the low value 0.67°K for T_{λ}^* , and with the lambda values of Roberts and Sydoriak⁹⁾¹⁸⁾ for concentrations larger than about 70% derived from their thermal conductivity measurements.

The spread of the experimental points with respect to the smoothed values derived from the leverage rule gives an idea of the overall non-systematic errors of the measurements. Systematic errors can be present in the temperature determination, in the amount of liquid condensed, in the amount of heat supplied and in the determination of the concentration. The largest uncertainty arises from the temperature determination, for the other quantities are more accurately known. The highest accuracy is

reached in the neighbourhood of 1°K. On the whole the accuracy is of the order of 5%, decreasing at lower temperatures and lower concentrations.

PART II: THERMODYNAMIC PROPERTIES OF LIQUID ^3He - ^4He MIXTURES DERIVED FROM SPECIFIC HEAT MEASUREMENTS BETWEEN 0.4°K AND 2°K OVER THE COMPLETE CONCENTRATION RANGE.

1. *Introduction.* In chap. I we ²⁰⁾ analysed the existing vapour-liquid equilibrium data and calculated the excess chemical potentials from the vapour pressure measurements of Roberts and Sydoriak ⁹⁾. At temperatures below 1°K the excess Gibbs function G^E could be expressed reasonably well by means of the formula:

$$G^E = X(1 - X)W \quad (1)$$

indicating an almost regular behaviour of the solution. However, it is known that the vapour-liquid equilibrium data are only moderately sensitive to deviations from regularity. Hence the fact that the experimental data conform to the criterion for regular solution does not exclude a more complicated behaviour in which $S^E \neq 0$. Furthermore, as we pointed out in chap. I ²⁰⁾ a regular solution would have a symmetric phase separation curve in disagreement with the existing data. Only direct caloric measurements can give us a picture of the real behaviour of the mixture.

In (2) we will derive the heat of mixing from our specific heat measurements and with this in combination with the vapour pressure data the excess entropy will be calculated in (3).

A theoretical discussion of the thermodynamic properties is given in (4). The discussion is divided into the same three sections A, B and C as in section (4) of part I.

The thermodynamic properties can be compared with the Pomeranchuk model ¹⁶⁾ for dilute mixtures of ^3He in liquid ^4He (see section 4A) and with Zharkov's model ¹⁷⁾ for dilute mixtures of ^4He in liquid ^3He (see section 4C).

For the definitions of the thermodynamic excess quantities we refer also to chap. I ²⁰⁾.

2. *The heat of mixing.* The heat of mixing $H^E(X, T)$ is defined as the heat required to keep the temperature T constant when X mole of pure liquid ^3He is added to $(1 - X)$ mole of pure liquid ^4He .

Since variations in the enthalpy are independent of the path described in a phase equilibrium diagram (see fig. 11), it is possible to derive the heat of mixing H^E from the specific heat measurements inside and outside the phase separation region by integrating the specific heat along different paths. When we cool one mole of a mixture of concentration \bar{X} ($0.15 < \bar{X} <$

< 0.954) to a temperature of 0.39°K , the mixture separates into two phases with concentrations $X_1 = 0.15$ and $X_u = 0.954$ containing respectively

$$\left(\frac{0.954 - \bar{X}}{0.954 - 0.15} \right) \text{ and } \left(\frac{\bar{X} - 0.15}{0.954 - 0.15} \right)$$

moles according to the leverage rule. The difference between the integration from 0.39°K to for example 0.9°K of the measured specific heat with average concentration \bar{X} condensed in the calorimeter and the sum of the integrations from 0.39°K to 0.9°K outside the phase separation curve of the specific heat of

$$\left(\frac{0.954 - \bar{X}}{0.954 - 0.15} \right)$$

moles at $X_1 = 0.15$ and of the specific heat of

$$\left(\frac{\bar{X} - 0.15}{0.954 - 0.15} \right)$$

moles at $X_u = 0.954$ gives the heat of mixing H^{E*} at 0.9°K of two liquids with starting concentrations of $X = 0.15$ and $X = 0.954$ and final concentration \bar{X} , since it is only in the first integration that the heat of mixing is

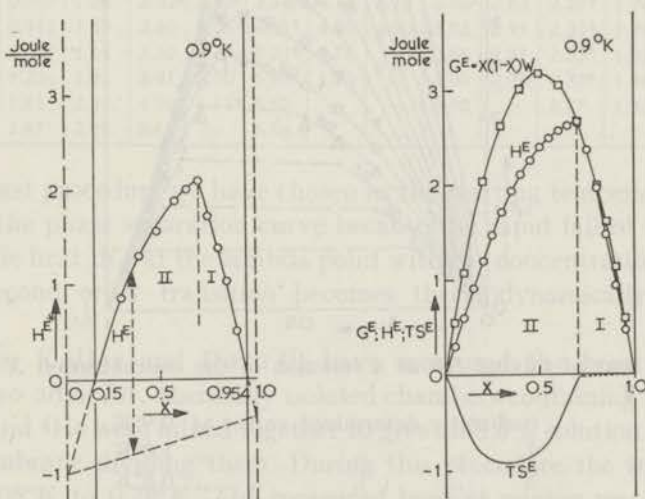


Fig. 13. H^{E*} , H^E , G^E and TSE as a function of the concentration X at 0.9°K
 $G^E = X(1 - X)W$; $W/R = 1.54^\circ\text{K}^{20}$

included and not in the integrations outside the phase separation curve PS. Thus the heat of mixing H^{E*} is given by the following equation.

$$H_{0.9^\circ\text{K}}^{E*}(\bar{X}) = \int_{0.39}^{0.9} C_{\bar{X}} dT - \left[\frac{\bar{X} - 0.15}{0.954 - 0.15} \int_{0.39}^{0.9} C_{0.954} dT + \frac{0.954 - \bar{X}}{0.954 - 0.15} \int_{0.39}^{0.9} C_{0.15} dT \right]. \quad (2)$$

Following this procedure we have calculated the heat of mixing H^{E*} at 0.9°K for the 10 concentrations \bar{X} between $X_1 = 0.15$ and $X_{11} = 0.954$ at which specific heat measurements were made (see fig. 13). By extrapolating H^{E*} to $X = 0$ and $X = 1$ the total heat of mixing H^E at 0.9°K is obtained (see figs. 13 and 14). The same procedure was also followed for 0.8°K and

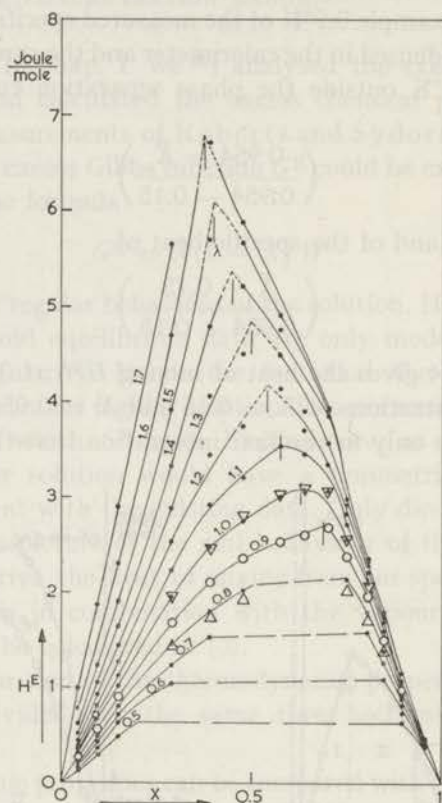


Fig. 14. The heat of mixing H^E as a function of the concentration X at different temperatures T

- directly determined values at 0.9°K
- ▽ " " " " 1.0°K
- △ " " " " 0.8°K
- Sommers, Keller and Dash²¹). Direct experimental point at $X = 0.086$ and $T = 1.02^\circ\text{K}$.

1°K and the extrapolated values of H^E obtained at these temperatures are plotted in fig. 14. If we now define the excess specific heat $C^E(T, X)$ by means of the following relation:

$$C(T, X) = XC_3^0(T) + (1 - X)C_4^0(T) + C^E(T, X)$$

it is possible to obtain the heat of mixing H^E at every other temperature

between 0.4°K and 2°K by integration of the excess specific heat using the relation

$$H_X^E(T) = H_X^E(0.9^\circ\text{K}) + \int_{0.9}^T C_X^E dT \quad (3)$$

The results obtained in this way are shown in fig. 14 and table III. In fig. 14 we see that there is reasonable agreement with the directly determined values of H^E at 0.8°K and 1°K. The correction for the pressure term appears to be negligible for the excess quantities.

TABLE III

Heat of mixing H^E (joule/mole)														
X_L	0.046 ⁶	0.094	0.15	0.29 ¹	0.39	0.47 ⁸	0.57 ⁵	0.63 ⁸	0.70	0.75	0.80 ⁵	0.84 ⁷	0.89 ⁴	0.95 ⁴
$T(^\circ\text{K})$														
0.4	—	—	0.472	—	—	—	—	—	—	—	—	—	—	0.364 ¹
0.5	0.129	0.299	0.551	—	—	—	—	—	—	—	—	—	0.635	0.394
0.6	0.165	0.362	0.631	1.04	—	—	—	—	—	—	—	1.085	0.734	0.413 ⁴
0.7	0.199	0.425	0.715	1.24	1.53	—	—	—	—	—	1.584	1.265	0.815	0.433 ⁴
0.8	0.234	0.489	0.805	1.45	1.80	2.01	—	—	—	2.13	1.79	1.39	0.885	0.452
0.9	0.270	0.560	0.90	1.68	2.10	2.35	2.52	2.60	2.68	2.37	1.95	1.50	0.94	0.47
1.0	0.309	0.636	1.01	1.94	2.47	2.74 ⁴	3.00	3.06	3.06	2.56	2.09	1.59	0.98	0.472
1.1	0.350	0.716	1.12	2.22	2.91	3.20	3.55	3.42	3.34	2.71	2.20	1.67	1.01 ⁴	0.472 ²
1.2	0.394	0.807	1.26	2.52 ⁶	3.43 ⁷	3.74 ⁵	4.14	3.70	3.56 ⁵	2.82	2.27 ²	1.74	1.03 ⁹	0.472 ³
1.3	0.444	0.913	1.43	2.88	4.06 ¹	4.41 ⁵	4.50	3.90	3.73	2.91	2.31 ⁹	1.79	1.05 ⁹	0.471 ⁵
1.4	0.512	1.051	1.64	3.32	4.79	5.21 ⁹	4.75	—	3.85	2.97	2.33 ⁸	1.82	1.06 ²	0.470
1.5	0.618	1.236	1.91	3.91	5.70	5.67	4.90	—	3.90	2.98 ³	2.32 ⁹	1.84	1.04 ⁹	0.467
1.6	0.777	1.51	2.31	4.70	6.71 ³	5.87	—	—	3.90	—	2.27	1.83	1.01	0.463
1.7	0.994	1.87	2.89	5.65	—	5.88	—	—	—	—	—	—	—	—

For this last procedure we have chosen as the starting temperature 0.9°K just above the phase separation curve because the rapid fall of the change of the specific heat ΔC_λ at the lambda point with the concentration indicates that the second order transition becomes thermodynamically of minor importance.

Sommers, Keller and Dash²¹) have measured the heat of mixing directly. Two adjacent, thermally isolated chambers containing pure liquid ³He and liquid ⁴He were mixed together to give an 8.6% solution by rupturing the membrane dividing them. During this procedure the temperature fell from 1.05°K to 0.78°K. The measured heat of mixing was estimated to be 0.71 joule/mole at 1.05°K which is in satisfactory agreement with our values determined from the specific heat measurements (see fig. 14 and fig. 17).

3. *The excess entropy.* The excess entropy S^E is defined by means of the relation:

$$S(T, X) = XS_3^0(T) + (1 - X)S_4^0(T) - R[X \ln X + (1 - X) \ln (1 - X)] + S^E(T, X).$$

As we have already calculated the excess Gibbs function G^E (20) in this temperature region from the vapour pressure measurements by Roberts and Sydoriak 9), using the relation $G^E = H^E - TS^E$ we can now calculate the excess entropy at 0.9°K and the excess entropy at other temperatures by means of the relation:

$$S_X^E(T) = S_X^E(0.9^\circ\text{K}) + \int_{0.9}^T \frac{C_X^E}{T} dT. \quad (4)$$

The results obtained are shown in table IV and fig. 15.

TABLE IV

		Excess Entropy S^E (joule/mole °K)													
X_L	$T(^{\circ}\text{K})$	0.046 ⁶	0.094	0.15	0.29 ¹	0.39	0.47 ⁸	0.57 ⁵	0.63 ⁸	0.70	0.75	0.80 ⁵	0.84 ⁷	0.89 ⁴	0.95 ⁴
0.4		—	—	-1.48											
0.5		-0.47	-0.93	-1.31											
0.6		-0.41	-0.84	-1.16	-1.90										
0.7		-0.36	-0.72	-1.03	-1.57	-1.73	—	—	—	—	—	—	-0.294	-0.159	-0.046
0.8		-0.31	-0.63	-0.91	-1.30	-1.37	-1.31	—	—	—	-0.30	-0.20	-0.127	-0.065	-0.021
0.9		-0.27	-0.55	-0.80	-1.02	-1.02	-0.91	-0.65	-0.39	-0.14	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0
1.0		-0.23	-0.47	-0.69	-0.75	-0.64	-0.50	-0.16	+0.10	+0.26	+0.20	+0.15	+0.097	+0.048	0.016
1.1		-0.19	-0.39	-0.58	-0.49	-0.22	-0.06	+0.37	+0.45	+0.53	+0.34	+0.25	+0.169	+0.080	0.023
1.2		-0.15	-0.31	-0.47	-0.22	+0.24	+0.41	+0.88	+0.70	+0.73	+0.44	+0.32	+0.222	+0.102	0.024
1.3		-0.11	-0.22	-0.33	+0.06	+0.74	+0.95	+1.77	+0.87	+0.86	+0.51	+0.36			
1.4		-0.06	-0.13	-0.18	+0.38	+1.28	+1.54	+1.35	—	+0.95	+0.55	+0.38			
1.5		+0.01	0.00	+0.01	+0.79	+1.90	+1.86	+1.46	—	+0.99	+0.56				
1.6		+0.11	+0.18	+0.26	+1.30	+2.56	+1.99	—	—	+0.90					
1.7		+0.24	+0.39	+0.62	+1.94	—	+2.06								

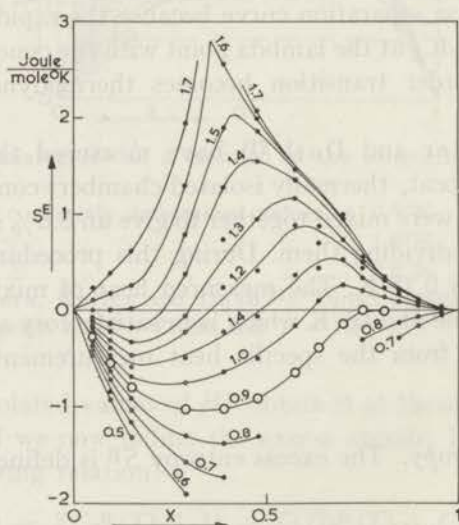


Fig. 15. The excess entropy S^E as a function of the concentration X at different temperatures T .

Thus all the thermodynamic excess functions have been determined.

We prefer to base our calculations on the excess Gibbs function G^E at 0.9°K and to use the integration of the specific heat to obtain the values at higher temperatures as we consider the values for G^E at 0.9°K the most reliable and for the very simple form $G^E = X(1 - X)W$ that is found at that temperature.

It is also possible to determine the excess entropy S^E directly from our specific heat measurements without using the excess Gibbs function derived from vapour pressure measurements. One can determine the entropy of mixing ΔS^* at 0.9°K for two liquids with starting concentrations of $X = 0.15$ and $X = 0.954$ and final concentration \bar{X} , by the same technique used in calculating the heat of mixing in section 2, using the formula:

$$\Delta S_{0.9^\circ\text{K}}^*(\bar{X}) = \int_{0.39}^{0.9} \frac{C_{\bar{X}}}{T} dT - \left[\frac{\bar{X} - 0.15}{0.954 - 0.15} \int_{0.39}^{0.9} \frac{C_{0.954}}{T} dT + \frac{0.954 - \bar{X}}{0.954 - 0.15} \int_{0.39}^{0.9} \frac{C_{0.15}}{T} dT \right]. \quad (5)$$

The excess entropy S^{E*} is determined by subtracting the ideal entropy of mixing from ΔS^* . By extrapolating S^{E*} to $X = 0$ and $X = 1$ the total excess entropy S^E is obtained. The results obtained in this way are given in fig. 16.

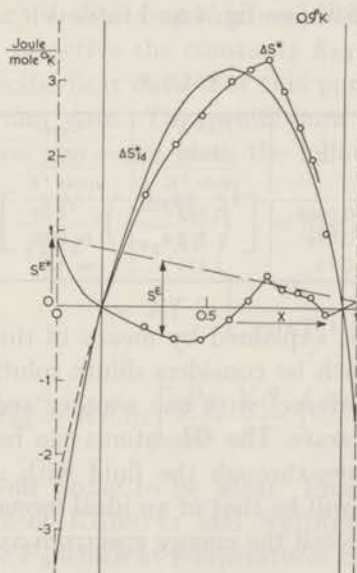


Fig. 16. The direct determination of the excess entropy at 0.9°K . ΔS^* , ΔS^*_{id} and S^{E*} as a function of the concentration X .

This method has some serious drawbacks. First the low temperature contribution to the integral is of more importance than in the case of the heat of mixing because of the factor $1/T$. This seriously affects the accuracy

of the final results of the integration. Furthermore, one does not obtain the excess entropy directly, but the result also contains the contribution from ideal mixing, which is of the same order of magnitude. This is especially so at the end of the concentration interval where this contribution makes the extrapolation to $X = 0$ and $X = 1$ rather difficult as can be seen from fig. 16. The extrapolation was performed in such a way as to obtain the best possible agreement with the calculations starting from G^E and H^E .

4. *Theoretical discussion of the thermodynamic properties.* For convenience we divide the theoretical discussion into three concentration regions:

A) dilute mixtures of ^3He in liquid ^4He : Experimental confirmation of the energy spectrum of Pomeranchuk¹⁶⁾ at temperatures below 1°K .

B) the intermediate region (phase separation region)

C) dilute mixtures of ^4He in liquid ^3He : the theory of Zharkov and Silin¹⁷⁾.

A) *Dilute mixtures of ^3He in liquid ^4He . Experimental confirmation of the energy spectrum of Pomeranchuk at temperatures below 1°K .*

a) *Introduction.* Measurements on the specific heat of ^3He - ^4He mixtures at concentrations of 4.66, 9.4 and 15% of ^3He in liquid ^4He show, between 0.4°K and 1°K , an almost constant contribution of the ^3He to the specific heat which is close to $\frac{3}{2}RX$ (see fig. 4 and table V).

TABLE V

X	$\frac{3}{2}RX$ joule mole $^\circ\text{K}$	C_{exp} joule mole $^\circ\text{K}$
0.0466	0.582	0.51
0.094	1.172	0.95
0.15	1.871	≈ 1.3

This behaviour can be explained by means of the theory of Pomeranchuk¹⁶⁾²²⁾²³⁾²⁴⁾, in which he considers dilute solutions and assumes that the ^3He atoms do not interact with one another and that the assembly of ^3He atoms is non-degenerate. The ^3He atoms can be treated as practically free particles which move through the fluid with an effective mass m_3^* . Hence the specific heat will be that of an ideal monatomic gas. To describe the properties in more detail the energy spectrum associated with the ^3He -atom is taken to be:

$$E = E_{03} + \frac{p^2}{2m_3^*} \quad (6)$$

where E_{03} is the effective potential and $p^2/2m_3^*$ is the kinetic energy associated with the translational motion through the superfluid of the ^3He atom which has an effective mass m_3^* . The statistical mechanics of the ^3He

atoms is nearly the same as for an ideal gas ²⁵⁾ and the internal energy U , the entropy S , the specific heat C and the partial chemical potentials μ_i , are equal to:

$$U = (1 - X) U_4^0 + X[NE_{03} + \frac{3}{2}RT] \quad (7)$$

$$S = (1 - X) S_4^0 + XR \left[\ln \left\{ \frac{g_3 V_4^0}{XN} \left(\frac{m_3^* kT}{2\pi h^2} \right)^{\frac{3}{2}} \right\} + \frac{5}{2} \right] \quad (8)$$

$$C = (1 - X) C_4^0 + X \frac{3}{2}R \quad (9)$$

$$\mu_4 = \mu_4^0 + RT \ln (1 - X) \quad (10)$$

$$\mu_3 = NE_{03} + RT \ln \left[\frac{XN}{g_3 V_4^0} \left(\frac{2\pi h^2}{m_3^* kT} \right)^{\frac{3}{2}} \right] \quad (11)$$

All quantities are expressed per mole; g is the statistical weight (degree of degeneracy). As the contribution of the ^4He to the specific heat is practically negligible at these temperatures, the experimental value of the specific heat should be equal to $\frac{3}{2}RX$. From table V and fig. 4 one sees that the experimental data approach this value in the limit of low concentrations and one concludes that it is only for dilute mixtures that Pomeranchuk's theory is satisfied.

b) *Analysis of the vapour-liquid equilibrium data.* It is clear (see eq. (9)) that it is not possible to derive the constants E_{03} and m_3^* of the energy spectrum from the specific heat data. For this purpose we reanalysed the vapour-liquid equilibrium data. The equilibrium condition between the liquid and vapour phase $\mu_{iL} = \mu_{iV}$ gives the following equation:

$$\begin{aligned} \mu_{3L} = NE_{03} + RT \ln \left[\frac{XN}{g_3 V_4^0} \left(\frac{2\pi h^2}{m_3^* kT} \right)^{\frac{3}{2}} \right] &= \mu_{3V} = \\ &= RT \ln \left[\frac{P_3}{g_3 (kT)^{\frac{3}{2}}} \left(\frac{2\pi h^2}{m_3} \right)^{\frac{3}{2}} \right] \end{aligned} \quad (12)$$

or

$$NE_{03} = RT \ln \left[\frac{P_3}{X} \frac{V_4^0}{RT} \left(\frac{m_3^*}{m_3} \right)^{\frac{3}{2}} \right] \quad (13)$$

if we assume the vapour phase to be ideal. From the smoothed vapour pressure measurements of Roberts and Sydoriak ⁹⁾ we calculated the partial vapour pressure P_3 which at temperatures below 1°K is nearly equal to the total pressure P_{tot} ²⁰⁾. With formula (13) we calculated the potential energy NE_{03} per mole and found its value between 0.6°K and 1°K to be independent of temperature. For the effective mass m_3^* we used the experimentally determined value $m_3^* = 2.7 m_3$ ²⁶⁻³¹⁾ (see later: second sound and the normal density). The values of NE_{03} obtained in this way are given in table VI as a function of temperature and concentration.

TABLE VI

The potential energy NE_{03} (joule/mole) as a function of temperature T and concentration X .					
$T(^{\circ}\text{K})$	0.6	0.7	0.8	0.9	1.0
X					
0.02	-21.5	-21.9	-22.1	-22.0	-21.6
0.04	-22.1	-22.6	-22.7	-22.7	-22.5
0.06	-22.6	-23.0	-23.1	-22.9	-22.9
0.08	-23.1	-23.3	-23.3	-23.3	-23.3
0.10	-23.5	-23.6	-23.6	-23.6	-23.5

Hence, below 1°K equation (13) is consistent with the experimental results, but at higher temperatures and concentrations NE_{03} changes slightly. Comparing this value with the corresponding value for pure ${}^3\text{He}$ of -21.2 joule/mole³²⁾ we see that the potential well of ${}^3\text{He}$ in a ${}^4\text{He}$ surrounding is only slightly larger, as one should expect in a cell model taking into account the zero point energy of the ${}^3\text{He}$ and the large compressibility of ${}^4\text{He}$.

NE_{03} , $U_{03}^0 = -L_{03}$, $U_{04}^0 = -L_{04}$ as functions of the molar volume are plotted in fig. 18 (see later e)). V_3 is the partial molar volume for a dilute solution of ${}^3\text{He}$ in liquid ${}^4\text{He}$ derived from the molar volume experiments by Kerr¹¹⁾.

c) *The thermodynamic excess functions.* Our aim is now to calculate all the thermodynamic excess functions for a dilute mixture, as defined in chap. I²⁰⁾, and to compare them with the experimental results. The heat of mixing H^E of a dilute solution is equal to:

$$H^E = H - H_{\text{ideal}} = X[H_3 - H_3^0] = X[NE_{03} + \frac{3}{2}RT - H_3^0(T)] \quad (14)$$

if we assume that for temperatures lower than 1°K , H is nearly equal to U .

The excess Gibbs function G^E is equal to:

$$G^E = X\mu_3 + (1 - X)\mu_4 - [X\mu_3^0 + (1 - X)\mu_4^0 + RT\{X \ln X + (1 - X) \ln (1 - X)\}] \quad (15)$$

in which μ_{3L}^0 is determined by the following equation:

$$\mu_{3L}^0 = \mu_{3V}^0 = RT \ln \left[\frac{P_3^0}{g_3(kT)^{\frac{1}{2}}} \left(\frac{2\pi h^2}{m_3} \right)^{\frac{3}{2}} \right]. \quad (16)$$

Inserting eqs. (16), (10), (11), (12) into eq. (15) gives the following result for the excess Gibbs function:

$$G^E = X \left[NE_{03} + RT \ln \left\{ \frac{RT}{P_3^0 V_4^0} \left(\frac{m_3}{m_3^*} \right)^{\frac{3}{2}} \right\} \right] = XRT \ln \left(\frac{P_3}{XP_3^0} \right). \quad (17)$$

The excess entropy S^E can now be determined by means of the relation

$G^E = H^E - TS^E$ from eq. (14) and (17).

$$S^E = X \left[R \ln \left\{ \frac{P_3^0 V_4^0}{RT} \left(\frac{m_3^*}{m_3} \right)^{\frac{1}{2}} \right\} + \frac{3}{2}R - \frac{H_3^0(T)}{T} \right] = \\ = X \left[-R \ln \frac{P_3}{X P_3^0} + \frac{NE_{03}}{T} + \frac{3}{2}R - \frac{H_3^0(T)}{T} \right]. \quad (18)$$

In the case of phase separation of two dilute mixtures (a ^3He rich upper phase u and ^4He rich lower phase l) one has in general that the concentration ratios of the upper phase X_u (if $X_u \rightarrow 1$) and the lower phase X_l (if $X_l \rightarrow 0$) are directly connected to the partial chemical excess potentials μ_{3l}^E since

$$\mu_{3l} = \mu_3^0 + RT \ln X_l + \mu_{3l}^E \quad \text{if } X_l \rightarrow 0, \text{ and} \quad (19)$$

$$\mu_{3u} = \mu_3^0 + RT \ln X_u \quad \text{if } X_u \rightarrow 1. \quad (20)$$

We have now the following equilibrium condition:

$$\mu_{3l} = \mu_{3u}. \quad (21)$$

The insertion of the eqs (19) and (20) into the equilibrium condition (21) gives the following result:

$$\frac{G_l^E}{X_l} \approx \mu_{3l}^E = RT \ln \frac{X_u}{X_l} = RT \ln \frac{P_3}{X_l P_3^0}. \quad (22)$$

Inserting of eq. (17) into eq. (22) gives the following result:

$$\frac{X_l}{X_u} = \left[\frac{P_3^0 V_4^0}{RT} \left(\frac{m_3^*}{m_3} \right)^{\frac{1}{2}} \right] e^{-\frac{NE_{03}}{RT}}. \quad (23)$$

In the same way, using the equilibrium condition $\mu_{4l} = \mu_{4u}$, one gets the following result:

$$\frac{G_u^E}{(1 - X_u)} \approx \mu_{4u}^E = RT \ln \frac{(1 - X_l)}{(1 - X_u)}. \quad (24)$$

As we have seen that the vapour-liquid equilibrium data for dilute solutions can be explained rather well by the Pomeranchuk model it seems advisable in this range of concentration to follow another procedure than was discussed in the previous section where we based our calculations on a regular excess Gibbs function. Especially at the lower concentrations the vapour-liquid equilibrium data agree better with the Pomeranchuk model than with a regular solution model. Hence in comparing data with the Pomeranchuk model we will derive the excess entropy from our heat of mixing data and from the Pomeranchuk excess Gibbs function.

d) *The excess Gibbs function G^E .* With formula (17) we have calculated G^E/X between 0.6°K and 1.2°K and with formula (22) we have calculated G^E/X for 0.3°K (see fig. 17).

e) *The heat of mixing.* The energy H_{03}^0 of liquid ${}^3\text{He}$ at 0°K is equal in magnitude to the latent heat L_{03} at 0°K , so that $H_{03}^0 = -L_{03} = -21.2$ joule/mole ³²). $H_3^0(T)$ can now be calculated by means of the following equation:

$$H_3^0(T) = -L_{03} + \int_0^T C_3^0 dT. \quad (25)$$

Hence it is now possible to calculate H^E/X by means of eq. (14). The result is shown by the hatched curve in fig. 17. We see that there is reasonable agreement with the experimental values of the heat of mixing for $X = 0.0466$, 0.094 and 0.15 derived from the specific heat measurements in the phase separation region, and with the direct measurement of the heat of mixing by Sommers, Keller and Dash ²¹) at 1.05°K for a 8.6% mixture.

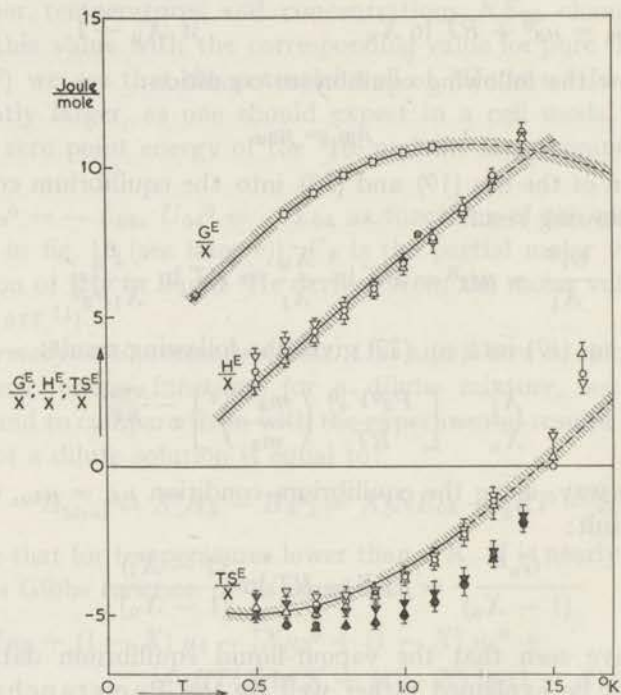


Fig. 17. G^E/X , H^E/X , TSE^E/X as a function of the temperature T for dilute mixtures in the Pomeranchuk region.

- G^E/X derived from the vapour pressure measurements of Roberts and Sydoriaik for a 10% mixture with formula (17)
 - ◇ G^E/X derived from the phase separation curve with formula (22)
 - ⊗ H^E/X direct experimental point of Sommers, Keller and Dash ²¹)
 - △ $X = 0.0466$
 - $X = 0.094$
 - ▽ $X = 0.15$
 - ▲ $X = 0.0466$
 - $X = 0.094$
 - ▼ $X = 0.15$
- } Experimental values of H^E/X and S^E/X , for the determination of S^E is used G^E as derived by means of formula (17).
- } Experimental values of S^E/X if we use a regular Gibbs function ²⁰).

Thus we see that the linear behaviour of H^E as a function of the concentration X as shown in fig. 14 and fig. 17 is in agreement with the predictions of eq. (14). The increase of the slope nearly proportional to the temperature is also in agreement with eq. (14).

f) *The excess entropy S^E .* Using formula (18) we have calculated the excess entropy S^E/X using eq. (25) for H_3^0 . The result is shown by the hatched curve in fig. 17. We see that there is reasonable agreement with our values for $X = 0.0466, 0.094$ and 0.15 . To show the influence of the choice of the Gibbs function we also plotted our results obtained from the regular solution Gibbs function (see table IV).

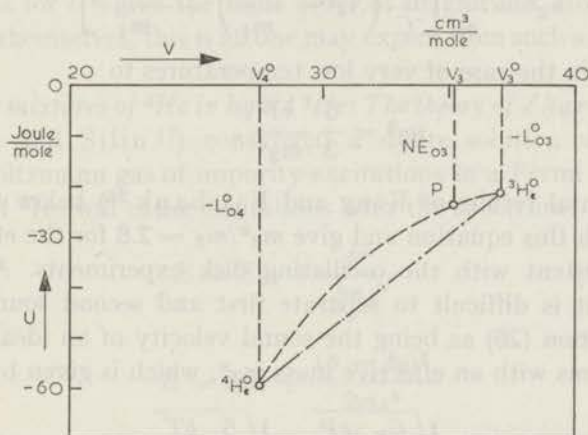


Fig. 18. $U_{03}^0 = -L_{03}^0$, $U_{04}^0 = -L_{04}^0$, NE_{03} as a function of the molar volume V . V_3 = partial molar volume for a dilute mixture of ^3He in liquid ^4He derived from the molar volume experiments by Kerr¹¹⁾.

g) *The phase separation curve.* The concentration ratio X_1/X_u of the phase separation at low temperatures can be calculated by means of eq. (23). Calculations at $T = 0.30^\circ\text{K}$ ($X_1 \approx 0.097$, $X_u \approx 0.97$) and at $T = 0.40^\circ\text{K}$ ($X_1 \approx 0.147$, $X_u \approx 0.955$) give $X_1/X_u = 0.104$ and 0.143 for the concentration ratio, while the extrapolated experimental values give the following ratios respectively $(X_1/X_u)_{\text{exp.}} = 0.100$ and 0.154 (See fig. 11(P)).

h) *The effective mass m_3^* , second sound and the normal density ρ_n in dilute ^3He - ^4He mixtures.* Since the dissolved ^3He atoms can readily collide with rotons and phonons, they always participate in the motion of the normal component and the density of the normal component ρ_n is equal to

$$\rho_n = \rho_{n,4} + \frac{m_3^*}{m_4} \rho X. \quad (26)$$

Below 1°K one has $\rho_{n,4} \ll m_3^* \rho X / m_4$ since the phonons and rotons make a negligible contribution, so that the normal fraction x is almost equal to $x \equiv \rho_n / \rho = (m_3^* / m_4) X$, and is determined by the constant density of the

^3He atoms. Pellam²⁹), Berezniak and Esel'son³⁰) and Dash and Taylor³¹) made extensive measurements of ρ_n in oscillating disk experiments by the Andronikashvili method and found an almost constant value for the effective mass, $m_3^*/m_3 = 2.7$.

The velocity of second sound in a dilute solution of ^3He in liquid ^4He has been measured by Lynton and Fairbank²⁷) and by King and Fairbank²⁸) between 0.2°K and the lambda temperature. From the thermohydrodynamical equations Pomeranchuk¹⁶) and Khalatnikov³³) have derived the following expression for the velocity of second sound

$$u_2^2 = \frac{\rho_s}{\rho_n} \left[\frac{T}{C} \left(S_4^0 + \frac{kX}{m_4} \right)^2 + \frac{kTX}{m_4} \right] \quad (27)$$

which reduces in the case of very low temperatures to

$$u_2^2 = \frac{5}{3} \frac{kT}{m_3^*}. \quad (28)$$

The experimental results of King and Fairbank²⁸) below 0.6°K are in agreement with this equation and give $m_3^*/m_3 = 2.8$ for the effective mass which is consistent with the oscillating disk experiments. At these low temperatures it is difficult to separate first and second sound. One may interpret equation (28) as being the sound velocity of an ideal monatomic gas of ^3He atoms with an effective mass m_3^* , which is given by

$$u = \sqrt{\frac{C_p}{C_v} \frac{\partial P}{\partial \rho}} = \sqrt{\frac{5}{3} \frac{kT}{m_3^*}}. \quad (29)$$

Recently Sandiford and Fairbank³⁴) have found two "sound" velocities for very low temperatures $T < 0.2^\circ\text{K}$ and small concentrations $X \approx 0.005$: the normal phonon velocity which is also observed in pure liquid ^4He and a velocity which is caused by the ^3He gas which moves through the superfluid according to eq. (29) as has to be expected if the interaction between the ^3He and the phonon is small.

In Feynman's theory²³) the motion of a ^3He atom through the superfluid is treated as a microscopic hydrodynamical problem and the effective mass m_3^* is the sum of the true mass of the ^3He atom and one-half of the mass of the displaced fluid. Thus $m_3^* = m_3 + \frac{1}{2}(V_3/V_4) m_4$ which gives $m_3^*/m_3 \approx 1.9$. In this model the backflow of the ^4He around the ^3He atom gives rise to the large effective mass m_3^* .

B. *The intermediate region (phase separation region)*. The thermodynamic properties are far more complicated in the intermediate region, as all types of interactions (*i.e.* ^3He - ^3He , ^3He - ^4He , ^4He - ^4He) become of importance. Furthermore, at higher temperatures the lambda phenomenon also plays an important role. Hence no simple description may be expected. At low

enough temperatures one may perhaps neglect the lambda phenomenon and try to describe the properties by means of the model of Prigogine, Bingen, Bellemans and Simon³⁶⁾³⁷⁾³⁸⁾.

They explained a positive excess Gibbs function by pointing out that, neglecting the collective motions, the difference between the pure isotopes is only due to the zero point energy, which gives rise to large differences in the molar volumes. In this picture the mixing becomes ideal if one has first brought the pure isotopes to the same molar volume as they have in the mixture. The excess Gibbs function is in this case equal to the work done by compressing the lightest isotope and by expanding the heavier one. These results for G^E give the right order of magnitude. However, as they pointed out themselves, this is all one may expect from such a model.

C). *Dilute mixtures of ^4He in liquid ^3He : The theory of Zharkov and Silin.* Zharkov and Silin¹⁷⁾ considered a dilute solution of ^4He in liquid ^3He as a Boltzmann gas of impurity excitations in a Fermi liquid. A small admixture of ^4He will cause excitations with the spectrum:

$$E = E_{04} + \frac{p^2}{2m_4^*} \quad (30)$$

or:

$$E = E_{04} + \frac{(p - p_0)^2}{2m_4^*} \quad (31)$$

where p is the momentum of the impurity excitation, p_0 and m_4^* are parameters that have to be determined experimentally. Eqs. (30) and (31) may be supported by the same line of reasoning that was used by Pomeranchuk¹⁶⁾ for the spectrum of impurities in liquid He II and the statistical mechanics of these two energy spectra are almost the same as those used in section A. For spectra (30) and (31) we have the following contributions to the specific heat:

$$C = XC_3^0 + (1 - X)C_4; C_4 = \frac{3}{2}R \quad (32)$$

$$C = XC_3^0 + (1 - X)C_4; C_4 = \frac{1}{2}R. \quad (33)$$

Spectrum (31) with a specific heat given by eq. (33) seems to satisfy reasonably the experimental specific heat data for the concentration of 95.4% of ^3He as one can see in fig. 8.

The heat of mixing H^E is now equal to:

$$H^E = (1 - X)[H_4 - H_4^0] = (1 - X)[NE_{04} + \frac{1}{2}RT - H_4^0] \quad (34)$$

in which

$$H_4^0(T) = -L_{04} + \int_0^T C_4^0 dT = -59.62 + \int_0^T C_4^0 dT \approx -59.62 \text{ joule/mole}^{35)}. \quad (35)$$

We have used eq. (34) to calculate the potential energy NE_{04} for a 95.4% mixture from the experimental heat of mixing $H^E = 0.47$ joule/mole at 1°K , and $H^E = 0.38$ joule/mole at 0.5°K . We find a temperature independent value of -53.6 joule/mole for NE_{04} . Comparing this value with the corresponding value for pure ^4He of -59.62 joule/mole³⁵), we see that the potential well of ^4He in a ^3He surrounding is only slightly less and we get a similar situation as for a dilute mixture of ^3He in liquid ^4He (see fig. 18).

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CHAPTER III

SOME THERMODYNAMIC CONSIDERATIONS ON THE PROPERTIES OF LIQUID ^3He - ^4He MIXTURES

Summary

The stratification curve for liquid ^3He - ^4He mixtures shows a singularity at the junction with the lambda curve as can be seen on the basis of pure thermodynamic considerations. If the lambda curve and the stratification curve meet each other under a finite angle, there is a discontinuity in the slope of the stratification curve and in the specific heat at this point. Furthermore, the entropy of dilute mixtures is discussed with respect to Nernst's theorem.

1. *Introduction.* In the previous chapters ¹⁾²⁾ where we discussed the thermodynamic properties of liquid ^3He - ^4He mixtures, we found a singularity in the specific heat at the point where the lambda curve meets the stratification curve. In this chapter we will derive the thermodynamic relations that are valid at this point. The general procedure will be to combine the equations for the first order stratification transition with the Keesom-Ehrenfest ⁴⁾⁵⁾ type relations for the second order lambda transition. The accuracy of the specific heat data around the lambda-transition does not allow a choice between a second order transition and the logarithmic singularity proposed by Buckingham and Fairbank ²⁵⁾. We prefer to continue to regard the transition as a second order one, instead of using the analogous relations valid for a transition with a logarithmic behaviour. From our considerations we obtain a discontinuity in the slope of the stratification curve and in the specific heat if the lambda curve and the stratification curve meet each other under a finite angle.

Furthermore, we would like to discuss two other aspects of the thermodynamic properties of these mixtures: one regarding Nernst's theorem, the other concerning the "short range ordering" above the lambda temperature.

In this chapter the same notation is used as in chapter I and II ¹⁾²⁾.

I. THERMODYNAMIC CONSIDERATIONS ON THE JUNCTION OF THE LAMBDA CURVE AND THE STRATIFICATION CURVE OF LIQUID ^3He - ^4He MIXTURES.

2) *The thermodynamic relations.* a) The stratification curve. By differentiating the equilibrium condition

$$\mu_{11}(X_1, T) = \mu_{1u}(X_u, T) \quad (1)$$

along both sides of the stratification curve (P.S.) one can derive the following expressions for the slope of this curve:

$$\left(\frac{dX_u}{dT}\right)_{\text{P.S.}} = \frac{\frac{\partial H_u}{\partial X_u} - \frac{H_u - H_1}{X_u - X_1}}{T \frac{\partial^2 G_u}{\partial X_u^2}}, \quad (2)$$

$$\left(\frac{dX_1}{dT}\right)_{\text{P.S.}} = \frac{\frac{\partial H_1}{\partial X_1} - \frac{H_u - H_1}{X_u - X_1}}{T \frac{\partial^2 G_1}{\partial X_1^2}}, \quad (3)$$

while the relation between the two slopes is given by:

$$\frac{\partial^2 G_u}{\partial X_u^2} \left(\frac{dX_u}{dT}\right)_{\text{P.S.}} + \frac{\partial(\mu_3 - \mu_4)_u}{\partial T} = \frac{\partial^2 G_1}{\partial X_1^2} \left(\frac{dX_1}{dT}\right)_{\text{P.S.}} + \frac{\partial(\mu_3 - \mu_4)_l}{\partial T}. \quad (4)$$

The subscripts u and l refer to the upper ^3He rich phase and the lower ^4He rich phase. For a complete derivation of eq. (2) and (3) see Rowlinson ³). According to the leverage rule the specific heat in the phase separation region is equal to ²):

$$\begin{aligned} C_{\bar{X}} &= \left(\frac{dH}{dT}\right)_{\bar{X}} = \frac{\bar{X} - X_1}{X_u - X_1} \left[\frac{\partial H_u}{\partial T} + \frac{\partial H_u}{\partial X_u} \frac{dX_u}{dT} - \frac{H_u - H_1}{X_u - X_1} \frac{dX_u}{dT} \right] + \\ &+ \frac{X_u - \bar{X}}{X_u - X_1} \left[\frac{\partial H_1}{\partial T} + \frac{\partial H_1}{\partial X_1} \frac{dX_1}{dT} - \frac{H_u - H_1}{X_u - X_1} \frac{dX_1}{dT} \right] = \\ &= \frac{\bar{X} - X_1}{X_u - X_1} \left[\frac{\partial H_u}{\partial T} + T \frac{\partial^2 G_u}{\partial X_u^2} \left(\frac{dX_u}{dT}\right)^2 \right] + \\ &+ \frac{X_u - \bar{X}}{X_u - X_1} \left[\frac{\partial H_1}{\partial T} + T \frac{\partial^2 G_1}{\partial X_1^2} \left(\frac{dX_1}{dT}\right)^2 \right]. \quad (5) \end{aligned}$$

b) The lambda curve (assuming a second order transition line). Stout ⁶), De Boer and Gorter ⁷) and Esel'son, Lazarev, Kaganov and Lifshitz ⁸)⁹) have developed relations between the thermodynamic properties at the lambda transition point by extending the Keesom ⁴)-Ehrenfest ⁵) relations to the case of a mixture. The entropy S , the chemical

potentials μ_i , the enthalpy H and the molar volume V are continuous along both sides of the lambda curve (λ), but their derivatives with respect to the temperature T and the concentration X show discontinuities at the lambda curve which are related to the slope of the lambda curve γ^{10}) in the following way:

$$\begin{aligned} \left(\frac{dT}{dX}\right)_\lambda &= -\frac{\Delta\left(\frac{\partial S}{\partial X}\right)_T}{\Delta\left(\frac{\partial S}{\partial T}\right)_X} = -\frac{\Delta\left(\frac{\partial(\mu_3 - \mu_4)}{\partial X}\right)_T}{\Delta\left(\frac{\partial(\mu_3 - \mu_4)}{\partial T}\right)_X} = \\ &= -\frac{\Delta\left(\frac{\partial H}{\partial X}\right)_T}{\Delta\left(\frac{\partial H}{\partial T}\right)_X} = -\frac{\Delta\left(\frac{\partial V}{\partial X}\right)_T}{\Delta\left(\frac{\partial V}{\partial T}\right)_X} \end{aligned} \quad (6)$$

in which $\Delta A = A(T_\lambda + 0) - A(T_\lambda - 0)$ indicates the difference between values of the quantity A at both sides of the transition curve. From this equation one obtains the following relations:

$$\Delta\left(\frac{\partial(\mu_3 - \mu_4)}{\partial T}\right)_X = \frac{\Delta\left(\frac{\partial H}{\partial T}\right)_X}{T} \left(\frac{dT}{dX}\right)_\lambda, \quad (7)$$

$$\Delta\left(\frac{\partial(\mu_3 - \mu_4)}{\partial X}\right)_T = \Delta\left(\frac{\partial^2 G}{\partial X^2}\right)_T = -\frac{\Delta\left(\frac{\partial H}{\partial T}\right)_X}{T} \left(\frac{dT}{dX}\right)_\lambda^2, \quad (8)$$

$$\Delta\left(\frac{\partial H}{\partial X}\right)_T = -\Delta\left(\frac{\partial H}{\partial T}\right)_X \left(\frac{dT}{dX}\right)_\lambda. \quad (9)$$

c) The junction λ^* of the lambda curve and the stratification curve. Suppose at T_{λ^*} we have a second order transition in the ^3He -rich upper phase. From eq. (2) one sees immediately that there is a discontinuity in the slope of the stratification curve of the ^3He -rich upper phase at T_{λ^*} , since there is a discontinuity in $(\partial H_u/\partial X_u)_T$ and $(\partial^2 G_u/\partial X_u^2)_T$. From the equations (2), (8) and (9), after some calculation it follows that the discontinuity in the slope of the stratification curve at the junction λ^* , is equal to:

$$\Delta\left(\frac{dX_u}{dT}\right)_{\text{P.S}^*} = \frac{\left[\left(\frac{dX_u}{dT}\right)_{\text{P.S}} \left(\frac{dT}{dX}\right)_{\lambda^*} - 1\right]}{T \frac{\partial^2 G_u}{\partial X_u^2} - \Delta\left(\frac{\partial H_u}{\partial T}\right)_X \left(\frac{dT}{dX}\right)_{\lambda^*}^2} \Delta\left(\frac{\partial H_u}{\partial T}\right)_X \left(\frac{dT}{dX}\right)_{\lambda^*}. \quad (10)$$

From eq. (3) it is clear that we have no discontinuity in the slope of the

stratification curve of the ^4He -rich lower phase at T_{λ^*} since there are no discontinuities in any of the thermodynamic quantities in the right hand side of eq. (3). However, from eq. (3) we see that there is a discontinuity in the derivative of the slope of the stratification curve of the lower phase at T_{λ^*} because of the discontinuity in $d[(H_u - H_l)/(X_u - X_l)]/dT$; hence we have at T_{λ^*} :

$$\Delta \left(\frac{dX_l}{dT} \right)_{P,S} = 0, \quad \Delta \left(\frac{d^2X_l}{dT^2} \right)_{P,S} \neq 0. \quad (11)$$

It is perhaps interesting to remark that eq. (10) can immediately be derived from eq. (4) using the relations (7) and (8) and the fact that there are no discontinuities in the right hand side of eq. (4), since:

$$\Delta \left[\frac{\partial^2 G_u}{\partial X_u^2} \left(\frac{dX_u}{dT} \right)_{P,S} + \frac{\partial(\mu_3 - \mu_4)_u}{\partial T} \right] = 0. \quad (12)$$

One can now derive from eq. (5) the discontinuity in the specific heat ΔC_{λ^*} using the relations (9) and (10). ΔC_{λ^*} appears to be equal to:

$$\begin{aligned} \Delta C_{\lambda^*} &= \frac{(\bar{X} - X_l) \left[\left(\frac{dX_u}{dT} \right)_{P,S} \left(\frac{dT}{dX} \right)_{\lambda^*} - 1 \right]^2 T \frac{\partial^2 G_u}{\partial X_u^2}}{(X_u - X_l) \left[T \frac{\partial^2 G_u}{\partial X_u^2} - \Delta \left(\frac{\partial H_u}{\partial T} \right) \left(\frac{dT}{dX} \right)_{\lambda^*}^2 \right]} \Delta \left(\frac{\partial H_u}{\partial T} \right) \\ &= \frac{(\bar{X} - X_l)}{(X_u - X_l)} \left[\frac{\left(\frac{dX_u}{dT} \right)_{P,S} \left(\frac{dT}{dX} \right)_{\lambda^*} - 1}{\left(\frac{dT}{dX} \right)_{\lambda^*}} \right] T \frac{\partial^2 G_u}{\partial X_u^2} \Delta \frac{dX_u}{dT}. \quad (13) \end{aligned}$$

If the lambda curve (λ) is tangent to the stratification curve (P.S.) one has:

$$\left(\frac{dX_u}{dT} \right)_{P,S^*} = \left(\frac{dX}{dT} \right)_{\lambda^*}. \quad (14)$$

Hence, we see from eq. (10) and (13) that in this case both the discontinuity $\Delta(dX_u/dT)_{P,S^*}$ in the slope of the stratification curve of the ^3He -rich upper phase and the discontinuity ΔC_{λ^*} in the specific heat are equal to zero:

$$\Delta \left(\frac{dX_u}{dT} \right)_{P,S^*} = 0, \quad \Delta \left(\frac{dX_l}{dT} \right)_{P,S} = \Delta \left(\frac{d^2X_l}{dT^2} \right)_{P,S} = 0, \quad \Delta C_{\lambda^*} = 0. \quad (15)$$

3) *Comparison with experiment.* The difficulty in discussing the singularity at T_{λ^*} from the experimental point of view is that the existing data for the location of the curves are not accurate enough to allow an unambiguous conclusion to the question of whether or not the stratification curve and lambda line meet each other under a finite angle. There is, however,

an indication that the slope of the stratification curve changes rapidly or discontinuously at λ^* . For this purpose we like to recall that the stratification curves, in general, obey a law of the rectilinear diameter³⁾. This appears also to be the case for the ^3He - ^4He stratification curve. However, the slope of this rectilinear diameter changes abruptly at T_{λ^*} as can be seen from fig. 1. If one assumes this change to be discontinuous one obtains $\Delta(dX_u/dT) \approx 0.23 \text{ deg}^{-1}$. The calculation of this quantity using relation (10) is rather arbitrary as neither $[(dX_u/dT)_{\text{PS}} (dT/dX)_{\lambda} - 1]$ nor $\Delta(\partial H_u/\partial T)$

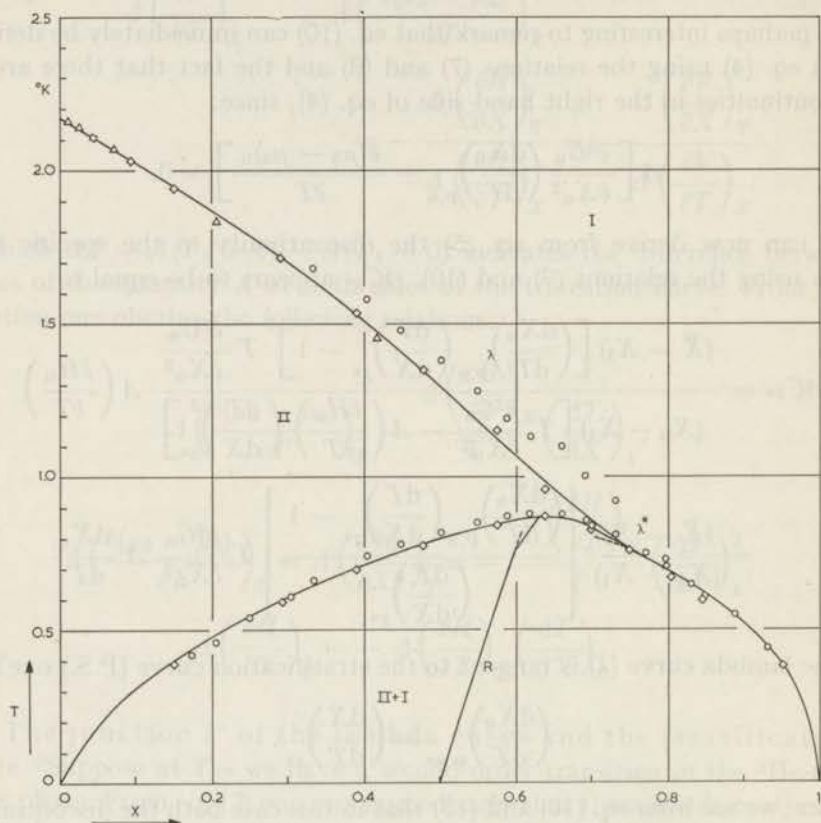


Fig. 1. The lambda and stratification temperatures as functions of the liquid concentration. The smoothed line denotes the values of Roberts and Sydoriak¹¹⁾.

△ Dokoupil¹²⁾

○ Zinov'eva and Peshkov¹³⁾

◇ Our experiments²⁾

R Curve of the rectilinear diameter.

nor $\partial^2 G_u / \partial X_u^2$ can be obtained with accuracy from experimental data. The value of $\Delta(\partial H_u / \partial T)$ lies between -1 and -0.1 joule/mole $^\circ\text{K}$, $\partial^2 G_u / \partial X_u^2$ between 8 and 5 joule/mole, hence from the change in the rectilinear diameter one should then obtain for $[(dX_u/dT)_{\text{PS}} (dT/dX)_{\lambda} - 1]$ a value

between 0.15 and 0.5, while the experimental data allow a maximum value of 0.5.

The other experimental indication is the measured discontinuity in the specific heat at this temperature. The difficulty here is that this singularity can be easily influenced by instrumental errors. In passing from the He I to the He II region all existing small temperature gradients in the upper phase disappear abruptly. The caloric effect might be comparable to the discontinuity as found experimentally²⁾. As in eq. (13) the square of the angle between the stratification curve and the lambda curve occurs, it is impossible to make a quantitative guess.

One should hope to obtain further information from a $C_{\bar{X}}$ versus \bar{X} plot²⁾ below and above T_{λ^*} . However, also in this case, the relations one can obtain from eq. (5) do not allow any quantitative comparison, although the experimental fact that the slope of these curves changes abruptly is in qualitative agreement.

II. THE BEHAVIOUR OF THE EXCESS ENTROPY AT VERY LOW TEMPERATURES.

In the foregoing chapter²⁾ we calculated the excess entropies at different concentrations and temperatures. The general trend is that this quantity becomes negative at low temperatures.

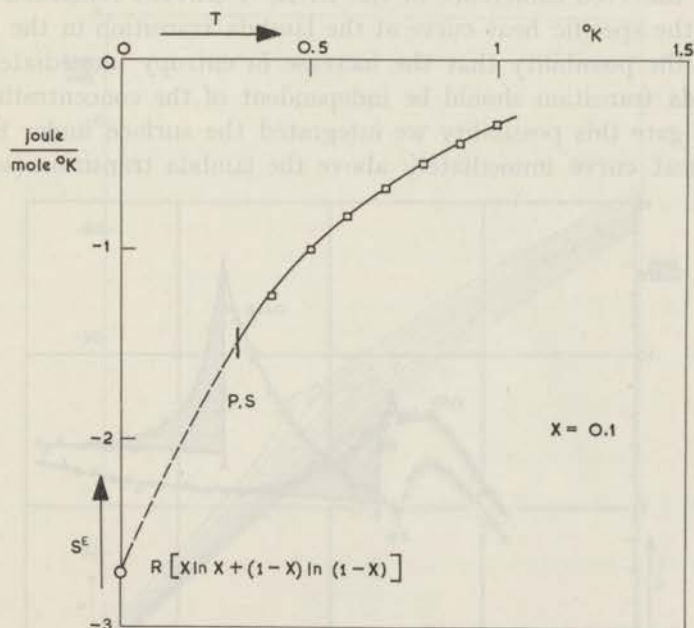


Fig. 2. The excess entropy S^E as a function of the temperature T for a dilute mixture of ^3He in liquid ^4He .

- S^E calculated from our experiments²⁾ ($X = 0.1$)
- $\lim_{\substack{T \rightarrow 0 \\ X=0.1}} S^E = +R[X \ln X + (1-X) \ln (1-X)]$ (Nernst's theorem).

For a dilute mixture of ^3He in liquid ^4He we like to point out that although this is in agreement with the model of Pomeranchuk it is a general property irrespective of the model.

Nernst's theorem states that the entropy at absolute zero should be equal to zero (third law of thermodynamics). In classical thermodynamics this is not the case for an ideal mixture, where there remains an entropy of mixing of $-R[X \ln X + (1 - X) \ln (1 - X)]$ (positive). In quantum statistics this difficulty does not arise as here this term goes to zero with decreasing temperature (because of the degeneracy)¹⁴⁾¹⁵⁾. Hence, if one describes the thermodynamic properties of a mixture in terms of classical excess functions one will obtain in the case where there is no phase separation the value of $+R[X \ln X + (1 - X) \ln (1 - X)]$ (negative) for S^E at $T = 0^\circ\text{K}$. For comparison with experiment we have plotted in fig. 2 the excess entropy S^E versus the temperature for a mixture of 10% ^3He ²⁾, where the phase separation occurs at a low enough temperature (0.31°K) that it does not confuse the situation too much. We see that the total entropy of mixing goes to zero with decreasing temperature, in agreement with what Nernst's heat theorem suggests.

III. THE "SHORT RANGE ORDERING" ABOVE THE LAMBDA TEMPERATURE.

During the 1960 conference of the I.I.R.¹⁶⁾ Gorter remarked that the shape of the specific heat curve at the lambda transition in the mixtures indicated the possibility that the increase in entropy immediately above the lambda transition should be independent of the concentration ¹⁷⁾¹⁸⁾. To investigate this possibility we integrated the surface under the extra specific heat curve immediately above the lambda transition (see fig. 3).

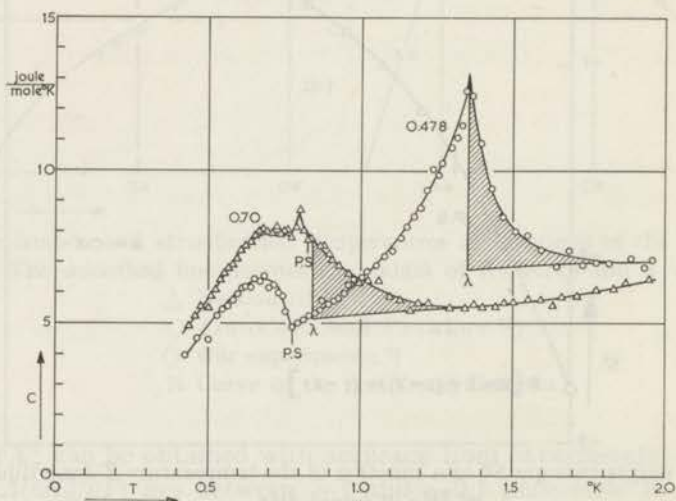


Fig. 3. The specific heat C as a function of the temperature T for the concentrations: $X = 0.478$, $X = 0.70$. The shaded area arises from the "short range ordering".

It is clear that such a procedure depends very much on the way in which one extrapolates the "ideal" specific heat curve. The data so obtained are given in table I. The remark of Gorter seems to be in agreement with the experimental data; however, one should treat these values with some caution.

TABLE I

The extra entropy due to "short range ordering" for different concentrations	
X	$\int_{T_\lambda}^{T > T_\lambda} \frac{C_{\text{extra}}}{T} dT$ joule mole °K
0	0.40-0.44
0.29	0.36
0.478	0.39
0.575	0.32-0.38
0.638	0.35
0.70	0.37
0.75	0.25-0.32
0.805	0.28-0.37

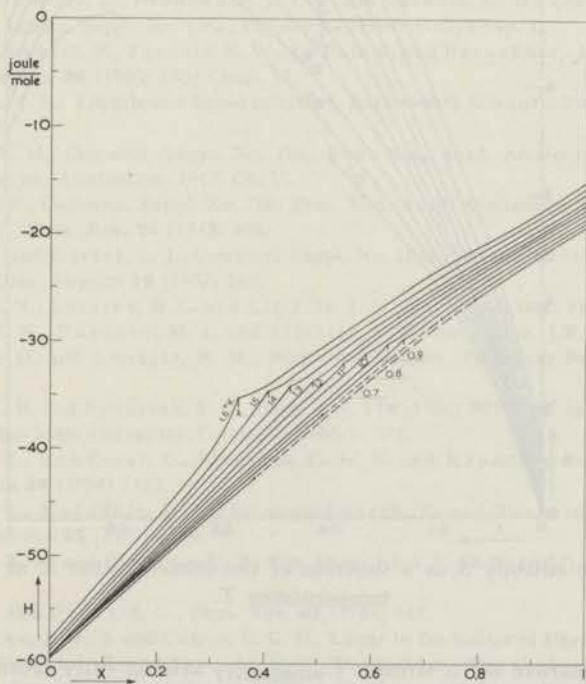


Fig. 4. The enthalpy H as a function of the concentration X at different temperatures T .

Buckingham and Fairbank²⁵⁾ write for the specific heat of ^4He around the lambda point:

$$C_{\text{observed}} = C_{\text{phonon}} + C_{\text{excitation}} + C_{\text{singularity}}$$

where the $C_{\text{singularity}}$ is a contribution to the specific heat that goes to infinity at the lambda point in such a way that the surface under the singularity remains finite. This results in an increase of the entropy already above the lambda point, which corresponds to the "short range ordering" we mentioned earlier. Our results for the mixtures do not allow an accurate analysis of the possible singularity in mixtures. However, the values for the "short range ordering" show that one cannot

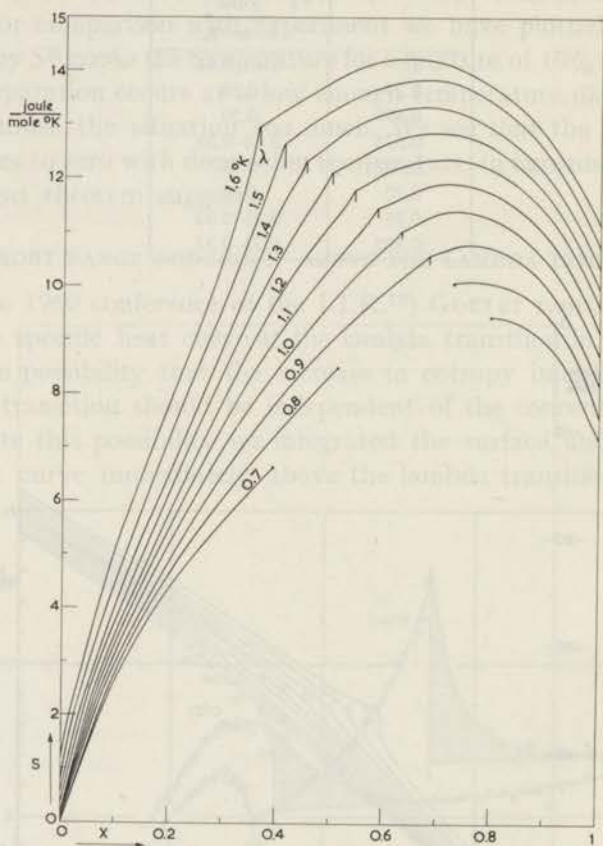


Fig. 5. The entropy S as a function of the concentration X at different temperatures T .

in this case separate off a similar $C_{\text{singularity}}$ arising only from the ^4He . In fact, our results have the tendency to be completely independent of the ^4He concentration.

IV. THE ENTHALPY AND ENTROPY DIAGRAM.

Finally, we like to add an enthalpy and an entropy diagram for the mixtures as calculated from our experimental excess data ²⁾ by means of the relations:

$$H(T, X) = XH_3^0(T) + (1 - X) H_4^0(T) + H^E(T, X), \quad (16)$$

$$H_i^0(T) = -L_{oi}^0 + \int_0^T C_{ip} dT, \quad (17)$$

$$S(T, X) =$$

$$= XS_3^0(T) + (1 - X)S_4^0(T) - R[X \ln X + (1 - X) \ln(1 - X)] + S^E(T, X). \quad (18)$$

In the calculation we have used the experimentally determined values for the pure components ¹⁹⁻²⁴⁾. The results are shown in figs. 4 and 5. From fig. 4 it is clear that the excess enthalpy is always small compared to the linear combination of the values of the pure components.

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SAMENVATTING

In dit proefschrift worden de thermodynamische eigenschappen van vloeibaar ^3He - ^4He mengsels over het gehele concentratie gebied besproken.

Soortelijke warmte metingen zijn uitgevoerd met een calorimeter, welke door middel van een ^3He cryostaat werd afgekoeld tot 0.35°K .

Het eerste hoofdstuk geeft een overzicht en analyse van de bestaande metingen van thermodynamische grootheden bij de aanvang van de onderzoekingen, welke in dit proefschrift beschreven zijn. Het fase-evenwicht tussen damp en vloeistof van ^3He - ^4He mengsels over het gehele concentratie gebied wordt geanalyseerd. Uit de kookpuntsbepalingen van Roberts en Sydorjak zijn de exces chemische potentialen berekend. In het temperatuur gebied rondom 1°K vertoont de exces Gibbsfunctie een bijna regulier karakter.

In het eerste gedeelte van het tweede hoofdstuk worden de soortelijke warmte metingen van vloeibaar ^3He - ^4He mengsels beschreven. Speciale aandacht wordt besteed aan de extra bijdrage tot de soortelijke warmte in het fasescheidingsgebied, welke een gevolg is van de menging van de beide fasen bij stijgende temperatuur. De resultaten van de soortelijke warmte experimenten worden uiteengezet en kwalitatief gediscussieerd aan de hand van het fasediagram. De hoogte van de soortelijke warmte piek in het lambda punt blijkt zeer snel bij toenemende concentratie af te nemen.

In het tweede gedeelte van het tweede hoofdstuk worden uit de soortelijke warmte metingen in het fasescheidingsgebied de mengwarmte en de exces-entropie berekend. Hierna wordt voor de verschillende concentratie gebieden een quantitative analyse gegeven van de thermodynamische excesfuncties. Voor de verdunde mengsels, waarbij een weinig ^3He is opgelost in het superfluide ^4He , schijnt voor temperaturen beneden ongeveer 1°K aan de theorie van Pomeranchuk te zijn voldaan. De ^3He atomen bewegen zich als vrije deeltjes met een bepaalde effectieve massa door het superfluidum. De extra bijdrage van het ^3He tot de soortelijke warmte is onafhankelijk van de temperatuur en gelijk aan de waarde, die voor éenatomig gas geldt. De ^3He atomen, welke opgelost zijn in het superfluidum bevinden zich in een effectieve potentiaal put, welke slechts weinig dieper is dan die van de ^3He atomen in zuiver vloeibaar ^3He .

In het derde hoofdstuk worden de thermodynamische relaties besproken, die geldig zijn in het punt waar de lambdaliijn de phasescheidingsliijn ontmoet. In dit punt vertoont de phasescheidingsliijn een knik, indien de lambdaliijn en de phasescheidingsliijn elkaar met een eindige hoek snijden. Verder wordt aangetoond, dat de excesentropie van verdunde mengsels aan de wet van Nernst voldoet.

