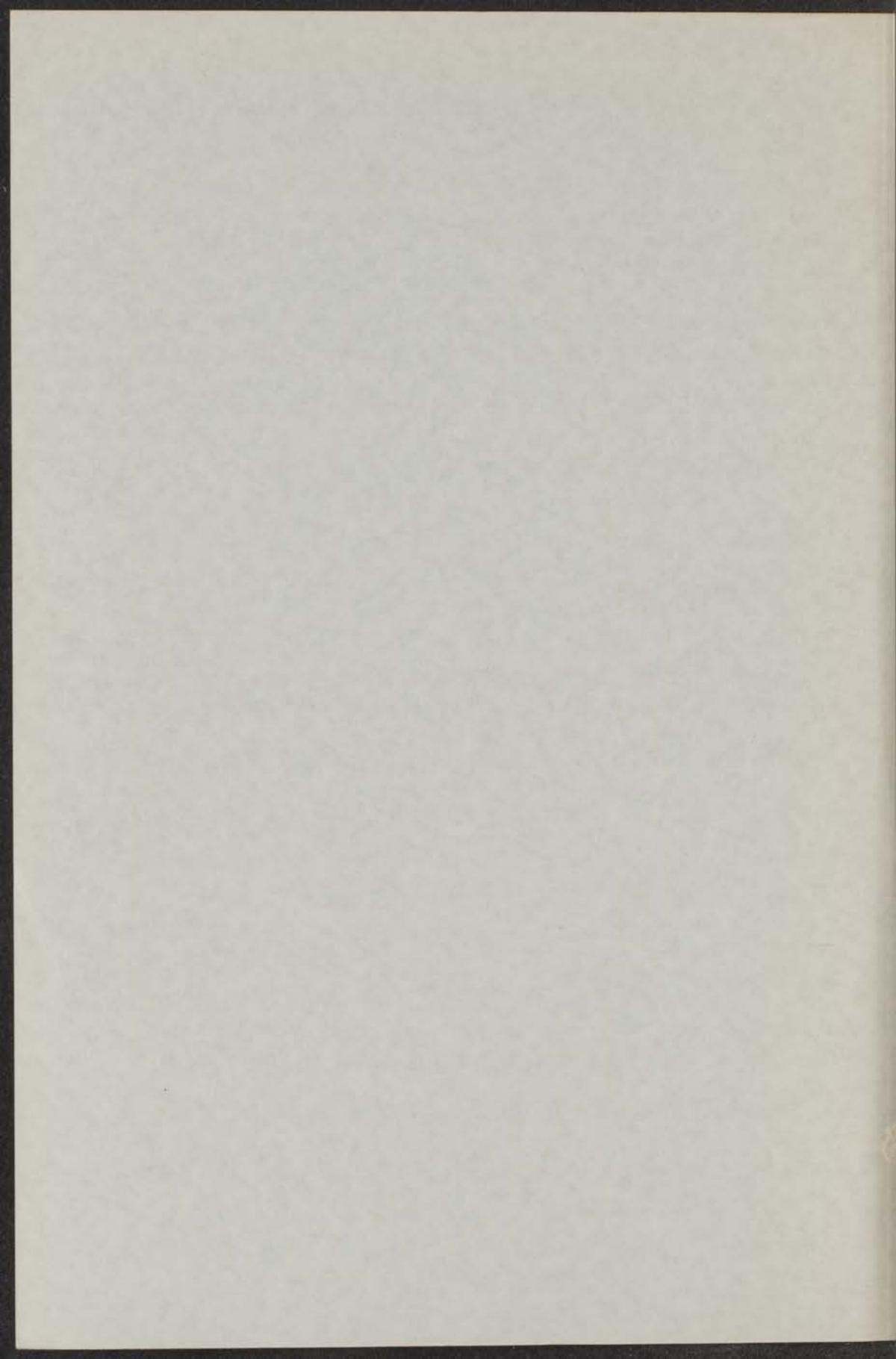


SPECIFIC HEATS
AT LOW TEMPERATURES

D. G. KAPADNIS, M.Sc.



SPECIFIC HEATS AT LOW TEMPERATURES

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN
DOCTOR IN DE WIS- EN NATUURKUNDE
AAN DE RIJSUNIVERSITEIT TE LEIDEN
OP GEZAG VAN DE RECTOR MAGNIFICUS
DR A. E. VAN ARKEL, HOGLERAAR IN DE
FACULTEIT DER WIS- EN NATUURKUNDE,
TEGEN DE BEDENKINGEN VAN DE
FACULTEIT DER WIS- EN NATUURKUNDE,
TE VERDEDIGEN OP
WOENSDAG 18 APRIL 1956
TE 16 UUR

DOOR

DATTATRAYA GOPALRAO KAPADNIS, M.Sc.

GEBOREN TE SOMPUR-DYANE, DIST. NASIK,
BOMBAY STATE, INDIA
IN 1923

PHYSICAL CHEMISTRY
AT LOW TEMPERATURES

Promotor: Prof. dr C. J. Gorter

To my Sanmitra-traya

Shri Vamanrao Chindhu Desai,

Dr. Natwarlal Amritlal Upadhyaya,

Shri Laxmanrao Manikrao Patil.

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As I was born in a farmer's family dwelling in a small village I had to shift from place to place for my education (due to lack of educational facilities within easy reach during the then-regime). I joined the Fergusson College, Poona, after getting through the matriculation examination in 1939. After a break of one year (1942-43) during the 'Quit India' movement of our national struggle for freedom, I continued my university studies in the Baroda College, Baroda, and was awarded the degree of *Bachelor of Science* (Phys. Maths.) of the University of Bombay in 1944. I served thereafter for three years as a science teacher in Maratha High School, Satana, Dist. Nasik, and simultaneously did the honorary work of R.S.D. Taluka Organizer, followed by that of a secretary of Taluka Congress Committee of The Indian National Congress till I left for higher studies.

Resuming the university studies again, I read physics (with advanced heat and thermodynamics as a special group) as a result of which the degree of *Master of Science* of the University of Bombay was conferred upon me in 1949. I was the recipient of the Bombay Government Special Scholarship (awarded on competitive basis) during my high school and undergraduate studies, while my postgraduate studies were facilitated by the demonstratorship in physics in the Faculty of Science of The Maharaja Sayajirao University of Baroda. During 1950-53 I did some research work on '*The Convective Heat Transmission*' under the guidance of Prof. D.V.Gogate, partly in the stated faculty and partly in The National Physical Laboratory of India, New Delhi.

In consequence of an award * of a Senior Research Fellowship from the M.S.University of Baroda, I joined the Kamerlingh Onnes Laboratory, Leiden, in March 1954. Since then I have been doing research work on '*Specific Heats at Low Temperatures*' under the responsibilities of Prof. C.J.Gorter and Prof. K.W.Taconis, benefiting from the kind co-operation of the members of that laboratory. Dr. Z.Dokoupil with whose co-operation the measurements

* A research assistantship from The State University of Leiden was made available to me for the last few months of my stay in this country.

included in chapter I were made, Dr. D. de Klerk and Dr. J. J. M. Beenakker with whom I had helpful discussions, Mr. R. Hartmans who kindly assisted during the major part of the research, Messrs A. Ouwerkerk, H. Kuipers and L. Neuteboom who helped in technical aspects, deserve a special mention.

This thesis is based upon a major part of the experimental work done in this laboratory during 1954-56. The work included in chapter I was carried under the supervision of Prof. Taconis and it was presented by Kapadnis and Dokoupil (read by Kapadnis) in the International Conference on Low Temperature Physics held in Paris in September 1955. The investigations included in the last three chapters were made under the supervision of Prof. Gorter.

Kamerlingh Onnes Laboratory,
Leiden, April 18, 1956.

Kapadnis

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Chapter I

Specific heat and entropy of helium II and of liquid mixtures of ^3He and ^4He

1. Introduction

Since its discovery in the solar atmosphere simultaneously from three places (*Guntoor, Jamkhindi and Bijapoor*) in *India* by *Janssen* ¹⁾, *Haig* ²⁾ and *Herschel* ³⁾ respectively and from *Malacca peninsula* by *Rayet* ⁴⁾ during the solar eclipse of the 18th of August, 1868, helium proved to be the most fascinating substance for the scientists. The charm in it was not dwindled after the successful attempt of its liquefaction by *Prof. H. Kamerlingh Onnes* of this laboratory (*Leiden*) on the 10th of July, 1908, but the light of that day saw the beginning of a new era in low temperatures. The liquid helium has kept the scientists spellbound since then.

Though the liquid helium is now widely used as an auxiliary research tool in various fields, still the so-called fourth state of aggregation, as represented by the superfluid state of helium (and by the superconducting state of electrons in certain metals and especially the very peculiar transfer phenomena which occur in this state) has partially defied the attempts made in order to understand the real mechanism of the phenomena and has attracted increasing interest. During the last nine years an attempt to study the superfluid phase on quite different lines, in addition to the existing ones, is being made. As the addition of even a small quantity of the rare isotope ^3He to liquid ^4He appreciably affects the behaviour of the latter, especially in the superfluid state, the study of the various properties of the liquid mixtures of helium isotopes should lead to a better understanding of the mechanism. This viewpoint led to the calorimetric determination of the specific heats of liquid mixtures of helium isotopes of mass 3 and 4, the experimental data of which form the bulk material of this chapter.

The nonavailability in substantial quantities of the rare isotope ^3He , which is only about 12×10^{-5} % abundant in the atmospheric helium (about 1.4×10^{-5} % abundant in well helium), ruled out the possibility of making use of any one of the familiar ways of building the calorimeter assembly ⁵⁾⁶⁾⁷⁾⁸⁾ for the present investigations. Because of the very small quantity of ^3He at our disposal, it was necessary to pay attention to the following main difficulties one is required to face with in the specific heat measurements of the liquids or liquid mixtures especially when one deals with small quantities. They are:

- (a) The thermal contact of the calorimeter with regions at higher temperatures, due to the filling capillary connecting the calorimeter with the outside filling system;
- (b) The evaporation of the liquid during the heating cycles;
- (c) The heat capacity and the compression of the vapour;
- (d) The change in the liquid concentration as a result of this evaporation, due to the different vapour pressures of the constituents of the liquid mixture.

The last arises only in the case of mixtures, while effects of the first three are usually negligible when one uses large amount of the liquid. It was, however, necessary in the present case to avoid the capillary connection with the regions at higher temperatures in order to minimize the heat leaks, and to decrease the vapour volume as far as possible in order to lessen the sources of error arising out of the difficulties mentioned above in (b), (c) and (d).

2. Experimental details

The above considerations led to the development of the following method *. A copper calorimeter **R** of about 250 mm^3 capacity, having a long narrow copper capillary tube **C** of about 0.2 mm internal diameter was first mounted separately in a liquid helium cryostat in such a way that part of the capillary passed through the cap of the cryostat to the outside filling system which was kept at room temperature. The ^3He - ^4He gas mixture of known concentration prepared previously in the storage balloon of the

* The principle of this method was developed by Dokoupil, Taconis, Beenakker and van Soest before I joined this laboratory.

filling system was, then, allowed to condense in the calorimeter R maintained at a temperature of about 1.9°K . The complete filling of the calorimeter and the immersed part of the capillary took about half an hour *. Subsequently the capillary was cut off as low as possible in order to minimize the vapour volume, the end was bent into a loop and surrounded completely by a silver solder. This proved to be sufficient to withstand the high pressure of about 1200 atmospheres as a result of the calorimeter attaining the room temperature after its removal from the cryostat. The amount of the gas mixture condensed in the calorimeter could easily be calculated from the decrease in pressure in the storage balloon.

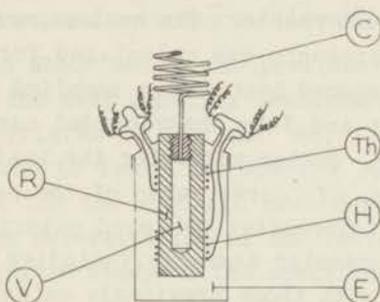


Fig. 1. The calorimeter.

After the removal of the calorimeter from the filling cryostat the capillary C was carefully spiralized (see figure 1) and the whole assembly consisting of the calorimeter, the phosphorbronze resistance thermometer wire Th and the constantan heating coil H which were previously wound round the calorimeter in the usual fashion, was mounted in a copper container as shown in figure 1. The space E surrounding the calorimeter was filled with helium gas exerting a pressure of about 3 cm of mercury at room temper-

* For the experiments with a higher concentration of 7.13 % of ^3He a still smaller calorimeter of only 54 mm^3 capacity was built up and used. In this case a new filling system with almost no dead volume was constructed. The storage vessel of this filling system contained the amount of the gas mixture just sufficient to fill the calorimeter and the capillary completely with the condensed liquid mixture. The time required for complete condensation in this case was relatively short and the amount of the gas mixture condensed was calculated from the volume of the storage vessel when all the gas mixture was displaced by mercury into the calorimeter.

ature, in order to have a good thermal contact between the heater the calorimeter and the resistance thermometer. This, in addition served in shielding the sensitive phosphorbronze thermometer wire from the vacuum space, thus reducing the effect of disturbing desorption of adsorbed molecules to a minimum. The container was finally mounted along with its contents in a vacuum jacket (not shown in the figure) in which a bit of exchange gas could be introduced in order to calibrate the thermometer against the bath pressure, and pumped out before the commencement of the measurements.

The actual measurements were made according to the standard technique followed for the heat capacity determinations in this laboratory. A part of the general experimental procedure will be described in the next chapter. The heat capacity of helium under saturated vapour pressure was calculated for different temperatures from the measured heat energy supplied by the heating coil to the calorimeter and from the recorded curves of temperature versus time before, during and after the heating periods. Measurements were made, of course, also of the heat capacity of the empty calorimeter (hereafter the word calorimeter will be used for the whole calorimeter assembly including the container) itself and compared with those previously calculated from the heat capacity determinations of pure copper by *Keesom* and *Kok*⁹⁾. The values at 1.1°K did not amount to more than 9 % of the total heat capacity of the calorimeter when filled. At higher temperatures, however, their influence was very small. Corrections were, of course, made for this. Corrections for the heat capacity of the exchange gas were also applied wherever necessary. As the calorimeter was practically full with the liquid (at least 96 % of it) it was not necessary to take into account the corrections due to the existence of the small vapour volume of about 10 mm³ at the end of the filling capillary. They were, however, computed and found to be negligibly small. At 1.1°K, for example, the correction to be applied for the amount of the heat energy used in the evaporation of a small fraction of the liquid during heating cycles amounts to about 0.4 %, that due to the compression of the vapour is about 0.05 % (moreover, it works in the opposite way). The heat capacity of the vapour evaporated gives rise to a correction of about 0.07 % at the same temperature. The correction due to a change in the liquid concentration depends on the concentration, nevertheless, it is comparatively very small. The net

effect of all these corrections shows a rapidly decreasing trend with an increase in the temperature.

In the case of the smaller calorimeter, however, the uncertainty due to the vapour volume was relatively large, giving rise to the necessity of applying the correction due to the evaporation of a small part of the liquid mixture. It amounted to about 2 % at 1.1°K. The rest arising out of the vapour volume were found to be much less than 1 % at the same temperature. At higher temperatures again, their effect was completely negligible.

3. Results and discussion

A. *The specific heat and entropy of liquid helium II*

Though the method described in the previous section was developed specially for the heat capacity measurements of small quantities of liquid mixtures of ^3He and ^4He , it was necessary to check its working and to learn the special features of the new method by trying it for the specific heat determination of pure ^4He . The independent determination of the latter was also essential for the comparative study of the specific heats of the mixtures.

The experimental results of specific heats of liquid helium II have been represented in figure 2. For the sake of legibility the data below 1.4°K have been shown in an enlarged form. The figure also includes the data obtained by various workers. The results of *Keesom and Clusius* ⁵⁾ and of *Keesom and miss Keesom* ¹⁰⁾ for the specific heat under saturated vapour pressure are included after correcting to 1948 temperature scale. As the main purpose of the work of *Keesom* and *miss Keesom* was to study the nature of the λ -transition and that of the specific heat in the neighbourhood of the λ -point, their experimental results centred round the λ -point of ^4He . As the temperature region we have covered is only from about 1 to 2°K, the figure 2 has been kept strictly limited to that range of temperatures only. In the region with which we are concerned the experimental points of *Keesom* and *Clusius* are rather scattered. The data of *Keesom* and *Westmijze* ¹¹⁾, the details of which were never reported, have not been included. Those of *Hull, Wilkinson* and *Wilks* ⁶⁾ were primarily concerned with the temperature region in which we have the least interest. But the smoothed values of their results above 1°K agree reason-

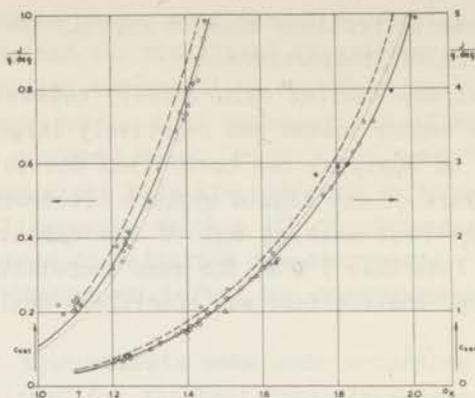


Fig. 2. The specific heat of liquid helium II as a function of temperature.

..... Gorter et al.; ——— Kramers et al.;
 - - - - - Hercus & Wilks; ● Keesom & Clusius;
 ▽ Keesom & miss Keesom △ Hull et al.;
 ○ This research.

ably well, if one keeps in mind that the closed capsule technique they developed is not very suitable for measurements in the temperature region with which we are concerned. The smoothed curve (fig. 2) representing the values published by *Gorter, Kasteleijn* and *Mellink*¹²⁾ who combined the specific heat data of *Keesom* and miss *Keesom* with the experimental formula of *Keesom* and *Westmijze* (for the estimation of the entropy), shows that below about 1.5°K their data are upto about 9 % lower, the agreement with the results of this research becoming closer as that temperature is reached. It starts deviating above about 1.6°K, thus giving values about 5 % higher near 1.8°K.

The comparison of our data with the smoothed curve given for liquid helium II by *Kramers, Wasscher* and *Gorter*⁷⁾ shows an excellent agreement within the limits of the experimental errors. The errors have been estimated to be within 4 % in the present case. Below about 1.2°K our values are about 8 to 10 % higher. The disagreement in this region of temperatures in which *Kramers* et al.'s results have been claimed to be the most accurate ones, is presumably due to rather poor accuracy we achieved in the measurements of the heat capacity of the empty calorimeter, because of its very small heat capacity, comparatively large heat leaks and the difficulties in getting adequate isolation in that region of temperatures.

It is a bit surprising that the results of the recent measurements by *Hercus* and *Wilks* ⁸⁾ are about 10 % higher throughout the temperature range we are concerned with. They claimed to have checked their results in some detail, finding thereby no reason to modify their values. They have also compared their results with the indirect specific heat determination by *Pellam* and *Hanson* ¹³⁾ from the velocity of second sound together with observations of the torque on a Rayleigh disc due to waves of second sound. But the evidence was inconclusive due to a rather large scatter of the points deduced by *Pellam* and *Hanson*. This discrepancy between the values of *Hercus* and *Wilks* and those of *Kramers et al.* is rather serious. Our experimental data (except below 1.2°K) as well as the indirect calculations from some of the recent fountain effect experiments, apart from any questions concerning the validity of the usual relation connecting the fountain pressure with the entropy, are in favour of the results of *Kramers et al.*

Starting with the absolute value of the entropy at 1.2°K (taken from the table of smoothed values of the entropy of liquid helium II given by *Kramers et al.*) and integrating graphically our c_{sat} versus T data between 1.2 and 2°K, we have computed the entropy of liquid helium II. A relative study of the entropy obtained directly by integrating the specific heat data and indirectly from the heat of transport experiments (assuming the validity of *H. London's* relations) is more instructive than a plot of the absolute values. Figure 3 gives such a plot with the smoothed curve obtained from our results above 1.2°K as a reference line. The same line serves the purpose of depicting the smoothed values of *Kramers et al.* All other data are shown in terms of percentage deviations from this line. The data collected from the specific heat experiments are smoothed, while those obtained indirectly by using *H. London's* relations, though there has been much discussion of the validity of those relations, are shown as individual points.

The results of computations by *Gorter et al.* ¹²⁾ are about 9 % lower at 1.2°K. The deviations diminish gradually with rising temperature, but above about 1.8°K they start increasing the other way, giving values upto about 3 % higher. The computations of *Gorter et al.* were, however, based on an erroneous extrapolation (due to the then available experimental data) of the specific heat - temperature curve of liquid helium, implicitly assum-

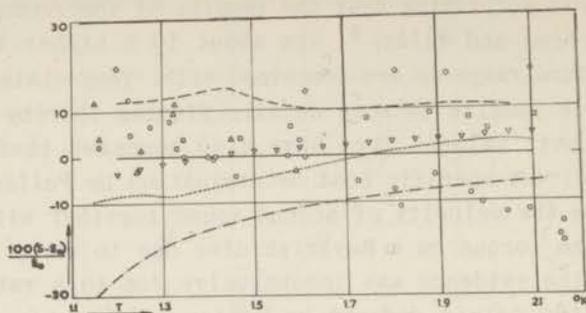


Fig. 3. Percentage deviations of the entropy data of other workers with respect to those of this research.

- This research (and also of Kramers et al.);
 Gorter et al.;
 - - - - - Hercus & Wilks;
 - · - · - · Stotal - Sphonons;
 □ Kapitza;
 ○ Meyer & Mellink;
 ◇ Chandrasekhar & Mendelssohn;
 △ Peshkov;
 ▽ Brewer et al.

ing the well-established conclusion that helium remains liquid down to 0°K . The entropy values deduced by *Hercus and Wilks*⁸⁾ from their specific heat data are about 12 % higher till 1.5°K above which they deviate by about 10 %.

The values computed from *Kapitza's* experiments¹⁴⁾ of thermo-mechanical effect are on the average about 6 % higher. The individual points show a rising trend of deviations from 2 to 8 %. The entropy taken into account in this case is as a matter of fact, the difference between the entropy of the bulk liquid and that of the liquid partaking in the superfluid flow. The comparison of the results of his computations with the entropy values deduced from the specific heat data prompted *Kapitza* to point out that the liquid taking part in superfluid flow has zero entropy. The fountain effect experiments of *Meyer and Mellink*¹⁵⁾ lead to values which are on the average about 4 % higher in the lower region of temperatures and about 10 % lower in the temperature region above about 1.8°K . Their data show a fair degree of scatter. Rather large scattering of the points especially above 1.8°K and very low values one gets from the data of *Meyer and Mellink* in that region of temperatures may probably be due to the experimental difficulty involved in such experiments near the λ -point. The difference in height between the liquid levels of helium II

in two vessels, per millidegree temperature difference increases with temperature and becomes very large in the vicinity of the λ -point. Therefore, only small differences in temperature are practicable, but at the cost of the accuracy. The heat of transport experiments of *Kapitza* were recently repeated by *Chandrasekhar* ¹⁶⁾ by replacing the superleak by a link of helium film. Those experiments lead to entropy values which (except one point at 1.4°K) are about 18 % higher. The measurements of the fountain effect carried out by *Peshkov* ¹⁷⁾ give points which show a scatter of ± 5 % on our reference line. The indirect measurements of the fountain effect carried out by *van den Meijdenberg et al.* ¹⁸⁾ lead to entropies scattering evenly on the reference curve by about 10 %. The agreement in spite of the large temperature differences they used in their method seems to be fair. The heat of transport experiments of *Brewer et al.* ¹⁹⁾ lead to values of entropy about 3 % lower at 1.2°K with a gradual trend to values about 4 % higher at 2°K. In spite of that the agreement with our results is fairly good.

The lowest curve in the figure gives the percentage deviations of the difference between the total entropy and that due to phonons. The phonon contribution has been computed from the data by *Kramers et al.* The figure clearly shows that the phonon contribution to the entropy, evidenced by the T^3 -dependence of the specific heat of liquid helium below 0.6°K, belongs to the normal component of helium II. As the agreement between the entropy determinations from the fountain effect experiments (taking the validity of *London's* relations for granted) and the specific heat data is not disappointing, we may express again that the normal constituent of liquid helium II carries all the entropy of the liquid.

Various theories have been proposed to explain the peculiar properties of liquid helium. The principal approaches to this problem are of considering the liquid to be either a gas in which the interatomic forces have become large, or a solid in which the binding forces are too weak to localize the atoms near the lattice points. For the review of different theories in connection with the specific heat and entropy of liquid helium we refer to the recent review articles ²⁰⁾²¹⁾.

Table I

T	ΔT	c_{sat}	T	ΔT	c_{sat}	T	ΔT	c_{sat}
X = 0.010								
(20-1-1955)			(27-1-1955)			(10-2-1955)		
1.073	7.01	0.326	1.249	5.26	0.462	1.163	4.24	0.328
1.074	7.67	0.295	1.255	5.12	0.475	1.174	11.6	0.363
1.073	7.20	0.316	1.261	5.07	0.480	1.181	3.81	0.368
1.073	8.13	0.275	1.265	5.05	0.482	1.187	7.84	0.356
1.078	14.1	0.324	1.274	16.1	0.541	1.194	11.0	0.386
1.078	14.2	0.324	1.292	30.0	0.584	1.199	7.54	0.375
1.082	20.7	0.270	1.312	28.2	0.623	1.205	7.35	0.382
1.093	39.5	0.249	1.325	14.0	0.627	1.209	10.5	0.406
1.083	21.2	0.258	1.335	13.2	0.668	1.213	7.18	0.396
1.097	43.2	0.254	1.346	13.1	0.675	1.221	12.8	0.447
1.088	23.1	0.247	1.357	12.4	0.710	1.227	8.86	0.453
1.322	9.98	0.595	1.366	12.3	0.715	1.232	17.3	0.466
1.328	8.64	0.696	1.377	11.9	0.747	1.244	16.9	0.476
1.339	19.0	0.627	1.387	21.8	0.821	1.255	17.4	0.461
1.350	17.1	0.706	1.405	21.1	0.845	1.085	11.5	0.240
1.386	14.8	0.817	1.562	6.24	1.47	1.095	11.0	0.252
1.401	13.9	0.871	1.615	52.6	1.73	1.102	11.8	0.257
1.410	14.4	0.838	1.646	22.4	1.83	1.110	16.2	0.258
1.802	18.5	3.00	1.658	21.0	1.95	1.115	10.1	0.277
1.818	18.2	3.05	1.672	20.1	2.04	1.117	9.85	0.285
1.836	17.4	3.21	1.683	19.0	2.16	1.114	9.78	0.289
1.858	38.2	3.75	1.869	35.4	3.56	1.111	5.44	0.254
1.889	32.2	3.95	1.889	33.9	3.72	1.118	5.15	0.271
1.913	31.0	4.11	1.911	31.4	4.03	1.131	5.03	0.276
1.958	24.4	5.30	1.934	29.4	4.31	1.137	5.07	0.273
1.981	22.4	5.80	1.964	53.5	4.74	1.145	13.6	0.312
2.003	23.1	5.60	1.994	23.6	5.38	2.127	16.1	8.20
2.026	21.7	5.96	2.009	22.2	5.72	2.146	15.6	8.43
2.048	19.8	6.55	2.025	20.7	6.15	2.165	30.8	8.53
2.065	18.4	7.07	2.037	20.7	6.16	2.232	120.5	2.13
2.087	31.5	7.99	2.053	19.3	6.60	2.289	49.8	2.56
2.114	29.1	8.08				2.332	52.4	2.42

Table I (continued)

T	ΔT	C_{sat}	T	ΔT	C_{sat}	T	ΔT	C_{sat}
$X = 0.025$								
(11-6-1955)			2.178	7.53	5.30	2.014	27.5	5.67
			2.193	9.20	4.32	2.035	25.4	6.23
1.073	9.40	0.238	2.207	11.62	3.40	2.057	24.1	6.59
1.077	9.35	0.229	2.218	12.28	3.22	2.073	21.6	7.35
1.080	17.22	0.265	2.260	55.80	2.85	2.099	38.2	8.33
1.080	17.08	0.271				2.115	17.8	8.94
1.084	17.35	0.264	(1-7-1955)			2.127	16.25	9.82
1.092	36.24	0.247				2.140	16.3	9.78
1.093	17.05	0.262	1.285	3.78	0.623	2.161	33.9	4.64
1.273	8.88	0.548	1.410	43.2	0.942	2.193	44.5	3.51
1.274	9.98	0.570	1.472	36.0	1.16	2.226	50.6	3.07
1.275	8.50	0.567	1.555	56.6	1.53	2.264	53.7	2.88
1.275	14.05	0.580	1.568	55.6	1.55	2.276	67.5	2.79
1.279	13.76	0.590	1.573	53.8	1.61			
1.281	17.46	0.594	1.638	45.0	1.92	(9-7-1955)		
1.285	18.15	0.569	1.661	43.0	2.06			
1.411	11.28	0.942	1.770	32.2	2.73	1.840	27.7	3.34
1.421	10.00	1.07	1.824	27.7	3.18	1.867	26.4	3.52
1.421	20.08	1.07	1.872	24.0	3.66	1.897	32.4	3.83
1.452	20.04	1.05	1.951	19.7	4.49	1.949	26.2	4.76
1.462	19.62	1.09	1.992	18.5	4.78	1.977	26.9	4.66
1.692	10.12	2.15	2.033	14.9	5.97	1.998	24.5	5.11
1.707	16.78	2.36	2.073	13.8	6.44	2.015	16.7	5.84
1.725	16.28	2.44				2.032	21.2	5.92
1.749	29.60	2.69	(9-7-1955)			2.052	20.6	6.14
1.775	27.68	2.89				2.069	18.1	6.96
1.975	16.55	4.87	1.787	30.9	2.86	2.115	34.8	7.87
2.002	24.52	4.97	1.814	28.1	3.11	2.121	41.1	9.02
2.029	14.39	5.60	1.840	26.4	3.30	2.164	55.8	4.95
2.054	27.48	6.05	1.866	24.2	3.61	2.201	26.8	3.39
2.071	24.60	6.65	1.887	22.4	3.90	2.223	28.9	3.13
2.105	22.62	8.17	1.910	21.3	4.11	2.230	30.3	2.98
2.128	20.04	9.06	1.927	20.8	4.18	2.245	31.8	2.83
2.145	17.02	9.94	1.936	35.5	4.45	2.268	33.0	2.73
2.165	4.08	9.88	1.967	32.3	4.80	2.292	32.6	2.76
2.169	5.13	7.82	1.992	29.2	5.43			

Table I (continued)

T	ΔT	c_{sat}	T	ΔT	c_{sat}	T	ΔT	c_{sat}
$X = 0.071_3$								
(26-5-1955)			1.950	3.00	5.03	1.323	5.23	0.845
			1.953	2.86	5.28	1.328	5.44	0.802
1.082	3.33	0.338	1.960	2.88	5.22	1.333	5.12	0.864
1.083	3.19	0.358	1.962	2.84	5.30	1.339	5.22	0.844
1.104	3.06	0.375	2.016	4.62	6.49	1.344	5.29	0.841
1.105	3.09	0.371	2.017	4.50	6.73	1.348	4.97	0.892
1.107	3.05	0.378	2.019	4.63	6.53	1.353	4.94	0.898
1.108	3.15	0.361	2.021	4.34	6.98	1.358	4.95	0.896
1.112	2.97	0.390	2.024	4.55	6.65	1.397	4.32	1.04
1.115	3.03	0.380	2.025	4.49	6.73	1.398	4.31	1.04
1.121	2.98	0.396	2.027	4.38	6.92	1.401	8.66	1.05
1.428	2.33	1.147	2.029	6.19	7.33	1.404	8.37	1.08
1.434	2.52	1.050	2.033	6.79	6.68	1.552	5.74	1.69
1.442	2.49	1.065	2.037	6.35	7.15	1.557	2.86	1.67
1.449	2.46	1.076	2.041	6.20	7.33	1.602	4.96	1.94
1.451	1.23	1.076	2.045	6.05	7.52	1.618	5.02	1.92
1.455	2.45	1.080	2.050	5.85	7.79	1.621	4.58	2.05
1.459	2.46	1.075	2.057	7.42	8.19	1.625	4.54	2.07
1.461	2.47	1.074	2.062	3.88	7.83	1.628	4.54	2.09
1.749	2.09	2.77	2.066	5.10	8.95	1.631	6.72	2.12
1.754	6.15	2.82	2.071	5.35	8.53	1.753	6.69	2.92
1.756	1.97	2.95				1.766	4.84	3.03
1.760	2.02	2.88	(3-6-1955)			1.786	4.61	3.20
1.765	2.00	2.90				1.791	3.05	3.22
1.929	3.07	4.89	1.123	3.23	0.392	1.800	4.47	3.29
1.931	3.01	4.99	1.124	2.98	0.410	1.806	4.45	3.30
1.938	3.10	4.86	1.126	3.12	0.390	1.817	4.29	3.43
1.941	3.08	4.89	1.302	11.6	0.750	1.823	4.29	3.45
1.944	2.93	5.13	1.308	5.72	0.756	1.958	2.78	5.30
1.947	2.94	5.12	1.316	5.65	0.770	2.002	4.67	6.39

(T is in $^{\circ}\text{K}$, ΔT is in millidegrees and c_{sat} is in joules per gram per degree)

B. Specific heats of liquid mixtures of ^3He and ^4He

The results of measurements of the specific heats of mixtures containing 1.0, 2.5 and 7.1₃ % of ^3He in a temperature range extending from 1 to 1.9°K have been given in table I and represented graphically in figure 4. This figure, in addition, shows the smoothed curve representing our specific heat data for pure ^4He presented in section A. The experimental results of the specific heat of liquid ^3He reported by Roberts and Sydoriak²²⁾ have also been included in the same figure. In spite of the fact that the

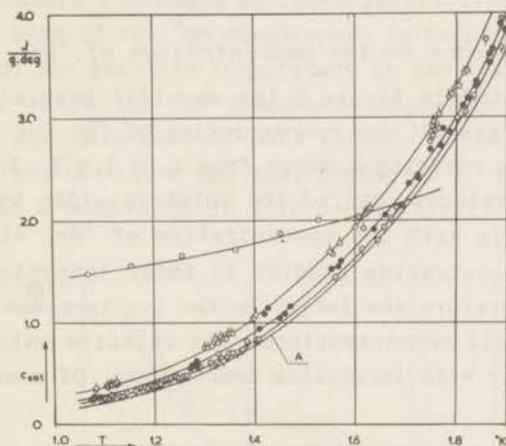


Fig. 4. The specific heat of liquid mixtures of ^3He and ^4He as a function of the temperature.
○ X = 0.010;
● X = 0.025;
○ X = 0.0713;
○ Liquid ^3He (Roberts & Sydoriak);
Curve A, liquid ^4He .

specific heat data for liquid ^3He are available from three different groups of research workers, this particular choice was made. The measurements of Osborn *et al.*²³⁾ were mainly concerned with the temperature region below 1°K. Though the experimental data of de Vries and Daunt²⁴⁾ cover a wide range of temperatures, the amount of ^3He they used was very small and it contained 4 % ^4He as an impurity. The quantity used by Roberts and Sydoriak was comparatively large and the results they arrived at in two different ways seem to be consistent.

Though the actual measurements we carried out were up to the

λ -point of each mixture (up to 2.3 K in the case of $X = 0.025$), the experimental data above 1.9°K have been excluded from figure 4. Due to the steep rise of the specific heat curves above 1.9°K, some uncertainty is introduced in the individual points in that region of temperatures, thus resulting in an encroachment of the points representing the heat capacities for $X = 0.010$ and 0.025. It is rather difficult to trace definite specific heat curves for the stated concentrations, especially above 2°K. The data for $X = 0.071_3$, on the other hand, lead to a well defined and distinct specific heat curve in that range of temperatures too. [X represents the molar fraction $N_3/(N_3+N_4)$.]

a. *Linear dependence on the concentration of ^3He*

We have plotted in figure 5 the specific heat at saturation vapour pressure against the concentration of ^3He for five different temperatures covering a range from 1 to 1.9°K. In the entire region of temperatures covered the total specific heat seems to increase linearly with the concentration of ^3He , at least upto the highest concentration studied in these investigations. The higher the temperature the larger is the net increase in the specific heat for all concentrations. Its relative value, however, decreases rapidly with increasing temperature, of course, for all concentrations.

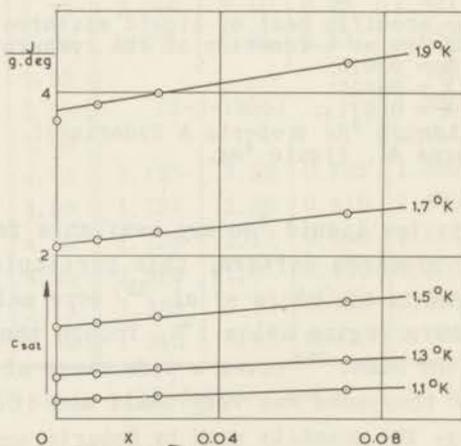


Fig. 5. The specific heat of the mixture as a function of concentration.
 ○ Experimental points (smoothed values).

b. *The relative increase in the specific heat*

Compared to the specific heat of pure ^4He that of each mixture is considerably large. The increase in the specific heat is relatively large at the lowest temperatures and it diminishes rapidly with a rise in temperature. Though the ^3He component present in the mixtures under study is small compared to the ^4He counterpart, its heat capacity especially below 1.4°K is large enough (viz., about 10 times that of liquid ^4He at 1.1°K) to make a substantial contribution to the specific heats of the mixtures. A rapid loss of its influence on the heat capacity of the mixture as the temperature increases is intelligible from the fact that the specific heat of the ^4He counterpart is proportional to about 5.6th power of the absolute temperature in the region we are concerned with, while the ^3He component lags far behind in this respect. The specific heat of pure liquid ^3He is chiefly due to the sum of a constant term and that linear in T . The contribution arising out of a term cubic in T is comparatively small.

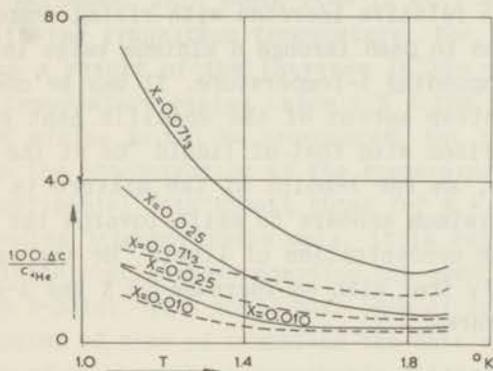


Fig. 6. An increase in the specific heat of the mixture with respect to that of pure ^4He , $\frac{100\Delta c}{c_{^4\text{He}}}$, as a function of

the temperature. The full curves include the contribution due to liquid ^3He , while the dashed curves are drawn after subtracting it.

The foregoing remarks are evident partially from figure 6. The curves in this figure give a ratio of the percentage increase in

the specific heat of the mixtures to that of pure ${}^4\text{He}$, $\frac{100 \Delta c}{c_{{}^4\text{He}}}$, as a function of the absolute temperature. We have represented the relative increase in the specific heat in two ways. The full curves in the figure include the contribution due to liquid ${}^3\text{He}$ components of the corresponding mixtures along with that as a result of mixing of ${}^3\text{He}$ in ${}^4\text{He}$, while the dashed curves are drawn after subtracting the contribution due to ${}^3\text{He}$ (computed by using the data given by *Roberts and Sydoriak*). The computations for the setting of these two types of curves have been made by using the smoothed data for the specific heats of the mixtures and of ${}^4\text{He}$.

The striking feature of this figure is the increasing influence of the specific heat of liquid ${}^3\text{He}$ with concentration, especially in the lower region of temperatures. At 1.8°K , for example, the relative increase is about 9 % for $X = 0.071_3$, 4 % for $X = 0.025$ and 2 % for $X = 0.010$; while at 1.1°K its values are about 78, 39 and 20 % for $X = 0.071_3$, 0.025 and 0.010 respectively. This is again a consequence of the relatively large heat capacity of liquid ${}^3\text{He}$ in that region. The curves do not show only a speedy diminution of the relative increase with rising temperature, but each of them seems to pass through a minimum value in the proximity of the corresponding λ -temperature. It may be connected with the relatively steep ascent of the specific heat curve of the mixture in comparison with that of liquid ${}^4\text{He}$ at the corresponding temperatures, as the λ -point of the mixture is approached. Moreover, this minimum appears to shift towards the low temperature side as the concentration of liquid ${}^3\text{He}$ increases. It indicates indirectly that with an increase in X the λ -point shifts to lower temperatures.

c. The specific heat of mixing

The dashed curves in figure 6 give the contribution arising out of the mixing of the two components. In order to gather more information about this contribution, we represent the total specific heat of the mixture by

$$c_{\text{total}} = X c_{{}^3\text{He}} + (1 - X) c_{{}^4\text{He}} + c_{\text{mix}}. \quad (1)$$

and plot c_{mix} , the term due to the mixing of ${}^3\text{He}$ and ${}^4\text{He}$, as a function of the ${}^3\text{He}$ concentration and temperature in figure 7. The specific heat of mixing for different concentrations in-

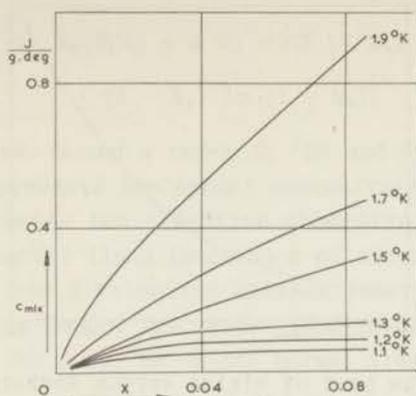


Fig. 7. c_{mix} versus X for different temperatures.

increases monotonously with rising temperature. This increase becomes rather large as the λ -temperature of the mixture is approached. The part of the c_{mix} versus T curve which represents somewhat rapid increase in c_{mix} undergoes a shift to low temperatures as X increases. This rapid rise in c_{mix} and its shift are connected with the transition temperature, the temperature that is lowered as a result of the increase in the concentration of ^3He . In the temperature region below 1.3 K the rise of the specific heat of mixing is not so pronounced, but it shows a marked increase with the concentration as the temperature increases.

As the experimental data except those for $X = 0.025$, extend to the corresponding λ -temperatures only, it is rather difficult to draw any definite conclusions regarding the specific heat of mixing above the λ -point. This would have been of interest especially from the point of view of comparing the data with the existing theories some of which predict remarkably different behaviour for the heat of mixing and the specific heat of mixing below and above the λ -temperature. The results for $X = 0.025$ however, show indications of negative c_{mix} above the λ -point of the mixture.

d. The heat of mixing

The heat of mixing for the concentrations we studied can be computed from the specific heat of mixing. The absolute values are, however, not possible in the present case as the experimental data extend to 1.08°K only. The relative values, nevertheless, show that the heat of mixing is positive and increases monoto-

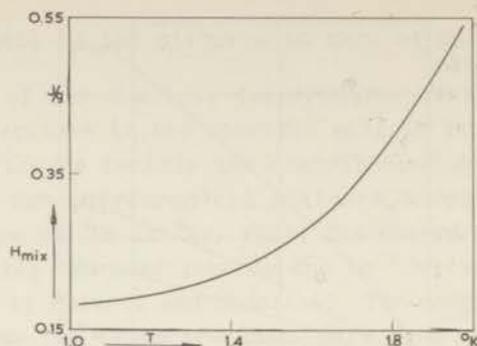


Fig. 8. The heat of mixing versus temperature for $X = 0.086$.

nously with temperature and concentration, of course, up to the λ -point of the mixture above which it will undergo a rapid decrease. In order to get some idea about the absolute heat of mixing versus temperature curve we made use of the results for the specific heat of mixing for $X = 0.086$ obtained by extrapolating our results, which were combined after graphical integration with the only available value of the heat of mixing for the same concentration of ^3He at 1.02°K reported by *Sommers et al.*²⁵⁾ Figure 8 shows the plot of the absolute values obtained in this way for $X = 0.086$.

C. Comparison with theories

Several theoretical attempts have been made to explain the properties of liquid mixtures of ^3He and ^4He . The earlier theoretical models were proposed mainly to explain the then-observed²⁶⁾ variation of the λ -temperature with the concentration of ^3He . It is now an established fact that the earlier observations of the shift of the λ -point were largely in error (refer to section 3.D) We shall, therefore, refrain from taking those models into consideration, with the exception of two of them.

a. Thermodynamic theories

With the *Taconis* and *Beenakker* hypothesis²⁸⁾, viz., ^3He dissolves in the normal part of liquid helium II only, as a basis *de Boer* and *Gorter*²⁹⁾ developed a schematical theory. The Gibbs' function of the classical thermodynamics can, in this case, be written in the form

$$G = (1 - X) G_4(T, x) + X G_3 + RT (X/X_e) [X_e \ln X_e + (1 - X_e) \ln (1 - X_e)] \quad (2)$$

where the suffixes 3 and 4 refer to ^3He and ^4He components respectively, X represents the actual concentration and $X_e = X/[X + x(1 - X)]$ denotes the effective concentration computed with respect to the normal fluid fraction x of the total number of ^4He atoms. Dropping the distinction between internal energy and enthalpy, and making use of the chosen functional dependence of the Gibbs' function for pure ^4He on the normal fraction x , viz.,

$$G_4(T, x) = - (6S_\lambda T_\lambda / 7) (1 - x^{7/6}) - xS_\lambda T \quad (3)$$

and assuming that in equilibrium G is minimum with respect to the variations of x at constant T and X , we get a positive quantity for the heat of mixing,

$$H_{\text{mix}} = - T^2 \partial(G/T) / \partial T = (1 - X) (6S_\lambda T_\lambda / 7) (x^{7/6} - x_0^{7/6}), \quad (4)$$

where x and x_0 represent the fraction of ^4He atoms comprising the normal fluid in solution and in the pure state, respectively. This expression gives relatively large values, especially near the λ -point of the mixture above which the values decrease rapidly to zero at the λ -point of ^4He . Except for seemingly dilute solutions the heat of mixing shows a strong dependence on the concentration of ^3He .

Differentiating equation (4) with respect to T , we get for the specific heat of mixing

$$c_{\text{mix}} = S_\lambda (1 - X) [T_\lambda x^{1/6} (\partial x / \partial T) - 6 (T/T_\lambda)^6], \quad (5)$$

S_λ being the entropy of pure ^4He at $T_\lambda = 2.186^\circ\text{K}$, x and $\partial x / \partial T$ are computed numerically by using the expression

$$S_\lambda T_\lambda x^{1/6} - S_\lambda T = RT \ln \{1 + X/[x(1 - X)]\}, \quad (6)$$

The expression (5) leads to a strongly concentration dependent specific heat of mixing which increases with the temperature but shows a decreasing trend as the temperature approaches the λ -point of the mixture. This is not supported by the experimentally observed behaviour. The choice of the Gibbs' function made in this theoretical model does not seem to be the proper one, as expression (3) gives temperature independent entropy for helium I.

This implies that liquid helium I has zero specific heat. Apart from the severe disagreement of the theoretical results with the present experiments (figures 9 and 10) it is interesting to note that as a result of the admixture of ^3He in ^4He , the excitation of ^4He atoms comprising the normal fluid takes place. The specific heat of mixing is, according to this theory, entirely due to this contribution.

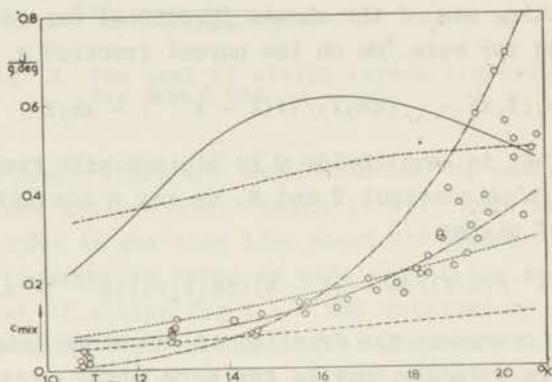


Fig. 9. C_{mix} (theoretical) versus T for $X = 0.025$.

- de Boer & Gorter;
- - - Nanda;
- · - Heer & Daunt;
- · · Mikura;
- · · Agarwal;
- - - Trikha & Nanda
- This research (experimental).

Recently *de Boer* and *Gorter*'s theory has been modified by *Nanda* ³⁰⁾ by taking into account the non-ideal behaviour of the solution above the λ -point. He introduced an extra term $X(1-X_e)W$ in expression (2), W being the interchange energy for which *Nanda* chose three different values. He used for G_4 the following expression ³¹⁾ involving a quadratic function for the term in T , viz.,

$$G_4(T, x) = -\frac{5}{14} T_\lambda S_\lambda (1 - x^{7/6}) - \frac{S_\lambda}{2 T_\lambda} T^2 x^{5/6}. \quad (7)$$

This choice is better compared to that made by *de Boer* and *Gorter* as it gives an entropy for helium I which increases linearly with the temperature, as has been observed experimentally ³²⁾. The

modification of the original theory on these lines leads to the following expression for the specific heat of mixing.

$$c_{\text{mix}} = \frac{S_{\lambda}}{R} (1 - X) \left\{ \frac{5}{6} T \frac{\partial X}{\partial T} \left[\left(\frac{T_{\lambda}}{T} \right) x^{1/6} + \left(\frac{T}{T_{\lambda}} \right) x^{-1/6} + \frac{3}{2} X_e^2 \frac{W}{RT} \right] + 2 \left(\frac{T}{T_{\lambda}} \right) x^{5/6} - 12 \left(\frac{T}{T_{\lambda}} \right)^6 \right\}, \quad (8)$$

where x and $\partial x / \partial T$ are given by

$$\left(\frac{T_{\lambda}}{T} \right) x^{1/6} - \left(\frac{T}{T_{\lambda}} \right) x^{-1/6} + 3 \ln (1 - X_e) + \frac{3 W X_e^2}{RT} = 0.$$

The specific heat of mixing computed by using expression (8) is rather very large and very strongly dependent on temperature and on the concentration of ^3He (refer to figures 9 and 10). The departure from the experimentally observed values is very great. Like that of *de Boer* and *Gorter* this theory also gives the specific heat of mixing which jumps from a large negative value above the λ -point of the mixture to a large positive value below that temperature. The different choice of the Gibbs' function for ^3He made in this modification and the introduction of the term involving the non-ideality parameter in the original theory to improve the situation above the λ -temperature seems to have served no useful purpose below the λ -point. The root cause of the severe disagreement of the original theory with the recent experimental results, therefore, seems to lie in the basic assumption of that theory.

Trikha and *Nanda*³⁷⁾ have very recently communicated a short note on the solution of ^3He and ^4He . They assume that ^3He mixes with the whole of ^4He , that the contribution to the entropy of mixing is due only to the thermal part of ^4He and that the solution obeys the laws of a strictly regular solution. They write the Gibbs function for the solution with these assumptions as the basis. The value for the parameter called the interchange energy is chosen by adjusting the shift of the λ -point of the mixture with that observed experimentally. Assuming the quadratic expression for G_4 , we get in this case the following expression for the specific heat of mixing.

$$c_{\text{mix}} = (1 - X) S_{\lambda} \left\{ \frac{4.5}{11} T \frac{\partial X}{\partial T} \left[\left(\frac{T_{\lambda}}{T} \right) x^{5.5} + \left(\frac{T}{T_{\lambda}} \right) x^{-5.5} + \frac{11}{4.5} \frac{XW}{T S_{\lambda}} \right] + \left(\frac{T}{T_{\lambda}} \right) x^{4.5} - 5.5 \left(\frac{T}{T_{\lambda}} \right)^{5.5} \right\}, \quad (9)$$

where x and $\partial x/\partial T$ can be computed from the relation

$$\frac{4.5}{11} S_{\lambda} \left[\left(\frac{T_{\lambda}}{T} \right) x^{5.5} - \left(\frac{T}{T_{\lambda}} \right) x^{-5.5} \right] + R \ln (1 - X) + \frac{XW}{T} = 0. \quad (10)$$

This expression gives very strongly temperature dependent specific heat of mixing which is rather too low in the lower region of temperatures and high in the upper region. The dependence of c_{mix} on the concentration of ${}^3\text{He}$ is stronger than that observed (refer to figures 9 and 10). It seems, however, that an approach made by changing the basic assumption of *De Boer and Gorter's* theory has improved the agreement with experiments. This in a way supports our views expressed in the previous paragraph.

b. Statistical theories

De Boer and Gorter tackled the problem of the solution of ${}^3\text{He}$ in ${}^4\text{He}$ by using the expression for an ideal mixture of classical liquids under the *Taconis* and *Beenakker* assumption, while *Heer and Daunt* ³³⁾ used a mixture of two model liquids and developed a theory by regarding the mixture of ${}^3\text{He}$ and ${}^4\text{He}$ as a mixture of an ideal *Fermi-Dirac* gas in a smoothed potential well $-\chi_3^0$ and of a degenerate ideal *Bose-Einstein* gas in a smoothed potential well $-\chi_4^0$. We get in this case

$$H_{\text{mix}} = \frac{3}{2} N_3 kT \left[\zeta(5/2)/\zeta(3/2) \right] (V_3^0/V_4^0) (T/T_{\lambda})^{3/2}, \quad (11)$$

for the heat of mixing for temperatures below the λ -point of ${}^4\text{He}$. $\zeta(3/2)$ and $\zeta(5/2)$ are the Riemann zeta functions, V_3^0 and V_4^0 are the atomic volumes per atom of ${}^3\text{He}$ and ${}^4\text{He}$ respectively, and T is the λ -temperature of liquid ${}^4\text{He}$. This expression holds good so long as ${}^4\text{He}$ is treated as degenerate and ${}^3\text{He}$ as nondegenerate in the pure state as well as in the solution. We get for c_{mix}

$$c_{\text{mix}} = \frac{15}{4} XR \frac{\zeta(5/2)}{\zeta(3/2)} \frac{V_3^0}{V_4^0} \left(\frac{T}{T_{\lambda}} \right)^{3/2}. \quad (12)$$

The theory gives comparatively low values for the heat of mixing and for the specific heat of mixing. Though the dependence of the specific heat of mixing on the concentration seems to be roughly of the right order of magnitude its rate of rise with the temperature is rather too small (see figures 9 and 10). This is not surprising. It is well known that the ideal *Bose-Einstein* gas model for ${}^4\text{He}$ leads to a third-order transition and gives a $T^{3/2}$ -

law for the specific heat. *Heer* and *Daunt's* model based on the *Bose-Einstein* statistics would naturally be affected seriously by these drawbacks.

Heer and *Daunt's* theory was modified by *Mikura* ³⁴). He ascribed each *Bose*-particle a much larger mass than that of a ⁴He atom and an energy gap $k\Delta_0$ between the ground state and the lowest excited state. In the case of pure ⁴He the introduction of two such parameters leads to the second order transition and to the specific heat resembling the experimentally observed curve for liquid ⁴He, but gives rather a small jump in the specific heat at the transition temperature ²⁰). In the revised model of his theory of modified *Bose Einstein* liquid *Mikura* assumed the mass factor ν to be independent of the concentration of ³He (other possibility is not excluded), while Δk the energy gap between the ground state and the lowest excited states is assumed to vary with the concentration and is given by

$$\Delta = \Delta_0 [N_4 V_4 / (N_3 V_3 + N_4 V_4)]^{0.4} \quad (13)$$

where V_3 and V_4 are molecular volumes and the exponent 0.4 is chosen by adjustment to give the shift of the λ -point equal to that observed. He gives the following expression for the total specific heat of the mixture.

$$c_v = (1 - m_3 N_3) \frac{k\Delta^2}{\rho_4} \left(\frac{2\pi M_4 k}{h^2} \right)^{3/2} T^{-1/2} \left(1 + \frac{3T}{\Delta} + \frac{15T^2}{4\Delta^2} \right) \exp(-\Delta/T) + c_v^3, \quad (14)$$

where c_v^3 is the direct contribution to the specific heat of the ³He component. In contrast to the situation found in pure liquid ³He, the assumption that ³He behaves as a nondegenerate ideal gas of the proper density at temperatures below the λ -point has been successfully applied in this theory in the case of specific heats and propagation of second sound in solutions. The contribution to the specific heat of mixing should according to this theory therefore, be partly due to a decrease in the energy gap that takes place when ³He is added to ⁴He. We have calculated the specific heat of mixing in this case by subtracting the individual contribution due to liquid ³He and ⁴He from the total specific heat computed by using expression (12). Figures 9 and 10 show a satisfactory agreement of the experimental results with the theoretical computations. The agreement in the close vicinity of

the λ -point of the mixture is only fair. The same is the case with the results below 1.3°K. The theoretical curve for c_{mix} versus X indicates that the agreement may deteriorate at higher concentrations of ^3He , may presumably be due to the departure from the assumed ideal nondegenerate gas behaviour of ^3He in the mixture.

Heer and *Daunt*'s theory has also been modified very recently by *Agarwal* ³⁵⁾ on the ground that the energy spectrum of a perfect gas may presumably be distorted in the liquid state. He suggests that the energy spectrum is given by $E(p) = Ap^{1/r}$, where $A = 1/2m$ and r is a simple function of the molar volumes of ^3He and ^4He , given by $r = r_0 V_3/V_4$, r_0 being the value of r for the perfect gas spectrum. This choice of r is made to get the proper shift of the λ -point. In connection with this modification we refer to the case of pure ^4He for the merits and drawbacks of the analogous theory of the self consistent field ²⁰⁾. Using *Agarwal*'s model we get for the specific heat of mixing

$$c_{\text{mix}} = 3r(3r+1)XR \frac{\zeta(3r+1)}{\zeta(3r)} \frac{V_3}{V_4} \left(\frac{T}{T_\lambda}\right)^{3r}. \quad (15)$$

This expression gives values which are somewhat higher in the low temperature region and the increase in c_{mix} in the neighbourhood of the λ -point is too slow. Except near the λ -point the theory gives stronger dependence of c_{mix} on X than that observed experimentally (refer to figures 9 and 10).

These three statistical models are based on the assumption that the deviations from the laws of perfect solutions are entirely due to the difference in statistics. The differences in masses of ^3He and ^4He as well as the differences in zero point energies will, according to the views of *Prigogine* ³⁶⁾, contribute effectively.

c. *Pomeranchuk's model for dilute solutions*

Pomeranchuk ³⁸⁾ treated ^3He in solution as a kind of impurity associated with the normal constituent of ^4He , and considered the effect of adding ^3He in small concentration to liquid ^4He . The specific heat of the solution is given in this case by the sum of the specific heat of pure liquid ^4He and the constant specific heat of the impurities (depending upon the concentration only). The *Pomeranchuk* model of dilute solutions, therefore, gives a linear dependence of the specific heat on the concentration of

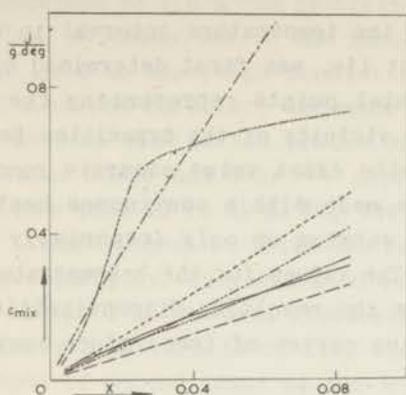


Fig. 10. c_{mix} versus X for $T = 1.5^\circ K$.

- De Boer & Gorter;
- Nanda;
- Heer & Daunt;
- Mikura;
- Trikha & Nanda;
- Agarwal;
- This research (experimental).

3He . Our experimental data plotted in figure 6 confirm this view at least upto $X = 0.071$, the highest concentration we studied. But this theory leads to a constant value of $3R/2$ for the derivative of the specific heat, while the experimental results give a value considerably greater than $3R/2$, increasing with the temperature and becoming very large near the λ -point of the mixture. King and Fairbank's experiments on second sound ³⁹⁾ lead to a confirmation of Pomeranchuk's model at very low temperatures. It seems from these experiments that the Pomeranchuk gas-like 3He excitations exist at very low temperatures at which other thermal excitations contribute very little in comparison. At higher temperatures, however, our experimental results seem to indicate that interactions of 3He excitations with those of phonons and rotons become prominent.

D. The influence of 3He on the λ -temperature

The interesting phenomenon of 3He not taking part in superfluid flow, observed by Daunt *et al.* ⁴⁰⁾ in dilute solutions of 3He in 4He , led to a new method of isotopic separation in the liquid phase by superfluid filtration, and also to the conclusion that the λ -temperature of liquid 4He would be a function of the concentration of 3He .

In our investigations, the temperature interval in which the λ -point of the mixture must lie, was first determined by a close scrutiny of the experimental points representing the specific heat of the mixture in the vicinity of the transition temperature. For the determination of its exact value separate runs through the transition point were made with a continuous heat supply, sometimes by the natural warming up only (especially when the bath level was very low). The values for the λ -temperature of the mixture were computed from the resulting discontinuities in the slopes of the corresponding curves of temperature versus time.

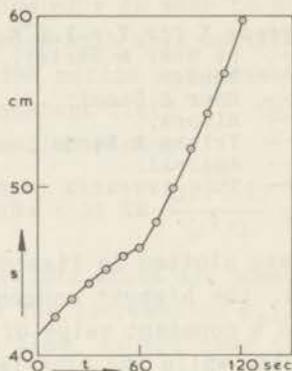


Fig. 11. A typical plot of the galvanometer reading versus time used to compute the λ -temperature of the mixture ($X = 0.010$).

Figure 11 shows such a typical plot used to compute the λ -temperature of the mixture. The values of the λ -points corresponding to $X = 0.010$, 0.025 and 0.071_3 are 2.171 , 2.149 and 2.080°K respectively, giving a negative shift of 1.48 degrees per mole concentration. The λ -transition is of the second order and there seems to be no appreciable change in the jump in the specific heat at the λ -point.

The early experimental observations of the lowering of the λ -point of ^4He due to an admixture of ^3He , reported by *Abraham et al.*²⁶⁾ for concentrations upto 28.2% ^3He by using a superleak formed around a platinum wire, seem to be largely in error, presumably due to the concentration gradient set up in the liquid mixture as a result of the heat flush effect. The value given for

the λ -temperature of 1.5 % ^3He by *Eselsohn* and *Lazarev* ²⁷⁾ is also somewhat low, probably due to the uncertainty of the concentration. They used an apparatus consisting of two reservoirs connected by a narrow capillary and made use of an observation of the supra-surface flow as the criterion for the existence of the λ -temperature. *Daunt* and *Heer* ⁴¹⁾ used in their experiments for concentrations from 42 to 89 % ^3He , the same criterion and determined the λ -temperatures at which the heat influxes to the reservoir changed abruptly. They expected that their results were not seriously affected by the heat flush effect.

The experimental results of *King* and *Fairbank* ³⁹⁾, using the disappearance of second sound at the λ -point as a criterion, for concentrations below 4.2 % ^3He revealed a linear dependence of the λ -temperature of the mixture on the concentration of ^3He , giving a slope of - 1.5 degrees per mole concentration. These observations led to the suspicion that the earlier observations were erroneous. It was confirmed by our measurements of the specific heats of liquid mixtures of ^3He and ^4He ⁴²⁾⁴³⁾ and later on by the oscillating pendulum experiments performed by *Dash* and *Taylor* ⁴⁴⁾, who obtained from their measurements of the behaviour of a torsion pendulum immersed in the liquids, transition temperatures of individual solutions by locating the discontinuity in slope of the torsion period versus temperature. This is equivalent to finding the temperature at which the normal fluid density becomes equal to the total density. Their experiments also give a linear shift of $- 1.47 \pm 0.03$ degrees per mole concentration for the whole concentration range (upto $X = 0.092$) they studied.

It may be pointed out that in the experiments of *King* and *Fairbank*, those of this research and of *Dash* and *Taylor* the principles involved in the methods to determine the lowering of the λ -point of ^4He due to the presence of ^3He in the mixture, are entirely different from each other. In spite of that the excellent agreement of the results suggests that the observed shift of - 1.48 degrees per mole concentration may be treated as an established fact.

Figure 12 shows the ratio of the λ -temperature of the mixture to that of pure ^4He as a function of the concentration of ^3He up to $X = 0.11$. The observed data as well as those computed according to different theories have been included in the figure. In this case also the theories (except two) proposed to explain the

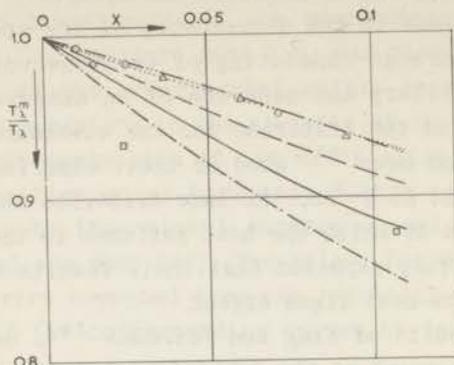


Fig. 12. $T_{\lambda}^m/T_{\lambda}$ as a function of X .

□	Abraham et al.;
◇	Esselsohn & Lazarev;
○	This research;
△	Dash & Taylor;
—	De Boer & Gorter;
- - -	Heer & Daunt;
- · - · -	Mikura;
- - - - -	Nanda;
· · · · ·	Agarwal (also Trikha & Nanda).

earlier erroneous observations of the shift of the λ -point have been omitted.

The Gibbs' function written according to the laws for perfect classical solutions leads to the second order λ -transition for liquid ${}^4\text{He}$, the λ -point of liquid ${}^4\text{He}$ remaining unaffected by the admixture of ${}^3\text{He}$. The experimentally observed change in the λ -temperature with the concentration of ${}^3\text{He}$ was accounted for, in the theory of *de Boer and Gorter* ²⁹⁾ by introducing the *Taconis* and *Beenakker* hypothesis. The λ -temperature of the mixture in this case is given by the expression

$$1 - X = \exp [S_{\lambda}(T - T_{\lambda})/RT]. \quad (16)$$

For given X the value of T satisfying (16) corresponds to T_{λ}^m , the λ -temperature of the mixture. The choice of G_4 as a function of T (linear or quadratic in T) and x in their theory does not help much in bringing the theoretical T_{λ}^m - X curve in close agreement with the experimentally observed values, at least upto $X = 0.1$. The theory also gives in both the cases of G_4 much higher values for the initial slope $(\partial T_{\lambda}^m/\partial X)_{X \rightarrow 0}$. The modification of this theory made by *Nanda* ³⁰⁾ leads to

$$1 - X = \exp \left[-\frac{1}{3} \left(\frac{T_\lambda}{T} \right)^{1/6} - \left(\frac{T}{T_\lambda} \right)^{1/6} + \frac{3WX^2}{RT} \right], \quad (17)$$

giving the variation of the λ -temperature with the concentration of ^3He . Figure 12 shows that this expression fails to improve the situation. The modification of the form of the Gibbs' function for pure ^4He or an entirely different approach to introduce the quantum nature of the liquid in the classical thermodynamic treatment is necessary.

Without resorting to the assumption made in the *Taconis Beenakker* hypothesis *Daunt and Heer*³³⁾ emphasized the role played by the type of statistics. They assumed the statistical independence of the *Bose-Einstein* and *Fermi-Dirac* systems in solutions of ^3He in ^4He and showed that the λ -temperature of the mixture is given by the degeneracy temperature of the *Bose-Einstein* system. The expression for the λ -temperature of the mixture in this case is

$$\frac{T_\lambda^m}{T_\lambda} = \left[\frac{1 - X}{1 + X \left(\frac{V_3^0}{V_4^0} - 1 \right)} \right]^{2/3} \quad (18)$$

The agreement with the experimental T_λ^m improves a bit in this case, but still it is very poor (see figure 12). This theory also leads to somewhat higher value for $(\partial T_\lambda^m / \partial X)_{X \rightarrow 0}$. The modifications of this theory made by *Mikura*³⁴⁾ and by *Agarwal*³⁵⁾ lead to a very close, rather very good fit of their T_λ^m versus X curves with the experiments. They have adjusted the parameters in their respective theories to that effect, i.e. the values assigned to the parameters were such that the theoretical initial slope was nearly the same as that observed experimentally. The λ -temperatures of the mixtures are given by

$$\frac{T_\lambda^m}{T_\lambda} = \left[\frac{1 - X}{1 + X \left(\frac{V_3^0}{V_4^0} - 1 \right)} \frac{F_{3/2}(\Delta_0 / T_\lambda)}{F_{3/2}(\Delta / T_\lambda)} \right]^{2/3}, \quad (19)$$

and

$$\frac{T_\lambda^m}{T_\lambda} = \left[\frac{1 - X}{1 + X \left(\frac{V_3^0}{V_4^0} - 1 \right)} \right]^{1/3} r \quad (20)$$

respectively, according to the theories of *Mikura* and *Agarwal*, *Trikha* and *Nanda* ³⁷⁾ in their theory based on the laws of regular solutions, substituted the experimentally observed value of the initial slope $(\partial X_{\lambda}^m / \partial T)_{X=0}$ in their expression for the λ -temperature of the solution in order to assign a value to the parameter called the interchange energy. This theory gives

$$\left(\frac{T_{\lambda}^m}{T_{\lambda}}\right)^2 - 6.896 \left(\frac{T_{\lambda}^m}{T_{\lambda}}\right) \log_{10} (1 - X) - 1 - 0.690 XW = 0, \quad (21)$$

for the λ -temperature of the mixture.

One gets according to *Pomeranchuk's* model ³⁸⁾ a negative shift of about 0.8 degrees per mole concentration, by using the effective mass derived from second sound experiments and taking for the λ -point the temperature at which the mass of the excited particles becomes equal to the total mass. This value is rather too low.

The experimental λ -temperatures are in very good agreement with the function $T_{\lambda}^m = T_{\lambda} (1 - X)^{2/3}$ given by *Goldstein* ⁴⁵⁾ from the asymptotic *Bose-Einstein* model by neglecting the effect of ³He on the total liquid density.

E. Concluding remarks

Though a number of phenomenological and molecular theories are available at present, there exists no completely satisfactory theory for the liquid mixtures of ³He and ⁴He. The phenomenological approach of *de Boer* and *Gorter* does not give any clue to the understanding of the molecular origin of the deviations from the laws of perfect solutions. A different choice of the Gibbs function and an introduction of a non-ideality parameter, as has been done by *Nanda*, make no appreciable improvement in the original theory. The root cause of the disagreement with the experiments seems to lie in the basic assumption of the theory. An approach to this problem made by *Trikha* and *Nanda*, with the assumption that ³He dissolves in ⁴He, normal as well as superfluid, improves the situation to some extent.

The theories based on the difference in the statistics are also unsatisfactory, though the approach made by *Mikura* leads to rather very good agreement with the experiments. The parameters involved in this model render it rather easy to arrive at the desired results by their suitable adjustment. One can also obtain the results in reasonable agreement with experiments, simply by

making S_λ and either E or n concentration-dependent in the relation

$$G_4 = -E (1 - x^n) - x S_\lambda T. \quad (3)$$

For the proper modification on this line the *Andronikashvili*-type or the *Hollis Hallett*-type experimental data for ^3He - ^4He mixtures will be of great help.

At least upto the highest concentration studied in these investigations, the observed λ -point shift of -1.48 degrees per mole concentration, is linear; the λ -transition is of the second order and there seems to be no appreciable change in the jump in the specific heat at the λ -point.

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Chapter II

Heat capacities of three paramagnetic alums at low temperatures

1. Introduction

Potassium chromic alum, ferric ammonium alum and recently chrome methylamine alum have been a subject of extensive study by both experimental and theoretical physicists. As they are inexpensive and can be grown easily into large single crystals they are frequently used in adiabatic demagnetization experiments as coolants and as magnetic thermometers. A knowledge of the position of the energy levels of the paramagnetic salts is of utmost importance in the demagnetization processes. The microwave resonance experiments supply direct information about this splitting of the ground state. This can also be achieved indirectly by the specific heat experiments which give a direct measure of interactions. As the specific heat contribution due to lattice vibrations is negligibly small below 1°K , the interest of the investigators centred round the specific heat of the spin system only. This is determined by the paramagnetic relaxation method which gives the precise data of the magnetic contribution to the specific heat, even by performing experiments at the liquid air temperatures. Therefore, with the exception of ferric ammonium alum no direct calorimetric measurements have been carried out with the stated alums in the liquid hydrogen and the liquid helium temperature region above 1°K . As a matter of fact one can compute the lattice- as well as the spin specific heat from such a direct determination of the total specific heat of the paramagnetic salt.

The results of an experimental study of the specific heats of these three paramagnetic alums (all in the polycrystalline form) in the temperature regions of 1 to 4.2°K and 11 to 21°K are presented and discussed in this chapter.

2. Experimental arrangement and procedure

Well established techniques of adiabatic calorimetry were followed in the present investigations. A cylindrical copper calorimeter K of 10.15 cm length and 3.35 cm outer diameter was constructed out of a sheet of 0.9 mm thickness. The phosphor-bronze and constantan thermometer wires T and C freely suspended from a sealed-in glass cross and separated by mica were mounted in a 8.81 cm long and 0.87 cm wide copper tube D which in turn was set in the calorimeter coaxially as shown in figure 1. A constantan wire R of 75 ohms resistance used for the energy input, was wound non-inductively round the central part of the calorimeter and cemented with glyptal lacquer. The thermometer tube was also connected to the outer shell by means of radial vanes made of copper used to facilitate heat distribution within the calorimeter. A small capillary S was attached to the cap to permit the introduction of the helium gas into the calorimeter for good

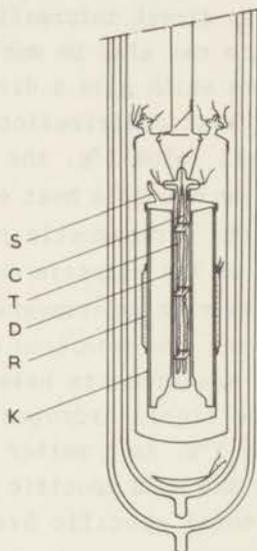


Fig. 1. The calorimeter assembly.

thermal contact. The thermometer connecting leads were brought out through a sealed-in glass cross. All the permanent joints were silver-soldered, the calorimeter was silver-plated and a very thin protective coating of lacquer was applied to its interior in order to prevent the possible deteriorating chemical action of the salts.

The value of the temperature coefficient of the resistance of the constantan thermometer was 0.6 percent per degree in the hydrogen temperature region and that of the phosphorbronze thermometer was 9 percent per degree at 4.2°K and 21 percent per degree at 1.08°K (the lowest temperature we usually attained). The temperature drift due to the combined effect of the measuring current and the heat leaks was small except in the region where the heat capacities of the salts under investigation were small.

In the temperature ranges available through the use of liquid helium and hydrogen the respective thermometers were calibrated against the vapour pressures of the corresponding bath before the commencement of each series of measurements. Sometimes the calibration was also made immediately after the completion of the experiment. For the determination of the temperatures the 1955 temperature scale was used for the helium region and the table * prepared by the thermometry group for the hydrogen region.

The thermometer resistance at various temperatures was determined during the calibration and measurements by comparing the potential drop between the ends of the thermometer wire with that across a standard resistance by means of a Disselhorst compensation apparatus with the aid of a galvanometer. Except during the calibration the null method was not used, but the differences from exact compensation were found from the sensitivity of the galvanometer.

An automatic relay system synchronizing the heating arrangement with time signals given by a pendulum clock was employed for switching the heating current on and off simply by pressing a key. The heat energy supplied during the period of heating was calculated from the milliammeter and millivoltmeter readings which were corrected for the instruments and for the current through the voltmeter. The correction for the resistance of the leads was negligible.

To measure the heat capacities the resistance of the thermometer (the corresponding galvanometer scale reading was observed during the measurement and converted afterwards into the thermometer resistance) was observed every 10 seconds till the drift

* This table was prepared by using formula B on page 9 of Leiden communication no. 217a assuming the boiling point of liquid hydrogen to be 20.380°K.

dR/dT was constant. The heating current was then switched on for a period of 10 seconds or multiples of it. The usual heating period ranged from 10 to 20 seconds in the helium temperature region and from 10 to 60 seconds in that of hydrogen. Thereafter the drift in temperature was again observed till a steady drift for a sufficiently long time was achieved. The process was then repeated. The recorded fore- and after-periods were extrapolated to the centre of the heating period in order to get the value of the increase in temperature due to the known amount of the heat energy supplied.

The empty calorimeter weighed 90.269 grams and the volume of the sample space was 75 cubic cm. The thermometer tube was filled with the helium exchange gas exerting a pressure of 3 cm of Hg at room temperature. The heat capacity of the calorimeter containing a known quantity of the exchange gas was experimentally determined between 11 and 21°K and also in the liquid helium temperature region. In the latter, however, we did not succeed in getting results of the accuracy desired.

Potassium chromic alum and ferric ammonium alum used in the present investigations were of the Analar grade supplied by *Hopkin and Williams Ltd.* Chrome methylamine alum was from *Johnson Matthey & Co.* The guaranteed purity of the samples was not less than 99.5 percent. They were recrystallized and the sample space of the calorimeter was filled with 0.127 mole of CrK alum crystals (later on with 0.132 and 0.0962 mole of $FeNH_4$ - and $CrCH_3NH_3$ alum respectively) of the average size of 30 cubic mm. The necessary precautions were taken to prevent excess water from being adsorbed on the crystals prior to the filling, and to avoid the loss of the water of crystallization during the filling and sealing of the calorimeter. About 3×10^{-5} mole of the helium gas was introduced to secure a quick and uniform heat distribution throughout the sample, the capillary end was silver-soldered and the whole assembly was mounted by Nylon threads in a polished brass vacuum jacket which could either be filled with the helium exchange gas or highly evacuated.

3. Results and discussion

Graphical plots of the measured specific heats as a function of temperature in the liquid helium region have been displayed

for potassium chromic alum, iron ammonium alum and chrome methylamine alum in figures 3, 4 and 5 respectively. These figures in addition, show the lattice- and spin specific heat components of the total specific heat. The heat capacities measured in the liquid hydrogen temperature region have been represented graphically in figure 6.

In these specific heat computations corrections were applied for the heat capacity of the empty calorimeter and also for that of the helium exchange gas, wherever necessary. The difference between the specific heats at constant pressure and at constant volume computed by using Nernst and Lindeman's empirical relation was found to be negligible throughout the temperature range investigated. The combined corrections at the liquid helium temperatures were found to constitute about 25 percent of the total heat capacity of the filled calorimeter in this range; while at hydrogen temperatures the corrections amounted to about 15 percent of the total value. The experimental errors of the results have been estimated to be within 3 percent. Due to comparatively large heat leaks and partly due to the desorption of the helium gas adsorbed on the crystal surfaces, the stated accuracy could not be achieved for the experimental points representing very low specific heats.

A. The separation of the lattice- and spin specific heat components

For the separation of the specific heat contributions due to the lattice vibrations and the electronic spins, usually the specific heat of the corresponding isomorphous diamagnetic salt is independently measured, taking it for granted that its lattice specific heat is equal to that of the corresponding paramagnetic salt; or the spin specific heat of the paramagnetic salt under investigation is determined by the paramagnetic relaxation method of measurements. One finds in reality that the lattice specific heats of the isomorphous salts slightly differ from each other. In the present case at least this difference is appreciable if one compares the specific heat data of the present investigations with those of the corresponding isomorphous diamagnetic alums presented in chapter III.

Instead of following any one of these two methods for the separation of the heat capacity into one portion due to lattice

vibrations of the crystal with the remaining portion assigned to the effect of the changing populations of electronic levels, we have attempted the following simple graphical method. It seems to serve the purpose satisfactorily.

At relatively high temperatures the individual contribution due to Stark effect, hyperfine structure and magnetic and exchange interactions to the specific heat of a paramagnetic salt is inversely proportional to the square of the absolute temperature¹⁾. The specific heat arising out of lattice vibrations may, at the liquid helium temperatures, be represented by a T^3 -law. Then the total heat capacity may conveniently be expressed as

$$\begin{aligned} C_{\text{total}} &= C_{\text{magnetic}} + C_{\text{lattice}} \\ &= b/T^2 + aT^3 \end{aligned} \quad (1)$$

where a and b are respectively the lattice- and spin specific heat constants to be determined from the experimental data. Assuming the validity of this relation in the liquid helium temperature region above 1°K, graphs of $c_p T^2$ versus T^5 were plotted for each alum and the corresponding values of a and b were determined graphically. Figure 2 shows such a typical plot for potassium chromic alum. For the sake of legibility the data upto $T \approx 2.7^\circ\text{K}$ have been replotted in an enlarged form (the upper curve in figure 2).

B. Potassium chromic alum

The specific heat data in the liquid helium temperature region are satisfactorily represented by

$$c = \frac{0.135}{T^2} + 4.11 \times 10^{-3} T^3 \quad \text{J/mole.deg} \quad (2)$$

The full curve in figure 3 depicts this relation, while the dotted curve shows the spin specific heat contribution, that due to the lattice vibrations is represented by a dashed curve in the same figure.

Our experimental results when extrapolated below 1°K agree fairly well with those of *Bleaney*²⁾ and of *Keesom*³⁾ in that temperature region. The lattice specific heat term gives the Debye characteristic temperature $\theta_{\text{thermal}} = 77.9^\circ\text{K}$. No elastic data at

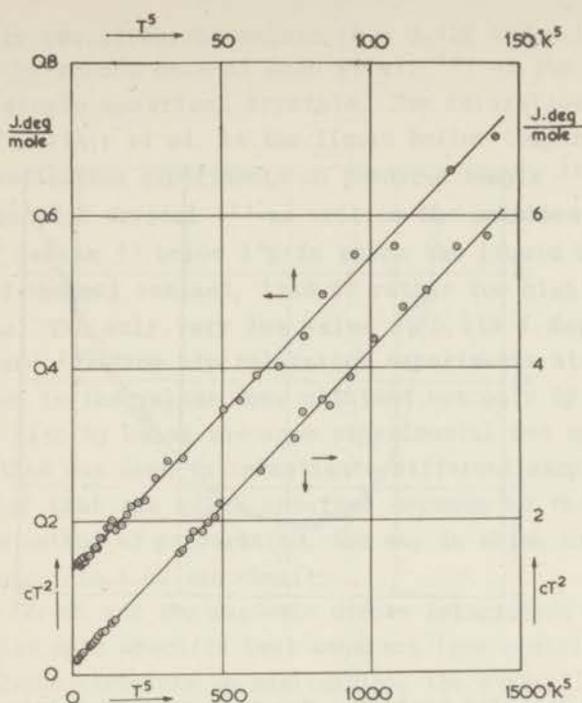


Fig. 2. $c_p T^2$ vs. T^5 for potassium chromic alum. The lower line represents the data upto $T \approx 4.3^\circ\text{K}$, while the upper one is an enlargement of the data upto $T \approx 2.7^\circ\text{K}$.

low temperatures are available, but the elastic constants of this alum at room temperature were determined by *Sundara Rao*⁴⁾ by the wedge method using ultrasonic frequencies. As the crystal anisotropy factor of this alum is nearly unity, *Bhatia and Tauber's*⁵⁾ method was preferred in the evaluation of θ_{elastic} from the available elastic data. The computation gives $\theta_{\text{elastic}} = 91.1^\circ\text{K}$. The method proposed by *Quimby and Sutton*⁶⁾ also gives nearly the same result. But *Blackman's* simple semi-theoretical formula⁷⁾ leads to $\theta_{\text{elastic}} = 98.5^\circ\text{K}$. This is not surprising because of the fact that the difference between the elastic constants c_{11} and c_{12} is relatively large in the present case. These θ_{elastic} values, however, indicate that the elastic constants at low temperatures may not probably lead to the observed θ_{thermal} . In other words, the true T^3 -region might presumably be at demagnetization temperatures in the present case.

The magnetic specific heat term gives the spin specific heat

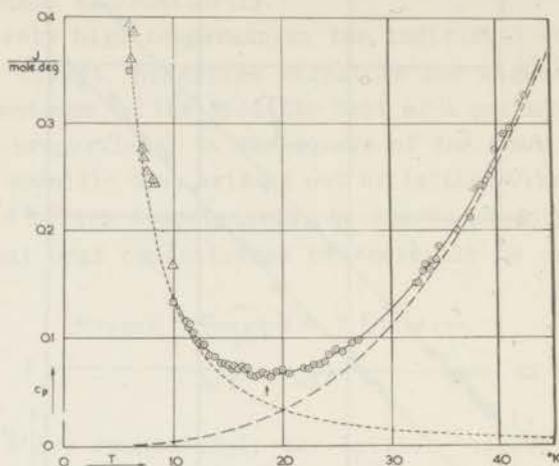


Fig. 3. The specific heat as a function of temperature for potassium chromic alum.

———— Graphical representation of equation (2).

----- The spin specific heat contribution.

- - - - The contribution due to lattice vibrations.

⊙ This research; Δ Keesom; ⊠ Bleaney.

constant, $b = 0.135$ J.deg/mole. The agreement of this value with those derived from the paramagnetic relaxation measurements of *Kramers et al.*⁸⁾ at the liquid helium temperatures (giving 0.139 J.deg/mole for b), of *Gorter et al.*⁹⁾ and of *Broer*¹⁰⁾ at the liquid nitrogen temperatures (leading to $b = 0.131$ J.deg/mole) is not disappointing. The spin specific heat constant computed from *Garrett's*¹¹⁾ data on the field dependence of adiabatic susceptibility at temperatures in the demagnetization range and also from *Bleaney's*²⁾ calorimetric measurements carried out by γ -ray heating, is $b = 0.133$ J.deg/mole. It is in very good agreement with our result. *De Klerk et al.*¹²⁾ in their adiabatic demagnetization experiments on a single spherical crystal arrived at $b = 0.139$ J.deg/mole; while *Ambler and Hudson*¹³⁾ gave $b = 0.138$ J.deg/mole from their demagnetization measurements by a.c. heat-

ing. One gets two different values ($b = 0.128$ and 0.138 J.deg/mole) from the recent data of *Beun et al.* ¹⁴⁾ on two different samples of single spherical crystals. The relaxation measurements ¹⁵⁾ of *Casimir et al.* at the liquid helium temperatures and their demagnetization experiments on powdered sample ¹⁶⁾ and on a single ellipsoidal crystal ¹⁷⁾ as well as the calorimetric measurements of *Keesom* ³⁾ below 1°K in which the liquid helium was used for the thermal contact, lead to rather too high and divergent results. The only very low value of 0.119 J.deg/mole was given by *Starr* ¹⁸⁾ from his relaxation experiments at 77°K . The inconsistency in the values thus obtained not only by different methods but also by using the same experimental set up in which the same method was used to investigate different samples, leads to the belief that the value obtained depends on the previous history (the method of preparation, the way in which the material is cooled down, etc.) of the sample.

If Stark effect and the magnetic dipole interaction alone contribute to the spin specific heat constant (the contribution due to the hyperfine structure is negligible), the crystalline splitting parameter δ can be calculated by making the usual assumption that all ions have the same splitting. Following *Hebb* and *Purcell* ¹⁹⁾

$$cT^2/R = b/R = \delta^2/4 + 2.40 \tau^2 \quad (3)$$

where $\tau = 0.0204^\circ\text{K}$ is the dipole interaction parameter. This gives the splitting parameter $\delta = 0.247^\circ\text{K} = 0.172 \text{ cm}^{-1}$ in the present case. The direct information given by the microwave resonance experiments about the ground state splitting of Cr^{+++} leads to two or three splittings at low temperatures. Consequently, the energy level separation so calculated for this alum has little significance.

C. Ferric ammonium alum

The experimental results between 1 and 4.5°K satisfy

$$c = \frac{0.112}{T^2} + 3.52 \times 10^{-3} T^3 \quad \text{J/mole.deg} \quad (4)$$

This expression is represented by a full curve in figure 4 in

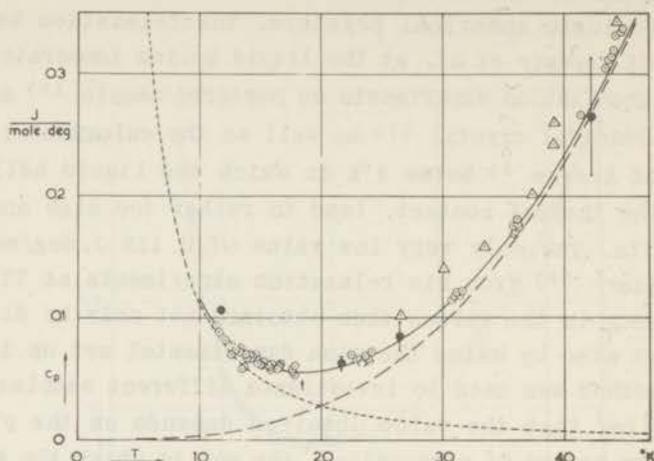


Fig. 4. The specific heat as a function of temperature for ferric ammonium alum.

- Graphical representation of equation (4).
 - - - - - The component due to the electronic specific heat.
 The lattice specific heat component.
 ○ This research; ● Casimir et al.; △ Duyckaerts.

which the lattice- and the spin specific heat components are also shown by a dashed and a dotted curve respectively.

Except in the lower region of temperatures the agreement with the results of *Casimir et al.*²¹⁾ arrived at in their demagnetization experiments and of *Duyckaerts*²²⁾ obtained by the calorimetric method is within the limits of experimental error. *Duyckaerts'* data below 3.5°K are about 12 percent higher than those of the present investigation. This is probably due to the method he followed in cooling the calorimeter by the condensation of the helium gas and then pumping it away. Considerable amount of the gas might have been absorbed during this process, the heat of desorption of which would lead to higher specific heat values. Neither the results of this investigation nor those of *Duyckaerts* reveal the presence of any hump in the specific heat-temperature curve obtained by *Van Dijk and Keesom*²³⁾ at about 3.8°K. The hump they got shifted slightly to the low temperature side with

the increase in the applied magnetic field. They suggested that this anomalous part of the specific heat might be of electrical rather than of magnetic origin, but this was not cleared up in further detail. They failed, however, to give a satisfactory explanation for this mysterious hump they observed. We think that probably some of the Fe ions in their specimen might be in the ferrous state, thus forming ferrous ammonium sulphate. This salt gives rise to two specific heat maxima ²⁴⁾, one at 3.8°K and another at 20.3°K. The very low specific heat values (in comparison with the data presented in this paper) observed by *Van Dijk* and *Keesom* below 1.5°K are a natural consequence of the magnetic dilution caused by the presence of an appreciable quantity of aluminium as impurity in the specimen of ferric ammonium alum they used.

The lattice specific heat contribution leads to the Debye temperature $\theta_{\text{thermal}} = 82.3^\circ\text{K}$ for the ferric ammonium alum, the spin specific heat constant for which is $b = 0.112 \text{ J.deg/mole}$. No elastic constants are available for the computation of θ_{elastic} . The paramagnetic relaxation measurements at the liquid helium temperatures carried out by *Du Pré* ²⁵⁾ give $b = 0.109 \text{ J.deg/mole}$, those by *Kramers et al.* ⁸⁾ give $b = 0.108 \text{ J.deg/mole}$, while *Benzie* and *Cooke* ²⁶⁾ find $b = 0.119 \text{ J.deg/mole}$ at the same temperatures. *Starr* ¹⁸⁾, *Dijkstra et al.* ²⁷⁾ and *Broer* ¹⁰⁾ get $b = 0.113$, 0.119 and 0.119 J.deg/mole respectively in the liquid nitrogen temperature range. The demagnetization experiments of *Casimir et al.* ²¹⁾ lead to $b = 0.106 \text{ J.deg/mole}$, while those of *Kurti* and *Simon* ²⁸⁾ on a compressed ellipsoid with an axial ratio of 1:3 lead to $b = 0.119 \text{ J.deg/mole}$.

As the only isotope with nuclear spin, ^{57}Fe , is only 2.2 percent abundant, the effects due to hyperfine structure are negligible. So the spin specific heat is represented by the relation

$$cT^2/R = b/R = 2\delta^2/9 + 2.40 \tau^2 \quad (5)$$

in which the first term arises from Stark splitting and the second from the spin-spin interaction. Substituting the value of b we obtained and the theoretical value of the interaction parameter, $\tau = 0.0472^\circ\text{K}$, in equation (5), we get $\delta = 0.192^\circ\text{K} = 0.133 \text{ cm}^{-1}$ for this alum. As has been shown by *Meyer* ²⁹⁾, one can ac-

count for the splitting observed by *Ubbink et al.*³⁰⁾ in paramagnetic resonance measurements on a magnetically diluted salt, by supposing that it is due to an electric field of cubic symmetry with a trigonal component in addition. *Meyer's* calculations of the zero field splittings lead to the crystalline splitting parameter, $\delta = 0.190$ to 0.201°K , which agrees with that derived from the specific heat data of this research.

D. Chrome methylamine alum

The observed specific heats at the liquid helium temperatures can be represented within the limits of experimental error by

$$c_p = \frac{0.162}{T^2} + 3.91 \times 10^{-3} T^3 \quad \text{J/mole-deg} \quad (6)$$

which is shown graphically by a full curve in figure 5, the spin and lattice specific heat contributions being represented by a dotted and a dashed curve respectively.

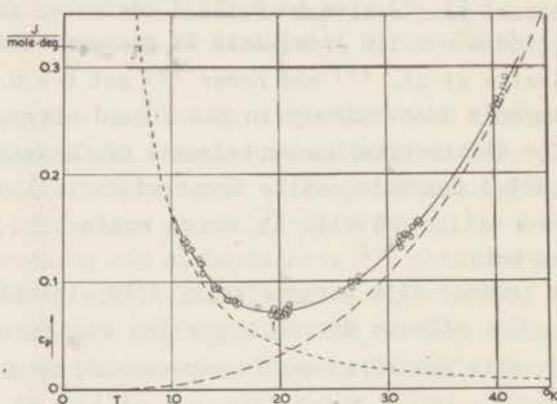


Fig. 5. The specific heat as a function of temperature for chrome methylamine alum.

- Graphical representation of equation (6).
- The spin specific heat.
- The lattice specific heat.

The Debye characteristic temperature computed for this alum is $\theta_{\text{thermal}} = 79.2^\circ\text{K}$, and the spin specific heat constant is 0.162 J.deg/mole . No estimate of θ_{elastic} can be made, as the elastic constants of this alum are unavailable. The value of b arrived at in this research agrees well with $b = 0.165 \text{ J.deg/mole}$, computed from the demagnetization experiments of *De Klerk and Hudson*³¹⁾ on a powdered sphere and also of *Beun et al.*³²⁾ on a single spherical crystal. The material used in the present investigation and that tried by *Beun et al.* were drawn from the same stock. The agreement of our result is also good with $b = 0.159 \text{ J.deg/mole}$ derived from the demagnetization data of *Gardner and Kurti*³³⁾ on a compressed powdered ellipsoid and of *Hudson and McLane*³⁴⁾ on one of the two samples they used.

By substituting the value of b we obtained and the theoretical value of $\tau = 0.0189^\circ\text{K}$ in equation (3), we find $\delta = 0.273^\circ\text{K} = 0.190 \text{ cm}^{-1}$. This result is in disagreement with $\delta = 0.245^\circ\text{K}$ given by *Bleaney*²⁰⁾ from his microwave resonance experiments. *Bleaney* calculated the stated value from the separation of the absorption lines in a strong magnetic field directed along the (111) axis, assuming a trigonal electric field with symmetry around this axis as was found in the rubidium and caesium alums. Measurements of *Baker*³³⁾ show that this assumption is far from reality.

E. Deviations from the Debye formula

The Debye characteristic temperatures of these three alums show a linear dependence on their molecular weights. The spin specific heat of these alums at the liquid hydrogen temperatures being very small (less than 1 in 10^4 at 15°K) the observed specific heat in this region of temperatures is practically due to the lattice alone. As these alums have the same crystal structure with only small difference in structural polymorphism, one expects a somewhat similar general behaviour of the lattice specific heat-temperature curves. The graphical representation of the experimental data in the hydrogen temperature range reveals marked deviations from the Debye formula. A c_p/T^3 versus T plot gives rather Schottky type curves which start rising from the normal at about 4°K , reach a maximum somewhere between 4°K and the liquid hydrogen temperatures and descend gradually. Such a Schottky type anomaly superimposed on the normal specific heat curve was ob-

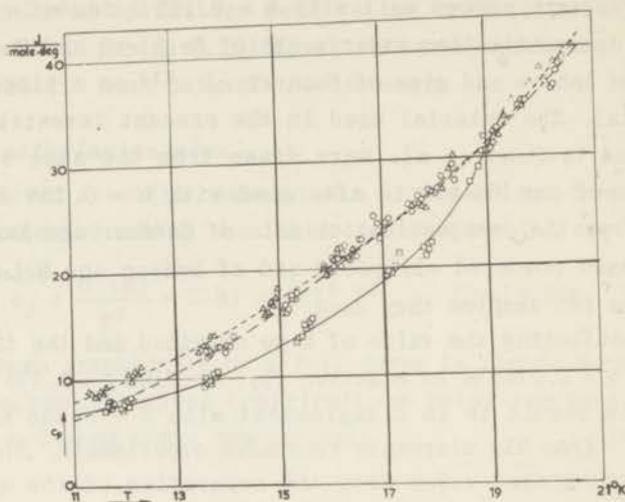


Fig. 6. A C_p vs. T plot at the hydrogen temperatures.
 ○ $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$; Δ $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$;
 □ $\text{CrCH}_3\text{NH}_3(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

served by *Duyckaerts* ²²⁾ in the case of ferric ammonium alum and by *Hill and Smith* ²⁴⁾ in that of ferrous ammonium sulphate. Recently *Gardner and Kurti* ³⁵⁾ reported in the Low Temperature Conference at Paris (1955) that ferric rubidium alum shows an anomalous non-magnetic specific heat. In the present case no measurements between 4.5 and 11°K were carried out. It is, therefore, rather difficult to give a precise account of the observed behaviour. The deviations are very pronounced in the case of ferric ammonium alum and chrome methylamine alum. The data below 14.5°K are, however, based on the extrapolation of the constantan resistance thermometer calibration curve in the liquid hydrogen temperature range. For these two alums the deviations at temperatures above about 18°K seem to increase again with temperature, this ascent being rapid in the case of chrome methylamine alum. The increasing deviations above 18°K are probably due to the internal excitations. As the specific heat data over a fairly wide

range of temperatures (upto the temperatures where the structural transitions take place) are not available at present, it is rather difficult to separate the contribution due to the excitations and to make a critical study of the remainder. It seems, however, that the qualitative nature of the observed deviations, excluding those due to excitations supplementary to the lattice specific heat, is somewhat similar to that of the face-centred cubic metals. The extension of the recently proposed theoretical models for monatomic crystals of this type to the case of these alums will be of interest.

A comparative picture and discussion of the results of this research along with those obtained for two diamagnetic alums will be given in the next chapter.

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*The low temperature heat capacities
of two diamagnetic alums*

1. Introduction

Certain diamagnetic alums play an important role in the realm of low temperatures when they are used for a replacement of some of the paramagnetic ions by equivalent diamagnetic counterparts, the so-called *dilution* of paramagnetic salts. Various properties of the latter undergo a modification. Extremely low temperatures have been reached by a single stage ¹⁾ or a two stage ²⁾ adiabatic demagnetization of diluted paramagnetic salts. The spin-lattice relaxation time is considerably longer ³⁾ and microwave absorption lines are narrowed ⁴⁾ in diluted salts. At very low temperatures the specific heat which is due largely to the magnetic and exchange interactions is decreased on dilution.

Experiments on magnetically dilute salts to study relaxation, absorption, demagnetization, etc., are in progress in this laboratory. For the satisfactory understanding of some of these phenomena and the demagnetization processes in general, data of the heat capacities of the dia- and paramagnetic salts are essential. A special interest in the diamagnetic alums is also due to the fact that ideally the only contribution at sufficiently low temperatures to their specific heats is that due to the lattice. This would enable us to try a direct comparison between the experimental results and the predictions of the lattice theory of specific heats. Therefore, the calorimetric determination of the heat capacities of potassium aluminium alum and ammonium aluminium alum in the liquid helium and hydrogen temperature ranges has been undertaken.

Heat capacities of potassium aluminium alum have been measured by *Baud* ⁵⁾ at temperatures above 288°K, by *Dewar* ⁶⁾ in a temperature range from 90 to 290°K and by *Nernst* and *Schwers* ⁷⁾ from the boiling point of liquid hydrogen to that of liquid oxygen. *Schomate* ⁸⁾ carried out specific heat measurements on this alum and also on ammonium aluminium alum from 50°K to room temperature. We have extended the measurements on both of these alums

to 1.1°K. The experimental data of these measurements have been presented in this chapter. This chapter also includes the discussion of the results of the experiments on paramagnetic alums presented in the previous chapter.

2. Experimental procedure

The experimental set up was the one which was used for the determination of the heat capacities of the paramagnetic alums⁹⁾.

The alums used in the present investigations were of the Analar grade supplied by *Hopkin & Williams Ltd.* The guaranteed purity of the samples was not less than 99.5 percent. The sample space of the calorimeter was filled with 0.149 mole of potassium aluminium alum crystals (later on with 0.134 mole of ammonium aluminium alum) of the average size of about 1 cubic mm. The necessary precautions were taken to avoid the loss of water of crystallization during the filling and sealing of the calorimeter. About 10^{-4} mole of helium gas was introduced in the filled calorimeter in order to secure a quick and uniform heat distribution throughout the previously filled sample.

The heat capacities of the alums under study were determined in the temperature regions extending from 1 to 4.2°K and 14 to 20°K. The 1955 temperature scale¹⁰⁾ was used to convert the liquid helium bath vapour pressures against which the phosphor-bronze resistance thermometer was calibrated before each series of measurements.

3. Discussion of the results

The experimental results for potassium aluminium alum and ammonium aluminium alum have been presented in figures 1, 2 and 3. The c_p vs. T data below 4.2°K have been shown for the respective alums in figures 1 and 2 and those in the liquid hydrogen temperature range for both alums in figure 3. Figure 4 gives a comparative picture of the heat capacity data for a series of substances, the experimental data of some of which have been presented in chapters II and IV. c_p/T^3 is plotted semilogarithmically as a function of temperature for these substances.

The measured specific heats of the two alums were corrected for the contribution due to the heat capacity of the empty

calorimeter and to that of the helium exchange gas. Especially below 3°K, the contribution due to the latter was also appreciable in comparison with the small heat capacity of the sample in this region. The exchange gas was treated as an ideal gas for the computation of the corrections. The contribution due to this source in the liquid hydrogen temperature range was, however, completely negligible. The corrections for the empty calorimeter and the helium transfer gas amounted to about 25 percent of the total heat capacity of the filled calorimeter in the liquid helium temperature region, while at hydrogen temperatures that due to the former was about 15 percent of the total value. The errors in the specific heat results are estimated to be within 4 percent. This accuracy could not be achieved for the experimental points in the temperature region below 2.5°K, due to comparatively large heat leaks and partly due to the desorption of the helium gas adsorbed on the crystal surfaces.

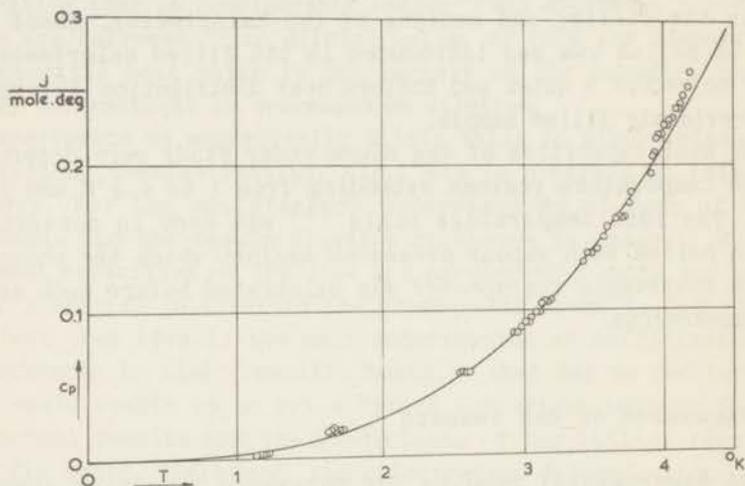


Fig. 1. C_p as a function of T for $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

In complicated crystals additional degrees of freedom corresponding to the internal vibrations of the groups of atoms or molecules exist. Though the actual frequency distribution curve is necessarily very complicated, the specific heat according to the general theory of vibrations for crystalline bodies containing atoms of different types can adequately be represented by the sum of three Debye terms and a number of terms arising out of single frequencies corresponding to the molecular vibrations. For the satisfactory representation of the data of cubic crystals however, only one Debye term is required along with a few Einstein

terms. In the liquid helium temperature region, however, the energy of the molecular vibrations of comparatively high frequency becomes negligible. The experimental results may, then, be represented by a Debye term only. This reduces to a simple T^3 -law at sufficiently low temperatures.

The experimental data of this research satisfy

$$c_p = 3.35 \times 10^{-3} T^3 \quad \text{J/mole. deg} \quad (1)$$

and
$$c_p = 3.18 \times 10^{-3} T^3 \quad \text{J/mole. deg} \quad (2)$$

for potassium aluminium alum and ammonium aluminium alum respectively. These equations are represented by full curves in the respective figures. They seem to fit the experimental points between 2 and 4°K within 3 percent. The experimental specific heat values below 2°K and also above 4°K deviate from the cubic.

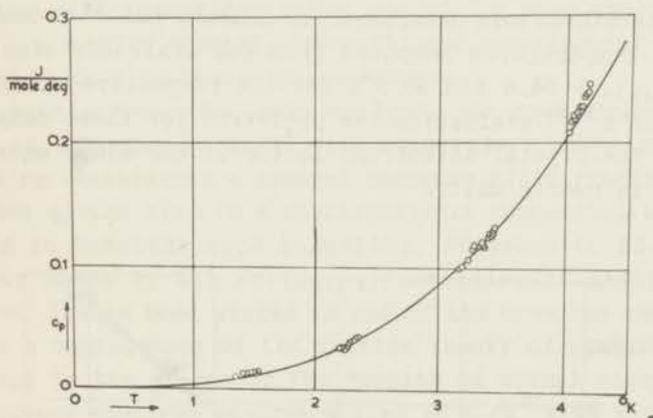


Fig. 2. c_p as a function of T for $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

This is contrary to what one expects according to the simple picture of the solid as an essentially isotropic continuum¹¹⁾. It is, therefore, unsatisfactory to treat the crystal as a continuum. The failure of Debye theory to account for these deviations is due to the assumption of a ν^2 -law for the frequency distribution.

Taking into account the crystal structure and the binding forces between the particles of ionic crystals and making use of a geometrical analysis, *Blackman*¹²⁾ gets two separate frequency distribution curves. His calculations and also those of others¹³⁾

show that the density of normal vibrations starting as a v^2 -law rises faster than v^2 immediately after the continuum region is passed. This seems to be the consequence of the lattice theory of *Born and Karman* ¹⁴⁾ and to be a property of all lattices in which short range forces are assumed. This property of the spectrum ensures a rise in c_p/T^3 with temperature. The amount by which it rises depends very much on the particular properties of the spectrum. The experimental curve should, therefore, as per *Blackman's* predictions, show a hump, giving rise to a spurious T^3 -region; and the thermal Debye characteristic temperature in the real T^3 -region should be equal to that computed from the elastic constants of the crystal at the absolute zero of temperature.

The T^3 -region observed in the present investigations leads to $\theta_{\text{thermal}} = 83.4^\circ\text{K}$ for potassium aluminium alum and 84.9°K for ammonium aluminium alum. No elastic data at low temperatures are available, but the elastic constants for both of these alums at room temperatures were determined by *Sundara Rao* ¹⁵⁾. The characteristic temperatures computed from the available elastic data are $\theta_{\text{elastic}} = 94.4$ and 95.5°K for the respective alums. *Bhatia and Tauber's* ¹⁶⁾ evaluation was preferred for these computations because, the crystal anisotropy factor of the alums under investigation is nearly unity.

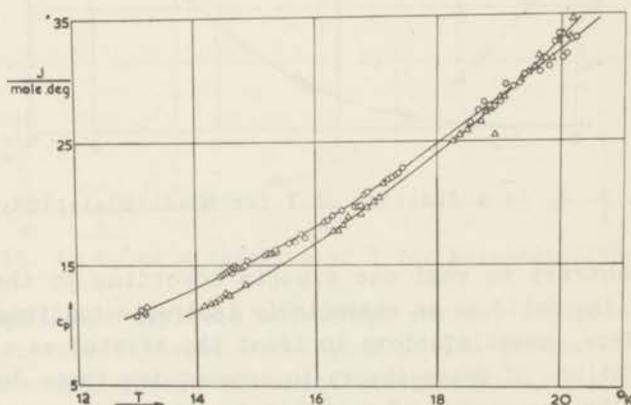


Fig. 3. C_p vs. T . \circ $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. Δ $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

If our experimental data in the liquid helium temperature region are represented in the form of (θ, T) curves, as is usually done by many investigators in this field, they indicate for both

alums the dip predicted by *Blackman* ¹²⁾. Such a curve for potassium alum passes through a minimum of about 77°K at 1.5°K and appears to rise sharply reaching a θ -value of about 98.4°K at 1.2°K. Because of very poor accuracy in the temperature region below 1.4°K, this should not be taken too seriously.

Figure 4 shows graphically c_p/T^3 as a function of $\log T$ for two diamagnetic alums of this research, three paramagnetic alums presented in chapter II and hydrated manganous bromide included in chapter IV. The entire liquid helium and hydrogen temperature regions have been covered. As no measurements have been carried out in the temperature range between about 4.5 and 11°K, the curves obtained from the observed data have been arbitrarily interpolated in this region. For the sake of comparison three curves representing three different groups of crystals have been included in the same figure. One is for lead ¹⁷⁾, a monatomic face-centred cubic metal; the second for potassium chloride ¹⁸⁾, the ionic crystal; and the third one is for zinc ammonium sulphate ¹⁹⁾, a complex crystal. The published experimental data have been used in drawing these typical curves.

All these curves show, more or less, the same general behaviour of an increase in c_p/T^3 with temperature, then undergoing with rising temperature a gradual decrease after reaching a maximum, thus giving rise to a characteristic shape similar to that observed in Schottky type anomalies. It seems to be a common behaviour shown by all solids, irrespective of their crystal structure. It has been stated in one of the previous paragraphs, that, as a consequence of the lattice theory of specific heats, the change in the v^2 -law of the density of normal vibrations of the frequency spectrum ensures a rise in c_v/T^3 with temperature. Some of the curves for the complex crystals seem to undergo a rising trend again above about 18°K. Others may show a similar change at still higher temperatures. The latter deviations are presumably due to the internal excitations of the groups of atoms.

The amount by which c_p/T^3 rises from its minimum value depends as has been stated, very much on the particular properties of the spectrum. Such detailed computations of the frequency spectrum of a monatomic face-centred cubic crystal lattice have been made by *Leighton* ²⁰⁾ and very recently by *Bhatia* ²¹⁾. The qualitative nature of our curves seems to be somewhat similar to their computations. *Leibfried* and *Brenig's* ¹³⁾ model applied to monatomic face-centred cubic crystals gives the same qualitative picture. The comparative study of the experimental curves in figure 4 also

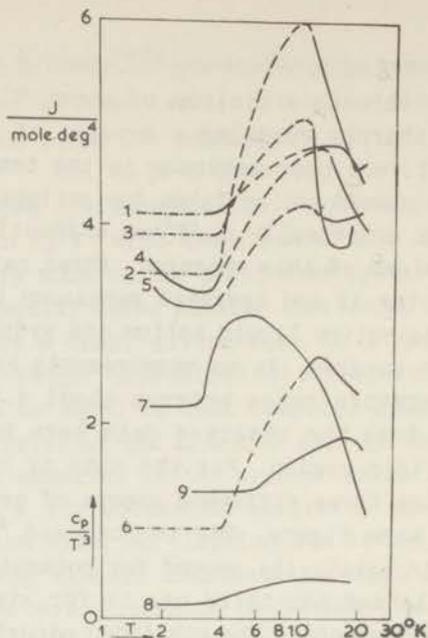


Fig. 4. C_p/T^3 as a function of absolute temperature for 1. potassium chromic alum, 2. iron ammonium alum, 3. chrome methylamine alum, 4. potassium aluminium alum, 5. ammonium aluminium alum, 6. hydrated manganous bromide, 7. lead, 8. potassium chloride and 9. zinc ammonium sulphate. The full curves have been drawn from the smoothed experimental data, the dashed curves have been drawn by arbitrary interpolation, while dashed-dotted curves represent the second term in the expression $bT^{-2} + aT^3$ which satisfactorily describes the specific heats of the four paramagnetic salts at temperatures between 1 and 4°K.

lead to a close qualitative resemblance between the curves for alums and that for lead having face-centred cubic crystal structure. Detailed computations according to any one of these models were thought inadvisable in the present case, because of the polyatomic crystal structure of the alums in which moreover, each octahedron of water molecules is believed to be slightly distorted along a trigonal axis of the unit cell. Moreover, the experimental data below 2.5°K are not of the accuracy desired and no results between 4.5 and 11°K are available for such deductions and comparisons.

In spite of the inherent difficulties and labour involved, a detailed computation of the frequency spectrum for the alums is necessary, along with the experimental specific heat data over a wide range of temperatures, for the satisfactory understanding of the observed deviations.

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Chapter IV

The low temperature specific heat and entropy of $MnBr_2 \cdot 4H_2O$

1. Introduction

The studies of antiferromagnetic H-T boundaries and apparent molecular fields for $MnBr_2 \cdot 4H_2O$ led Henry ¹⁾ to conclude that this salt undergoes an antiferromagnetic-paramagnetic transition at 2.2°K. The magnetic absorption experiments carried out by Bolger ²⁾ and the susceptibility measurements made by Gijssman ³⁾ on single crystals of this hydrated salt show rather high anisotropy, considerable deviations from the Curie-Weiss law and a critical temperature of 2.14°K (according to 1955 temperature scale) at which the transition takes place.

This type of order-disorder transition is accompanied by a continuous increase in entropy, thus giving rise to an excess of specific heat which leads to a λ -type specific heat anomaly at the transition temperature. With a view to study the behaviour of this excess specific heat characterised by the ordering of the magnetic moments of Mn^{++} ions the present investigation has been undertaken. Manganous bromide tetrahydrate has a notable advantage over the antiferromagnetic substances previously studied in this laboratory ⁴⁾⁵⁾. From the experimental point of view the anomaly in this salt is ideally situated for unambiguous studies of the nature of the magnetic specific heat contribution extending over both sides of the Néel temperature.

2. Experimental details

The experimental set up assembled for the heat capacity measurements of a series of alums was used in the present investigation. The calorimeter and its accessories have been described in chapter II. The usual precautions were taken to avoid the loss of water of crystallization while filling the calorimeter with this sample. The quantity used was 0.363 mole of polycrystalline manganous bromide, the average size of each crystal being about

30 cubic mm. In order to ensure good thermal contact 10^{-5} mole of the helium exchange gas was introduced in the calorimeter.

Because of the deliquescent nature of the crystals the filled calorimeter assembly was maintained throughout at low temperatures. The specific heat measurements were carried out in the temperature regions extending from 1 to 4.5°K and from 11 to 20°K. The 1955 temperature scale was used to convert the liquid helium bath vapour pressures against which the phosphorbronze resistance thermometer was calibrated before and after the measurements.

Corrections were applied for the heat capacity of the empty calorimeter and the exchange gas, wherever necessary. In the liquid hydrogen temperature region they amounted to about 10 % of the total heat capacity of the calorimeter filled with the material under investigation. The corrections for the same in the liquid helium temperature region were, however, completely negligible except above 2.5°K, where the values did not amount to more than 2 percent of the total heat capacity. The experimental errors have been estimated to be within 2 percent.

3. The experimental results

A. The specific heat

The experimental data extending from 1 to 20°K have been depicted graphically in figures 1 and 2. In the liquid helium temperature region the specific heat increases rapidly with temperature, its ascent becoming steeper as it approaches the antiferromagnetic-paramagnetic transition temperature. At 2.13°K it reaches a value of about 48 J/mole.deg and seems to continue its very steep ascent still further, reaches a maximum value and suddenly undergoes an abrupt descent. Within a temperature interval of ten millidegrees the specific heat appears to fall from about 48 J/mole.deg to about 12 J/mole.deg, then continues to descend gradually with increasing temperature, thus giving rise to a characteristic tail of the λ -shaped anomaly.

The experimental points representing the specific heat of the salt in the neighbourhood of the transition point reveal when carefully scrutinized, the temperature interval of 2.126 to 2.147°K in which the Néel point must lie. In order to determine the precise value of the transition temperature a separate run through the transition point was made with a continuous heat

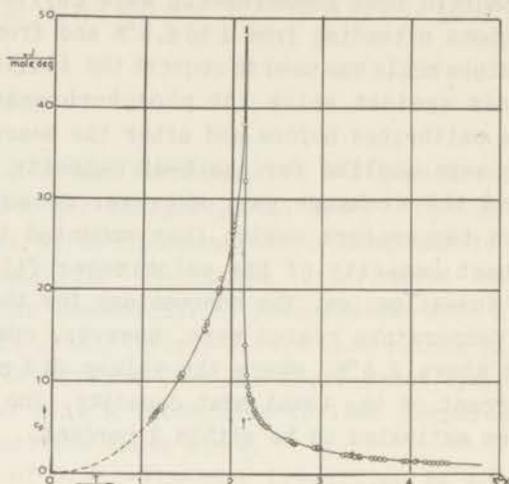


Fig. 1. The specific heat as a function of temperature below 4.5°K.

supply. The value of $(2.136 \pm 0.003)^\circ\text{K}$ was found for the Néel temperature from the resulting discontinuity in the slope of the temperature versus time curve. This value assigned to the Néel point is in good agreement with those obtained by others ¹⁾²⁾³⁾ in their investigations of the magnetic properties of this salt. A comparison of this value of the critical temperature for $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ with that for the isomorphous * $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ shows that in this case the transition temperature becomes higher the greater the mass of the combining atoms.

Because of the sharpness of the peak a quantitative estimate of the specific heat at the Néel point is rather difficult. It is certainly higher than 48 J/mole.deg, while an observed experimental point at 2.136°K gives a c_p value of 31.86 J/mole.deg which is rather too low. This point was affected by the transition which took place during the heating cycle of this experimental point. This fact is evident from the nature of its after-period.

* Private communication of Prof. Mac Gillavry to Prof. Gorter.

Moreover, the specific heat at each experimental point represents the value at the mean temperature.

The thermal anomalies of the λ -type are generally associated with the processes where there is essentially co-operative ordering. In the present case the hydrated manganous bromide undergoes a transition from the antiferromagnetically ordered state to the paramagnetically disordered state while the salt is warmed through the region of the Néel temperature. This anomaly is, therefore, presumably associated with a drastic change in the degree of order among the magnetic moments of the Mn^{++} ions. The characteristic tail formation due to the gradual decrease in the specific heat above the Néel point indicates the diminution of the short-range order that exists beyond the transition temperature at which long-range ordering disappears. The persistence of this short-range ordering above the Néel point must be connected with the observed deviations from the Curie-Weiss law.

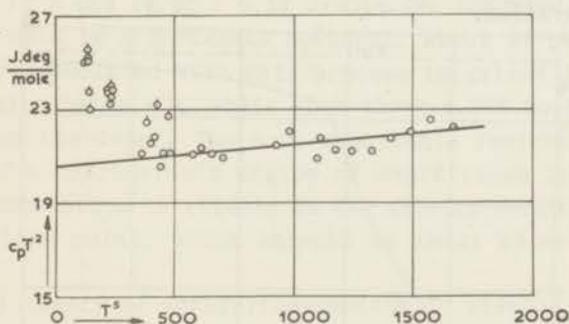


Fig. 3. $C_p T^2$ vs. T^5 plot. \odot Points used to compute the lattice- and spin specific heat constants.

To separate the magnetic contribution from the total specific heat observed in the liquid helium temperature range a quantitative estimate of the small lattice contribution is necessary. A c_p/T^3 versus T plot of the experimental data in the liquid hydrogen temperature region in which the magnetic specific heat contribution is negligibly small shows deviations from the Debye formula. Somewhat similar deviations have been observed in a number of alums ⁶⁾ the details of which are given in ch. II & III. It was, therefore, thought unadvisable to extrapolate these results to the liquid helium temperature region in order to compute the lattice specific heat below 4.5°K.

Assuming that (1) the magnetic specific heat above the Néel point is inversely proportional to the square of the temperature and that (2) the lattice contribution to it is given by a T^3 -law in this temperature region, the total specific heat can be represented by $c_p = b/T^2 + aT^3$, where b and a are respectively the spin- and the lattice specific heat constants. The Debye continuum theory as well as the lattice theory of specific heats support the second assumption, while the first is due to the belief that $MnBr_2 \cdot 4H_2O$ in the paramagnetic state obeys the relations derived by Van Vleck ⁷⁾ to describe the behaviour of a system of paramagnetic ions with magnetic dipole-dipole and exchange coupling. Figure 3 gives a plot of $c_p T^2$ vs. T^5 showing that the assumptions made are not far from reality. The experimental points deviate from linearity as the Néel point is approached. The method of least squares gives $b = 20.5 \pm 0.3$ J.deg/mole and $a = (9.36 \pm \pm 0.15) \cdot 10^{-4}$ J/mole.deg⁴. This value of a was made use of in the lattice specific heat computations in the temperature region under consideration.

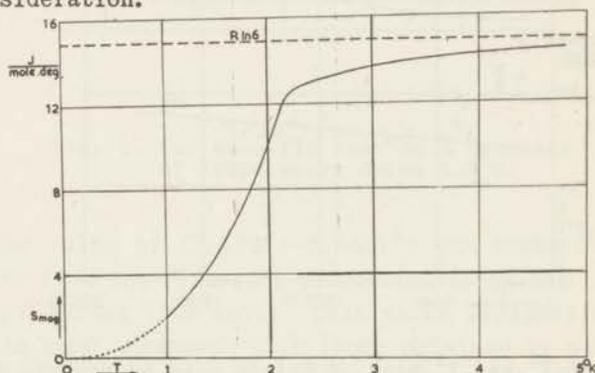


Fig. 4. The spin entropy as a function of temperature.

As the contribution due to the lattice vibrations to the total specific heat is quite small at liquid helium temperatures, a relatively large error in its determination will not affect the evaluation of the magnetic specific heat very much.

Figure 3 in one way confirms the $1/T^2$ dependence of the paramagnetic contribution to the specific heat above the Néel point, the validity of which was not clearly brought out in the heat capacity measurements of $MnCl_2 \cdot 4H_2O$ ⁵⁾, while it was taken for granted in those of $CuCl_2 \cdot 2H_2O$ ⁴⁾.

The experimental points representing the specific heat between 1 and 1.5°K satisfy the relation

$$c_{\text{mag}} = (4.57 \pm 0.06) T^{(2.30 \pm 0.01)} \quad \text{J/mole.deg}$$

the lattice specific heat being completely negligible in this temperature region. This expression was used to extrapolate the specific heat curve to 0°K. The expression $c_{\text{mag}} = (20.5 \pm 0.3)/T^2$ J/mole.deg was employed to extend the curve representing the paramagnetic contribution to infinity.

B. The spin entropy

The entropy change associated with the antiferromagnetic-paramagnetic transition in $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ is expected to be $R \ln(2S+1)$ which gives $R \ln 6$, since the ground state of Mn^{++} is ${}^6S_{5/2}$. The results of the computation of the entropy gained are shown graphically in figure 4. An excellent agreement between the expected value of $R \ln 6$ and 14.90 ± 0.18 J/mole.deg computed from the experimental data is a fortunate accident. About 14 percent of the net entropy associated with this process is gained in the extrapolated region below 1°K, while that above 4.5°K contributes only 3 percent of the total. The most remarkable feature of the persistence of a considerable degree of short range ordering above the Néel temperature is evident in the entropy contribution above the transition point, which amounts to about 20 percent of the net value.

The Néel theory of antiferromagnetism ⁸⁾ gives a rather broad specific heat peak of the magnitude of about 20 J/mole.deg at the Néel point above which the excess specific heat should, according to this theory, be zero. Thus the complete magnetic entropy of $R \ln 6$ should have been acquired at this temperature. The experimental results do not support this view. The gradual diminution of the short-range order persistent above the Néel point and the very sharp specific heat peak observed at this temperature seem to be a common feature of antiferromagnetic-paramagnetic transitions and should be properly accounted for in a satisfactory theory of antiferromagnetism.

It is curious to note that at least for $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$; $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ the spin specific heat constant b varies directly as the square of the Néel temperature, the constant of proportionality being about 4.5 J.deg/mole. The excess specific heat

data of *Friedberg* and *Wasscher* ⁵⁾ for hydrated manganous chloride and those of manganous bromide of the present investigation fail to agree when plotted in reduced coordinates (c/R versus T/T_N). The former give rather systematically bit low values. This discrepancy might perhaps be due to a shift in the calibration curve and to somewhat poor accuracy of their experimental data.

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Samenvatting

Deze dissertatie behandelt de soortelijke warmte van verscheidene stoffen bij lage temperaturen. Aangezien de onderzochte problemen verschillend van aard zijn, vormt elk hoofdstuk een apart geheel. In elk hoofdstuk vindt men, na een uiteenzetting van het doel van het behandelde onderzoek, de experimentele bijzonderheden, een overzicht van de behaalde resultaten en de discussie daarvan.

Het eerste hoofdstuk betreft de soortelijke warmte van vloeibaar Helium II en vloeibare mengsels van ^3He en ^4He . Een korte behandeling van een nieuwe methode, speciaal ontwikkeld met het oog op de geringe hoeveelheden mengsels (paragrafen 1 en 2), wordt gevolgd door een vergelijking van de experimentele gegevens voor de soortelijke warmte en de entropie van vloeibaar Helium II (paragraaf 3 A) met die van verschillende andere onderzoekers. De resultaten van onze experimenten bevestigen die van *Kramers et al.*

In § 3B vindt men een verslag van onze metingen en de behaalde resultaten voor drie verschillende concentraties van ^3He en ^4He (tot 7,13 % ^3He) in het temperatuurgebied van ongeveer 1 tot 2,2°K. De soortelijke warmte van het mengsel hangt lineair af van de concentraties van ^3He (fig. 6), terwijl de temperatuurafhankelijkheid ongeveer dezelfde is als die van zuiver ^4He . De extra bijdrage tot de soortelijke warmte ten gevolge van het bijmengen van ^3He in ^4He (hier meng-soortelijke warmte genoemd) wordt betrekkelijk groot in de buurt van het Θ -punt van het mengsel.

Vergelijking van de verkregen gegevens met de bestaande theorieën wijst uit, dat slechts een min of meer bevredigende overeenstemming gevonden wordt met het door *Mikura* voorgestelde, gewijzigde *Bose-Einstein* model van de heliumvloeistof (§ 3C). De metingen betreffende de λ -temperaturen worden in de laatste paragraaf behandeld. Zij blijken een verschuiving te vertonen van -1,48 graden per grammeconcentratie, hetgeen in uitmuntende overeenstemming is met de door *King* en *Fairbank* behaalde resultaten met second sound en de experimenten van *Dash* en *Taylor* met een slingerende bol.

De soortelijke warmte van drie paramagnetische aluinen wordt

in hoofdstuk II behandeld. Deze werden gemeten op de voor lage temperaturen gebruikelijke methode (met de adiabatiscbe calorimetrie voor lage temperaturen). De resultaten tussen 1 en 4.2 °K worden bevredigend voorgesteld door de betrekking $C_p = b/T^2 + aT^3$, waarin het eerste, respectievelijk het tweede lid, de rooster- en spinsoortelijke-warmtes aangeven (§ 3A). De karakteristieke Debye-temperatuur θ en de kristalsplitsingsfactor δ zijn voor elk van de aluinen berekend; de laatste werden vergeleken met de overeenkomstige waarden, verkregen uit experimenten met paramagnetische relaxatie, paramagnetische resonantie en adiabatiscbe demagnetisatie. De θ -waarden zijn 77,9, 82,3 en 79,2 °K, terwijl voor δ werd gevonden 0,247, 0,192 en 0,273 °K resp. voor kaliumchromaluin, ferriammoniumaluin en chrommethylamine-aluin. Een vergelijking van de thermische Debye-temperaturen met die berekend uit de beschikbare elastische constanten, leidt tot de conclusie dat het werkelijk T^3 -gebied voor de aluinen wellicht bij de demagnetisatie-temperaturen ligt. Schottky-afwijkingen van de Debye-formule zijn voor deze aluinen waargenomen (discussie in hoofdstuk III) in het gebied van de waterstoftemperaturen (§ 3E).

Bij lage temperaturen werd eveneens de soortelijke warmte van twee diamagnetische aluinen gemeten, waarvan het verslag te vinden is in het derde hoofdstuk. De resultaten in het gebied van vloeibaar helium werden voorgesteld door een T^3 -wet. De θ -waarden zijn resp. 83,4 en 84,9 °K. De afwijkingen van de Debye-formule, welke waargenomen zijn bij para- en diamagnetische aluinen (fig. 4), worden besproken in het licht van de roostertheorie van de soortelijke warmte.

De resultaten van de soortelijke warmte van $MnBr_2 \cdot 4H_2O$ in de paramagnetische en anti-ferromagnetische toestand zijn weergegeven in het laatste hoofdstuk. De soortelijke warmte bleek duidelijk een verschijnsel te vertonen, analoog aan het λ -verschijnsel hetgeen wijst op een antiferromagnetische-paramagnetische overgang; het Néel-punt bleek 2,136 °K te zijn. De staartvorming, kenmerkend voor een geleidelijke vermindering in de soortelijke warmte boven het Néel-punt, wijst op het blijven bestaan van een korte afstands-ordening boven de overgangstemperatuur. De netto verandering van de entropie bij dit proces bleek ongeveer $14,9 \text{ J m}^{-1} \text{ grd}^{-1} = R \ln 6$ te zijn, waarvan een vijfde deel boven dit Néel-punt plaats vindt.

Stellingen

I

Het verdient aanbeveling de soortelijke warmte van mengsels van ^3He en ^4He boven het λ -punt te bepalen.

II

Het door *Van Dijk* en *Keesom* opgegeven maximum in de soortelijke warmte van ferri ammonium aluin is waarschijnlijk toe te schrijven aan verontreiniging met ferro ammonium sulfaat.

Van Dijk H. and Keesom W.H., *Physica* **7** (1940) 970.

III

Het is van belang de soortelijke warmte van antiferro-magnetische stoffen in uitwendige magneetvelden te onderzoeken.

IV

De wijziging, die *Nanda* heeft aangebracht in de formules van *De Boer* en *Gorter* voor de thermodynamische grootheden van vloeistofmengsels van ^3He en ^4He is in sommige opzichten beneden de overgangstemperatuur geen verbetering; een enigszins analoge wijziging kan echter wel een verbetering geven.

Nanda V.S., *Phys. Rev.* **97** (1955) 571.

V

Het is wenselijk, dat de soortelijke warmte van de aluinen tussen 4 en 12°K gemeten wordt.

VI

Onze voorlopige onderzoeken in het temperatuurgebied van vloeibaar helium tonen aan, dat een anomalie optreedt in de soortelijke warmte van vast deuterium, welke overeenkomst vertoont met die welke door *Hill*, *Ricketson* en *Simon* in vaste waterstof is waargenomen.

Hill R.W., Ricketson B.W.A. and Simon F., *Rept. Conf. Phys. basses Temp. Paris* (1955) 317.

VII

Een onderzoek van de magnetische susceptibiliteit van vast ^3He in het temperatuurgebied beneden 0.5°K zou nuttig zijn.

VIII

Op het gebied van kleinbeeldfotografie is de laatste bijdrage van het Ernst Leitz model *Leica M₃* een goede benadering van een volmaakte camera.

IX

De uitdrukking

$$\Delta \log \left(\frac{1}{A} \frac{dq}{d\theta} \frac{d\theta}{dt} \right) = (n - 1) \Delta \log D$$

kan worden afgeleid uit de vergelijking van Nusselt. Deze is experimenteel geverifieerd voor lichamen van verschillende vorm en afmetingen in een homogene evenwijdige luchtstroom. Uit deze betrekking volgt, dat zeer dunne draden gebruikt moeten worden om de temperatuur van het stromende medium met een thermoëlement te meten.

Kapadnis D.G., *Ind.J.Phys.* **27** (1953) 77; *Ibid.* **29** (1955) 296.

X

De beweging van landschenking, waartoe *Vinoba Bhave* in *India* het initiatief nam, vormt een vruchtbare bodem voor democratisch socialisme, gebaseerd op liefde en offer.

XI

Het tientallig stelsel is, zowel wat de getalsymbolen betreft, als wat betreft de plaatsing van de cijfers, het eerst geformuleerd en gebruikt door de Hindoe-wiskundigen. Het duurde geruime tijd eer zij vanuit *India* via *Bagdad* de westerse wereld bereikten.

Smith D.E. and Karpinsky L.C., *The Hindu-Arabic Numerals*, Ginn & Co. (Boston, 1911).

Datta B. and Singh A.N., *History of Hindu Mathematics*, (1935).

Hogben L., *Mathematics for the Million* (London, 1942).

XII

Achter de verscheidenheid van de zes Brahmaanse stelsels der filosofie in *India*, de zogenaamde *Darshanas* (*Nyaya*, *Vaishesika*, *Samkhya*, *Yoga*, *Mimansa* en *Vedanta*), schuilt een gemeenschappelijke achtergrond, die nationale en algemene filosofie genoemd kan worden en waaruit de denkers der verschillende stelsels ieder naar eigen inzichten putten.

XIII

Het vrijwel ontbreken van studententehuizen in *Nederland* moet als een gemis beschouwd worden voor de karaktervorming der studenten.

