The low temperature heat capacities of potassium chloride, nickel and gadolinium sulfate

C. W. CLARK

THE LOW TEMPERATURE HEAT CAPACITIES OF POTASSIUM CHLORIDE, NICKEL AND GADOLINIUM SULFATE

THE LOW TEMPERATURE HEAT CAPACITIES OF POTASSIUM CHLORIDE, NICKEL AND GADOLINIUM SULFATE

PROEFSCHRIFT

TER VERKRIJGING VAN DEN GRAAD VAN
DOCTOR IN DE WIS- EN NATUURKUNDE
AAN DE RIJKSUNIVERSITEIT TE LEIDEN, OP
GEZAG VAN DEN RECTOR MAGNIFICUS
Dr. W. VAN DER WOUDE, HOOGLEERAAR IN
DE FACULTEIT DER WIS- EN NATUURKUNDE,
VOOR DE FACULTEIT DER WIS- EN NATUURKUNDE TE VERDEDIGEN OP VRIJDAG 12
JULI 1935 DES NAMIDDAGS TE 2 UUR

DOOR

CHESTER WILLIAM CLARK,

GEBOREN TE SAN FRANCISCO

DRUKKERIJ OUDSHOORN — LEIDEN — 1935

AAN MIJN OUDERS
AAN JESSIE MAY

Promotor: Prof. Dr. W. H. KEESOM

CONTENTS

INTRODUCTION.

In common with other branches of experimental science, the study of specific heats is a study of exceptions to a "normal" behavior. A normal behavior is determined by a sufficiently large group of substances following this behavior to within a reasonable degree of accuracy, the latter depending on the type of research and the state of perfection of the technique available. There is therefore usually sufficient confirmation for the normal behavior and further measurements showing similar behavior, while furnishing substantiation and strengthening the explanatory hypothesis advanced, do little to uncover other new and interesting phenomena. It is the finding and explanation, or attempted explanation, of exceptions to the normal behavior which stimulate new lines of thought and suggest other subjects for investigation.

When, in 1819, P. L. DULONG and A. T. PETIT advanced their law that the product of the specific heat and atomic weight is approximately a constant for nearly all the solid elements, there were already exceptions noted, which could not at the time be explained. Subsequent work at lower temperatures demonstrated that these exceptions were but easily found examples of a general behavior, a new normal behavior.

SCHRÖDINGER, about a year ago, wrote that, "Thirty years ago nobody was particularly interested in asking how the thermal capacity of a body changes with the temperature . . . . . . But once NERNST put forward his famous 'third law of thermodynamics', the whole situation suddenly altered." These sentiments were more recently echoed by LINDEMANN. This is true in a certain sense; the interest of chemists was drawn to the study of heat capacities at low temperatures. Actually I think such experiments followed rather closely upon the availability of the necessary low temperatures. Within about two or three years after the perfection of the Linde air liquefier, U. BEHN in Berlin had published the results of heat capacity measurements on some eight metals down to liquid air temperatures. His article ended with the remark, "Stellt man die Abnahme der specifischen Wärmen mit der Temperatur graphisch dar, so erscheint es als möglich, dass sämmtliche Curven bei der absoluten Temperatur 0° sich schneiden, dass also die specifischen Wärmen dort alle den gleichen sehr kleinen Werth (0?) annehmen".

Although this behavior was further well substantiated, principally by the work of DEWAR and by the many experiments of NERNST and his collaborators, there was as yet no quantitative explanation presented.

In the study of radiation, there was an outstanding anomaly which defied explanation by means of the then existent theories. Why was the energy of the radiation from a black body not concentrated in the short wave region of the spectrum? The genius of PLANCK supplied the answer, out of which so much was to grow. From the explanation of this exception the fertile mind of EINSTEIN found the key to the classically unexplainable observations of the manner in which the energy of certain substances varied with temperature. DEBIJE, whose influence has been felt in so many fields of physical science, amplified and refined this explanation, and provided *the* normal behavior which has withstood the attacks of now vigorously agressive experimental groups the world over for many years.

The discovery at Leiden of the remarkable thermometric properties of certain wires of phosphor-bronze, an alloy formerly valued only because it made excellent springs, has given an invaluable tool to workers interested in the energy of material systems at very low temperatures. Since a temperature rise of the order of magnitude of 0.02° or less at liquid helium temperatures may now be accurately determined, the measured heat capacity very closely approaches the defined quantity $\frac{dQ}{dT}$. The heat capacity being determined, it is compared with the "DEBIJE specific heat", and if there is a difference, it is to be explained.

Thus we find the study of heat capacities offering data, through the disclosure of "anomalies," to those who are studying the behavior of electrons in metals, magnetism, phase changes and supraconductivity.

I find that others have expressed the aim of specific heat work in a far better manner, and in fewer words, than I am able to do. In 1819 PETIT and DULONG wrote, " . . . . . it is absolutely indispensable to clarify the question of specific heats as much as possible, and from it, to deduce all the conclusions to which it can lead concerning the knowledge of the structure of bodies".

CHAPTER I.

THEORY OF VIBRATIONAL HEAT CAPACITIES.

All general considerations of specific heat work begin with the work of DULONG and PETIT and the repetition of their experimentally found law that, "The atoms of all simple bodies have exactly the same capacity for heat"[1]). This is justly so. Their experimental work was of a high degree of accuracy, (they claimed an accuracy of 0.005° in the reading of temperatures) and they were well aware of the advantage of carrying out a series of similar researches under exactly reproducible conditions. With but few exceptions, previous work had yielded a rather confused jumble of figures, with differences between values given by different workers amounting at times to 200—300%. Furthermore, the aim of their work, quoted in the introduction of this thesis, although originally enunciated more than a century ago, is still valid. It is unfortunate that this brilliant collaboration was broken up by the death of Petit in 1820 when only 29 years of age.

This law, that the atomic heat[2]) of monatomic solids is equal to approximately 6.2 cal/deg. was first given a theoretical foundation by BOLTZMANN[3]). In the classical kinetic theory the

---

[1]) A. T. PETIT and P. L. DULONG, Ann. Chim. Phys., **10**, 395, 1819.

[2]) Heat capacity is used in the most general sense, the thermal reaction of bodies to the addition of heat energy, excluding, however, changes of state. Specific heat is used as the abbreviation for the longer term, specific heat capacity, usually referred to one gram of a substance; but often also when speaking in a general sense. Similarly, atomic heat means atomic heat capacity, but without reference to the constancy of any variables.

[3]) L. BOLTZMANN, Wiss. Abh., **1**, p. 288; Wien. Ber., **63** (2), 731, 1871.

MAXWELL law of the equipartition of energy tells us that the average kinetic energy of a degree of freedom is $^1/_2\,kT$, or when referred to a gram-atom, $^1/_2\,RT$. Corresponding to the three coordinate axes, each atom has three degrees of freedom, so the average kinetic energy of 1 gram-atom of a solid is equal to $^3/_2\,RT$. There is also a potential energy since the particle is assumed to perform a simple, harmonic vibration about a rest point, under the influence of a restoring force. If the restoring force follows the simple HOOKE's law, the average potential energy is equal to the average kinetic energy. The total energy content of a gram-atom is then $U = 3\,RT$ or $C_v = \left(\frac{\partial U}{\partial T}\right)_v = 3\,R = 5.959$ cal/deg., thus independent of temperature.

The difference between 6.2 and 5.959 is, of course, the difference between the measured C_p and the calculated C_v. The present considerations deal only with the energy content of a body in virtue of the vibrations of its constituent parts, or the vibrational heat capacity.

The measurements of BEHN, definitely showing that specific heats of solids were not independent of temperature, have already been mentioned in the introduction¹). DEWAR extended specific heat measurements down to the temperatures attainable with liquid hydrogen, and it was decided that the C_p *vs* T curve had the form "of an old English S".

In 1900 PLANCK proposed the idea that the average total energy of a harmonically vibrating particle was not simply kT, but $U = \dfrac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$. This formula was derived for electrically charged oscillators emitting electromagnetic waves, but EINSTEIN saw that it could be applied equally as well to the vibrations of atoms in solids vibrating about their equilibrium positions²).

---

¹) U. BEHN, Wied. Ann., **66**, 237, 1898.

²) A. EINSTEIN, Ann. d. Phys., **22**, 180, 800, 1907.

Assuming that all atoms in a body vibrate with the same frequency, ν, one gram-atom possesses the energy

$$U = 3N \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} = 3RT \frac{\frac{h\nu}{kT}}{e^{\frac{h\nu}{kT}} - 1} = 3RT \frac{\frac{\theta}{T}}{e^{\frac{\theta}{T}} - 1} \tag{1}$$

in which θ has been introduced in place of $\frac{h\nu}{k}$. From this, the atomic heat is obtained immediately,

$$C_v = 3R \frac{\left(\frac{\theta}{T}\right)^2 e^{\frac{\theta}{T}}}{\left(e^{\frac{\theta}{T}} - 1\right)^2}. \tag{2}$$

This is generally known as the EINSTEIN function. The values of θ were chosen from experimental data to give the best agreement between the observed and calculated values. The function represented the general course of the observed specific heat curves quite well, but it soon appeared that systematic deviations set in at low temperatures. EINSTEIN recognized that the assumption of a monochromatic vibration frequency was necessarily incorrect and the deviations were attributed to this fact. Nevertheless, it was a great advance in the theory of specific heats, and pointed the way for future developments.

NERNST and LINDEMANN[1]) found that if one assumed that half of the atoms vibrated with a frequency ν and half with a frequency $\frac{\nu}{2}$, the resulting formula for C_v represented the course of the experimental values quite well. Its range of validity was much greater than the EINSTEIN formula, but at low temperatures the deviations from the experimental values began to be rather large. It showed, nevertheless, that the assumption of more than one vibration frequency was more nearly correct.

Since the motion of an atom in a solid is influenced by the motions of its neighbors, the motions of the atoms in a solid

---

[1]) W. NERNST and F. A. LINDEMANN, Berl. Ber., 494, 1911.

are necessarily very complicated. It is impossible to determine precisely the spectrum of the vibration of the atoms in a body. Approximations and simplifying assumptions must be introduced in order to be able to handle the problem at all.

The success of the DEBIJE theory over a period of many years is excellent proof that the assumptions made by DEBIJE were not far from the true state of affairs within the type of body he treated.

DEBIJE ¹) assumed firstly that the body could be treated as a continuum. In this way, elastic theory as applied to a continuum could be employed for the analysis of the modes of vibration within the body. It was further assumed that the radiation principle of RAYLEIGH-JEANS, that the number of modes of vibration, dZ, lying in a given frequency range, $d\nu$, is proportional to $\nu^2 d\nu$, was applicable to a solid continuum, as well as to the vacuum or aether for which it was derived. A third assumption was that the spectrum was characterized by its upper limit, ν_m, determined by the limitation of the total number of modes of vibration to $3N$ per gram-atom and the application of the relation $dZ \propto \nu^2 d\nu$.

In the solid, there will be both longitudinal and transverse wave motions, and from the principle of RAYLEIGH-JEANS,

$$dZ = 8\,\pi V \left(\frac{1}{C_t^3} + \frac{1}{2\,C_l^3} \right) \nu^2 d\nu, \tag{3}$$

C_t and C_l being the velocities of the wave motions in transverse and longitudinal directions respectively.

According to the third assumption $\int_0^{\nu_m} dZ = 3\,N$; performing the integration, solving for ν_m, and substituting back in (3), we find

$$dZ = \frac{9N}{\nu_m^3}\,\nu^2 d\nu \tag{4}$$

---

¹) P. DEBIJE, Ann. d. Phys., **39**, 789, 1912.

We find then that the total vibrational energy of the body is the integral of equation (4), multiplied by the **Planck** expression for the average energy of any harmonic oscillator of frequency ν. For simplicity, the usual symbols, $\theta = \frac{h\nu_m}{k}$ and $x = \frac{h\nu}{kT}$ are introduced. For 1 gram-atom then

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = 9R\left[4\left(\frac{T}{\theta}\right)^3 \int_0^{\frac{\theta}{T}} \frac{x^3}{e^x - 1}\, dx - \frac{\theta}{T}\,\frac{1}{e^{\frac{\theta}{T}} - 1}\right]. \quad (5)$$

The indicated integration cannot be expressed in finite terms and for an actual evaluation it must be expressed in series. Actually, one always makes use of the published tables of this function[1]).

According to **Debije** then, the heat capacity and energy of such simple solids is a function of a single parameter θ, which is, as will be discussed later, dependent solely on the elastic properties of the solid. The parameter θ has the dimensions of temperature and is usually referred to as the characteristic temperature.

At high temperatures, the function approaches the classical value $3R$, and at low temperatures, the famous T^3 law, valid in the range $\frac{\theta}{T} \geqq 12$, is obtained.

Almost simultaneously with the **Debije** theory, a similar theory due to **Born** and **von Karman**[2]) was deduced. These authors took the crystal lattice of the substance into consideration, and by means of an extremely involved and difficult mathematical analysis, calculated the vibrational spectrum of the body. This theory is based on more fundamental grounds than the **Debije** theory, but there are only data enough available to permit its

---

[1]) W. **Nernst**, Grundlagen des neuen Wärmessatzes, pp. 200—207.
Handbuch d. Physik, Vol. **10**, p. 367.
Landolt-Börnstein, Ergänzungsband, 1927, p. 705.

[2]) M. **Born** and **Th. v. Karman**, Phys. Zs. **13**, 297, 1912; **14**, 15 and 65, 1913. There was apparently only a difference of a few days in the publication of the theory of **Debije** and that of the latter.

application to relatively few substances. The principal differences between this theory and that of DEBIJE occur at high temperatures. The assumption of a continuum and a continuous distribution of frequencies according to the RAYLEIGH—JEANS formula is no longer valid when the higher frequencies are excited. The shorter wave lengths are then more comparable with the distances apart of the atoms in the lattice and dispersion effects occur, introducing a tendency for the frequencies to pile up toward the high frequency end of the vibrational spectrum. At low temperatures, however, this theory also furnishes the same T^3 law as the DEBIJE theory.

At low temperatures, i.e., as $\frac{\theta}{T} \rightarrow \infty$, the second term in the brackets in eq. (5) approaches zero and when the integration limits for the other term are changed to 0 and ∞, one can obtain

$$C_v = 3\,Nk\;\frac{12\,\pi^4}{15}\left(\frac{T}{\theta}\right)^3 = 464.4\left(\frac{T}{\theta}\right)^3. \qquad (6)$$

This approximation begins to deviate from eq. (5) at about $\frac{\theta}{T} < 12$. Most low temperature measurements have followed this law quite well although a number of deviations, quite beyond the experimental error, have been noted[1]).

It has generally been considered, however, that the T^3 law should be more correct than the more complicated function derived for higher temperatures. At low temperatures, only the low frequency or long wave length vibrations have any appreciable energy, and as these are long compared to the inter-atomic distances, dispersion effects may be neglected and the body treated as a continuum.

Recent theoretical considerations by BLACKMAN in which a geometrical method of analysis is employed, have indicated that in simple cubic crystals of the $NaCl$ type, the distribution of

---

[1]) W. H. KEESOM and H. KAMERLINGH ONNES, Comm. Leiden, No. 147a.
W. H. KEESOM and J. N. v. D. ENDE, Comm. Leiden, Nos. 213c and 219b.
W. H. KEESOM and J. A. KOK, Comm. Leiden, No. 219d.

frequencies in the elastic spectrum is controlled by two parameters[1]). This furnishes two separate frequency distribution curves for the substance, whose sum yields a curve showing two maxima. If the spectrum is approximated by assuming the two maxima to represent monochromatic frequencies, expressions for the vibrational energy and heat capacity of the NERNST-LINDEMANN type are obtained.

This analysis has been so far applied only to the $NaCl$ type of crystal and will be considered further in Chapter III.

It must be borne in mind that all these considerations deal only with the energy content of a body in virtue of the oscillations of its constituent particles and under certain assumptions and limiting conditions. At high temperatures, for example, the vibrations become so violent that the force of restitution can no longer be represented by the simple HOOKE's law, and deviations will occur.

Excluding physical changes of state, there are still other causes which introduce additional energy terms which are of importance at low temperatures. Metals, on becoming supraconductive, show a discontinuity in heat capacity; ferromagnetics have an additional energy term in virtue of their intrinsic magnetization; the free electrons in metals and the "term splitting" in paramagnetics contribute to the heat capacity. There is also the sharp rise in the heat capacities of certain salts and solid gases, as yet not fully explained, similar to the lambda phenomenon in liquid helium. Some of these are of interest in connection with the present measurements and will be considered as they are encountered.

---

[1]) M. BLACKMAN, Proc. Roy. Soc. London, (A) **148**, 365, 1935; **149**, 117, 1935.

CHAPTER II.

EXPERIMENTAL METHODS AND APPARATUS.

This work deals with the low temperature heat capacities of $Gd_2(SO_4)_3 \cdot 8H_2O$, KCl and Ni. The experimental arrangements are the same for the first two substances, but necessarily somewhat different for Ni. The following discussion will first treat the experimental methods for the crystalline compounds and then those for Ni, insofar as they differ from the first mentioned.

§ 1. General.

The idea of a vacuum calorimeter seems to have originated with PETIT and DULONG. Their polished silver calorimeter was suspended in a space in which the air was exhausted to a pressure of 2 mm "to reduce the rate of cooling for the purpose of ease of observation". JOULE, after his discovery of the relation between mechanical and electrical energy units, was the first to suggest the use of electrical heating in calorimetry.

These two ideas seem not to have been combined and applied to specific heat work until about 1896 when CALLENDAR[1]) developed his method of continuous electric calorimetry for the investigation of the heat capacity of H_2O and Hg. He "regarded the vacuum jacket as a most essential part of the experiment and expected a great improvement to result from its use".

When the knowledge of low temperature heat capacities became of importance in connection with the NERNST heat

---

[1]) H. L. CALLENDAR, Phil. Trans. Roy. Soc., A **199**, 55, 1902.
cf. also W. JAEGER and H. DIESSELHORST, Wiss. Abh der P.T.R. III, 269, 1900.

theorem, EUCKEN[1]) applied the combination of a calorimeter suspended in a vacuum and electric heating to the measurement of the low temperature heat capacities of several inorganic salts.

The advantages of such a system are obvious. Under good experimental conditions the heat exchange between the calorimeter and its surroundings, due to gaseous conduction, can be practically eliminated by maintenance of a high vacuum in the space surrounding the calorimeter. This is especially important at low temperatures, where, because of the small heat capacities, a quantity of energy furnished to the calorimeter would be quickly dissipated to the surroundings if any gas were present.

There remains only the heat exchange through radiation and conduction to or from the calorimeter along the connecting wires and suspension device. Since its original use, this type of calorimeter has naturally undergone much development and its form and the disposition of its constituent parts is varied to permit adaptation to the particular use for which it is desired. This method has been used in these experiments.

The quantities which must be experimentally determined are (1) the temperature rise in the system under consideration, (2) the energy supplied which caused the temperature rise, and (3) the average temperature over which this rise occurred.

Numbers (1) and (3) are usually determined by the same thermometric device, which is sometimes also used as the intermediary for supplying the energy in (2).

§ 2. Experimental Details.

a. The thermometer. For low temperature calorimetric work, the helium or hydrogen gas thermometer, the resistance thermometer or thermo-electric couple may be used. A research program is at present under way at the KAMERLINGH ONNES Laboratory for the investigation of thermo-electric couples at liquid helium

---

[1]) A. EUCKEN, Phys. Zs. **10**, 586, 1909.

temperatures[1]), but in practice, the thermo-electric couple is not used in calorimetry at these temperatures because of its lack of sensitivity. The helium gas thermometer may be used for temperature measurements down to a little below 1°K[2]), but for calorimetric measurements it is in general not practicable because of its inherent slowness[3]).

For resistance thermometers at low temperatures, platinum, gold, lead, constantan, manganin and phosphor-bronze wires are used. Recent measurements have shown that cadmium can also be employed. Lead becomes supraconductive at 7.2°K and requires an external magnetic field for its use below this temperature; this is not always convenient or desirable. At helium temperatures, the ratio R_T/R_0 of platinum has become so small that it is difficult to make accurate temperature measurements with its aid without having taken an inconveniently large resistance at room temperature. It is still very good at liquid hydrogen temperatures. Constantan and manganin retain most of their resistance down to helium temperatures but have the disadvantage of a rather small $\frac{dR}{dT}$ per ohm, which makes it difficult to determine accurately small changes in temperature. The discovery of the very desirable thermometric properties of certain samples of phosphor-bronze[4]) wire has greatly increased the fineness of work possible at liquid helium temperatures. Accurate determinations of temperature rises of the order of 0.003° have been made in specific heat measurements. It has thus been possible to determine the precise course of the specific

---

[1]) G. Borelius, W. H. Keesom and C. H. Johansson, Comm. Leiden, No. 196a.
G. Borelius, W. H. Keesom, C. H. Johansson and J. O. Linde, Comm. Leiden, Nos. 206a, b; 217c, d, e.
W. H. Keesom and C. J. Matthys, Comm. Leiden, No. 238b.

[2]) W. H. Keesom, Sophus Weber and G. Schmidt, Comm. Leiden, No. 202c.
W. H. Keesom and G. Schmidt, Comm. Leiden, No. 226b.

[3]) See however N. Kürti, Zs. f. Phys. Chem. B. **20**, 305, 1933, where clever and ingenious use is made of a helium gas thermometer for calorimetric measurements down to 1.6°K.

[4]) W. H. Keesom and J. N. v. d. Ende, Comm. Leiden, No. 203c.

heat curve of liquid helium in the vicinity of the "lambda-point"[1]), and the specific heat of thallium[2]) in the region around its supraconductive transition point. While at higher temperatures a ΔT of 1° or more is quite acceptable for determining true specific heats with but very little error, it is obvious that in the cases above mentioned a ΔT of even 0.05° would have yielded erroneous results. The disadvantages of phosphor-bronze are that its $\frac{dR}{dT}$ becomes zero in the vicinity of 7°K, its resistance is greatly affected by a magnetic field, and its resistance is dependent on the measuring current.

In this work phosphor-bronze (hereafter called *Ph-br*) and constantan wires were used. The necessity of making measurements in the range from 6-10°K required the adoption of constantan in preference to gold or platinum, the usual thermometer in the liquid hydrogen region[3]). The *Ph-br* had a resistance of about 16 ohms at 4.2°K and 13.7 ohms at 1.2°K. The $\frac{dR}{dT}$ per ohm was 0.0572 at 4.2°K and 0.0516 at 1.2°K. It was used in all measurements below 6°K, usually with a measuring current of 0.51 milliamperes. The constantan wire, which was used in measurements above 6°K, had a resistance of 10.651 ohms at 20.4°K, 10.586 ohms at 14°K and 10.461 ohms at 4.2°K, the corresponding $\frac{dR}{dT}$ per ohm being 0.000794, 0.001092 and

---

[1]) W. H. KEESOM and Miss A. P. KEESOM, Comm. Leiden, Nos. 221d; 235d.

[2]) W. H. KEESOM and J. A. KOK, Comm. Leiden, Nos. 230c, e; 232a.

[3]) The $\frac{dR}{dT}$ of gold tends toward zero below 10°K. Platinum has desirable thermometric properties in this range, but in order to have a resistance of 1 Ω at 10°K one would have to begin with about 1600 Ω at 0°C. The R *vs* T curve of cadmium is similar to that of platinum in this region; to have 1 Ω at 10°K would require about 200 Ω at 0°C. For calorimetric purposes, it is necessary to have a thermometer with an appreciable resistance in the range where it is used, as well as a large $\frac{dR}{dT}$. Otherwise the current necessarily employed to measure the potential drop with sufficient accuracy would develop too much heat in the wire.

0.001048. A measuring current of 1.02 milliamperes was used.

The two wires were connected in series but were so arranged that the resistance of each could be determined separately. A common current carrying wire was soldered to the junction of the *Ph-br* and constantan thermometers and at either end of the resistances, two more wires were soldered, one of each for current carrying, and the other two for determining the potential drop across the system. The measuring current could then be made to pass through either thermometer, and the resistance was determined by comparing the potential drop across the thermometer in question, with that across a standard 10 ohm resistance by means of a Diesselhorst compensation apparatus, with the aid of a Zernike or Diesselhorst galvanometer. No attempt was made to employ a null-method, the differences from exact compensation being found from the sensitivity of the galvanometer in the usual manner. This was such that under usual experimental conditions 1 cm on the scale was equivalent to about 0.01°K, this figure varying slightly, of course, with the change in $\frac{dR}{dT}$. In the case of the constantan wire, however, 1 cm was equal to about 0.05°K.

In the temperature ranges available through the use of liquid and solid hydrogen and liquid helium, 20.4° to about 12°K and 4.2° to 1.1°K respectively, the thermometers were calibrated by direct comparison with these substances in equilibrium with their saturated vapour at different pressures. The temperatures were determined from the vapour pressure formulae[1]). (Below about 12°K one is never certain of temperature equilibrium throughout the solid hydrogen). For the calibration of the range between 4.2° and 12°K, the calorimeter, with the thermometer in place (see paragraph *c*) was provided with a capillary and a manometer system and used as a constant volume helium gas thermometer. This was calibrated in the

---

[1]) W. H. Keesom, Sophus Weber and G. Schmidt, Comm. Leiden, No. 202c.
W. H. Keesom, Comm. Leiden, No. 219a.
W. H. Keesom, A. Bijl and Miss H. v. d. Horst, Comm. Leiden, No. 217a.

liquid helium and hydrogen ranges at the same time as the first thermometer calibrations and the P *vs* T curve was very nearly a straight line. An empirical procedure of this type avoids the necessity of correcting for the noxious volume of the capillary, since the temperature differences within the cryostat must be rather small and the ratio of the volume of the gas thermometer to that of the capillary is large, 93 to 0.088. It is then simply a matter of reading the pressure of the gas thermometer and the resistance of resistance thermometers simultaneously, and reading the corresponding temperatures from the P *vs* T curve. The calorimeter was brought to and maintained at the desired pressure (or temperature) by proper manipulation of the current through the heating wire.

The results of the calibrations were treated in the following way. A large scale graph of R against T was prepared and the values of R for each 0.1° were tabulated (for *Ph-br*, each 0.05°). The first differences, ($\frac{\Delta R}{\Delta T}$, for the range considered) and second differences were smoothed, and then assuming one of the calibration points as fixed, the other R's for each 0.1° or 0.05° were calculated from the smoothed $\frac{\Delta R}{\Delta T}$ values. The calculated curve is made to agree with the observed one to within 0.002°K and cumulative differences are avoided so that $\Sigma \frac{\Delta R}{\Delta T} \Delta T$ over the whole range is equal to the observed ΔR over the same range.

One is thus provided with a tabulation of the values of R for the thermometer for each 0.05° or 0.1° and also with the values of the $\frac{dR}{dT}$ over the whole range; the temperature corresponding to any observed resistance may then be calculated. This is no artificial procedure but serves to eliminate the errors of calibration and personal errors in reading from graphs.

The resistances of the *Ph-br* and constantan thermometers did not remain constant but on each measuring day showed a small increase over that of the previous measuring day. This necessitated a calibration of the thermometers at the end of each measuring day. The change was not caused by the magnetic fields used in the measurements. A check calibration at 4.2°K showed exactly the same resistance at the start of the measurements as at the end some 6 or 7 hours later, during which time magnetic fields up to 7500 gauss had been employed.

b. Energy Input. 55 Ohms (at 20°K) of constantan wire was wound non-inductively on the outside of the calorimeter, covering a central portion 3 cm in length. It was made to adhere to the calorimeter by a cellulose lacquer. To avoid radiation losses due to a large temperature head in the case of non-adherence of the wire or poor heat contact due to other causes, the heating unit was surrounded by a closely-fitting copper shield which was soldered at the bottom to the calorimeter. A study of the heating curves (galvanometer scale readings against time) showed a lag of a maximum of two seconds between the heating wire and the thermometer, this including the inertia of the galvanometer.

Heat capacities may be expressed in any energy units per unit of temperature, but the energy units usually employed are the joule and the calorie. The latter, an empirical unit which must be referred to the specific heat of water over a certain range of temperature, is the unit mostly employed. In these measurements the 15° calorie or 4.186 joules was used as the unit of energy.

Two wires were soldered at each end of the heating unit, one of each set for current carrying and the other two for determining potential drop across the heating unit. The current and voltage were measured by a millivoltmeter and a milliammeter, both specially calibrated against a Weston standard cell. Time was measured by a pendulum clock and was recorded by a telegraph instrument and checked by a stop-watch.

An electrical system was employed for starting and stopping the heating current. The clock was wired to give an electrical impulse through a relay during alternate seconds. Two telegraph keys were provided, one for starting and one for stopping. When depressed, a circuit was completed through the clock relay which actuated a magnetically operated switch, and at the start of the next contact made by the clock the heating circuit was opened or closed, depending upon the key used. The recording telegraph instrument was employed as follows. It consisted of a magnetically actuated recording pencil, which in alternate seconds made a pencil mark on a tape pulled past by a small synchronous motor. During the time either of the telegraph keys was depressed, the magnet actuating the recording pencil was short-circuited and the pencil made no mark. Releasing the key again closed the circuit and the alternate pencil marks and blank spaces were again begun.

When it was desired to start heating, one would depress the starting key in the second when there was no current in the clock circuit; this also short-circuited the telegraph instrument. At the start of the next second, contact is made in the clock circuit and the magnetic switch in the heating circuit is thrown, completing the heating circuit. Just after the end of this second, the telegraph key is released and at the start of the next second, the recording instrument again begins to register. The effect has been the omission of the pencil mark on the tape during the first second of the heating period. When one wishes to end the heating period the process is repeated with the other key. Thus the heating period may be any multiple of two seconds. The usual heating period was 60 seconds.

The millivoltmeter was connected in parallel with the heating circuit and since it has necessarily a finite resistance part of the current passes through the voltmeter itself and a correction must be made for this. This takes the form of a correction factor f, equal to the resistance of the voltmeter circuit, divided by that resistance plus that of the heating wire.

The energy input is then equal to

$$\frac{E \times I \times t \times f}{4.186} \text{ calories,}$$

where E is the recorded potential drop, I the recorded current, and t the time in seconds, the product of these with f giving joules developed in the heating wire, and 4.186 is the latest published factor for converting joules to 15° calories[1]).

c. The Calorimeter. The calorimeter assembly is shown in Fig. 1.

The calorimeter C was a cylindrical copper can with rounded ends, inside diameter 34 mm outside diameter 35 mm, length along outside edge 103 mm, and total volume 93 cm^3. The resistance thermometer assembly, in a copper tube T, diameter 7 mm, length 80 mm, was placed in the calorimeter coaxially with the long axis of the latter. Within the tube the thermometer wires were separated by mica. The end of the tube was closed off but the tube itself was pierced with several small holes to permit the influx of helium gas admitted for heat conduction. The 55 ohms constantan wire H used for energy input, was wound non-inductively on the central portion of the outside of the calorimeter. To facilitate heat distribution within the calorimeter, four radial vanes of copper connected the outer shell to the thermometer tube. On the top of the calorimeter, was a "Contracid" capillary to permit the introduction of helium gas into the calorimeter for heat conduction. This capillary was also used to connect the calorimeter to the manometer system when employing the calorimeter as gas thermometer. The top of the calorimeter was also provided with a sealed-in glass cross K, through which the thermometer connecting wires were brought[2]). On the bottom of the calorimeter, was a flanged hole for filling the calorimeter, provided with a cap which could be soldered on. There was also attached to the bottom a piece of brass F, in which was bored a conical hole; this fitted into a piece of the reverse shape on the inside of the bottom of the container (see following paragraph). This was for the purpose of providing

---

[1]) Nature, **135**, 417, 1935.

[2]) The glass cross was made from Normal Jena 16III glass, which can be sealed directly on platinum, which was in turn soldered to the calorimeter.

heat contact with the outside bath without the use of helium gas. In order to better this contact, MR. FLIM, chief of the laboratory technical staff, devised an ingenious spring device *M* for pressing the calorimeter down into better contact, which could be operated from the outside. This was not used in the *KCl* measurements.

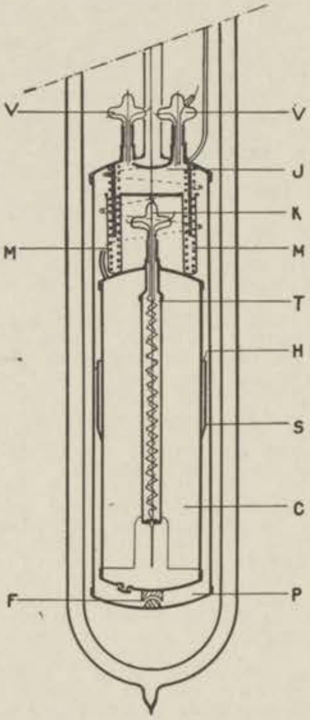

Fig. 1. The calorimeter and cryostat assembly used for heat capacity measurements on crystalline materials.

The calorimeter was suspended in a cylindrical, highly-polished brass container *P*, fitted with a metallic vacuum line. Just below the junction of the vacuum line and the container, a copper disc *J*, in contact with the container but not blocking the vacuum line, was placed for shielding off radiation from above. Two glass crosses *V* were sealed into the top of this container for bringing out connections from the thermometer and heater wires.

Three sharply pointed pieces of metal were soldered on the outer surface of the calorimeter to maintain the latter in an upright position with respect to the container.

Outside the container the connecting wires were formed into a many-coiled spiral, giving the wires a much longer contact with the bath of liquefied gas, thus minimizing the heat leak from above.

The whole calorimeter assembly was attached to a head which served the triple purpose of supporting the calorimeter, holding the Dewar flask which surrounded the calorimeter assembly and making connection with the vacuum line used for reducing the pressure under which the liquefied gas boils. The connecting wires were brought out through a glass and sealing-wax seal and the metallic vacuum line was attached to a glass line just above the head.

With a vacuum of $< 10^{-6}$ mm Hg, the heat leak into the calorimeter (in heat capacity measurements on $Gd_2(SO_4)_3 \cdot 8H_2O$) was,

on June 12, 1934	at 15.225°K	0.00666 cal/min
on Oct. 18, 1934	at 0.52°K (calc)	0.000049 „ „
on Oct. 18, 1934	at 1.19°K	0.000074 „ „
on Oct. 18, 1934	at 1.71°K	0.000044 „ „

These figures are only given to show how small the heat leak can be in spite of 7 wires and a metallic capillary leading to the calorimeter from the outside. At temperatures attainable with liquid hydrogen, the radiation interchange between the calorimeter and its surroundings, due to a temperature difference of one or two degrees, is of the order of magnitude of 5% of the heat leak observed. At liquid helium temperatures, the radiation interchange for a like temperature difference is less than 1% of that observed. The average heat developed by the *Ph-br* thermometer with a measuring current of 0.51 milliamperes is 5×10^{-5} cal/min. The constantan thermometer, with a measuring current of 1.02 milliamperes develops on the average 0.00016 cal/min.

d. Heat distribution within calorimeter. At the temperature of liquid helium, the heat conductivity within a mass of loosely packed crystals is quite poor. In the calorimeter, even with the radial copper vanes present, the distribution of the heat added would be undesirably long if this process were not assisted by the presence of helium gas. Further, there would be no heat equilibrium with the thermometer. The practical limit of heat conductivity with helium gas or the saturated vapour of liquid helium is not easily defined, but it was found to be definitely insufficient at about 0.6°K. In some of the first experiments in which adiabatic demagnetization was used to obtain a low starting temperature, there was present helium calculated sufficient to cover the surface of the gadolinium sulfate crystals with a layer 1 molecule thick (the crystal surface being estimated at 1300 cm^2) and enough extra so that the excess was expected to liquefy at 0.9°K. This was found to be insufficient to give equilibrium with the thermometer below 1°K. More gas was added until the total present (in 50 cm^3 unoccupied space in the calorimeter) was 8.4×10^{-5} mols. This allowed measurement of temperatures in the calorimeter by means of the resistance thermometer, estimated at about 0.6°K. This question is further discussed in Chapter VI.

e. *Experimental details peculiar to Nickel.* For the purpose of measuring the heat capacities of metals, and especially at low temperatures, a cylindrical block of the metal under consideration is made to act as its own calorimeter. The most convenient method of temperature measurement and energy input in this case is to have the agencies used for these purposes in a separate core, which is brought into thermal contact with the metal block.

The calorimetric arrangement used is shown diagramatically in Fig. 2.

(1) The thermometer core.

A section of the thermometer core is shown in Fig. 3.

It is cylindrical in shape, made principally of *Cu*, and the cylindrical surface is threaded so that it may be screwed into a threaded cylindrical recess in the block of metal. The thermometers, again *Ph-br* and constantan, are suspended in an atmosphere of *He* gas in a closed-off space in the center of the core. The heating-unit, 50—60 ohms of insulated constantan wire, may be wrapped around an inner cylinder and then sheathed with a hollow cylinder bearing the screw threads, or it may be placed at the bottom of the core, below the space containing the thermometers. The wire is packed in copper amalgam to insure good thermal contact.

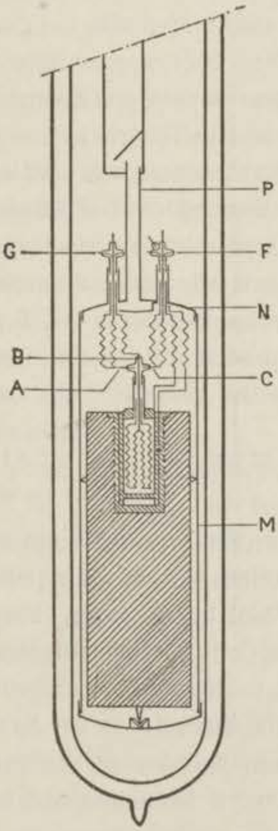

Fig. 2. Calorimetric assembly used in heat capacity measurements on metals.

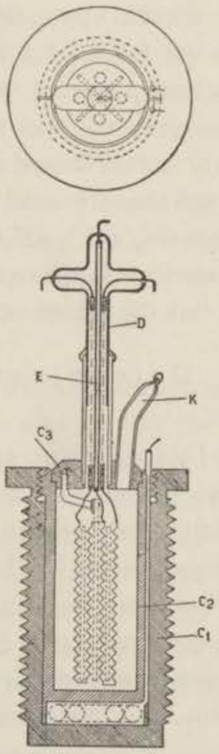

Fig. 3. The thermometer core.

Both types of cores were used in these measurements. The core used for the measurements in the liquid helium range, gave above 10°K after-periods which led to erroneous results. Another core was substituted and the measurements in the liquid hydrogen range were repeated.

The calibration of the thermometer wires was carried out in the same manner as already described. For the range 4°-10°K, the thermometer core was screwed into the calorimeter which had previously been used for measurements of the heat capacity of liquid helium (volume ca. 83 cm^3), and this was used as a gas thermometer.

(2) The calorimeter (Nickel block).

The nickel upon which the measurements were carried out was in the form of a cylinder, 100 mm in length and diameter 38 mm and provided with a cylindrical recess into which the thermometer core was screwed. The thermal contact so obtained between the Ni block and the core was quite satisfactory.

Beyond these points, the method and apparatus described for KCl and $Gd_2(SO_4)_3 \cdot 8H_2O$, are equally applicable to Ni. Some of the numerical values quoted are somewhat different in the case of Ni, but the order of magnitude is the same in both cases.

§ 3. Determination of temperature scale below 1°K.

The Leiden temperature scale for the liquid helium region, in terms of the pressure of the saturated vapour in equilibrium with liquid helium boiling at a certain temperature, has been determined down to 0.90°K with the helium thermometer. The vapour pressure curve is expressed in the form of the theoretical vapour pressure curve. In experiments carried out by KEESOM[1]) lower temperatures have been attained by reducing the pressure down to 3.6μ, these low pressures having been attained by the

---

[1]) W. H. KEESOM, Comm. Leiden, No. 219a.

use of mercury vapour pumps of special design, having a capacity of 675 liters helium gas per second. The corresponding temperature, 0.71°K was calculated by application of the formula derived for temperatures from 2.19° to 0.9°K. It is, however, considered that the temperature scale is not definitely established below 0.9°K.

In later similar experiments[1]) the resistance of a *Ph-br* wire was measured down to 0.75°K and showed no discontinuity in its resistance.

For certain of the measurements on $Gd_2(SO_4)_3{\cdot}8H_2O$ temperatures below 1°K were attained by means of the magnetic cooling process. For calculating these measurements, the $R\ vs\ T$ curve for *Ph-br* was extrapolated below 1°K. This procedure is, of course, open to all objections against extrapolations into practically unknown regions. The measurements of KEESOM just noted have shown that the resistance of *Ph-br* suffers no discontinuity down to about 0.7°K and the course of the heat capacity measurements indicated no irregularities which could be attributed to a discontinuous change of resistance. Nevertheless, the non-agreement of the $C_p\ vs\ T$ curves below 1°K representing the measurements on two different days, and calculated on the basis of an extrapolated $R\ vs\ T$ curve, shows that the procedure is not entirely trustworthy.

In using a paramagnetic substance whose magnetization is known as a function of temperature or which may be safely extrapolated to temperatures below which it is known, the temperature may be determined by determining the force on a sample in a magnetic field of known properties, or by measuring the change in self-induction in a coil surrounding the sample. Knowing the magnetization function, the corresponding temperature may be calculated. This method has, of course, the undesirable feature that the temperatures so determined are based on an extrapolation.

A method, which does not depend on extrapolations and which

---

[1]) W. H. KEESOM, Comm. Leiden, No. 230a.

gives temperatures in the thermodynamic scale was proposed by KEESOM[1]). This method is especially applicable to the present calorimetric set-up and may be used for calibration of the resistance thermometers. If the magnetization of a substance is known as a function of temperature, the entropy change caused by magnetization in a given magnetic field strength and temperature may be calculated. Let adiabatic demagnetizations be carried out from several different field strengths, $H_1, H_2, H_3, \ldots$ from a common temperature, T, and at the temperatures reached, T_1, T_2, $T_3, \ldots$ measure the resistance of the thermometer, R_1, R_2, $R_3, \ldots$ and then heat up to the common starting temperature, T, measuring the calories required to do this $Q_1, Q_2, Q_3 \ldots$ Then since $\frac{dQ}{dS} = T$, $\frac{\Delta Q_1 - \Delta Q_2}{\Delta S_1 - \Delta S_2} = T_{1,2} = \frac{T_1 + T_2}{2}$, if it can be assumed that for a small temperature difference the arithmetic average is the true average temperature. If then, the average of R_1 and R_2 corresponds to this calculated temperature, this gives points on the R *vs* T curve.

The application of this method is further discussed in Chap. VI.

§ 4. Method of Measurements.

The usual procedure in measuring a point is as follows. The thermometer resistance is nearly balanced by the compensation apparatus, the lack of balance being indicated in the usual manner by a galvanometer. A series of galvanometer readings is begun, readings usually being made each 10 seconds, and this indicates the manner in which the resistance or temperature in the calorimeter is changing. When sufficient readings have been made so that one is certain that the true rate of change has been determined, the fore-period is ended and the heating is begun. During the heating period, the readings are continued or the change in resistance is compensated for, depending upon

---

[1]) W. H. KEESOM, Jour. de Phys., **5**, 373, 1934. Phys., Zs. **35**, 928, 1934.
cf. also, P. DEBIJE, Phys. Zs., **35**, 923, 1934.
N. KÜRTI and F. SIMON, Proc. Roy. Soc London (A), **149**, 161, 1935.

the amount of the change. In the after-period the readings are continued until it is certain that the true equilibrium rate has been ascertained.

If the fore and after-periods are linear or nearly so, extrapolation to the time at the middle of the heating period gives the resistances at the start and end of the heating corrected for the warming or cooling due to heat exchange. More strictly, the extrapolation should be performed by the tangents at the start and end of the heating period. This is done when the fore or after-periods show a definite curvature.

To determine the rise in temperature, ΔT, the centimeters rise on the galvanometer scale is converted to ΔR from the sensitivity, and the ΔR converted to ΔT by multiplication with the $\frac{dT}{dR}$ of the R *vs* T curve at that point. The average temperature is calculated from the resistance at the middle of the heating period. If the compensation method is used, the resistances at the start and end of the heating period are determined and converted to temperatures, from which the ΔT and average temperature are obtained.

The heat capacity of the system in then $\frac{\text{ENERGY INPUT}}{\Delta T}$.

If the vacuum between the container and the calorimeter is not good, there is a large heat exchange between the calorimeter and its surroundings. During heating, an increasing amount of the energy added is dissipated as the temperature rises, and after the heating period the temperature falls until eventually the calorimeter has the temperature of its surroundings. A method was developed by KEESOM and KOK¹) for calculating heat capacities from such points. Under the assumptions that:

1. the heat capacity of the calorimeter is constant during the period considered,
2. the temperature throughout the calorimeter is uniform,
3. the heat exchange is proportional to temperature difference,

---

¹) W. H. KEESOM and J. A. KOK, Comm. Leiden, No. 219c.

4. the heat production is constant in the heating period,
5. the temperature of the surrounding bath is some regular function of time,

an expression was derived for the amount of energy lost to the surroundings during the heating period. Fig. 4 shows a time-galvanometer readings curve to which this method was applied, taken from the measurements on the heat capacity of the empty calorimeter at liquid helium temperatures.

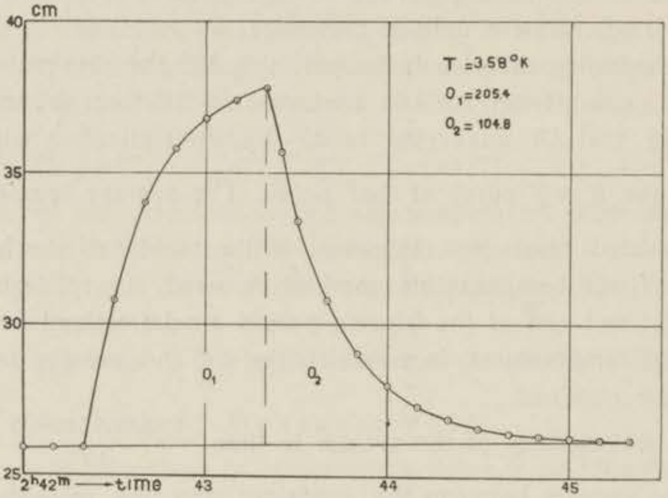

Fig. 4. Measurements with large heat exchange.

If E is the amount of energy added during the heating period, the amount which caused the observed temperature rise is equal to

$$E \times \frac{O_2}{O_1 + O_2}$$

where O_1 and O_2 are the areas of the surfaces, indicated by these letters in the figure. The areas of the surfaces are determined planimetrically.

CHAPTER III.

THE HEAT CAPACITY OF POTASSIUM CHLORIDE[1]).

§ 1. Introduction.

Among the metals whose heat capacities have been measured at liquid helium temperatures at the KAMERLINGH ONNES Laboratory only *Pb* showed a nearly constant θ value when the results were considered in the light of the DEBIJE theory. All the others, *Hg*, *Bi*, *Sn*, *Ag*, *Zn* and *Tl* exhibited relatively large changes of θ in this region. The earlier measurements on *Cu* showed a noticeable deviation from a constant θ even at liquid hydrogen temperatures.

This effect was most marked in the cases of *Ag* and *Zn*. Taking silver as an example, the value of θ rises slowly from 209 at 20°K to a maximum of 226 at 5.4°K, and then rapidly falls off to 165 at 1.35°K, the lowest temperature reached in the measurements. This is the dotted curve in Fig. 6.

In making the measurements it had been necessary to admit helium gas into the space surrounding the metal block, in order to be able to cool it down to the temperature of the surrounding bath. It was thought that perhaps the metal surface had adsorbed a layer of helium gas and that it was the heat necessary for desorption that had caused the (relatively) higher heat capacities and the low θ values.

This was checked in two ways[2]). The silver was remeasured after having been cooled down only by a mechanical thermal contact, without the aid of helium gas. Holes were bored into the zinc block to increase the ratio of surface to weight (it was

---

[1]) This research was carried out under the direction of Prof. Dr. W. H. KEESOM and is published as W. H. KEESOM and C. W. CLARK. Comm. Leiden, No. 238c.

[2]) W. H. KEESOM and J. A. KOK, Comm. Leiden, No. 232d.

increased by a factor 4), and the heat capacity was remeasured. In both cases the results were negative.

It was then concluded that the contribution of the free electrons to the heat capacity was the cause of the effect. The basis for this contribution is discussed in Chap. IV, and need not be further considered here.

The θ values for silver were extrapolated from higher temperatures to the liquid helium region. Heat capacities were recalculated from the θ values so derived and the differences between the observed and calculated values were compared with the heat capacity expected for one free electron per atom. The agreement was quite good up to about 3°K, but the extra atomic heat appeared then to fall off to zero at about 6°K.

In the case of zinc, the heat capacity expected for one free electron per atom was subtracted from the observed values, and the θ values corresponding to these "corrected" heat capacities were determined. The θ values now rose very rapidly on going to lower temperatures — from 200 at 20°K to 335 at 2°K.

It was considered advisable to investigate the heat capacity of a non-conductor of electricity in order to see if this behavior was confined to metals. Potassium chloride, KCl, is almost surprisingly suitable for a comparison of its heat capacity with that of silver. It crystallizes in the same system as silver, and down as far as liquid hydrogen temperatures, the θ values of KCl are about the same as those of Ag. Further, the two constituent atoms, or more strictly, ions, have nearly the same masses, $K = 39.10$, $Cl = 35.457$.

§ 2. Material.

The KCl employed in this research was the "Puriss" grade, purchased from Brocades, The Hague.

The average dimension of the crystals was 0.2-0.3 mm.

A quantity of the material was dried in an oven for three hours at 140°C, taken out and allowed to cool in a dessicator. When cooled, the whole quantity was weighed and the calorimeter filled. The remainder was again placed in the dessicator and later weighed, the amount in the calorimeter being obtained by difference. The quantity of *KCl* used was 76.959 grams, or 1.032 mols.

After the calorimeter was filled and put in place in the cryostat assembly, it was pumped and a high vacuum maintained for a day to remove any water which may have been taken up by the crystals.

For assuring heat conduction among the crystals and thermal contact with the thermometer wires, a small quantity of helium gas, 3.4×10^{-5} mols, was admitted to the calorimeter. This was done by means of a small gas pipette (volume 10 cm^3) which was attached to the capillary leading to the calorimeter. The pipette, in the form of a cross, was provided with a small manometer and three stopcocks, which permitted connection with or shutting-off from the calorimeter, the vacuum pump and the supply of helium gas.

§ 3. Heat capacity of empty calorimeter.

The heat capacity of the empty calorimeter, being of the same order of magnitude as that expected for the *KCl*, had to be determined carefully in the liquid helium region. It was filled with the same quantity of *He* gas that was employed in the *KCl* measurements.

Due to the very small heat capacity of the calorimeter and a vacuum which was not "perfect", there was a large heat exchange between the calorimeter and the container which was at the temperature of the surrounding liquid helium. This made it impossible to measure below 2.5°K.

The experimental data were calculated according to the method developed by KEESOM and KOK (see Chap II) and the points so obtained lay on a rather good curve. Previous measurements had covered the range 9° to 20°K, and the two curves were joined to obtain the values for temperatures between 4.2° and 9°K. The measured values in the liquid helium region and points from the smoothed curve above 4.2°K are given in Table I.

For the few *KCl* points below 2.6°K, the measured curve was extrapolated.

TABLE I.

Heat Capacity of Empty Calorimeter.

Measurements in liquid helium. April 16, 1935.

Point	ΔT	T_{av}	C_p
Ia	0.0948	2.68	0.00176
b	0.0994	2.68	0.00174
c	0.0521	2.86	0.00197
d	0.0826	2.89	0.00204
e	0.0605	3.23	0.00284
f	0.0769	3.25	0.00255
g	0.0991	3.56	0.00339
h	0.1258	3.58	0.00328
i	0.1236	3.83	0.00364
j	0.1443	3.84	0.00356
k	0.1139	4.16	0.00463

Points above 4.2°K.

T	C_p	T	C_p
5.0	0.0071	13.0	0.0810
6.0	0.0112	14.0	0.0995
7.0	0.0166	15.0	0.119
8.0	0.0234	16.0	0.141
9.0	0.0316	17.0	0.166
10.0	0.0412	18.0	0.194
11.0	0.0513	19.0	0.226
12.0	0.0660	20.0	0.262

§ 4. Results.

Three series of measurements were carried out. On March 8, 1935 measurements were made from 3° to 9.2° K. The measurements were started at 1.5°K, but the heat exchange with the surroundings was too large to allow any use of the data obtained below 3°K. On March 14, another attempt was made to obtain points in the liquid helium region. Again the heat exchange was rather large, but it was possible to calculate some of the points by the method of KEESOM and KOK. Three of the five points so handled appeared to extend the curve of the measurements of March 8 very nicely, but the other two points lay rather far off.

Measurements were carried out in liquid hydrogen on March 15 and extended from 9.5° to 19°K. These points are rather less accurate than is to be expected from the appearance of the heating curves, with their fore and after-periods.

The results of all the measurements and the corresponding

TABLE II.

Heat capacity of *KCl*. Liquid helium region.

Point	ΔT	T_{av}	C_v cal/deg per $\frac{1}{2}$ mol.	θ
Measurements of March 8, 1935.				
Ig	0.101	2.99	0.00103	229.2
h	0.0874	3.16	0.00125	226.6
i	0.1147	3.28	0.00138	228.1
j	0.1085	3.37	0.00145	230.2
k	0.1019	3.43	0.00157	229.0
l	0.0956	3.52	0.00169	229.0
m	0.1423	3.62	0.00179	231.0
n	0.1347	3.71	0.00188	232.9
o	0.1272	3.81	0.00200	233.8
p	0.1211	3.86	0.00212	233.0
q	0.1166	3.92	0.00221	232.7
r	0.1723	4.01	0.00235	233.3
s	0.1642	4.10	0.00246	235.2
t	0.3856	4.29	0.00277	236.5
Measurements of March 14, 1935.				
Ig	0.308	2.345	0.000468	233.6
i	0.2845	2.415	0.000542	229.4
IIb	0.136	2.440	0.000710	211.7
c	0.0454	2.618	0.000972	204.8
d	0.0405	2.71	0.000806	225.4

TABLE III.

Heat capacity $^1/_2$ mol *KCl*. 4.6°—17°K.

Point	ΔT	T_{av}	C_v cal/deg.	θ
Measurements of March 8, 1935.				
Iu	0.309	4.60	0.00362	232.0
v	0.269	4.87	0.00419	233.8
w	0.332	5.14	0.00505	231.8
x	0.297	5.40	0.00559	231.5
y	0.479	5.72	0.00727	228.7
z	0.419	6.14	0.00791	233.6
IIa*)	0.385	6.24	0.00888	232.9
b	0.353	6.52	0.00957	237.7
c	0.341	6.73	0.00951	246.0
f	0.222	7.45	0.0164	227.1
g	0.306	7.65	0.0184	224.3
h	0.287	7.89	0.0195	227.1
i	0.255	8.00	0.0230	218.0
j	0.252	8.22	0.0234	222.6
k	0.234	8.33	0.0249	221.5
l	0.287	8.46	0.0252	223.2
m	0.265	8.70	0.0272	223.9
n	0.250	8.94	0.0288	226.3
o	0.232	9.23	0.0310	227.8
Measurements of March 15, 1935.				
IIa	0.296	9.53	0.0376	220.1
b	0.279	9.81	0.0402	221.7
c	0.345	10.06	0.0419	224.8
d	0.197	13.01	0.107	212.0
e	0.347	13.22	0.113	211.5
f	0.329	13.55	0.119	212.5
g	0.406	13.85	0.123	212.0
h	0.372	14.20	0.135	214.0
i	0.353	14.47	0.142	213.5
j	0.328	14.73	0.155	212.0
k	0.403	15.84	0.180	218.0
l	0.349	16.34	0.212	212.0
m	0.336	16.67	0.219	214.0
n	0.374	17.09	0.229	216.0

---

*) Constantan thermometer used from here on.

θ values are collected in Tables II and III[1]). Curves of $\frac{\theta}{T}$ *vs* C_v calculated from the T^3 law, $C_v = 464.5 \left(\frac{T}{\theta}\right)^3$, were used to determine the θ values. All calculations are on a basis of $^1/_2$ mol KCl.

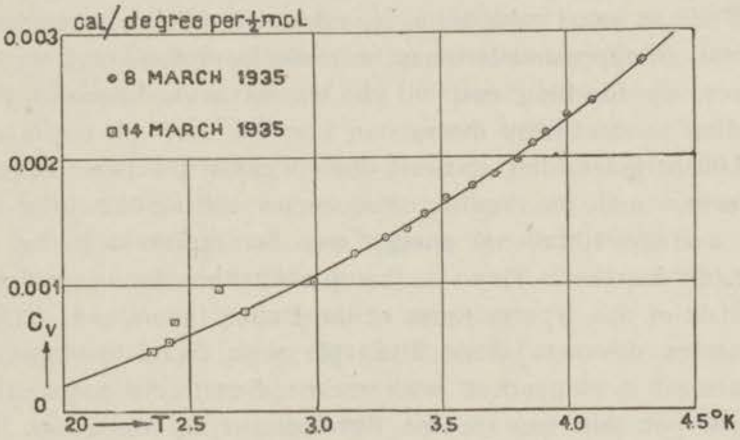

Fig. 5. Heat capacities, $\frac{1}{2}$ mol KCl. Liquid helium temperatures.

§ 5. Discussion.

a. Theoretical. The crystal structure of KCl is well known from crystal analysis. It may be considered as a whole as a simple cubic lattice, with alternating K^+ and Cl^- ions, or as being composed of two interpenetrating, face-centered cubic lattices, one of K^+ and one of Cl^-. There is no molecule formation. Both ions have closed electron shells, the electron in the 4*s* shell of the K going over to complete the 3*p* shell of the Cl both then having the extranuclear structure of A. The compound contains thus no free electrons. This is confirmed by its electrical conductivity, ca. $2.5 \times 10^{-14}\,\mathrm{cm}^3/\Omega$ [2]).

---

[1]) It was not necessary to make any correction for the difference between C_p and C_v.

[2]) F. Quittner, Zs. f. Phys., 56, 597, 1929.

The theory of BORN and V. KARMAN deals with the vibrational spectrum and heat capacity of such binary crystals. There appear in general two frequency branches, the low frequency (so-called "acoustical") and high frequency (optical), each characterized by three limiting vibration frequencies, one for the longitudinal and two for the transverse waves.

While an exact calculation is extremely difficult in an actual crystal, an approximation may be made for not too high temperatures, by handling each of the six maximum frequencies according to the DEBIJE theory.

If the particles differ relatively little in mass the two frequency branches and the limiting frequencies differ but little, and the average vibrational energy may be represented by one DEBIJE function. This is the justification for considering crystals of this type in terms of the DEBIJE theory and at temperatures down to those attainable with liquid hydrogen the agreement is as good as with metals. DEBIJE did not consider crystals of this type in the development of his theory. The application was made later when it was found that the heat capacity of KCl and $NaCl$ were well represented by the DEBIJE function.

In spite of the definite anisotropy of the KCl, it is expected, in the theories of DEBIJE and of BORN and V. KARMAN, that at very low temperatures it may also be considered as a continuum and will follow the T^3 law to which both of these theories reduce. The same reasoning employed in the justification of this law for metals (Chap I, p. 9) is valid here.

BLACKMAN has recently made calculations on the general features of the spectrum of such crystals by means of a relatively simple type of geometrical analysis¹). He definitely disagrees with the continuum distribution of frequencies (i.e., density of vibrations proportional to ν^2) except at the very lowest temperatures. Whereas in the DEBIJE theory, the T^3 law is supposedly

---

¹) M. BLACKMAN, Proc. Roy. Soc. London A, **148**, 405, 1935; **149**, 122, 1935.

valid in the range $\frac{\theta}{T} \geqq 12$, BLACKMAN claims that the range cannot exceed $\frac{\theta}{T} \geqq 50$, thus in general only a few degrees absolute.

There are present according to this theory, even in compounds in which the atoms are as nearly of the same mass as in KCl, the two frequency branches, the "acoustical" and the "optical". The distributions of frequencies in these two branches are determined by two different parameters which are in turn dependent on the binding forces between the different particles. The sum of these two curves yields a curve of the variation of the density of the vibrational frequencies with the frequency. The curve displays two maxima, i.e., two regions in which the density of vibration frequencies is very high.

If, instead of multiplying by the PLANCK-EINSTEIN expression for the energy of an harmonic oscillator and summing the energy over the whole curve, the two maxima are assumed to be monochromatic frequencies, and these are multiplied by the PLANCK-EINSTEIN expression, an expression for the energy of the NERNST-LINDEMANN type is obtained. This is probably simplifying too much, but is does give some theoretical explanation for the success of the NERNST-LINDEMANN theory.

The consequences of BLACKMAN'S theory as applied to the low temperature heat capacity of KCl will be discussed later¹).

b. Comparison of results with silver. A comparison of the θ values obtained for KCl with those determined from the smoothed atomic heats of Ag is given in Fig. 6.

The difference is at once evident. The θ values for KCl do not descend rapidly with descending temperature as do those

---

1) A paper by J. H .C. THOMPSON on this same subject has recently appeared in Proc. Roy. Soc. London A, **149**, 487, 1935. The mathematics on which the theory is based are given and the equations required for the calculations of the frequencies are developed. The calculations have not yet been carried out.

for *Ag*. If the heat capacity of one free electron per atom, as given by SOMMERFELD's formula[1], is deducted from the measured atomic heats of *Ag* and the "corrected" heat capacities are converted to θ values, the resulting θ *vs* T curve reproduces all the features of that found for *KCl*. This is the dashed curve in Fig. 6.

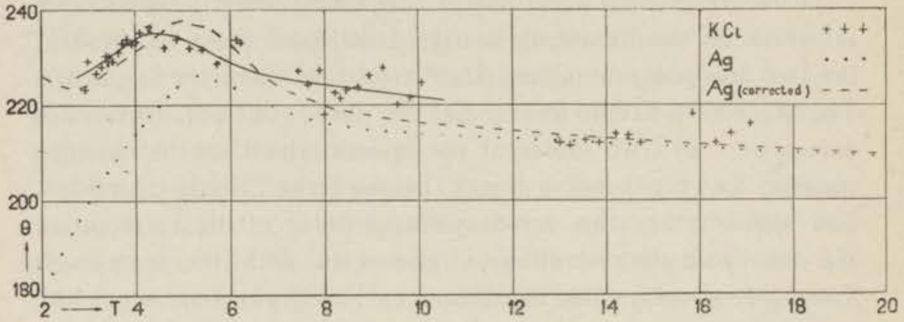

Fig. 6. θ values for *KCl*, *Ag* (uncorrected) and *Ag* (corrected).

One point of uncertainty concerning the heat capacity measurements of *KCl* in the liquid helium range must be considered. As mentioned in § 2 of this chapter, it was necessary to admit a small quantity of helium gas to the calorimeter and its contents. This was undoubtedly adsorbed on the crystal surfaces to some extent at liquid helium temperatures. If, during the calorimetric experiments, desorption occurs, the measured heat capacities will be too high and the corresponding θ values too low. The extent of the adsorption is unknown, as is the desorption heat, but a rough estimate based on the assumption of complete adsorption indicates the possibility of an additional heat capacity term of the same order of magnitude as that attributed to *KCl*. This is perhaps the explanation of the decrease of the θ values on the low temperature side of the maximum. This can only be decided by further measurements with varying amounts of helium gas present in the calorimeter or by measurements on larger crystals, thereby reducing the total surface. Should the thermal

---

[1] Cf. Chap. IV, p. 51. For *Ag* at liquid helium temperatures, this amounts to $1.526 \times 10^{-4}\ T$ cal/deg. per gram-atom.

conductivity of *KCl* prove to be sufficiently good at these temperatures, the measurements could be carried out on one large crystal.

Nevertheless, the θ values determined for *KCl* are minimum values (i.e., the heat capacities, if not correct, must be smaller), so the difference between the θ *vs* T curves for *KCl* and *Ag* is real. This is considered to be a corroboration of the presence of an additional heat capacity term due to the free electrons in *Ag*.

With the experimental material at present available, it is not possible to draw any further conclusions from this type of comparison. *Pb* has the same type lattice as *Ag*, but is supraconductive below 7.2°K. The exact correction for the heat capacity of the "supraconductive electrons" is not known.

Zn, a hexagonal crystal, as has already been mentioned, shows a rising θ value on going to lower temperatures when corrected for an electronic heat capacity. *Tl*, also hexagonal, exhibits falling θ values from 4.2° to 2.36°K, at which point it becomes supraconductive. *Bi* is also a hexagonal crystal, but because of its unusual diamagnetic properties, the correction for an electronic heat capacity is uncertain. Any correction, however, would result in rising θ values with falling temperatures.

White tin, a tetragonal crystal, shows a minimum at about 10°K with a rather rapid rise to the temperature at which it becomes supraconductive.

c. Comparison with BLACKMAN'S *theory*. According to the theoretical considerations of BLACKMAN, the θ *vs* T curve of binary ionic crystals should pass through a minimum at fairly low temperatures (liquid hydrogen temperatures), and then rise to a final higher value, corresponding to the true continuum region. This latter is expected to extend over only a few degrees absolute.

The present measurements confirm these predictions to some extent. The θ values rise on going to lower temperatures, but on reaching a maximum at about 4.5°K fall off toward lower temperatures. A possible reason for this latter behavior has been discussed.

However, considering the fact that the lattice heat capacity of *Ag* (assuming that the measured heat capacity, less that calculated due to the electrons, represents the lattice heat capacity) shows a similar behavior, the effect may be real. Further, BLACKMAN mentions the possibility of such an occurrence.

If a DEBIJE curve of the distribution of the density of vibrations as it varies with frequency is plotted on the same diagram as a curve of the type proposed by BLACKMAN, the BLACKMAN maxima will project above the DEBIJE curve, and between the maxima, the curve will fall below the DEBIJE curve. Call this latter area, minus, and those contained in the maxima, above the DEBIJE curve, plus. BLACKMAN then says, " . . . . if it (the minus area) is very much larger (than the first plus area), θ attains a maximum value and then falls . . . .".

The prediction that the continuum region (constant θ) will not extend to higher than a few degrees absolute, is partially confirmed in the case of *KCl*. This also seems to be the case with the "corrected" lattice heats of *Ag*. That is to say, the θ values are definitely changing down to 4° or 5°K. Therefore, the continuum region cannot extend further than from 0° to 5°K.

CHAPTER IV.

THE HEAT CAPACITY OF NICKEL.[1])

§ 1. Material.

The laboratory was presented with liberal samples of very pure *Ni* by the International Nickel Co. of Canada, and the Mond Nickel Co., Ltd. Both samples were of substantially the same purity, at least 99.9% *Ni*. That furnished by the latter firm was used, being in the form of small pellets and more convenient for small scale melting and casting operations.

The metal was melted and cast in the form of a cylinder in the Metallurgical Laboratory of the Technische Hoogeschool at Delft, by Prof. Ir. M. H. CARON. In order to assure a coherent casting, 0.05% *Mg* was added. An analysis of turnings from the completed cylinder was carried out by Miss M. E. VAN DE KLEINEMULDER, Chem. Eng., and showed 99.81% *Ni*, the principal impurities being *Cu* 0.017%, *Fe* 0.083%, *Mg* 0.037% and *C* 0.04%[2]).

§ 2. Results.

The results of the measurements are collected in Tables IV and V, and are represented graphically in Figs. 7 and 8.

In all, three series of measurements were carried out in the liquid helium region, 1.1° to 4.2°K, on two different days. These

---

[1]) This research was done under the direction of Prof. Dr. W. H. KEESOM. W. H. KEESOM and C. W. CLARK, Physica **2**, 513, 1935, and Comm. Leiden, No. 235e.

[2]) The sample was so pure that the usual method of *C* determination, oxidation of the sample in a stream of O_2 at 950°C, did not work. It was necessary to go to 1300°C.

all agreed quite well. Only one series of measurements was carried out from 4.2° to 9.5°K. Another series of measurements was made from 9.5° to 20°K, but it was necessary to discard these completely because the long after-period gave entirely erroneous results. The measurements from 14° to 19°K were later repeated with another thermometer core.

TABLE IV.

Atomic Heat of Nickel. Liquid Helium Region.

Measurements of Jan. 25, 1935.

Point	ΔT	T_{av}	Atomic heat cal/deg.	Point	ΔT	T_{av}	Atomic heat cal/deg.
Ia	0.040	1.11	0.00174	Iv	0.190	3.37	0.00616
b	0.072	1.14	0.00183	w	0.183	3.46	0.00641
c	0.206	1.23	0.00204	x	0.178	3.57	0.00657
d	0.184	1.31	0.00229	IIa	0.0426	1.10	0.00186
e	0.173	1.41	0.00244	b	0.0434	1.10	0.00182
f	0.161	1.48	0.00261	c	0.0432	1.10	0.00184
g	0.152	1.52	0.00277	d	0.0983	1.14	0.00187
h	0.142	1.67	0.00297	e	0.107	1.18	0.00171
i	0.135	1.77	0.00312	f	0.137	1.66	0.00302
j	0.274	1.92	0.00343	g	0.166	3.49	0.00615
k	0.246	2.08	0.00383	h	0.159	3.63	0.00642
l	0.240	2.24	0.00392	i	0.156	3.73	0.00652
m	0.218	2.39	0.00430	j	0.148	3.83	0.00690
n	0.208	2.49	0.00451	k	0.142	3.89	0.00718
o	0.254	2.56	0.00460	l	0.139	3.97	0.00735
p	0.240	2.71	0.00488	m	0.153	4.05	0.00750
q	0.228	2.81	0.00515	n	0.155	4.04	0.00740
r	0.232	2.82	0.00504	o	0.149	4.12	0.00769
s	0.216	3.00	0.00543	p	0.146	4.20	0.00785
t	0.203	3.15	0.00579	q	0.145	4.27	0.00794
u	0.196	3.26	0.00596	r	0.143	4.31	0.00802
Measurements of Feb. 6, 1935.							
Ia	0.202	3.11	0.00557	f	0.272	3.78	0.00658
b	0.191	3.26	0.00589	g	0.326	4.03	0.00735
c	0.186	3.37	0.00606	h	0.234	4.16	0.00767
d	0.289	3.51	0.00621	i	0.229	4.27	0.00782
e	0.276	3.71	0.00649				

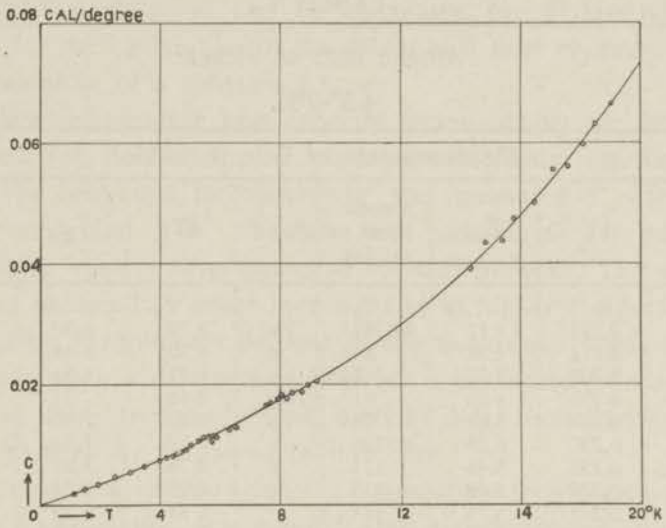

Fig. 7. Atomic heat of nickel. 1.1° — 19.0°K.

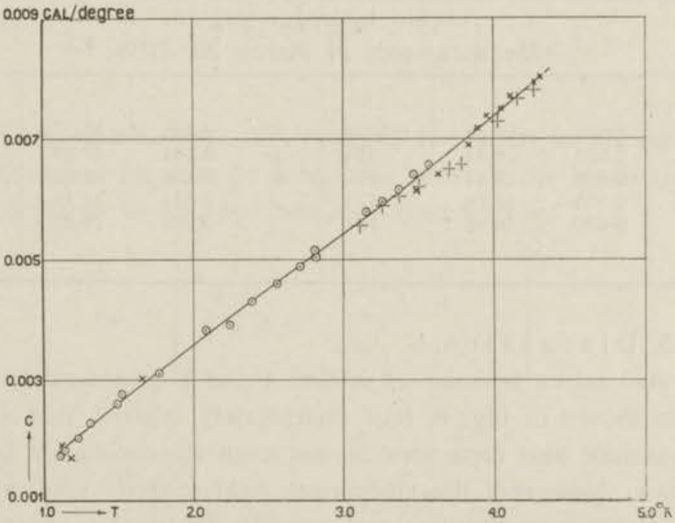

Fig. 8. Atomic heat of nickel. Liquid helium range.

⊙	Series I	Jan. 25, 1935.
×	Series II	
+	Series I	Feb. 6, 1935.

TABLE V.

Atomic heat of nickel. 4.3°-9°K.							
Measurements of Feb. 6, 1935.							
Point	ΔT	T_{av}	Atomic heat cal/deg.	Point	ΔT	T_{av}	Atomic heat cal/deg.
Ij	0.221	4.42	0.00811	Iw	0.202	6.30	0.0124
k	0.211	4.58	848	x	0.201	6.48	128
l	0.205	4.70	873	y	0.255	6.54	128
m	0.275	4.86	917	IIm	0.180	7.51	164
n	0.257	5.01	981	n	0.282	7.69	169
p	0.237	5.28	0.0106	o	0.271	7.93	175
q	0.226	5.45	111	p	0.263	8.05	181
r	0.229	5.62	113	q	0.268	8.21	176
s	0.221	5.75	114	r	0.344	8.39	186
t	0.220	5.86	114	s	0.340	8.70	187
u	0.241	5.72	104	t	0.320	8.91	198
v	0.225	5.90	111	u	0.310	9.22	204
Liquid hydrogen region. Measurements of March 26, 1935.							
Ia	0.676	14.34	0.0391	If	0.564	17.07	0.0555
b	0.610	14.84	434	g	0.563	17.59	559
c	0.601	15.41	437	h	0.538	18.08	597
d	0.555	15.78	474	i	0.631	18.49	630
e	0.620	16.46	501	j	0.596	19.02	663

§ 3. Discussion.

a. Anomalous behavior of Nickel. From a consideration of the points shown in Fig. 8, it is immediately evident that the low temperature heat capacities do not even approximately follow a T^3 law. However, the vibrational heat capacity must make an appreciable contribution, and in order to be able to determine the amount of the anomalous or additional heat capacity present, the amount of the usual vibrational heat capacity must be deducted. If the value of the characteristic temperature, θ, is known from other thermal data, or can be calculated, the T^3 law may be applied for the calculation of the vibrational heat capacity, with the assumption of a constant θ.

The low temperature heat capacity measurements are usually employed for determining θ, since at sufficiently low temperatures the correction for converting the measured C_p to C_v may be neglected. It is, of course, not possible to use the low temperature results here measured for this purpose. The measurements obtained by other investigators at higher temperatures are likewise inapplicable because of the anomalous behavior.

There is often a discrepancy between θ calculated from elastic data and that determined from thermal data. Nevertheless, the θ (elastic) must be employed in this case.

b. Calculation of characteristic temperature from elastic data. In Chap. I, an equation was given for the distribution of vibration frequencies in a solid when the solid may be considered as a continuum.

$$dZ = 8\,\pi V \left(\frac{1}{C_t^3} + \frac{1}{2\,C_l^3} \right) \nu^2 d\nu. \tag{3}$$

Since the total number of vibrations is limited to $3N$ for 1 gr. atom, equation (3) may be integrated between the limits 0 and ν_m and equated to $3N$, and one may then find ν_m.

$$\nu_m = \left[\frac{9\,N}{8\,\pi V} \; \frac{2\,C_l^3\,C_t^3}{2\,C_l^3 + C_t^3} \right]^{1/3} \tag{7}$$

or since $\theta = \dfrac{h\nu_m}{k}$.

$$\theta = \left[\frac{9\,Nh^3}{8\,\pi V k^3} \; \frac{2\,C_l^3\,C_t^3}{2\,C_l^3 + C_t^3} \right]^{1/3} \tag{7'}$$

According to elastic theory,

$$C_l = \sqrt{\frac{\lambda + 2\mu}{\varrho}} \; ; \; C_t = \sqrt{\frac{\mu}{\varrho}}$$

where μ is the principal rigidity, λ the LAMÉ constant and ϱ the density. The two elastic constants are expressible in terms of elastic quantities usually measured, the compressibility $\varkappa$ and POISSON's ratio σ, the ratio of relative change of diameter of a bar to its unit change in length under an axial load which does not stress it beyond the elastic limit. Making these substitutions in (7′), putting in the numerical values for the universal constants and eliminating the atomic volume V by the introduction of the atomic weight A, (8)

$$\theta = \frac{3.62 \times 10^{-3}}{\varkappa^{1/2} \varrho^{1/6} A^{1/3} \left\{ \left[\frac{(1+\sigma)}{3\,(1-\sigma)}\right]^{3/2} + 2 \left[\frac{2}{3} \frac{(1+\sigma)}{(1-2\sigma)}\right]^{3/2} \right\}^{1/3}}$$

For the compressibility, 57×10^{-12} was used, density 8.81 gr/cm^3 and atomic weight 58.7. For POISSON's ratio, two figures were available, the value given by GRÜNEISEN[1]) 0.309, and that given by the I.C.T., 0.33.

If $\sigma = 0.309$ $\quad\theta = 442.4$
$\sigma = 0.33$ $\quad\theta = 413.$

The value of θ is then roughly inversely proportional to that chosen for σ. The latter value, $\theta = 413$ has been adopted, since in general the characteristic temperature calculated from the elastic constants exceeds that determined from thermal data in the T^3 region.

c. *Difference between observed heat capacities and C_v calculated.* The differences between C_v ($\theta = 413$) and a number of the measured points were calculated and the results are collected in Table VI.

The graphical representation in Fig. 9 shows that they follow a straight line rather well, i.e., the additional heat capacity is proportional to T. In the liquid hydrogen range, the accuracy of the measurements is less, and this linear relation fails. The differences found at liquid hydrogen temperatures are more sensi-

---

[1]) E. GRÜNEISEN, Ann. d. Phys., 25, 845, 1908.

TABLE VI.

Additional Atomic Heat of Nickel.
$C_{\text{observed}} - C_{\text{vibrational}}$ ($\theta = 413$).

T	$C_{\text{obs.}}$	$C_{\text{vibr.}}$	$C_{\text{obs.}} - C_{\text{vibr.}}$
1.10	0.00184	0.00001	0.00183
1.48	0.00261	0.00002	0.00259
2.08	0.00383	0.00006	0.00377
2.49	0.00451	0.00010	0.00441
3.00	0.00543	0.00018	0.00525
3.46	0.00641	0.00027	0.00614
3.97	0.00735	0.00041	0.00694
4.20	0.00785	0.00049	0.00736
4.58	0.00848	0.00063	0.00785
5.01	0.00981	0.00083	0.00898
5.62	0.0113	0.0012	0.0101
6.30	0.0124	0.00165	0.01075
6.54	0.0128	0.0018	0.0110
7.69	0.0169	0.0030	0.0139
8.70	0.0187	0.0043	0.0144
9.22	0.0204	0.0052	0.0152

tive to the value chosen for θ than are those at lower temperatures.

If $\theta = 442.4$ is taken for this calculation, the agreement is rather better and the same linear proportionality valid from 1°-10°K is approximately valid in the liquid hydrogen region.

The straight line in the figure is $C_{\text{add}} = 0.001744\ T$.

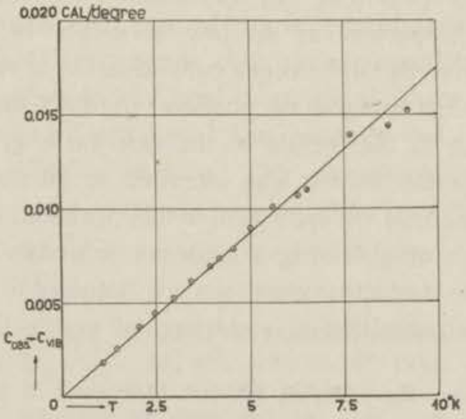

Fig. 9. Additional atomic heat of nickel.

d. Ferromagnetism according to quantum mechanics. The electron exchange interaction theory sketched by HEISENBERG[1]) was a first attempt to lay down a quantum theoretical basis for the discussions of ferromagnetism. He showed that the exchange of electrons in atoms, which is characteristic of quantum mechanics, is capable, under certain conditions, of giving rise to those effects which have been partially correlated by the WEISS molecular field hypothesis. The exchange forces are electrostatic but are formally equivalent to large spin coupling. In order that ferromagnetism may appear (instead of paramagnetism), an atomic magnet must have several possible states giving positive contributions to the medium, and must have enough immediate neighbors so that its energy of interaction with these may be considerable. The electron exchange is a mutual effect of two electrons, one in atom A and one in atom B, by which the states permissible to each are reduced in number, and the state of parallelism is made more probable.

The interaction is expressed formally by the complicated HEITLER-LONDON exchange integral, introduced in the theory of the chemical bond. SLATER[2]) introduced into the theory the idea that the probability of interaction increases as the ratio of interatomic distance to radius of incompleted electron shell increases, thus providing an explanation for the occurence of these unique properties in so few elements in the family of atoms. Similarly, BETHE[3]), from a consideration of the requirement that the exchange integral be positive, predicts that ferromagnetism will occur in the metals of the rare earth group.

The HEISENBERG theory was intended to do no more than to indicate the method of approach to the problem. The mathematical difficulties of obtaining a rigorous solution are admittedly insurmountable and approximations are required to obtain results which may be submitted to experimental verification.

---

[1]) W. HEISENBERG, Zs. f. Physik, **49**, 619, 1928.

[2]) J. C. SLATER, Phys. Rev., **35**, 509, 1929; **36**, 57, 1930.

[3]) H. BETHE, Leipziger Vorträge, Magnetismus, 1933.

BLOCH[1]) undertook to solve the problem, for temperatures approaching the absolute zero, where the observed saturation is very nearly the true saturation. For this purpose he applied a method of solution developed a short time previously by SLATER[2]). For the approach to saturation at very low temperatures he developed the formula

$$\frac{\sigma_T}{\sigma_0} = 1 - \gamma \left(\frac{T}{T_c}\right)^{3/2} \tag{9}$$

where T_c is the order of magnitude of the Curie temperature and equal to $\frac{J}{k}$ (J is the interaction energy and k BOLTZMANN'S constant) and

$$\gamma = \frac{1}{(4\pi)^{3/2}} \sum_{n=1}^{n=\infty} \frac{1}{n^{3/2}} = 0.0587.$$

Measurements on Ni by WEISS and FORRER[3]) down to temperatures attainable with the use of liquid air, showed that the approach to absolute saturation followed the law

$$\frac{\sigma_T}{\sigma_0} = 1 - A' \left(\frac{T}{T_c}\right)^2 - B' \left(\frac{T}{T_c}\right)^4.$$

More recent measurements by FALLOT in WEISS'[4]) laboratory, down to temperatures obtainable with liquid hydrogen, have shown that at these lower temperatures the data are much better represented by a law of the type proposed by BLOCH.

It is reasonable to expect that the interaction energy might give a contribution to the heat capacity at these temperatures.

e. Calculation of additional heat capacity due to interaction of electrons, according to BLOCH. The equations of BLOCH from which the approach to absolute saturation at low temperatures was derived yield an expression for the average electronic interaction energy involved[5]).

---

[1]) F. BLOCH, Zs. f. Phys., **61**, 206, 1930. Handbuch der Radiologie, VI, 2, p. 469.

[2]) J. C. SLATER, Phys. Rev., **35**, 509, 1929; **36**, 57, 1930.

[3]) P. WEISS and R. FORRER, C. R., **186**, 822, 1928.

[4]) P. WEISS, C. R., **198**, 1893, 1934.

[5]) Our thanks are due to Dr. J. DE BOER for the communication of this result.

$$\overline{E} = \frac{N\,(kT)^{5/2}}{J^{3/2}} \times 0.045 \tag{10}$$

The corresponding heat capacity term is[1])

$$\frac{d\overline{E}}{dT} = \frac{5}{2}\;\frac{Nk\,(kT)^{3/2}}{J^{3/2}} \times 0.045 \text{ ergs/deg.} \tag{11}$$

For the purpose of estimating this, use is made of the relation given by BLOCH $T_c = \frac{J}{k}$, were T_c is Curie temperature.

This yields the simple relation

$$\left(\frac{k}{J}\right)^{3/2} = \left(\frac{1}{T_c}\right)^{3/2} \tag{12}$$

Substituting this in eq. (11), and putting Nk equal to 1.98 cal/deg., we derive,

$$C_\mathrm{i} = 1.8 \times 10^{-5}\; T^{3/2} \text{ cal/deg.}$$

Comparing this to the measured heat capacities we find[2])

$T = 1.23$	$C_\mathrm{obs.} = 204 \times 10^{-5}$	$C_\mathrm{i} = 2.4 \times 10^{-5}$
$T = 4.2$	$C_\mathrm{obs.} = 785 \times 10^{-5}$	$C_\mathrm{i} = 15 \times 10^{-5}$

The present measurements do not necessarily exclude the possibility of such a contribution to the atomic heat being present. It is perhaps masked by the larger effect due to some other cause. Further, the data show that the accuracy of the measurements is of the same order of magnitude as the interaction contribution sought.

f. A linear heat capacity. The free or conduction electrons in metals are considered statistically as a gas and it remained for long unexplained why they did not make an appreciable contribution to the heat capacity of metals. For the most elementary explanation of electrical conductivity, the conduction electrons must be assumed to move more or less freely among the atoms, thus introducing three more degrees of freedom; if

---

[1]) This equation was developed for a simple cubic lattice but will give the correct order of magnitude for *Ni* also.

[2]) In the original paper concerning these measurements, (W. H. KEESOM and C. W. CLARK. Physica **2**, 513, 1935) the value of *J* was assumed to be 0.02 electron-volts, which accounts for the higher value of *Ci* given there.

the MAXWELL-BOLTZMANN distribution function were applicable, an additional heat capacity of $^3/_2\,R$ should be present at all temperatures.

On the assumption that the free electrons in a metal act statistically as a degenerate gas, and must therefore be considered from the standpoint of the FERMI-DIRAC statistics, SOMMERFELD derived a formula for the energy of the free or conduction electrons in metals. This yields a heat capacity proportional to the first power of T. (13)

$$C_e = \frac{\pi^2 n m k}{h^2} \left(\frac{8 \pi V}{3 n N}\right)^{2/3} RT = 3.26 \times 10^{-5}\, V^{2/3}\, n^{1/3} T \text{ cal/deg.}$$

in which n denotes the number of free electrons per atom, V the atomic volume, and the other symbols have their usual significance[1]).

Strictly speaking, this heat capacity is not proportional to T, since the atomic volume changes somewhat with temperature. This is, however, a secondary effect of minor importance, and for the small temperature interval here considered, may be neglected.

Since in its simplest form, the heat capacity so introduced is proportional to the cube root of the number of free electrons, variation in n does not greatly change the amount of this contribution.

For simplifying the calculation n is here assumed as 1, and 30.4×10^{-6} has been used for the coefficient of cubical expansion of Ni when calculating the atomic volume at low temperatures. Eq. (13) then reduces to

$$C_e = 1.15 \times 10^{-4}\ T \text{ cal/deg.} \qquad (14)$$

This is only 6.6% of the additional heat capacity determined experimentally. This was derived for electrons which are entirely free. Actually in the interior of a metal, the movement of the

---

[1]) A. SOMMERFELD, Zs. f. Phys., 47, 1. 1928.
In the formula as given by SOMMERFELD, n was the number of electrons per cm^3 and equal to N/V, and only 1 free electron per atom was considered. The formula has here been rearranged to cover the case of more than one electron per atom.

electrons cannot be considered free of forces. When an electron leaves a metallic atom, it leaves behind a positive ion and there is, of course, an attraction between the two.

For the more general case, leaving open the question of the forces to which the conduction electrons are subject, the formula is[1])

$$C_e = \frac{2\,\pi^2}{3}\,N\,(\zeta_0)\,k^2\,T \tag{15}$$

where $N(\zeta_0)$ is the number of quantum states per energy interval per cm^3. From this equation, one may derive the equation valid for entirely free electrons by substituting in the value $N(\zeta_0)$ applicable to that case[2]).

As with the fully free electrons, this yields a heat capacity proportional to T. It increases with the number of quantum states per energy interval dE.

The conduction electrons are responsible for the temperature independent paramagnetism observed in many metals (according to BETHE it was PAULI'S theory of this effect which gave the impulse to the modern electron theory of metals) and this paramagnetism may be calculated from the assumption of entirely free conduction electrons. In the calculation, the volume susceptibility is directly proportional only to the number of quantum states per energy interval. The observed temperature independent paramagnetism of many metals greatly exceeds this calculated quantity, the greatest difference being in the cases of *Cr*, *Pd* and *Pt*, the ratio of observed to calculated being 32 to 1 in the extreme case of *Pd*. One derives from this that the number of quantum states per energy interval is greater than follows from the assumption of free electrons.

---

[1]) A. SOMMERFELD and H. BETHE, Hdb. d. Physik, **24**, 2, p. 430.

[2]) A. SOMMERFELD and H. BETHE, Hdb. d. Physik, **24**, 2, p. 353, eq. (5.8) and p. 336, eq. (2.6).

By analogy, the same is assumed to be the case with Ni and the additional heat capacity term found in these measurements is attributed to such an effect.

The FERMI statistics go over to the classical MAXWELL-BOLTZMANN statistics at a temperature T'' defined by

$$T'' = \frac{h^2}{2\ mk} \left(\frac{3\ N}{8\ \pi V}\right)^{2/3}$$

which is greater than 10^4 °K. Thus the electron gas in the metals should be subject to this statistical method at all temperatures below the melting point. If the additional heat capacity here observed is to be attributed to the change in energy of some of the electrons, it should be expected that the effect would continue up to the melting point.

It is particularly difficult in Ni to determine precisely if this is so. With the exception of the very lowest temperatures (1-10°K) the choice of θ exerts a large effect on the determination. At the higher temperatures (500-600°K) where the DEBIJE atomic heat approaches the classical value of 3R (plus the correction for C_p - C_v) and the choice of θ within reasonable limits should make little difference, the vibrations of the atoms can no longer be considered harmonic. The classical value is exceeded for this reason and it is not possible to evaluate exactly this additional heat capacity. Further, there is a magnetic specific heat present below the Curie point. The disappearance of this term at the Curie point is predicted quantitatively by the WEISS theory of the internal field but it is not possible to say how far below this temperature the assumptions of WEISS are valid for calculating this magnetic term.

Measurements of the atomic heat of Ni from the temperatures obtainable with liquid air to about 100° above the Curie point were recently carried out in WEISS' laboratory by Mme. LAPP¹). It appeared that the measured heat capacity was rather higher

---

¹) P. WEISS, C. R., **187**, 1, 12, 1928.
E. LAPP, Ann. de Phys., **12**, 442, 1929.

than might reasonably be expected. Calculations were made to determine as accurately as possible the amounts of the different terms enumerated in the preceding paragraph. θ was taken to be 380 as estimated from the heat capacity at the lowest temperature measured. The correction for the high temperature deviation from the DEBIJE formula (BORN-BRODY anharmonic oscillator) was obtained by comparison with *Cu*. The magnetic term was calculated according to WEISS' assumption concerning the nature of the internal field. After these and the correction for $C_p - C_v$ were deducted there remained aquantity whose origin was unexplained. This "unknown term" so determined increased with temperature, from 0.029 cal/deg. at 98°K to about 1.0 cal/deg. at the Curie point, and appeared to remain constant up to the limit of the measurements, 743°K.

Had a somewhat higher value been chosen for θ, for example, the 413 calculated from the elastic constants, the amount of this "unknown term" would be of the same order of magnitude as the additional heat capacity determined in these measurements. However, even above the Curie point where the magnetic term has disappeared and the temperature is sufficiently high so that a difference of 50 in the value of θ makes relatively little difference, the correction for the anharmonic oscillator is still a source of considerable uncertainty. The difficulty of evaluating the corrective terms must therefore leave this concordance open to some doubt.

CHAPTER V.

THE HEAT CAPACITY OF GADOLINIUM SULFATE.

§ 1. Introduction.

The heat capacity of gadolinium sulfate became of interest after DEBIJE[1]) and GIAUQUE[2]) suggested a process for attaining temperatures below 1°K with the aid of this well-known paramagnetic salt. Its heat capacity was measured from temperatures attainable with liquid hydrogen to room temperature in order to be able to estimate its heat capacity at still lower temperatures, and from this to estimate the amount of cooling to be expected under certain conditions[3]). At the time these estimates were made, it was stated that the neglect of the energy considerations introduced by "term-splitting" would yield higher estimates for the reduction in temperature than would be realized experimentally.

These measurements were extended by KÜRTI[4]) to liquid helium temperatures (down to 1.6°K), and he succeeded in demonstrating the anomalous thermal behavior of this substance at these temperatures. Because of this interesting behavior and the original connection of this compound with the magnetic cooling process, it was considered desirable to extend the measurements to still lower temperatures. The knowledge of its low temperature thermal properties was rendered further desirable by the announce-

---

[1]) P. DEBIJE, Ann. d. Phys., **81**, 1154, 1926.

[2]) W. F. GIAUQUE, Journ. Amer. Chem. Soc., **49**, 1865, 1927.

[3]) W. F. GIAUQUE and C. W. CLARK, Journ. Amer. Chem. Soc., **54**, 3135, 1932.

[4]) N. KÜRTI, Zs. f. phys. Chem., B. **20**, 305, 1933.

ment by KEESOM[1]) of a scheme for determining the absolute temperature scale below 1°K by essentially calorimetric methods. These various topics will be considered in more detail later.

§ 2. Material.

The gadolinium sulfate employed in these measurements was obtained from the stock of the late Prof. CHARLES JAMES of the University of New Hampshire, through the cooperation of Dr. H. S. Miner of the Welsbach Co., and was stated to have been of atomic weight purity.

The material, originally in the form of very small crystals, was recrystallized in order to reduce the surface.

With the cooperation of Dr. J. J. M. VAN SANTEN, the absorption spectrum of a 0.2 N chloride solution, prepared from the recrystallized material, was photographed as a verification of the purity. The absorbing layer had a thickness of 115 mm, and exposures of 2, 15 and 25 seconds were made. The only bands found, in the range from below 2200 Å to 5700 Å, were those previously attributed to the gadolinium ion. The impurities usually associated with gadolinium are terbium and europium and no absorption could be found in the regions where absorption bands are to be expected for these two elements.

137.9 gr. were used in the measurements.

§ 3. Experimental.

The low starting temperatures for measurements beginning at 1.1° K were obtained in the usual manner, i. e., the calorimeter and its contents were placed in thermal contact with the surrounding bath of liquid helium boiling under reduced pressure. For obtaining still lower starting temperatures the obvious procedure was to employ the magnetic cooling process. This was carried out in a simple manner. A Weiss type electro-magnet with flat-pole pieces (diameter 190 mm) was placed so that the calorimeter and its contents were centrally and symmetrically

---

[1]) W. H. KEESOM, loc. cit., See Chap. II, p. 25.

situated between the pole pieces. With the calorimeter at 1.5° K and in contact with the surrounding liquid helium, by means of the mechanical contact maintained by the spring device mentioned in Chap. II, a field of 5500 gauss was switched on. When equilibrium with the outside bath appeared to have been reached, the thermal contact was broken, the magnetic field switched off and the magnet removed.

The first attempt to do this was unsuccessful because the helium gas present for thermal conductivity was completely adsorbed and the thermometer was isolated. For the following attempt, a device was prepared by means of which any required amount of helium gas could be measured and admitted to the calorimeter. This enabled the low temperatures reached, estimated by extrapolation of the *R vs T* curve at 0.5°-0.6° K to be measured with the *Ph-br* resistance thermometer.

§ 4. Results.

Four series of measurements were carried out in the liquid helium range:

(1) June 8, 1934	from	1.3° to 3.9°K.
(2) June 28, 1934		(0.72°) to 4.6°K.
(3) July 6, 1934		3.7° to 4.5°K.
(4) Oct. 18, 1934		(0.5°) to 1.8°K.

The temperatures at which the measurements began on June 28 and October 18 are uncertain because these temperatures were determined by extrapolation of the *R vs T* curve below 1°K. The above results are summarized in Table VII.

One series of measurements was made between 4.6° and 10°K on July 6, 1934. Measurements from 10° to 20.5°K, temperatures attainable with solid and liquid hydrogen, were carried out on June 1 and June 12, 1934. The results of the measurements from 4.6° to 10°K, and points taken from the smoothed curve for temperatures above 10°K are given in Tables VIII and IX.

All the results are based on $^1/_2$ gr. molecule $Gd_2(SO_4)_3 \cdot 8H_2O$.

TABLE VII.

Heat capacity of $^1/_2$ mol $Gd_2(SO_4)_3 \cdot 8H_2O$.
Measurements in liquid helium.

June 8, 1934.

Point	T_{av}	C_p cal/deg.	Point	T_{av}	C_p cal/deg.
Ia	1.61	0.1986	IIf	2.36	0.1114
b	1.73	0.1765	g	2.41	0.1093
c	1.77	0.1829	h	2.40	0.0999
d	1.80	0.1642	i	2.47	0.1030
e	1.84	0.1658	j	2.60	0.0914
f	1.88	0.1593	k	2.72	0.0835
g	1.93	0.1492	l	2.81	0.0778
h	1.97	0.1512	m	2.89	0.0758
i	2.02	0.1408	n	3.00	0.0723
j	2.28	0.1164	o	3.17	0.0680
IIa	1.38	0.2640	p	3.45	0.0636
b	1.39	0.2857	q	3.58	0.0591
c	1.40	0.2887	r	3.68	0.0545
d	1.42	0.2688	s	3.78	0.0596
e	2.30	0.1163	t	3.89	0.0535

June 28, 1934.

Point	T_{av}	C_p cal/deg.	Point	T_{av}	C_p cal/deg.
If	1.03	0.4179	IIf	1.04	0.4406
g	1.23	0.3373	g	1.11	0.4046
h	1.33	0.2975	h	1.19	0.3711
i	1.43	0.2662	i	1.27	0.3250
j	1.60	0.2193	j	3.87	0.0504
k	1.77	0.1962	k	3.94	0.0506
l	1.93	0.1575	l	4.02	0.0460
m	2.09	0.1349	m	4.11	0.0537
n	2.23	0.1221	n	4.30	0.0544
o	2.37	0.1128	o	4.57	0.0535
p	2.57	0.1027			

July 6, 1934.

Point	T_{av}	C_p cal/deg.	Point	T_{av}	C_p cal/deg.
Ia	3.77	0.0632	Ic	4.28	0.0536
b	4.15	0.0512	d	4.48	0.0572

TABLE VII, cont.

October 18, 1934.					
Ij	1.01	0.4031	Ip	1.45	0.2479
k	1.08	0.3810	q	1.52	0.2276
l	1.15	0.3540	r	1.60	0.2141
m	1.22	0.3272	s	1.67	0.2007
n	1.30	0.2974	t	1.74	0.1874
o	1.38	0.2725	u	1.81	0.1777
Points below 1°K obtained with extrapolated temperature scale.					
June 28, 1934.					
Ia	0.74	0.711	IIa	0.73	0.768
b	0.78	0.636	b	0.78	0.640
c	0.83	0.547	c	0.83	0.588
d	0.87	0.520	d	0.89	0.510
e	0.95	0.480	e	0.97	0.460
October 18, 1934					
Ia	0.51	0.727	If	0.75	0.568
b	0.54	0.709	g	0.81	0.506
c	0.59	0.668	h	0.87	0.473
d	0.64	0.643	i	0.94	0.442
e	0.69	0.601			

TABLE VIII.

Heat capacity of $^1/_2$ mol $Gd_2(SO_4)_3 \cdot 8H_2O$.

Measurements between 4.6° and 10° K.

July 6, 1934.

Point	T_{av}	C_p cal/deg.	Point	T_{av}	C_p cal/deg.
Ie	4.68	0.0595	Ii	5.75	0.0760
f	4.88	0.0605	l	8.49	0.227
g	5.13	0.0648	m	9.04	0.238
h	5.25	0.0657	n	9.99	0.310

TABLE IX.

Measurements in solid and liquid hydrogen.

Points taken from smoothed curve of measurements of June 1 and June 12, 1934.

T	C_p	T	C_p
10.5	0.354	16.0	1.245
11.0	0.426	16.5	1.346
11.5	0.500	17.0	1.451
12.0	0.576	17.5	1.563
12.5	0.657	18.0	1.685
13.0	0.730	18.5	1.817
13.5	0.811	19.0	1.955
14.0	0.892	19.5	2.102
14.5	0.977	20.0	2.249
15.0	1.063	20.5	2.395
15.5	1.152		

The results for the whole temperature range here investigated are shown graphically in Fig. 10. The results in the liquid helium range are separately presented in Fig. 11.

It is evident from the divergence of the points below 1° K shown in Fig. 11, that the extrapolation of the R *vs* T curve below temperatures at which it has been calibrated is not to be trusted. The divergence is due to the fact that extrapolations based on two different sets of calibration points obtained on two different days did not agree. The points have been included because they are certainly of the correct order of magnitude.

These results show consistently lower heat capacities than those reported by Kürti in the liquid helium region. In Kürti's experiments, the heat capacity of the salt present is a relatively small part of the total heat capacity measured; the most unfavorable ratio occurs at 5°K where the heat capacity of the salt is less than $20^{0}/_{0}$ of the total; at the lowest temperature of the measurements, 1.6°K, the heat capacity of the salt was about $80^{0}/_{0}$ of the total. Since there was helium gas present there is also the possibility of a desorption heat in the liquid helium range.

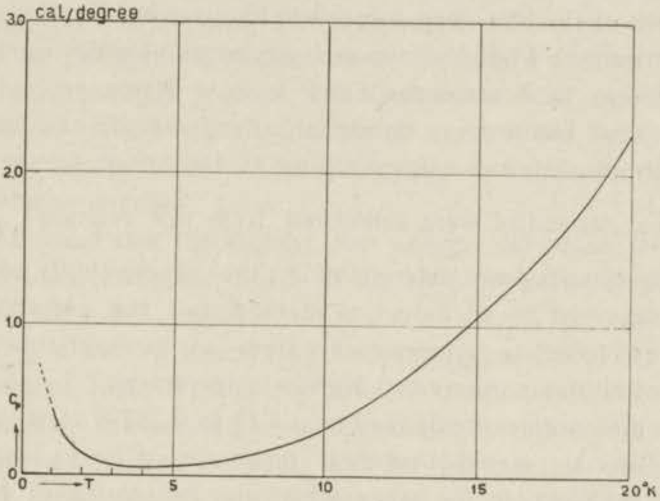

Fig. 10. Heat capacity $Gd_2(SO_4)_3{\cdot}8H_2O$. 0.5° to 20.0°K.

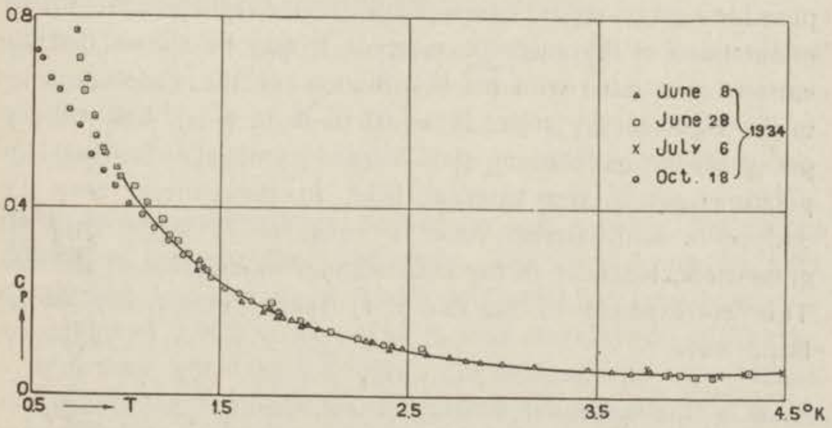

Fig. 11. Heat capacity $Gd_2(SO_4)_3{\cdot}8H_2O$. 0.5° to 4.5°K.

The heat capacity of $Gd_2(SO_4)_3 \cdot 8H_2O$ was determined by GIAUQUE and MAC DOUGALL[1]) in an entirely different manner. A quantity of the salt was subjected to a series of adiabatic demagnetizations from a common temperature, employing a series of different field strengths; and from a determination of the temperature reached on demagnetization and the calculation of the entropy loss on magnetization at the initial temperature[2]), the heat capacities were calculated from the relation $\frac{dS}{dT} = \frac{Cp}{T}$. For the temperature determination, the susceptibility of the salt was measured by an induction method and the susceptibilities were converted to temperatures from an extrapolation of the susceptibilities measured at higher temperatures.

The measurements extended from 1.7° to 0.287°K. GIAUQUE and MAC DOUGALL stated that their results were lower than those found by KüRTI in the range where the two series of measurements overlapped; but the numerical data were not given.

§ 5. Discussion.

a. The cause of the anomaly. In the absence of a magnetic field the gadolinium ion possesses, at usual temperatures, eight possible energy states, corresponding to the eight possible spatial orientations of the magnetic moment. It may be shown that the entropy associated with the distribution of the gadolinium ion in the eight energy states is equal to $R \ln 8 = 4.13$ cal/deg. per gram-ion gadolinium, (i.e., $N\ Gd^{+++}$ ions) at not too low temperatures and in zero external field. In the general case, the entropy in zero external field is equal to $R \ln(2J + 1)$ per gram-atom, where J is the total angular momentum of the ion. This corresponds to the $(2J + 1)$ spatial degeneracy of the basic level.

---

[1]) W. F. GIAUQUE and D. P. MAC DOUGALL, Phys. Rev., **44**, 235, 1933.

[2]) The thermodynamical basis of the magnetic cooling process and the methods of calculation of the entropy loss on magnetization are considered in the following chapter.

According to the NERNST heat theorem the entropy content must be zero at the absolute zero, and all the ions will then be in the lowest energy state. When energy is added to the substance, the distribution of the ions to the higher energy states will take place. This process will continue until an equilibrium distribution is attained and no further energy will then be required for this activation. This energy is, of course, in addition to the lattice energy.

It is evident that the smaller the energy difference between the individual levels, the closer to the absolute zero this process of distribution will begin.

Nothing is known concerning the splitting pattern of the basic level except that it splits up into 8 components, nor of the mechanism of the interaction which eventually reduces the magnetic entropy content to zero. For the purpose of comparing the data here obtained with some kind of a theoretical curve, assumptions concerning these questions must be made and considered statistically.

b. The SCHOTTKY *thermally excited "quantum jumps"*. From a simple statistical consideration of an equilibrium between the basic level and one higher level, SCHOTTKY[1]) developed an expression for the heat capacity term introduced.

This is

$$\Delta C_v = \frac{R\left(\frac{\theta_u}{T}\right)^2 e^{\frac{\theta_u}{T}}}{\left(1 + e^{\frac{\theta_u}{T}}\right)^2}$$

were θ_u is a temperature defined by u/k, u being the energy difference between the two levels. The two levels are here considered to have equal statistical weights. This reaches a maximum of $0.44R$ at $T = 0.42\ \theta_u$ and decreases on either side.

SCHOTTKY tested this formula on the heat capacity observations that were then available for the paramagnetic metals, *Na*, *K*, *Mg* and *Ca* and found fair agreement.

---

[1]) W. SCHOTTKY, Phys. Zs., **23**, 448, 1922.

SIMON¹) has extended these comparisons to a variety of other substances and has found a number of cases where such "quantum jumps" are apparently taking place.

An extension of this type of formulation to more than two levels may be made for studying the anomaly in the gadolinium ion.

c. Theoretical calculation of the anomaly for Gd^{+++}²). The simplest assumption to make for the purpose of this calculation is that the eight levels in question are equally spaced and are acting independently. This was done by SIMON and KÜRTI for comparison of the measurements of KÜRTI; an expression was developed for the entropy due to the orientation of the gadolinium ion in the eight states, each separated by the energy ε (or $N\varepsilon$ per gram-ion), which is only a function of ε/T. The measurements of KÜRTI could be represented by this expression with $N\varepsilon = 0.52$ cal/gr. ion. According to this relation, about 98% of the final entropy has been attained at 2°K. The entropy corresponding to the heat capacities determined in the present measurements lies below this theoretical curve down to 1°K. Our results agree fairly well, but not exactly, with such a function with $N\varepsilon = 0.494$ cal/gr. ion. This corresponds to a wave number of 0.17 cm^{-1}.

GIAUQUE and MAC DOUGALL (loc. cit.) calculated the theoretical change in entropy by considering the interaction of two gadolinium ions, treated as simple magnets. For the purposes of calculation, "the magnets were assumed to have clockwise and counter-clockwise directions along the interatomic direction and along three symmetrically placed lines, making an angle of 60° with the interatomic direction". The total number of configurations is thus 64 and when the energies of the different configurations are considered, eight discrete groups are found which correspond to the eight energy levels. The expression

---

¹) F. SIMON, Sitz. Preuss. Akad., 33, 477, 1926.

²) The two formulae corresponding to the treatment here sketched, have, so far as I know, not been published. Prof. KEESOM derived and discussed them for his class lectures during the spring semester, 1934.

for the entropy is then developed, but contains the distance between the two coupled atoms as an unknown. This distance was determined from some of the experimental data. The entropies corresponding to their measured heat capacities agreed well with the theoretical curve over the whole range. Such a treatment is not rigidly valid down to the absolute zero, since the lowest level has an *a priori* weight 2, corresponding to an entropy, $^1/_2\ R$ ln 2 at the absolute zero. Some assumption must be made concerning the mechanism necessary to reduce this so that it eventually disappears from the expression. The authors say that the results also agree with the SIMON-KÜRTI curve.

GIAUQUE says that the agreement between their data and their theoretical curve does not necessarily imply that their geometrical assumptions are correct. It shows rather that any reasonable assumption concerning the interaction of the atoms, or the distribution of the energy levels will give a theoretical curve of the correct order of magnitude.

The extensive experiments of DE HAAS and WIERSMA¹) on the attainment of low temperatures by the application of the magnetic cooling process have demonstrated that many other paramagnetic salts are more suitable than the originally discussed gadolinium sulfate for reaching very low temperatures ($T < 0.05°K$). For many experimental purposes, however, the presence of the anomalous heat capacity is a distinct advantage. Reasonably low temperatures, of the order of magnitude of 0.2°K, can be reached with the aid of gadolinium sulfate, and the higher heat capacity would act as a buffer against energy entering the system. Its high magnetic moment is also an advantage since the available entropy change is then greater. The temperature range attainable through the use of Gd^{+++} may be extended by the use of more dilute salts, as for example, the ethyl sulfate or other organic compounds.

---

¹) W. J. DE HAAS and E. C. WIERSMA, Comm. Leiden, Nos. 231e and 236a. Physica 1, 779, 1934; 2, 91, 1935.

CHAPTER VI.

TEMPERATURE SCALE BELOW 1°K.

§ 1. Introduction.

The process proposed by KEESOM for placing temperatures below 1°K on the thermodynamic scale was briefly outlined in Chap. II.

In order that the principles underlying this proposal may be clearly understood, the theory of the magnetic cooling process in the ideal case will be reviewed.

The combination of the first and second laws of thermodynamics yields

$$dU = TdS + dA. \tag{16}$$

Considering now a magnetizable substance, if we change its magnetic moment σ, by an amount $d\sigma$, in the magnetic field, H, the work done on it is $Hd\sigma$[1]) and eq. (16) may be rewritten

$$dU = TdS + Hd\sigma \tag{17}$$

assuming that the volume change dV and the corresponding term for the work done by the body against an external pressure, PdV can be neglected.

Equation (17) may be written

$$dS = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_\sigma dT - \left(\frac{\partial H}{\partial T}\right)_\sigma d\sigma \tag{18}$$

and when this is integrated, the total entropy is represented as the sum of two parts. The first is the usual vibrational entropy, and the second is the magnetic part

$$S_m = -\int\left(\frac{\partial H}{\partial T}\right)_\sigma d\sigma. \tag{19}$$

---

[1]) W. H. KEESOM, Leiden Suppl., No. 32a, 1913.

Considering now a paramagnetic substance at a temperature T, and with a total entropy content S. If the substance is magnetized isothermally, the total entropy will change by an amount $-\Delta S_m$. If it is then demagnetized adiabatically, the total entropy must remain the same, and in the ideal case, the magnetic entropy of the substance will regain its former value at the expense of the vibrational entropy. The substance will then cool down by an amount corresponding to the amount of entropy it has lost during magnetization at the higher temperature[1]).

If a substance is subjected to this process and has cooled down to a temperature, T_1, because of an entropy loss ΔS_{m_1} at the temperature T, we can determine experimentally the heat required Q_1, to bring the substance to the starting temperature T. Similarly, the substance may be cooled down to a lower temperature T_2, corresponding to an entropy loss ΔS_{m_1} ($\Delta S_{m_2} > \Delta S_{m_1}$) and the amount of heat Q_2, required to reheat to the starting temperature may be determined. The difference, $Q_2 - Q_1$, is the amount of heat which is required to give back to the substance the entropy $\Delta S_{m_2} - \Delta S_{m_1}$. Since according to the second law, the amount of heat required to increase the entropy by a certain amount is a function of temperature we have the necessary data for determining the temperature, thermodynamically.

The process was carried out in the following manner. The gadolinium sulfate contained in the calorimeter was subjected to isothermal magnetizations and adiabatic demagnetizations from the initial temperature, 1.50°K, employing magnetic fields up to 7500 gauss. At each low temperature reached, the resistance of the thermometer was measured. The calorimeter and its contents were then heated up to 1.50°K and the amount of energy Q, required to do this was measured. A graph was then

---

[1]) For a more complete and detailed consideration of the magnetic cooling process, reference should be made to the original papers of GIAUQUE and DEBIJE (see page 55) or more recent summaries as:

W. MEISSNER, Phys. Zs., **35**, 303, 1934.

P. DEBIJE, Phys. Zs., **35**, 923, 1934.

N. KÜRTI and F. SIMON, Proc. Roy. Soc. London, A, **149**, 154, 1935.

made in which the calculated entropy change ΔS_m, was plotted against the corresponding Q. The slope dQ/dS at any point should then give the corresponding absolute temperature T.

§ 2. Calculation of entropy change on magnetization.

The equation for the entropy change caused by a magnetic field H, at a temperature T, has already been given. If we may put $\sigma = f\,(H/T)$, the equation may be written as follows:

$$\Delta S_m = -\int \frac{H}{T}\, d\sigma. \tag{20}$$

a. The LANGEVIN *formula.* The measurements of WOLTJER and KAMERLINGH ONNES[1]) showed that the magnetization of gadolinium sulfate was rather well represented by the LANGEVIN function at temperatures down to 1.31°K and in magnetic fields up to 24000 gauss. The formula proposed by LANGEVIN for the approach of paramagnetics to saturation is

$$\frac{\sigma}{\sigma_\infty} = \coth a - \frac{1}{a} \tag{21}$$

in which σ_∞ is the magnetic moment at complete saturation, and $a = \mu H/kT$, μ being the magnetic moment of one "carrier". This agreement was considered rather surprising since the formula was developed on a classical basis from the consideration of a paramagnetic gas, the molecules of which are supposed to exert no influence on each other and can have a continuous distribution of their magnetic axes. When subjected to the action of a magnetic field the molecules tend to orient themselves with their magnetic axes in the direction of the field. This tendency will be counteracted by the thermal agitation of the molecules, and depending on the magnetic field strength H, and the temperature T, there will be an equilibrium distribution. It is the formulation of this equilibrium which gives the LANGEVIN expression for the total magnetic moment in the field direction.

---

[1]) H. R. WOLTJER and H. KAMERLINGH ONNES, Comm. Leiden, No. 167c.

The ions of the rare earths possess their magnetic moments as a result of the incompletely filled $4f$ electronic shell, and these electrons are surrounded by 8 electrons of higher principal quantum number. That these $4f$ electrons are but little affected by the fields of other atoms is attested to by the well-known difficulty of the chemical separation of the rare earth compounds, in spite of the fact that the number of $4f$ electrons varies from 0 to 14. In a compound such as $Gd_2(SO_4)_3 \cdot 8H_2O$, the magnetic ions are further separated by the negative ions and the molecules of water of crystallization.

In order to evaluate the change in entropy upon magnetization according to formula (20) with the aid of the LANGEVIN formula, let $H/T = x$ and $\sigma = f\,(x)$. We then have

$$\Delta S_m = - \int x\, f'(x)\, dx = - x\, f(x) + \int f(x)\, dx$$

and when the indicated integration is carried out one obtains,

$$\Delta S_m = nk \left[\ln \frac{\sinh a}{a} + 1 - a \coth a \right]. \qquad (21)$$

This is the change in entropy caused by the change in the parameter a, from $a = 0$ to $a = a$.

DEBIJE[1]) pointed out that this expression conflicted with the usual concept of the finiteness of entropy. If equation (21) is developed in a series for large values of $a\,(T \rightarrow 0,\ a \rightarrow \infty)$ it contains the term $-nk \ln 2a$, which would become infinite at $T = 0$. However, in this work the field strengths and temperatures employed were such that the value of the parameter a, did not exceed 3, and the experimental points were well represented by the LANGEVIN curve in this range.

The LANGEVIN formula is employed here only as an interpolation formula. The same result could be obtained by preparing a graph of the experimental data, in which H/T is plotted against σ. The area under the curve, from $\sigma = 0$ to the σ corresponding to the value of H/T used, is the entropy and this may be

---

[1]) P. DEBIJE, Ann. d. Phys., 81, 1154, 1926.

determined simply by graphical integration. In this case then, the use of a formula which represents the data is only for convenience in calculation[1]).

b. Quantum theory. It should be mentioned that the difficulty of the infinite decrease in entropy upon magnetization at the absolute zero, which is a consequence of the LANGEVIN formula, disappears when the restrictions of the quantum theory are introduced. Whereas on the classical theory, any orientation of the elementary moment is assumed possible, in the quantum theory only certain angles with the direction of the field are permitted. The experiments of GERLACH and STERN gave direct evidence of such space quantization of the directions of an elementary moment with respect to the direction of an external magnetic field. The effect of the assumption of fewer possible orientations is a more rapid approach to saturation.

However, for the values of H/T used in these experiments, the entropies calculated on the basis of the LANGEVIN formula agree quite well with those calculated from formulae based on the quantum theory.

The calculation of the entropy changes involved in these experiments has been based on the LANGEVIN formula.

§ 3. Experimental.

All the magnetizations performed prior to the adiabatic demagnetizations were done at 1.50°K. The magnetic fields employed were not entirely homogeneous. The magnet was calibrated before the experiments and was recalibrated after the experiments were completed. At the extremities of the calorimeter the field was about 1% less than at the center. A correction for this has been applied in the calculations.

The first experiments were carried out on Nov. 12, 1934. No gas was admitted to the space surrounding the calorimeter, an attempt being made to conduct away the heat developed during magnetization through the mechanical contact. Had this been

---

[1]) Except in so far as the assumption $\sigma = f(H/T)$ has been made.

possible, it would not have been necessary to evacuate before demagnetization. The mechanical contact was apparently not sufficiently good, because equilibrium with the surroundings (kept at 1.50°K) was never attained.

The experiments were again carried out on Nov. 22, 1934. Gas was now admitted into the space surrounding the calorimeter during magnetization and equilibrium with the surroundings was attained rather rapidly. As soon as the calorimeter was again at 1.50°K, the gas was pumped out. The demagnetization was carried out when a fair vacuum had been attained, usually after 10 to 15 minutes.

In round numbers, the field strengths employed were 7500, 6500, 5500, 4000, 2500 and 1500 gauss. On demagnetization from the first three field strengths, the *Ph-br* indicated the same temperature, indicating probably that the helium gas present had been "frozen out".

It was then thought that if a much larger quantity of helium gas were present, there would be sufficient liquid present between the crystals at the lowest temperatures to provide thermal contact. Accordingly, the quantity of gas in the calorimeter was increased from 8.4×10^{-5} to 0.0113 mols and on Nov. 30, measurements similar to the above were carried out, beginning with a field of 4000 gauss at 1.50°K. The thermometer reading agreed with that found under the same conditions the previous week, but the thermometer now indicated a large heat leak into the calorimeter, in spite of an excellent vacuum. A repetition of the experiment with a field of 7500 gauss gave the same result. Here, the initial reading of the thermometer indicated a somewhat lower temperature than was reached with the same field the previous week in spite of the additional heat capacity introduced by the larger quantity of helium present, indicating that the presence of the larger quantity of gas did assist in the attainment of better thermal equilibrium.

Following this, about 75% of the helium gas was pumped out of the calorimeter and the experiment with 7500 gauss was repeated. There was again a heat leak but it was only about half that observed in the preceding experiment.

Similar experiments were carried out on January 17, 1935, but the same phenomenon occurred. The cause of this is not known. It might be supposed that the thermometer wire was entirely isolated and that the observed "heat leak" was only a heat leak down the thermometer wire. This heat leak was not present however, on November 22, when a much smaller quantity of helium gas was present in the calorimeter. Further, the thermometer responded to energy added to the calorimeter through the heating coil.

§ 4. Consideration of experiments of November 22, 1934.

The quantity of gadolinium sulfate employed in the experiments was 137.9 gr. In the calculation of the entropy change on magnetization as derived from the Langevin formula, the value of the saturation magnetization of $^1/_2$ gr. ion $Gd_2(SO_4)_3 \cdot 8H_2O$ was taken to be 38.65 Weiss magnetons. The value of the parameter a is then $5.223 \times 10^{-4}\ H/T$. The field strengths employed, corrected for the inhomogeneity of the field, the value of a, the calculated entropy change and the amount of heat required to heat up the calorimeter and its contents to 1.50°K are given in Table X.

TABLE X.

<table>
<tr><th colspan="4">Adiabatic demagnetizations followed by calorimetric experiments</th></tr>
<tr><th colspan="4">Basis — 137.9 gr. $Gd_2(SO_4)_3 \cdot 8H_2O$.</th></tr>
<tr><th>H</th><th>a</th><th>$-\Delta S_m$</th><th>Q</th></tr>
<tr><td>1474.6</td><td>0.5135</td><td>0.03140</td><td>0.03408</td></tr>
<tr><td>2438.1</td><td>0.8489</td><td>0.08225</td><td>0.0892</td></tr>
<tr><td>3856.1</td><td>1.3427</td><td>0.1871</td><td>0.1483</td></tr>
<tr><td>5416.7</td><td>1.8861</td><td>0.3226</td><td>0.2130</td></tr>
<tr><td>6455.2</td><td>2.2477</td><td>0.4146</td><td>0.2467</td></tr>
<tr><td>7462.0</td><td>2.598</td><td>0.5006</td><td>0.2778</td></tr>
</table>

These values of ΔS_m were plotted against the corresponding Q, and the slopes of the curve were determined by the method employed for determining the slopes of the R *vs* T curve (Chap. II, p. 16). According to the experimental conditions, the slope dQ/dS at the origin, $Q = 0$, $\Delta S_m = 0$, should equal the starting temperature 1.50°K. Instead of this value, about 1.0°K was found and no method of drawing the curve, without unnatural distortion, would change this value greatly.

There was one very good check available for the two points in which the field strengths, 1500 and 2500 gauss, had been employed. The first cooled down to 1.169°K from 1.50°K as determined by the *Ph-br* thermometer. The heat capacity of gadolinium sulfate is known in this range (see preceding chapter), and an integration of the Cp *vs* T curve from 1.169° to 1.50°K would give the quantity of heat necessary to bring the substance from the lower to the higher temperature. This was determined and agreed quite well with that found in the demagnetization experiments. The same method of comparison was carried out for the point in which 2500 gauss had been used, the temperature reached (as determined by extrapolation) being 0.86°K. The agreement between the measured Q and that determined from the previous heat capacity measurements was also good here considering that it was partially based on an extrapolation. We can further compare the calculated entropy loss on magnetization with that determined calorimetrically in the range over which the cooling took place. In Fig. 12, the entropy determined calorimetrically in the range from 0.85° to 1.50°K is shown, so that these values may be compared with the calculated entropy loss on magnetization. The entropy loss (thermal) on going to lower temperatures, has been shown with zero placed at 1.50°K. These values were determined by graphical integration of a C_p/T *vs* T curve.

It was found in the two cases where a control was possible, that the calculated entropy change on magnetization was greater than the thermal entropy change in the range over which the cooling took place.

For the first point (1500 gauss and 1.50°K) the entropy change on magnetization (see Table X) was 0.0314 Clausius and the entropy loss on cooling was 0.0279 Clausius. For the second point, the calculated loss was 0.08225 Clausius and the observed change was 0.0764.

It thus appears that in this case, the magnetic cooling process is not as effective as is expected.

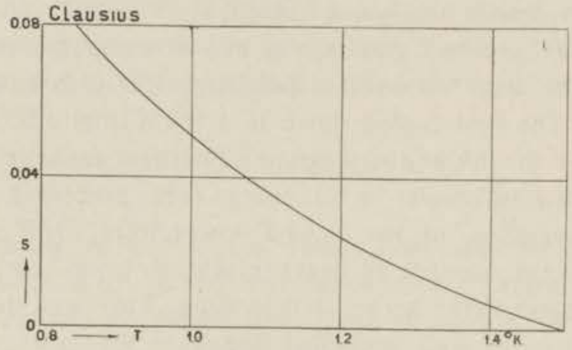

Fig. 12. Calorimetrically determined entropy loss of 137.9 gr. $Gd_2(SO_4)_3 \cdot 8H_2O$.

§ 5. Possible causes for discrepancy.

a. Incorrect evaluation of the magnetic field. In order to check this the magnet used was recalibrated with the same currents passing through the coils as when the demagnetization experiments were carried out. This calibration agreed with a previous calibration carried out completely independently. The inhomogeneity was determined by measurements at two field strengths along three radii at right angles.

b. Incorrect calculation of ΔS_m. This was checked by calculating the change in entropy upon magnetization by three different methods, (1) according to the LANGEVIN function, (2) according to the quantum theory of paramagnetism and (3) by graphical integration of the H/T *vs* σ curve as given by the measurements of WOLTJER and KAMERLINGH ONNES. Although all agreed fairly well, the LANGEVIN function gave the lowest values.

If, of course, there had been present some undetectable error in the basic measurements of the susceptibility, an error would be introduced into the entropy calculation. In the calculation of susceptibilities from the data obtained in some of the more recent measurements, the correction for the demagnetization factor has been neglected[1]). The data of WOLTJER and KAMERLINGH ONNES, recalculated on this basis and corrected to the temperature scale now in use, show a magnetization curve which would give a smaller entropy change on magnetization than the curve previously given. The difference though is much smaller than the order of magnitude of the discrepancy noted in these experiments.

c. *Non-reversible demagnetization.* If the demagnetization were carried out too rapidly, the change of magnetization of the gadolinium sulfate would cause an electromotive force to be induced in the pole pieces of the magnet. Assuming that the magnetization was reduced to zero in 10 seconds, and that the pole pieces offered a resistance of 0.01Ω, the order of magnitude of the energy dissipated is 10^{-7} to 10^{-8} calories. This figure is inversely proportional to the time assumed for demagnetization and the resistance assumed for the pole-pieces.

d. *Purity of material.* This point was considered in Chap. V, § 2.

§ 6. Assumption of an internal field.

It seems possible however, to give a quantitative explanation of the discrepancy noted by the assumption that the external field H evokes an opposing internal field H_0. Proceeding under such an assumption, it is possible to calculate the field H_0 from the difference between the calculated entropy change in the field H at a temperature T and the observed entropy change which occurs on adiabatic demagnetization. The calculation is essentially the determination of the effective field which would operate to produce the observed entropy change at 1.5°K and the comparison of this field with that actually employed.

The quantum theoretical formula for the approach to saturation

---

[1]) JEAN BECQUEREL, W. J. DE HAAS and J. v. D. HANDEL, Comm. Leiden, No. 231a. C. J. GORTER, W. J. DE HAAS and J. v. D. HANDEL, Comm. Leiden, No. 222d.

was employed for the calculation of the entropy change on magnetization since this now has a sounder theoretical basis than the LANGEVIN formula[1]).

The calculations show the following:

(1) Field applied, H = 1474.6 gauss. Calculated entropy change, 0.0329 Clausius. Observed entropy change, 0.0279 Clausius. Apparent opposing internal field, H_0 = 114 gauss.
(2) Field applied, H = 2438.1 gauss. Calculated entropy change, 0.0857 Clausius. Observed entropy change, 0.0764 Clausius. Apparent opposing internal field, H_0 = 135 gauss.

It is not possible to decide from these two points if this apparent field increases with the external field, or if it remains approximately constant. Such a field would, of course, have to be zero when the external field is zero and more points would have to be measured to determine the course of such an internal field from zero to the values here determined. The interpretation of the field H_0 is rather difficult but is does give a possible interpretation of the discrepancy noted in these measurements.

In consequence of these uncertainties the following calculations have more of a tentative character and it should not be considered that they lead to well established fact. They are to be considered merely as an example of the way in which the thermodynamic scale in the region below 0.9°K can be fixed and specific heats can be determined on the basis of that scale if more exact experimental facts are available. We are sorry that lack of time has prevented our extending the experimental data.

For these calculations it has been assumed that H_0 has a value of 125 gauss for all external fields greater than that value, and that $H_0 = H$ from $H = 125$ to $H = 0$. The ΔS_m values have been recalculated on this basis for reconsidering the *Q vs S* curve. The results are given in Table XI.

---

[1]) J. H. VAN VLECK, The theory of electric and magnetic susceptibilities, Oxford, 1932, p. 257.

R is the resistance of the *Ph-br* thermometer after the demagnetization had taken place. It will be noted that in the last three points the resistance of the *Ph-br* remains approximately constant; this is most likely due to the lack of heat conduction within the calorimeter.

TABLE XI.

Calculations on basis of assumption of internal field.
Temperatures determined from demagnetization experiments.

$H - H_o$	$-\Delta S_m$	Q	R	$T=dQ/dS$
1349.6	0.0277	0.0341	13.7627	1.21
2313.1	0 0775	0.0892	13.5477	0.82
3731.1	0.1817	0.1483	13.3412	0.54
5291.7	0.3146	0.2130	13.2280	0.39
6330.2	0.4062	0,2467	13.2282	0.36
7337.0	0.4923	0,2778	13.2274	0 33

§ 7. Heat capacity determinations.

These data may be employed to obtain heat capacities. One has the quantities of heat Q_1, Q_2, etc., required to heat up the system from T_1, T_2, etc., to the starting temperature T. The data treated arithmetically, i.e., $\frac{Q_a-Q_b}{T_a-T_b}$, will give average heat

TABLE XII

Heat capacities determined from demagnetization experiments
Basis —137.9 gr. $Gd_2(SO_4)_3 \cdot 8H_2O$.

$T=dQ/dS$	$C_p = dQ/dT$	C_p (calorimetric)
1.4	0.119	0.099
1.2	0.130	0.128
1.0	0.142	0.164
0.8	0.167	0.213
0.6	0.246	0.281
0.4	0.695	

capacities in the range T_a to T_b. For more accurate treatment of the data, a Q *vs* T curve can be drawn and the slope of this, dQ/dT, gives the heat capacity of the system. The data given in Table XI were treated in this manner and the results are given in Table XII. The heat capacities determined calorimetrically are also given for the purposes of comparison.

The heat capacities so determined do not lie on a good curve and do not agree particularly well with those determined calorimetrically. The origin of the irregularities is undoubtedly the original Q *vs* S curve; it was not possible to draw a smooth curve and give equal weight to the six measured points. Measurements of more points would make possible a better determination of the curve.

I am fully grateful to the Faculty of Mathematical and Natural Sciences and to the Senate of this University for having given favorable advice for obtaining the permission, without which it would not have been possible to complete this thesis.

For his kindness, patience, continued thoughtfulness and sure guidance while the material which forms the basis of this thesis was being gathered, and during the actual preparation of the thesis, I am greatly indebted to my promotor, Prof. Dr. W. H. KEESOM.

I extend my hearty thanks to my colleagues, Dr. J. A. KOK, Miss A. P. KEESOM, Mr. C. J. MATTHIJS and Mr. H. VAN LAER for the help they have given me in carrying out the measurements. I wish also to express my appreciation to Mr. FLIM and his staff for the great profit I have derived from their fund of technical skill and experience.

SAMENVATTING.

In dit proefschrift worden beschreven metingen, bij zeer lage temperaturen, van de soortelijke warmten van $Gd_2(SO_4)_3 \cdot 8H_2O$, van KCl en van Ni, benevens demagnetisatieproeven met eerstgenoemde stof, ter vastlegging van de thermodynamische temperatuurschaal beneden 1°K.

Hoofdstuk I. Hierin wordt een overzicht gegeven van de formules voor de soortelijke warmte eener stof, volgende uit de theorieën, waarin warmte als een vorm van beweging wordt opgevat, te beginnen met den theoretischen grondslag, door Boltzmann aan den regel van Dulong en Petit gegeven. Einstein gaf met behulp der quantumtheorie een verklaring van de afwijkingen van dezen regel bij lage temperaturen; hij nam hierbij aan, dat alle atomen van een lichaam met dezelfde frequentie trillen en dat de gemiddelde energie van een vibrator door de formule van Planck gegeven wordt. De op zijn werk volgende berekeningen, die van Nernst en Lindemann, van Debije, van Born en von Karman, gingen steeds in de richting eener nauwkeuriger vaststelling van het spectrum der trillingen van het beschouwde lichaam; hier wordt de afleiding der formule van Debije gegeven, daar nog steeds de uitkomsten van metingen van soortelijke warmten met deze formule worden vergeleken.

De nieuwere theoretische gevolgtrekkingen van Blackman betreffende de soortelijke warmte van kristallen van ionen, zooals KCl, bij lage temperatuur, worden in het kort behandeld; zijn resultaten komen met die van Debije overeen voor de allerlaagste temperaturen, bij hoogere wijken zij daarvan af. Hetzelfde geldt met betrekking tot de resultaten van Born en von Karman.

Hoofdstuk II. In dit hoofdstuk zijn de toestellen, meetmethoden en wijzen van berekening beschreven.

De soortelijke warmten van het gadoliniumsulfaat en van het kaliumchloride werden bepaald met behulp van een dunwandigen, cylindrischen, koperen calorimeter van 93 cm^3 inhoud. Om dezen was de weerstandsdraad ter verwarming van de stof gewonden; hij was ter vermijding van stralingsverliezen door een dun koperen scherm omgeven. De hoeveelheid warmte, die per seconde aan de stof werd toegevoerd, werd berekend uit de sterkte van den stroom door den weerstandsdraad en het potentiaalverschil aan diens uiteinden, af te lezen op gecalibreerde milliampère-of millivoltmeters. Twee weerstandsthermometers werden gebruikt: de een van phosphorbrons, voor de temperaturen beneden 6°K, de ander van constantaan, voor die daar boven. Ze waren in een cylindrische buis op de as van den calorimeter geplaatst. Hun ijking geschiedde met behulp der bekend zijnde dampspanningen van vloeibaar helium, van vloeibare en vaste waterstof, en bovendien nog door den calorimeter zelve als heliumthermometer van constant volume te gebruiken. De weerstand van een thermometer, bij een meting, werd afgeleid uit de verhouding der potentiaalverschillen aan zijn uiteinden en aan die van een standaardweerstand van 10Ω, in serie geschakeld.

De metingen aan nikkel geschiedden volgens de gebruikelijke Leidsche methode: het nikkel in cylindervorm werd gebruikt als zijn eigen calorimeter, terwijl de thermometer- en de verwarmingsdraad zich bevonden in een afzonderlijke kern, die in een uitholling in het nikkel geschroefd kon worden.

Hoofdstuk III. De uitkomsten der metingen aan KCl, van 2.3° tot 17°K, worden hierin gegeven.

Het was wenschelijk, de soortelijke warmte van een niet-geleider voor electriciteit bij zeer lage temperatuur te bepalen. De θ *vs* T-kromme van sommige metalen toch vertoont een vrij scherpe daling, waarvan de warmtecapaciteit van vrije electronen in geleiders de oorzaak zou kunnen zijn. De kromme voor een niet-geleider, als *KCl*, kon een beslissing geven omtrent dezen invloed der vrije electronen.

De waarde voor θ neemt volgens onze metingen bij *KCl* toe van 220, bij 10°K, tot 236, bij 4.5°K, en daarna af tot ongeveer 230, bij 2.3°K; de waarden beneden 4.2°K zijn minimumwaarden, daar er een mogelijkheid is van een desorptiewarmte in verband met het gasvormige helium, dat tot den calorimeter voor verkrijging eener goede warmtegeleiding toegelaten was.

De waarde van θ voor zilver neemt volgens Keesom en Kok langzaam toe van 209, bij 20°K, tot 226, bij 5.4°K, en dan snel af tot 165, bij 1.35°K; de mogelijkheid eener desorbtiewarmte was wegens de inrichting der proeven uitgesloten.

Wordt de warmtecapaciteit van één vrij electron per atoom berekend met de formule van Sommerfeld, dit bedrag afgetrokken van de gemeten soortelijke warmte van *Ag*, en vervolgens een θ *vs* T-kromme uit de verkregen verschillen berekend, dan gelijkt deze kromme zeer op die van *KCl*. De metingen aan *KCl* steunen blijkbaar de hypothese, dat de sterke daling der θ *vs* T-kromme van *Ag* aan de warmte-capaciteit der vrije electronen te wijten is.

Hoofdstuk IV. Hierin vindt men de resultaten voor *Ni*.

De afwijkingen van een Debije-kromme zijn groot; de verschillen tusschen de uitkomsten en de Debije-kromme voor $\theta = 413$ kunnen, tusschen 1 en 9°K, worden voorgesteld door $C_{add} = 0.001744\ T$. Aangetoond wordt, dat deze verschillen niet geheel kunnen worden toegeschreven aan de energie der wisselwerking, die het ferromagnetisme veroorzaakt; dan toch zouden deze volgens de theorie evenredig met $T^{3/2}$ moeten zijn en hun orde van grootte bovendien veel kleiner dan de waarnemingen leeren.

Het feit, dat deze bijkomende warmte-capaciteit bij lage temperaturen evenredig met T is, leidde tot de veronderstelling, dat zij verband houdt met de energie der geleidingselectronen. Zij is vele malen grooter dan uit de formule van Sommerfeld voor vrije electronen zou volgen, hetgeen doet zien, dat in den overeenkomstigen energieband de dichtheid der mogelijke energietoestanden tamelijk groot is. Een bevestiging van het afwijkende gedrag der soortelijke warmte van nikkel wordt misschien gevonden in metingen over deze grootheid, door Mevrouw LAPP in het laboratorium van WEISS bij hoogere temperaturen verricht.

Hoofdstuk V. Dit hoofdstuk bevat de uitkomsten van metingen over de soortelijke warmte van $Gd_2(SO_4)_3 \cdot 8H_2O$ van beneden 1° tot 20.5°K. Beneden 4°K ongeveer neemt de soortelijke warmte van hooger naar lager temperatuur toe. Deze anomalie is te danken aan de energie noodig om de ionen te brengen op de hoogere energie-niveau's, waarin het grondniveau gesplitst is. De verdeeling der ionen over deze energie-niveau's zal des te dichter bij het absolute nulpunt beginnen, naarmate de energieverschillen tusschen de niveau's geringer zijn. Als de evenwichtsverdeeling bereikt is, is voor dit doel geen energie meer noodig.

De uitkomsten zijn vergeleken met twee theoretische krommen, voor welker berekening beurtelings het volgende is verondersteld:

a. de acht niveau's liggen op gelijke afstanden en zijn onafhankelijk van elkaar;

b. de energie is noodig, om te overwinnen de wisselwerking tusschen paren van gadolinium-ionen, die behandeld worden als eenvoudige magneten.

Er bestaat in beide gevallen vrij goede overeenstemming tusschen waarneming en berekening, maar aangezien er geen onafhankelijk experimenteel gegeven betreffende het splitsingspatroon van het grondniveau is, kunnen geen gevolgtrekkingen gemaakt worden.

Hoofdstuk VI. Dit proefschrift wordt besloten met een beschrijving der proeven, die bedoelen, de thermodynamische temperatuurschaal beneden 1°K vast te leggen. De gang van zaken, aangegeven door KEESOM, is als volgt:

Een gemagnetiseerde paramagnetische stof wordt bij herhaling adiabatisch gedemagnetiseerd, steeds uitgaande van dezelfde temperatuur T, maar van telkens andere velden H; de sterkte van alle eindvelden is nul. Na iedere demagnetisatie wordt de hoeveelheid warmte Q bepaald, die noodig is om de stof weer op de temperatuur T te brengen. Het verschil in entropie, ΔS, van de stof in twee begintoestanden, kan met een eenvoudige thermodynamische formule worden berekend. Dit verschil en dat, ΔQ, tusschen de twee correspondeerende gemeten warmtehoeveelheden Q geven ons de temperatuur T volgens de formule $T = \frac{\Delta Q}{\Delta S}$ Op deze wijze kunnen de temperaturen bepaald worden over het geheele gebied der magnetische koeling.

De begintemperatuur werd 1.50°K gekozen; in het hoogste deel van het vast te leggen gebied kon de temperatuur van het gadoliniumsulfaat dan ook nog met een reeds geijkten weerstandsthermometer worden gemeten. De uit de demagnetisatieproeven berekende temperaturen bleken steeds lager dan die volgende uit de aanwijzingen van den weerstandsthermometer. Mogelijke oorzaken hiervoor worden opgegeven. Het verschil zou verklaard kunnen worden door aan te nemen, dat het uitwendige veld een tegengesteld gericht, inwendig veld opwekt. Temperaturen en soortelijke warmten zijn met deze veronderstelling berekend; wegens tijdgebrek konden niet voldoende experimenteele gegevens omtrent dit inwendige veld verzameld worden; in verband daarmede dragen deze berekingen een voorloopig karakter.

STELLINGEN

I

De quantumtheoretische formule voor de magnetisatie van een ideale paramagnetische stof, door VAN VLECK de BRILLOUIN-functie genoemd, zou met meer recht de GIAUQUE-functie kunnen heeten.

J. H. VAN VLECK, The theory of electric and magnetic susceptibilities, Oxford, 1932, blz. 257.

II

De bewering van ANDRADE, dat de waarde voor de verzadigingsmagnetisatie van gadoliniumsulfaat bepaald is op twee *onafhankelijke* wijzen, te weten met behulp der constante van CURIE en uit metingen der verzadiging, is niet juist.

E. N. da C. ANDRADE, The structure of the atom, 3rd Edition, Bell, London, blz. 604.

III

De waarnemingen van BEEBE, dat op 400 voet beneden het oceaanoppervlak alleen het blauw voor ons oog zichtbaar is, terwijl het violet daar in de spectroscoop overheerscht, kan verklaard worden door de vorm der zoogenaamde "zichtbaarheidskromme", ~~en de verschuiving van haar maximum naar langere golflengten voor geringere intensiteit.~~

W. BEEBE, Science, 80, 495, 1934.

IV

Van het licht der Finsenlamp kan het niet-gewenschte gedeelte van het spectrum verwijderd worden door twee prisma's in het optische stelsel der lamp aan te brengen.

V

Geactiveerd Al_2O_3 is voor algemeen laboratoriumgebruik een zeer geschikt droogmiddel.

VI

De eenvoudigste wijze om corrosie bij waterkoeling te voorkomen, is de toevoeging aan het water van een geringe hoeveelheid K_2CrO_4 of $K_2Cr_2O_7$.

VII

Een minimum in de weerstands-, temperatuurkromme van metalen, bij lage temperaturen, moet waarschijnlijk aan chemische onzuiverheden worden toegeschreven.

H. A. Baarse and H. Niewodniczanski,
Nature **135**, 827, 1935.

VIII

De bewering van Lapp, dat de karakteristieke temperatuur θ volgens Debije, die temperatuur is, waarbij de frequentie ν_m begint op te treden, is niet juist.

E. Lapp, Ann. de Phys., **12**, 492, 1929.

IX

Het bewijs materiaal, dat Simon aanvoert voor het optreden van „quantumsprongen" is in eenige gevallen niet zeer overtuigend.

F. Simon, Sitz. Preuss. Akad., **33**, 477, 1926.
Ergeb. d. exakt. Natuurwis, **9**, 257, 1930.