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THE LOW TEMPERATURE SPECIFIC HEAT
OF FINELY DIVIDED SODIUM CHLORIDE

by

James Humphrey Barkman, Jr.

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

Thesis Director's signature:

A handwritten signature in cursive script, reading "John E. Kilpatrick". The signature is written in dark ink and is positioned below the text "Thesis Director's signature:". The signature is written over a horizontal line.

Houston, Texas
October, 1963

Dedicated to my wife, Alma.

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INTRODUCTION

A. Summary

It has been found experimentally by numerous investigators that finely divided materials possess a larger specific heat than do large crystals of the same substance. Dynamic lattice theory predicts that such an excess specific heat should exist and that it should vary directly as the surface area and approximately as the square of the absolute temperature. There is, however, a limited amount of experimental data suitable for a critical test of the theory. The data that is available is not in especially good agreement with the theory. For example, some measurements on finely divided sodium chloride (1, 2) indicate that the excess specific heat is three to four times larger than predicted. The question of whether the excess specific heat is proportional to the surface area has not yet been completely settled.

The purpose of this research is to furnish some additional experimental specific heat data on finely divided sodium chloride. It is hoped that the present disagreement between theory and experiment may at least be partly resolved. Furthermore, a knowledge and understanding of the thermal properties of surfaces may conceivably be of use in the study of other surface phenomena.

It was decided to carry out these experiments on finely divided sodium chloride since the experimental specific heat of the bulk material is in good agreement with theory and is well known over the whole temperature range above 3° K. Also, sodium chloride is probably

the simplest compound that has been prepared in large quantities with a sufficiently high specific surface area. Measurements on finely divided sodium chloride have been previously reported above 10° K but the results were not entirely conclusive. Another goal was to prepare a larger specific surface area than previous workers and to extend the temperature range to 4° K or lower.

B. Experimental history of the problem

The first experimental evidence of an excess specific heat which could be associated with the surface was obtained by Simon and Swain (4) in 1935. They found that the specific heat of activated charcoal lay above that of graphite. Two years later Glauque and Archibald (5) discovered the specific heat of a high surface area magnesium oxide sample to be higher than had been found earlier for large crystals by Parks and Kelley (6). This was more recently confirmed by Barron, Berg and Morrison (7).

The preceding experiments, however, were not made with the purpose of investigating a surface effect and cannot be used to test the theory. Lien and Phillips (8) have measured the specific heat of magnesium oxide of 166 m.²/g. between 1.5° and 4° K. They found an excess specific heat which had the expected temperature dependence but was about 3.8 times larger than predicted.

More extensive measurements have been carried out on sodium chloride by Patterson, Morrison and Thompson (1) between 10° and 20° K and by Morrison and Patterson (2) between 12° and 270° K. Three different samples were investigated in the lower temperature range. They found that all three samples had approximately the

expected temperature variation; however, the excess specific heat was much larger than predicted and was not quite proportional to the surface area.

C. Theoretical history of the problem

A general problem of the theory of specific heats is to find the frequency distribution of the normal modes of vibration. That is, to find $g(\nu) d\nu$, which is the number of normal modes in the frequency range $d\nu$ at ν . Then the specific heat is given by the equation

$$C_v = k \int_0^{\nu_L} \frac{g(\nu) \left(\frac{h\nu}{kT} \right)^2 d\nu}{\sinh^2 \left(\frac{h\nu}{2kT} \right)}$$

where ν_L is maximum or cut-off frequency. The maximum frequency is usually chosen so that the total number of modes will be equal to three times the number of atoms in a crystal. The Debye theory considers the crystal to be a continuous isotropic elastic medium with perfectly reflecting, rigid boundaries. Debye showed that the frequency distribution of the normal modes was then given by

$$\nu = \frac{c}{2} \left[\left(\frac{m_x}{L_x} \right)^2 + \left(\frac{m_y}{L_y} \right)^2 + \left(\frac{m_z}{L_z} \right)^2 \right]^{1/2}$$

where c is the longitudinal or transverse wave velocity, m_x is the half wave length in the x direction, and L_x is a crystal dimension. Now consider the reciprocal space defined by the vector

$$\hat{r} = \frac{2\nu}{c}$$

which is made up from the basis vectors m_i/L_i . If we allow m_i to take on integral values an array of points is thus generated in our

reciprocal space which corresponds to the normal modes of vibration. The number of normal modes will be approximately one-eighth the volume of the ellipsoid generated by this vector, since there is on the average one point per unit volume in the positive octant. The number of modes of frequency ν or less is thus

$$N(\nu) = \frac{1}{8} \cdot \frac{4}{3} \pi \left(\frac{2\nu}{c} \right)^3 L_x L_y L_z$$

$$g(\nu) = \frac{dN}{d\nu} = \frac{\pi}{2} \left(\frac{2\nu}{c} \right)^2 L_x L_y L_z$$

This distribution leads to the well known T-cubed law at low temperatures.

The first theoretical expression for the surface specific heat was given by Montroll (9) in 1950. It had been previously shown by Bolt (10) and Maa (11) that the Debye method of counting the normal modes was slightly in error for a crystal of finite dimensions. They pointed out that the points in the coordinate planes were underestimated since they actually were shared by 2 octants. The correction to be added to $N(\nu)$ involves ν^2 and the surface area. Montroll showed that this leads to an additional specific heat term which varies as the square of the temperature and is proportional to the surface area. His expression for the surface specific heat is given by

$$C_s = \frac{9}{4} \zeta(3) (12\pi)^{1/3} k \frac{\left[1 + 2 \left(\frac{c_l}{c_s} \right)^3 \right]^{2/3}}{\left[1 + 2 \left(\frac{c_l}{c_s} \right)^2 \right]} \left(\frac{m}{V} \right)^{2/3} S \left(\frac{T}{\theta_D} \right)^2$$

where S is the specific surface, θ_0 is the observed Debye theta, n is the number of atoms, C_l and C_t are the longitudinal and transverse wave velocities, $\zeta(3)$ is the zeta function of argument 3, which has the value 1.202, V is the volume, T is the absolute temperature, and k is Boltzmann's constant.

It is clear that Montroll's boundary conditions are not entirely realistic. A transverse wave upon reflection is transformed into both a transverse and a longitudinal wave and vice versa. Brager and Schuchowitsky (13) carried out the calculation with free boundary conditions for an incompressible medium. Stratton (14) extended the calculation to include compressible media. He took as his model thin plates with stress free boundaries perpendicular to the short axis and periodic boundary conditions in the other two directions.

Dupuis, Mazo and Onsager (3) have also treated the isotropic elastic solid using free boundary conditions but have employed a different mathematical method than Stratton. The expression they give for the surface contribution to the specific heat is

$$C_s = 3\pi \frac{h^3}{h^2} \zeta(3) \frac{2c_x^4 - 3c_x^2 c_t^2 + 3c_t^4}{c_x^2 c_t^2 (c_t^2 - c_x^2)} S T^2$$

where h is Planck's constant and the other symbols have the same meaning as before.

As will be shown in section IV, the Onsager expression yields a surface specific heat that is about twice as large as the Montroll result. This is not unexpected since it is well known that placing additional restraints (in this case the rigid boundary conditions) on a vibrating system raises the frequencies of the normal modes and

thus lowers the specific heat. However, the higher specific heats from Onsager's equation are still lower than any experimental results to date. Stratton has shown in a more recent paper (14a) that after correction of some minor errors in (14) that his results are identical with those of Dupuis, Mazo and Onsager. This is expected as both employ essentially the same model and boundary conditions.

One might wish to go a step further in searching for a model that gives results in closer agreement with experiment. Victor (15) has assumed the crystal can be separated into two parts, the bulk, and the surface layer. He then treats the surface as a continuous vibrating membrane and neglects surface-bulk interaction. Victor's expression for the surface specific heat is

$$C_s = S \left(\frac{M\rho}{N} \right)^{1/3} (C'_s - C_b)$$

where ρ is the bulk density, S is the specific surface area, C_b is the observed molar heat capacity of the bulk salt, N is Avogadro's number, M is the molecular weight, and C'_s is the heat capacity of a mole of surface atoms. C'_s is given by

$$C'_s = 6nk \left(\frac{T}{\theta_D} \right)^2 \int_0^{\theta_D/T} \frac{e^x x^3}{(e^x - 1)^2} dx$$

where n is the number of surface atoms, k is the Boltzmann constant, and θ_D may be taken as the observed Debye theta. This expression yields values of the surface specific heat which are about twice that given by the Onsager expression.

Jura and Pitzer (16) have developed an interesting theory that treats the individual crystallites as if they were molecules possessing rotational and translational degrees of freedom. They use the Debye expression for calculating the frequencies but do not assume a continuous frequency distribution as most others have. Their expression for the specific heat is summed rather than integrated over the normal modes. They argue that the rotation and translation of ionic or metallic particles should remain classical to about .001°K. This implies a constant specific heat term down to that temperature having the magnitude $6Nk$, where k is Boltzmann's constant and N the number of particles. This constant specific heat has not yet been observed experimentally. Possibly it was not detected by Lien and Phillips (8) due to the fact that magnesium oxide possesses a porous structure rather than a loose, granular nature. As will be shown, it is too small to be measured in the samples used in this research.

Of the various theories that have been considered so far the one due to Stratton and to Dupuis, et al, is probably based on the most realistic physical model, namely free boundaries and a compressible medium. Their theory represents a fair degree of refinement based on the assumptions already mentioned.

One should not expect to obtain complete agreement between experiment and the theories which have been developed to date. For one thing, surfaces are known to be quite irregular, possessing lattice defects, peaks, crevices, and non-stoichiometric proportions. The imperfections of surfaces are probably even more extensive than those of the internal crystal. Also, crystal surfaces are probably not ideal reflecting boundaries, either clamped or free. Another

assumption that is implicit is that the elastic constants and the density are the same in the first few surface layers as in the bulk crystal. It is possible that the atomic force constants in the first dozen or so layers may be appreciably different from those in the bulk. Finally, we are dealing with discrete atoms, not a continuum, and many of the same criticisms that apply to the Debye theory for bulk materials are applicable here.

II

CALORIMETRIC APPARATUS

A. Mechanical

The mechanical details of the calorimeter are discussed elsewhere by Anderson (17). The purpose of this section is to provide a brief description so that the experimental results can be conveniently evaluated.

The calorimeter is of the isothermal variety. This means that the sample container is maintained in an isothermal environment while energy is supplied to it, and its resultant temperature rise is measured. It is capable of operating in the range of about 1.2° - 21° Kelvin and requires a bath of liquid helium at all times. A high speed Kinney pump provides the temperatures below 4.2° K by cooling the bath.

The working thermometers are ordinary carbon radio resistors of the 1/2 watt Allen-Bradley variety with the covers removed and a glyptal coating applied (12,20). The main thermometer, which is located in the sample, is calibrated at the end of each run by means of a gas thermometer which actually forms the upper half of the sample container. Also, a vapor pressure thermometer is adjacent to and used to calibrate the gas thermometer. The thermometer calibration is discussed in another section.

The connections between the shield and the sample container consist of a nylon suspension, three stainless steel capillary tubes, and two leads each for the thermometer and the heater. They were, of course, designed to minimize heat leaks. The insulating vacuum is

provided by an oil diffusion pump, and no stopcocks or other restrictions are present in the one inch pumping line. The vacuum was generally of the order of 10^{-7} mm. of Hg. or better. The Newton coefficient of the apparatus was such that fore and after drifts of less than a millidegree per minute were obtained for all heating intervals.

The shield can be set quickly at any desired temperature above that of the bath and does not drift more than a few thousandths of a degree during a heating interval. This excellent control is accomplished by having a calibrated heat leak from the bath to the shield which is balanced by a heating current which is controlled by a six decade resistance box.

For the purpose of bringing the sample container into thermal equilibrium with the bath, as in the initial cool down period, a mechanical heat switch is available. It consists of a pedestal which rises from the bottom of the can to squeeze the sample container between it and the top of the can. This is preferred over the method of using an exchange gas, which may lead to spuriously high values of the heat capacity due to desorption effects.

B. Electrical circuits and components

1. Energy and thermometer circuits

All the critical potential measurements in this research were made with a "White" type double potentiometer manufactured by the Gray Instrument Company. The measurement of two potentials could be made in rapid succession. The galvanometer was actually a combination of a Beckman model 14 breaker-amplifier and a Leeds and Northrup Speedomax recorder. The amplifier is a highly linear device which

receives the unbalance of the potentiometer in the microvolt range and amplifies it to the millivolt range for the recorder. The recorder pen can be watched for the purpose of balancing the potentiometer, and drifts are easily obtained from the chart paper.

Figure 1 is a schematic of the circuitry involved. The resistors designated as standard are manufactured by the Leeds and Northrup Company; the $1000\ \Omega$ and $1\ \Omega$ models have been further calibrated at the National Bureau of Standards. The broken lines surround components that are located in the low temperature region. The heating current is supplied from a single nickel-alkaline Edison cell, and the thermometer current comes from a telephone dry cell.

Two standard resistors across the heater form a voltage divider and a correction must be made for the current which they carry. The calculation is straightforward since the resistances are known.

Critical circuits have been protected by shielding so that the noise as seen on the galvanometer is about $.02\ \mu\text{v}$. It was also necessary to suspend the preamplifier portion of the Beckman amplifier independent of its normal chassis mounting. Apparently, microphonic noise of the magnitude of $.1\ \mu\text{v}$ from the breakers or their motor was otherwise transmitted.

The design of these circuits permitted the use of all four decade knobs on the potentiometer for almost all current and EMF measurements; thus, maximum precision was obtained.

The thermometer current was in the range of 1-10 microamperes which, according to the formula of Berman (22), produces a negligible amount of self-heating in the thermometer. The temperature rise due to self-heating can be estimated, and for these experiments it should

FIGURE I

be on the order of 10^{-5} degrees or less. It was unobservable experimentally.

2. Trigger and timing circuit

The trigger and timing equipment is essentially the same as that described by Johnson (23) and Taylor (24,25). It consists of a pendulum clock and phototube-amplifier which deliver voltage pulses at precise one second intervals to an Eccles-Jordan "flip-flop" circuit. With this equipment the heating current can be switched back and forth at will between the sample heater and a dummy resistor of the same magnitude. An electric clock which is accurate to about one-hundredth of a second is simultaneously triggered and its purpose is to keep track of the number of pulses, which is the actual time standard. By having the current flowing through one resistor or the other at all times (except during the very short switching period) transients are minimized.

Several modifications were necessary. The pulses were obtained from the clock in a nearby laboratory, but due to the long connecting wire a capacitive load was introduced on the amplifier output which resulted in unstable behavior. This was eliminated by installing a cathode-follower at that point, and no further trouble was experienced.

The circuit failed to trigger properly as it was initially constructed. The reason became clear upon examining it with a triggering type oscilloscope. Although the input pulse was normal as it arrived at the 6H6 rectifier tube, it had a large negative tail as it reached the 6SN7 tube grid where the switching takes place. The result of this was that the effect of the positive portion of the pulse was quickly reversed by the negative portion, so that no permanent

switching took place. It was reasoned that the negative tail resulted from a differentiation of the normal positive input pulse whose duration was about .2 millisecond. A parallel 10 megaohm resistor and .1 microfarad capacitor were installed between the output of the 6H6 tube and ground. They changed the time constant of the circuit in such a way as to produce a slow decay of the input pulse. Then after differentiation the pulse was sharp and positive as it reached the 6SN7 tube and possessed no negative portion. The width of the corrected pulse is about .2 millisecond and its height is 2 volts. The switching was quite reliable thereafter. The accuracy of the resulting time intervals is of the order of a millisecond or about .0001 %.

3. Shield heater

The power for the shield heater was available at 1.5 to 40 volts from a bank of Edison cells. Control was accomplished by a six decade resistance box and shunt combination as indicated in Figure I.

4. Ion gauge

The ion gauge was constructed according to the plans of Hariharan and Bhalla (26). In conjunction with an R.C.A. 1949 tube it could measure pressure over the range 10^{-3} to 10^{-8} mm. of Hg. This particular circuit has the advantage of possessing a nearly logarithmic pressure scale and a low sensitivity to the ion current adjustment. The circuit requires one 2500 megaohm resistor which was not readily available. It was constructed from a small strip of stiff cardboard with a nut and bolt terminal at each end connected by a thin graphite pencil line, which formed the electrical path. The ion gauge was calibrated against a sensitive McLeod gauge from time to time and was not found to drift significantly.

5. Level detector

A simple electronic level detector was constructed which sensed the presence of liquid helium near the top of the dewar and just above the top of the can. It was convenient for use during the liquid helium filling period and as the run progressed toward the point where the helium was nearly depleted.

The sensing elements are the same type carbon thermometers as used in the calorimeter and are connected in series with an ammeter and a dry cell. As the sensor becomes immersed in the liquid its resistance rises sharply and the current drops. The ammeter was calibrated so that the presence of liquid could be detected at a glance.

III

PREPARATION OF THE SAMPLE

A. Introduction

It has been possible to prepare finely divided sodium chloride with a specific surface of $96 \text{ m.}^2/\text{g.}$ by precipitation of the vapor in a high voltage precipitator. The method is similar to that described elsewhere (27,28,29). The salt is kept molten in a platinum crucible while a stream of dry nitrogen is directed across the surface. The resultant aerosol is carried to an electric precipitator where it collects and then is pushed into a sample container located in a dry box. As will be seen presently, the exclusion of water vapor is of the utmost importance if salt of a high specific area is to be obtained.

A variety of means were employed before a satisfactory result was obtained. The final form of the apparatus used to prepare the calorimetric sample is shown in Figure II. Some earlier versions will be discussed briefly toward the end of this section.

B. The Apparatus

The dry nitrogen gas was obtained from a storage dewar which held 25 liters of liquid nitrogen. An electric heater of chromel wire mounted on a glass tube and controlled by a 0-115 volt a.c. powerstat was employed to boil off the required nitrogen gas from the 25 liter dewar. With this equipment the volume flow could be varied over the range 0-60 liters (S.T.P.) per minute; having been set, it did not drift more than 1 liter per minute per hour.

FIGURE II
APPARATUS FOR PRODUCTION
OF SMALL PARTICLES
(NOT TO SCALE)

The flow meter is a simple type consisting of a steel ball in a tapered glass tube. After leaving the flow meter the stream was broken into two segments each of which was controlled by a stopcock. One was directed at the molten surface at a 45 degree angle and the other was pointed directly at the furnace outlet. Thus it was possible to control the total flow independently of the amount of gas striking the sample (29).

The heart of the furnace is a 10 cc. platinum crucible which is surrounded by alundum cement containing a nichrome heater. The heating element consists of No. 22 wire wrapped in a tight coil. Leads of No. 18 wire were welded on and were used to come out of the cement for extra mechanical strength. A platinum apron was welded to the crucible and served to inhibit the diffusion of hot sodium chloride vapor toward the heating element. The above section is contained in a 250 cc. nickel crucible mounted on a tripod which reaches to the bottom of the glass envelope. The life of the nichrome element was inconveniently short, but on the whole it functioned better than a platinum element or a gas-air flame which were also tried. Platinum, having a large temperature coefficient of resistance, develops hot spots; the use of a torch directly on the crucible produced a good deal of extraneous heat, and it was difficult to adjust it to the temperature tolerances needed. All glass is of the ordinary pyrex variety. About 4 amperes at 70 volts a.c. was required to keep the salt molten under typical flow conditions.

The precipitator was constructed from three-inch glass pipe with one-inch side arms and flange connections. A central wire, about three feet of No. 36 nichrome, was spring mounted between two terminals

situated at right angles to the flow. The terminals were mounted with epoxy resin through small holes drilled in the side of the glass pipe. A heavy copper foil sheet was tied around the outside of the pipe to provide the ground potential. About 10,000 volts a.c. was supplied from a transformer. The top of the precipitator was sealed with a brass plate and flange arrangement that admitted a long push rod through a double O-ring sleeve. At the end of the rod was a teflon split-ring which aided in the removal of salt from the walls. The bottom of the precipitator opened directly into a dry box which contained the calorimeter sample container and sealing facilities.

C. Water Vapor

Previous workers in this field have noted the remarkable growth or sintering of small alkali halide crystals in the presence of water vapor. Papee (30,31) has found the growth to follow first order kinetics. Moffat and McIntosh (32) have also investigated sintering by water vapor under a variety of conditions. From these studies it is evident that 40 percent relative humidity, the usual condition in many laboratories, will reduce a high specific surface area by a factor of ten or more in a matter of minutes. It is therefore imperative that the particles not be allowed to come into contact with moist air.

An attempt was made to use a centrifugal fan to re-cycle the dry gas to the furnace after it left the precipitator. This would have the obvious advantage of conserving gas; however, consistently mediocre ($5 - 25 \text{ m.}^2/\text{g.}$) surfaces were obtained with this set up despite extensive

efforts to tightly seal the fan housing. It was only after the present design or else cylinder nitrogen was used that large areas (from 50 - 96 m.²/g.) were produced.

D. Parameters

The purpose of the following set of experiments was to attempt to determine which parameters had an influence on the production rate and the specific surface area.

Table I is a summary of the trial runs made with the final apparatus. Stopcock "A" is the one pointing at the molten surface and the ratio of B:A refers to the volume flow ratio as estimated with the flowmeter. All runs were approximately of 30 minutes to one hour duration. The samples, which weighed about one gram or less, were collected in an adsorption cell and immediately evacuated to 10^{-6} mm. pressure unless otherwise noted. The precipating voltage was within 10% of 10,000 v.a.c. No attempt was made to vary the surface temperature but rather an effort was made to maintain the surface in a barely molten condition. This was done by first setting the flow rate and then adjusting the heating powerstat until the solid phase was barely visible at the point on the surface where the flow was aimed. The level of the molten salt apparently has an effect on the production rate if not the surface area. The experiments are listed in chronological order.

In conclusion, it can be said that these tests show no clear dependence of the surface area on any of the parameters considered except possibly the temperature. This is contrary to the results of Balk and Benson (29) who used a similar double stream flow and reported

TABLE I

The Effect of Various Parameters on the Surface Area

Ratio of B:A	Total Flow l./min.	Prod. Rate g./hr.	Specific Surface m. ² /g.	Remarks
2:1	22	.60	73.0	Cylinder N ₂ used.
2:1	30	1.18	62.3	Surface temperature too hot.
2:1	30	.96	77.5	-----
1:4	30	.50	75.6	-----
1:1	35	.94	84.6	Product had a dirty, cream-yellow appearance.
1:1	35	1.00	77.1	Appearance of product again normal, snow-white.
1:1	35	.95	80.5	Special effort made to dry apparatus. Molten salt low.
1:1	35	1.30	86.8	NaCl level in crucible raised to near top. Special drying efforts made.
1:1	40	.90	88.4 77.7	The first specific surface taken immediately; the latter after salt was exposed in dry box for 20 hours.
1:1	30	.90	96.4	-----

that high flows through stopcock A generally yielded the higher specific surface areas. It is possible that still higher surface areas in excess of $100 \text{ m.}^2/\text{g.}$ may be obtained by taking extraordinary precautions to eliminate water vapor.

As mentioned earlier a direct current potential was tried, but it failed to collect a large amount of the aerosol; however, the reason for this is not clear. Rose and Wood (33) state that effective precipitation occurs only when a discharge corona is present to impart a charge to the particles; furthermore, they derive an expression for the minimum voltage required to produce a corona as a function of the geometry of the apparatus. For this apparatus the starting voltage is found to be about 5,700 volts, a figure which rises rapidly as the diameter of the central wire is increased. Employing the equations found in (33) it is estimated that this apparatus should collect about 75% of a stream of $300 \text{ \AA}$ particles. No attempt was made to verify this quantitatively, but it does not appear to be inconsistent with the amounts collected.

E. Surface Area Measurement

All surface areas were determined from an adsorption isotherm of nitrogen gas at 77° K. The general method and a discussion of its validity is given by Emmett (34). Pressure, volume, and temperature measurements are made on the nitrogen gas in order to determine the number of moles of gas adsorbed at various pressures; this data, when fitted to the well known B.E.T. equation, yields the number of moles of gas in a monolayer. A molecular cross section for nitrogen of

$9.76 \times 10^4 \text{ m.}^2/\text{mole}$ is assumed, consistent with the value that has been generally accepted.

The isotherm data fit quite well a linear form of the B.E.T. equation:

$$\frac{p}{N_a(p_o - p)} = \frac{1}{N_{ml} \cdot C} + \frac{C - 1}{N_{ml} \cdot C} \cdot \frac{p}{p_o}$$

where p is the equilibrium pressure, p_o is the barometric pressure, N_a is number of moles adsorbed, C is an undetermined constant which depends on the heat of adsorption, and N_{ml} is the number of moles in one monolayer. In practice the intercept $1/N_{ml} \cdot C$ could be neglected and a single point isotherm used to get an approximate area on preliminary trial samples. The equilibrium pressure range was assumed to extend from .01 to .1 p/p_o . This is somewhat lower than is usually used for other materials but leads to more reliable results in the case of NaCl as reported by Benson (35). The reproducibility of these surface areas is better than .5%. Emmett (34) has reported that for non-porous materials such as sodium chloride the accuracy of this method is fairly good; for example, the results compare favorably with results obtained by other means such as electron micrographs and X-ray scattering.

F. The Calorimetric Sample

The sodium chloride sample was prepared in 28 hours of actual running time which was spread over a period of 3 days. The salt was allowed to accumulate in the precipitator for about 3 hours after which time the furnace heat was reduced temporarily and the salt pushed into

the sample container in the dry box. After carefully packing the salt the container was placed in a special glass jar and evacuated to a pressure of .1 micron or better. This process was repeated until the sample container was filled with about 28 grams of salt. A small portion of each batch was placed in an adsorption cell which received precisely the same treatment as the main sample. It was on this representative sample that a B.E.T. area was determined immediately after production was finished. The surface was found to be $78.30 \text{ m.}^2/\text{g.}$ from a four point isotherm that extended from 1 to 66 mm. pressure.

Next the sample container top and bottom were sealed together inside the dry box with Wood's metal and rosin flux. The sample was evacuated to 10^{-6} mm. pressure and removed from the dry box to the cryostat.

For the lower surface area run a choice existed between preparing a new sample and sintering the old one. The latter alternative was chosen because of convenience and the feeling that certain indeterminate factors which are introduced during preparation, such as surface roughness, would tend to cancel out on the same sample. The sample was placed in contact with moist air of about 3% relative humidity for 48 hours. At the end of this time the surface had been reduced to $41.80 \text{ m.}^2/\text{g.}$ The sample was re-evacuated as usual and the specific heat determined.

Following the specific heat measurements the sample was analyzed for nitrites, nitrates and pH characteristics. It was found to contain .05% sodium nitrate and .001% sodium nitrite by weight. This amount of nitrogen impurity is considerably less than found by Moffat and McIntosh (32) in their samples. The pH values of .1 molar solutions

of the finely divided sample and bulk reagent grade salt were 7.49 and 6.62 respectively. Since the starting material was analytical grade sodium chloride it can be assumed that the nitrite and nitrate impurities are formed from trace quantities of oxygen in the nitrogen stream under the influence of high temperatures and high electric fields. Van Zeggeren, et al (36) have found that the nitrate concentration rises significantly at 7,000 volts and higher with only .05% oxygen in the nitrogen carrier. If the positive pH change is assumed to result from sodium atoms in the crystal lattice, the impurity would be approximately .0001 %. The sample had a clean, snow white appearance, although it was rather crusty due to the packing and sintering process.

Although no electron micrographs of the calorimetric sample were taken, the early trial runs were photographed extensively. Two typical examples are seen in Figure III. In general the individual particles appear nearly cubical but have somewhat rounded edges. Absorbed water probably accounts for this as it is very difficult to transport a sample to the electron microscope without exposing it to the air for at least several minutes. It has already been mentioned that the kinetics of water adsorption and sintering are very rapid.

FIGURE III

ELECTRON MICROGRAPHS OF SODIUM CHLORIDE POWDER

40,000 X

10,000 X

IV

EXPERIMENTAL SPECIFIC HEATS

A. Method of Measurement

1. Calibration of the thermometer

The temperature region between the liquid hydrogen and the liquid helium range is one where no completely satisfactory thermometer or practical temperature scale exists. The most accurate primary standard is the gas thermometer, but its use is tedious and difficult and therefore it is usually avoided. To date, the carbon radio resistor has found widespread use as a secondary thermometer due to its convenience and availability; germanium may be a successor (2). Semiconductors have the distinct advantage that, unlike platinum and other metals, their sensitivity actually increases at these temperatures. The principal drawback is that their calibration changes significantly upon warming to room temperature, thus requiring a more or less complete re-calibration. At least one scheme (18) has been devised which employs a one-point recalibration, but it does not appear to be accurate enough for the more precise calorimetric measurements. Germanium resistors have shown considerable promise in this respect; however, they were generally unavailable at the time this research was begun.

Once a resistance thermometer is decided upon its calibration in terms of some temperature scale presents numerous problems. The most outstanding is that no convenient vapor pressure scale exists between about 4.2°K and 13°K . In fact, this region is often avoided altogether and workers have tended to make measurements below 4.2°K

or above 13° K. Those (19) who have taken specific heat measurements in this region have usually calibrated their thermometer from helium and hydrogen vapor pressure scales and have made some sort of extrapolation in the rather wide region between. In this research a gas thermometer was employed to cover the temperature range above 4.2° K. Temperatures which are determined in this manner are probably more reliable than those based on an extrapolation in the region between 4.2° K and 13° K.

The sample container contained a gas thermometer and a vapor pressure thermometer. The calibration was carried out after each specific heat run as follows. The gas thermometer was filled with helium gas near the normal boiling point of helium and the vapor pressure of the helium was measured. This enables one to determine the number of moles of gas, and thus bases the gas thermometer measurements on the accuracy of the helium vapor pressure scale. The alternative procedure of filling the thermometer at the ice point is not possible since the thermometer is part of the sample container and should not contain any gas during the specific heat measurements. The vapor pressure scale employed is the 1958 He⁴ scale as reported in a National Bureau of Standards Monograph (37). Any temperature above 4.2° K up to about 22° K could be determined from two pressure measurements on the external gas burets. Further details of the gas thermometer measurements including the derivation of fundamental equations are given in Appendix I. Against each gas thermometer determination the resistance of the carbon thermometer was measured. In the range from 4° K to 20° K it was common to take about nine calibration points. In order to promote equilibrium the

shield was set near the desired calibration temperature; thus, the temperature of the sample container, which was suspended from the shield, remained approximately constant. In practice it was convenient to have two people, one to take potentiometric data and the other to read the cathetometer.

The second aspect of the problem is to find an equation which relates resistance to absolute temperature for the purpose of interpolating between the calibration points. Several have been proposed and used by various workers, and four have been tested with data from this laboratory. These equations along with the references are given as follows.

$$\left(\frac{\log R}{T}\right)^{1/2} = A + B \log R \quad (21)$$

$$\log R = A + B/T + C/T^2 \quad (19)$$

$$\log R = A + B/T + C/\log R \quad (12)$$

$$\log\left(\frac{R}{R_f}\right) = A + B/T + \frac{C}{D + \log\left(\frac{R}{R_f}\right)} \quad (18)$$

For purposes of comparison, a sample calibration is treated with each of the four equations, and the results are illustrated in Figure IV. It should be noticed that equation (18) due to Hoare, et al is actually a modification of Clement's equation (12). It has one additional parameter and a reduced resistance, R/R_f , where R_f is the resistance at some arbitrary fixed point such as the normal boiling point of helium. In the case of the first three equations the constants were determined by choosing two or three calibration points (depending on the number of

FIGURE IV

constants) which spanned the temperature range and solving the resulting simultaneous equations. The latter equation (18) was treated by a linear regression analysis program on a computer to determine the best values of its four constants.

It is seen immediately from Figure IV that Clement's equation (12) and its modification (18) give the best fit to the calibration data. Of these the modification is the better, which is to be expected considering its similar form and extra parameters. The other two equations seem unsatisfactory for our particular thermometer; however, this would not necessarily be the case for a resistor of a different origin and treatment.

Actually, equation (18) was not discovered until the final stages of this research and therefore Clement's equation (12) is used exclusively. A plot of the form of Figure IV was made for each calibration run and was used to correct each temperature calculated from the interpolation equation.

2. Method of taking specific heats

The method employed in this research is quite similar in many respects to the method which has been used for many years in the range 13° - 300° K. The theory has been developed in numerous sources (23,24,38,39) and will not be repeated in detail here.

Generally speaking, an experimental specific heat is a measured heat input divided by the resultant temperature rise. However, certain realities, such as the impossibility of isolating the sample from its surroundings, make it necessary to take a more sophisticated approach than first suggests itself. In particular one must take into account the fact that there is always a transfer of thermal energy between

the sample container and its surroundings by radiation, conduction along leads and suspensions, and by residual gas in the insulating vacuum. In principal, this could be done by writing down an expression for the above heat leaks, integrating over the heating interval, and adding this correction to the measured joule heat input. However, it can be shown under certain assumptions that an equivalent procedure is to extrapolate the fore and the after drift to the midpoint of the heating interval and take the temperature change at that point. For example, Taylor (25) has taken the reasonable set of assumptions:

- 1) The temperature of the shield is changing linearly with time and at a very slow rate.
- 2) The surface temperature of the sample rises linearly during the heating period.
- 3) Before and after the heat input the rate of change of the sample temperature is proportional to the temperature difference between the shield and the sample container.

From this starting point he shows that the true specific heat is given by the expression

$$C = \frac{\Delta H}{\Delta T} \left\{ 1 + \frac{1}{\theta} \left(\frac{\lambda t}{C} \right)^2 + \dots \right\}$$

where ΔH is the measured electrical heat input, ΔT is the resultant temperature change obtained by extrapolating the drifts to the midpoint of the interval, λ is the Newton heat exchange coefficient for the calorimeter, C is the approximate specific heat, and t is the length of the heating interval. We are interested in knowing the magnitude of the factor in order to see if it may be safely ignored. For example near 20° K, λ is about .004 joules/deg-min., t is 20 minutes, and C is 4 joules/deg. Thus the factor is 1.00005 and can certainly be neglected.

The drifts and their extrapolation require some comment. Using the set of assumptions in the preceding paragraph it is shown in (25) that in a state of equilibrium or very near equilibrium the temperature of the sample will be changing with time as given by the equation:

$$T = a + bt + ce^{-\alpha t^2}$$

where t is the time and α is proportional to the Newton coefficient. For a properly designed calorimeter, α will be small and the exponential term may very nearly be neglected. That is to say, the drifts can be extrapolated in a linear fashion and the result will be almost the same as if a fit of the data to the above equation were made. Now this is desirable since for a finite number of points there is much less error introduced by extrapolating a straight line than one with a significant curvature. There is another reason for wanting nearly linear drifts. Immediately following the heating interval there will be a period of time when the temperature of the sample is changing very rapidly due to the internal thermal gradients. It is convenient to watch the after drift as it approaches linearity in order to estimate the arrival of equilibrium or steady state conditions.

However, it sometimes happens in the case of measuring the specific heat of materials such as powders that the equilibrium times are of the order of an hour. It is not accurate enough to ignore the small curvature when making such a long extrapolation. If the exponential term is expanded and the cubic and higher order terms ignored, the temperature is seen to vary quadratically.

$$T = a + bt + ct^2$$

For example, Scales (39) in his measurements on bulk salts extrapolates all his drifts by fitting them to a quadratic least squares curve. Taylor (24) mentions the use of second differences in calculating his temperature drifts which is equivalent to considering a quadratic term.

In this research it was found that the drifts were usually linear to a very good approximation. Only in the case of the high area ($78 \text{ m.}^2/\text{g.}$) salt at temperatures below about 10° K was it necessary to extrapolate quadratically. Equilibrium was achieved in ten minutes or less with the empty sample container and the low area salt and within 30 minutes for the high area salt above 10° K ; in these cases virtually the same answer was obtained whether the after drift was extrapolated linearly or quadratically. In every case the fore drift could be treated linearly.

The arrival of equilibrium can usually be judged by following the progress of the drift. Immediately after the heating interval the temperature is changing very rapidly. As the curvature becomes smaller it approaches a rate of change (on the order of a millidegree per minute) which can be calculated in advance from the Newton coefficient, the temperature of the shield, and the approximate heat capacity of the sample. Some approximate equilibrium times for the various runs were as follows: empty, almost instantaneous; the low area salt, from 10 to 20 minutes; the high area salt, from 20 to 80 minutes. Shorter times in all cases were experienced at about 9° K and higher. More specific detail concerning the calculation of equilibrium times as a function of temperature is given in Appendix II.

The power supplied to the sample heater was determined by measuring the current and voltage at Gaussian times (41). Gaussian times

are generally irrational fractions of the total interval. The benefit derived from taking measurements at such peculiar intervals is that N observations can be used to calculate the exact time average of a $(2N - 1)$ degree polynomial. For example, if the voltage is drifting as a cubic equation in time two observations at Gaussian times will yield the correct time average as compared to three observations taken at equally spaced intervals.

The average power is then set equal to the average current times the average voltage. There is a slight error introduced by defining the average power in this way rather than as the average of the product of voltage times current. It is shown in Appendix III that the error is negligible.

Certain other corrections of a small magnitude were applied. They concern lead heating and curvature. The curvature correction is necessary to convert the experimental specific heat, measured across a finite temperature change, to the true or differential specific heat. An analytical expression for this factor is derived in Appendix IV. The correction at no time amounted to more than .5% of the total specific heat and was usually less.

The phenomenon of lead heating is discussed for example in the papers by Clement, Logan and Jeffers (42) and by Langmuir and Taylor (43). In calorimetry experiments it is common to measure the voltage drop across the sample heater plus two leads between the sample and the shield. A certain amount of the joule heat that develops in the leads flows to the sample and the rest is lost to the surroundings by conduction or radiation. Now if radiation can be neglected it is an elementary problem to show that exactly half of the joule heat

leaves each end of the lead. It then follows that the correction factor to the energy input ΔH is

$$f = \left(1 - \frac{r}{2R_H} \right)$$

where R_H and r are the resistances of the heater and the leads respectively. In this calorimeter R_H is about 180Ω and r is about 1.6Ω . Thus, f is .9956, a correction of $\sim .4\%$.

The main problem is to decide whether it is really legitimate to ignore radiation from the leads. It is not practical to attempt a theoretical calculation, and therefore the effect must be measured. Scales (39) has determined the heat loss due to radiation from the leads in a liquid helium calorimeter very similar in some respects to the one used in this research. Due to his very long and resistive leads about 62% of the joule heat in his leads was lost as radiation. However, by comparing the surface area, the length, and the resistance of his leads to the leads of this calorimeter it is estimated that no more than 3% of this heat is lost by radiation. This means that the first approximation of the factor, which was .9956, will be lowered to about .9955, which represents a change of only .01%. Therefore, a radiation correction for lead heating need not be applied in this case.

B. Experimental Results

The specific heat of a powdered sodium chloride sample was determined between 4° and 20° K for two specific surface areas, 41.8 and $78.3 \text{ m}^2/\text{g}$. The preparation and sintering of the sample has already been discussed in Section III. An excess specific heat over and above that of bulk sodium chloride has been found. To a first

approximation it has the predicted temperature dependence and is an extensive property of the surface area.

The primary results, expressed in cal./deg.-mole (one defined calorie = 4.1840 joules), are given in Tables II and III. The "surface specific heat" is simply the difference between the observed specific heat of the powder and the smoothed specific heat of the bulk salt. It was decided to employ the data of Morrison, Patterson and Dugdale (44) for the bulk salt. This procedure is most likely of sufficient accuracy since the excess specific heat ranges from 3 - 30% of the total specific heat of the salt and is usually 10% or more. Furthermore, their measurements are of recent origin and were made with a calorimeter and carbon thermometer similar to the one used in this research. One point of difference is that they used an earlier helium vapor pressure scale (45) than the one used here (37); however, the correction should not be significant. Their data is smooth to .3% and they claim a reliability of better than 1%.

The sample was prepared initially at $78.3 \text{ m.}^2/\text{g.}$ After the specific heat of this sample (Table III) was determined the sample was reduced to the lower area and the specific heat as listed in Table II was taken. The purity and appearance of the sample has already been described in Section III.

Both runs were made without an exchange gas and under a vacuum of 10^{-7} mm. or better. Nonetheless, equilibrium was achieved in a workable length of time. This is in contrast with some earlier experiments on sodium chloride powders by Patterson, Morrison and Thompson (1) where an exchange gas was used. This point will be discussed in the next section.

TABLE II

Specific Heat of NaCl of 41.8 m.²/g.

Temperature (°K)	Total Specific Heat of Salt (cal/deg-mole)	Specific Heat of Bulk Salt (cal/deg-mole)*	Surface Specific Heat (cal/deg-mole)
5.410	.005202	.004552	.00065
5.698	.006175	.005326	.00085
6.267	.008225	.007148	.00108
7.060	.01163	.01027	.00135
8.103	.01712	.01566	.00146
9.189	.02539	.02318	.00222
10.235	.03538	.03260	.00279
11.391	.04998	.04626	.0037
12.604	.06820	.06463	.0036
13.877	.09416	.08970	.0045
15.138	.1268	.1203	.0065
16.573	.1705	.1638	.0067
18.215	.2346	.2261	.0085
19.614	.3030	.2921	.0109

* Smoothed values based on the data of Morrison, Patterson and Dugdale (44).

TABLE III

Specific Heat of NaCl of 78.3 m.²/g.

Temperature (°K)	Total Specific Heat of Salt (cal/deg-mole)	Specific Heat of Bulk Salt (cal/deg-mole)*	Surface Specific Heat (cal/deg-mole)
4.501	.003610	.002604	.00101
4.792	.004601	.003150	.00145
5.428	.005927	.004597	.00133
5.695	.006900	.005361	.00158
6.097	.008582	.006542	.00204
6.741	.01167	.008905	.00277
7.406	.01530	.01188	.0034
8.111	.01924	.01571	.0035
8.916	.02498	.02109	.0039
9.800	.03284	.02835	.0045
10.844	.04522	.03941	.0058
11.930	.06081	.05376	.0071
13.169	.08438	.07495	.0094
15.066	.1316	.1184	.0132
16.504	.1763	.1615	.0148
18.126	.2400	.2223	.0177

* Smoothed values based on the data of Morrison, Patterson and Dugdale (44).

A separate run was made on the empty sample container to determine its contribution to the total specific heat. A careful record of weighings was kept so that small differences in its weight from run to run (due to gains and losses in the solder) could be corrected for. The specific heat data was subjected to a linear regression analysis and fitted to a five term polynomial in odd powers of temperature. The first and second terms represent the electronic and the Debye contributions respectively; higher power terms have some theoretical justification (46) and are necessary to obtain a fit to .1%. The purpose of finding a polynomial fit was to provide a convenient analytical function so that the empty could be subtracted off the total specific heat as part of the computer program. A smooth graph was drawn of the empty data to make certain that the polynomial function yielded correct values at all temperatures. In general, the empty sample container contributed about 70% to the total specific heat. This is somewhat unfavorable but was partly a result of the extremely low density of the powders. It is interesting to note that the sample container is about 98% copper, and its specific heat is in fair agreement with measurements that have been made on copper of about 99% purity (47).

A plot of the surface specific heat divided by the specific surface and the square of the absolute temperature is displayed in Figure V. Also, several theoretical curves are plotted for comparison. This particular plot is valuable since it shows immediately the extent to which the excess specific heat is an extensive property of the surface and illustrates the form of the temperature dependence. It can be seen that the points of the high surface area sample lie

FIGURE V

slightly above the lower surface area points. These observations are illustrated in Figure VI which displays, among other things, smoothed linear curves of the data points of this research. This does not imply that the surface specific heats of this research should fit a straight line, but rather it is done for clarity and to provide an easy comparison with the other data in Figure VI. It should be emphasized that the experimental scatter, as illustrated in Figure V, is large enough to account for the apparent non-zero slopes and the differences between the two samples.

The total specific heat of the powder runs was smooth to about .4% and the empty was smooth to .1%. As the value of the surface specific heat is of the order of 5% of the total specific heat it is estimated that the scatter in the surface heats should be about 10%. This in fact is consistent with the actual scatter as seen in Figure V. The uncertainty due to the use of the bulk NaCl data of Morrison, et al (44) should be no more than 10% based on their estimate of 1% accuracy for their data. The error in fixing the temperature in an absolute sense is somewhat more difficult to estimate. It is certainly limited to an accuracy of not better than .1% due to purely mechanical factors such as measuring volumes and pressures. Referring to the gas thermometer equations in Appendix I it can be seen that to a first approximation the percent error at any given temperature is equal to the percent error in determining the calibration temperature. Thus, if the helium vapor pressure temperature scale is in error by 5 millidegrees at the normal boiling point where the fill takes place, then the calculated temperature near 20° K will be in error by $\sim .02^\circ$ K. These errors are probably much smaller than scatter which is discussed above.

FIGURE VI

The theoretical curves in Figures V and VI were determined by calculating the specific heat at several points over the temperature range and joining them with a straight line, which represents the points to 1% or better. The equations have been given explicitly and discussed in the theoretical portion of Section I. In all cases the values for the elastic constants were extrapolated from the data of Overton and Swim (48) and a density of 2.209 g./cm.³ was assumed. The integral which occurs in Victor's equation was evaluated by numerical integration. Where the Debye theta occurs, the experimental values for the bulk salt were used.

Also found in Figure VI is a representative sampling of the data of Patterson, Morrison and Thompson (1). The relation of their data to the data of this research is discussed in the next section.

DISCUSSION AND CONCLUSIONS

One purpose in undertaking this research was to answer the question of whether or not the excess or "surface" specific heat is an extensive property of the surface. Earlier measurements (1) on sodium chloride failed to establish this point as an examination of Figure VI will show. Patterson, Morrison and Thompson attribute their inconsistencies to variations in the preparation of their samples. Their 39 m.²/g. sample, whose excess specific heat was especially large, was prepared in a higher electric field than the other two. However, even their two samples which were prepared under supposedly similar conditions did not have a strictly extensive surface specific heat. On the basis of the data in this research and within the limits of the experimental error, the excess specific heat appears to be proportional to the specific surface area. Whether or not this will be found true in future measurements may depend on the method of sample preparation.

It should be born in mind that idealized crystal models by no means represent the real state of affairs. If it were possible to make a detailed examination of real surfaces one would not find perfect crystalline planes, but peaks, crevices, lattice defects, and adsorbed gases. One cannot know the detailed extent of these irregularities, but it is almost certain that their occurrence is dependent upon the conditions of preparation. However, it seems possible that for a particular sample the number of surface imperfections may be nearly proportional to the surface area. In other words, the imperfections of a given sample may be reduced during the sintering process

approximately in the same proportion as the surface area is reduced. Using this simple picture one might expect a contribution proportional to the surface area due to surface imperfections. This would lead to an observed excess specific heat of larger magnitude than predicted by theory but still proportional to the surface area provided that the same sample was used for all measurements. This was the case in this research. This concept may explain why previous workers who have used different samples for each surface area have observed that the excess specific heat is not exactly proportional to the surface. Furthermore, it is believed that the sample used in this research was prepared under milder conditions of temperature and electric field. It contains fewer impurities than the sodium chloride used in earlier research (1).

One might wish to consider edge effects or bending modes of the crystals. Dupuis, Mazo and Onsager (3) have estimated both of these to be much smaller than the surface contribution. Jura and Pitzer (16) have pointed out that for sufficiently small particles the gross translational and rotational motion will contribute a significant amount to the specific heat. In the case of the $78.3 \text{ m.}^2/\text{g.}$ sample there are about 5×10^{17} crystallites per mole. The contribution in question will be six times the number of particles times the Boltzmann constant, or about 10^{-5} calories per degree-mole. This is about an order of magnitude smaller than the experimental scatter and therefore it is not possible to verify whether or not it exists in this sample.

It may be further concluded that within the limits of experimental error the excess specific heat of both samples varies approximately as

the square of the absolute temperature. Actually, none of the theories predict that the temperature dependence is exactly quadratic. All imply some additional dependence which arises from the temperature variation of the elastic constants or the Debye theta. In fact, the various theories do not agree on the direction of the deviation from the T^2 approximation as Figure VI illustrates.

Several interesting points relate to the thermal conductivity of powders and the use of exchange gases. No exchange gas whatever was used in this research in order to eliminate the possibility of having any desorption phenomena interfere with the measurements. Patterson, et al (1) used various amounts of exchange gas in their sodium chloride samples but were never able to maintain a sufficiently high thermal conductivity below about 9° K. In this research a similar decrease in thermal conductivity with temperature was observed in both samples, as evidenced by the equilibrium times. Patterson, et al attribute this phenomenon to the adsorption of a large fraction of their exchange gas. Nonetheless, they state that a hundredfold increase in the amount of exchange gas used failed to significantly improve their equilibrium times below 9° K. Helium appears to be adsorbed in a completely regular fashion between 1° and 20° K as indicated by the spacing of its isotherms (50). It would seem that if the helium gas were making a contribution to the thermal conductivity just above 9° K a hundredfold increase would result in a somewhat improved conductivity below 9° K.

The observed decrease in thermal conductivity of the powder samples may be simply due to the rise in thermal resistance of the individual crystals. It appears to be quite general that the thermal conductivity of a dielectric material rises slowly with decreasing

temperature, levels off at some temperature of the order of 20° K, and decreases very rapidly as absolute zero is approached (51). The rapid decrease in thermal conductivity at the lowest temperatures is thought to be due to the decrease in the specific heat, which is nearly proportional to T^3 . At higher temperatures, of the order of 30° K and above, certain processes which involve anharmonic scattering of the elastic waves predominate. Unfortunately, the thermal conductivity of sodium chloride does not appear to have been measured below 80° K so it is not possible to tell if the low temperature decrease in thermal conductivity occurs in the vicinity of 10° K. However, any such comparison must take into account the particle size effect. At low temperatures, reducing the crystalline dimensions increases its thermal resistance and shifts the thermal conductivity maximum toward a higher temperature. This has been observed, for example, in the case of potassium chloride (52).

In addition to the size effect of individual crystals there is a temperature independent variation of the thermal conductivity with the porosity of the whole sample (51). This is a function of the packing and the extent to which the crystallites are fused together. The $41.8 \text{ m.}^2/\text{g.}$ sample possessed a higher thermal conductivity than it did at $78.3 \text{ m.}^2/\text{g.}$ It is suggested that the sintering process was largely responsible for this, possibly through the partial fusion of the individual particles and the formation of thermally conducting chains. Lien and Phillips (8) report finding fairly short equilibrium times with magnesium oxide of $166 \text{ m.}^2/\text{g.}$ from 1° - 4° K while using no exchange gas. This might be somewhat surprising unless it is remembered that magnesium oxide is thought to possess a structure that tends

to be more porous than granular. Naturally, the increased size of the particles in the $41.8 \text{ m.}^2/\text{g.}$ sample would also contribute to the improved thermal conductivity but probably not so much as the increased porosity.

In the case of thermodynamic properties of the surface a real discrepancy appears to exist between the results of theory and experiment. This difference is principally in the absolute magnitude of these quantities. A smaller discrepancy concerns the temperature and surface area dependence but at the present time this is attributable to experimental error. The theory has been developed by Stratton and by Dupuis, et al, to a fair degree of refinement for the ideal continuum model. Future developments in the theory should perhaps take into account lattice defects on the surface and the change in the atomic force constants from the interior to the surface layers. Experimentally, the data which is suitable for a critical test of the theory is still limited. There are probably numerous salts that can be prepared in a state of high specific surface by electrostatic precipitation of the vapor. Future experiments should attempt to minimize lattice defects, perhaps by more careful control of the preparation conditions.

APPENDIX I

GAS THERMOMETRY

The construction and layout of the gas thermometers in this research is described in detail by Anderson (17). Located in the sample container there is a main volume of about 128 cc. and a much smaller compensating volume of about 4 cc.; however, they are designed so as to have approximately the same surface area. By taking measurements on both systems with the pressures equalized it is possible to eliminate from the final expression such indeterminate quantities as the amount of gas adsorbed on walls and the amount present in the connecting capillaries, which lie in a temperature gradient. In other words, if the pressures in the two systems are almost the same, the amount of gas adsorbed will be the same in each system.

Pressure measurements were corrected for capillary depression, temperature, the acceleration of gravity, and the position of the movable background behind the mercury meniscus. A calculation showed that the thermo-molecular pressure effect is negligible for this apparatus. Observed volumes were corrected for the meniscus height of the mercury in the burets.

The fundamental equation is derived as follows. The helium gas obeys the virial equation of state to a good approximation at these temperatures if two terms are retained.

$$PV = nRT + nBP$$

B is the second virial coefficient and n is the number of moles of gas. Let the subscript m refer to the main thermometer. c to the compensating thermometer and b to the burets which are at room temperature.

The primes designate any part of the compensating system.

$$N(\text{total}) = N_m + N_b + N(\text{capill.}) + N(\text{adsorb.})$$

$$N'(\text{total}) = N'_m + N'_b + N'(\text{capill.}) + N'(\text{adsorb.})$$

Now if $P \cong P'$

$$N(\text{capill.}) + N(\text{adsorb.}) = N'(\text{capill.}) + N'(\text{adsorb.})$$

$$\Delta N_t = N(\text{total}) - N'(\text{total}) = N_m + N_b - N'_m - N'_b$$

$$\Delta N_t = \frac{PV_b}{RT_b} - \frac{P'V'_b}{RT_b} + \frac{PV_m}{RT + BP} + \frac{P'V'_c}{RT + BP'}$$

The unsubscripted T refers to the temperature of the thermometer in the cryostat. It is not necessary to include the second virial term in the denominator of the first two terms since B is small at room temperature. Furthermore, since RT is several magnitudes larger than BP, we may replace BP' by BP in the last term with only negligible error provided the pressures P and P' have been properly adjusted. Now we have the expression for the filling constant with T* being the temperature (determined from the He vapor scale) at which the thermometers are filled.

$$R\Delta N_t = \frac{PV_b - P'V'_b}{T_b} + \frac{PV_m - P'V'_c}{T^* + \frac{BP}{R}}$$

Any temperature can be calculated from the equation

$$T = \frac{PV_m - P'V'_c}{R\Delta N_t + \frac{P'V'_b - PV_b}{T_b}} - \frac{BP}{R}$$

The values for the second virial coefficient were taken from the tabulated theoretical values of Kilpatrick, et al (49). These values are in good agreement with experiment.

In practice, the calculations are straightforward but laborious, especially the application of the capillary depression corrections. The entire calculation, including necessary tabulated constants, was written as a program for the I.B.M. 1620 computer. The original data can be punched onto cards and the final answers obtained rapidly.

APPENDIX II

EQUILIBRIUM TIMES

As mentioned earlier, the approach to equilibrium can be followed by observing the magnitude of derivative of temperature with time and the rate at which it changes. During a period of time following the heating interval the temperature of the sample will change rapidly and non-linearly due to thermal gradients and lack of internal equilibrium. As equilibrium is approached, the temperature drifts must become almost linear and of a magnitude dependent upon the Newton coefficient, the heat capacity, and the temperatures of the shield and the sample container. The heat leak to the sample container from its surroundings is approximately given by

$$\dot{Q} = \lambda (T - T_s)$$

where λ is the Newton coefficient and T_s is the shield temperature. The temperature drift of the sample is given by

$$\frac{dT}{dt} = \frac{\dot{Q}}{C_v}$$

where t is the time and C_v the heat capacity. Eliminating the heat leak $\dot{Q}$ we obtain

$$\frac{dT}{dt} = \frac{\lambda}{C_v} (T - T_s)$$

In practice the quantity λ can be calculated for various temperatures from the empty run, where no internal equilibrium problem exists. It is of the order of 10^{-3} joules/deg.min. The quantities

T and T_s are directly measurable during a drift and the heat capacity C_v can be estimated sufficiently well. Thus the magnitude of the equilibrium drift can be calculated and compared to the observed drift. The drift data was taken after these two values substantially agreed.

Table IV gives some equilibrium times for the two runs at various temperatures. It should be noted that the amount of joule heat added during the heating interval will certainly influence the equilibrium time. No attempt has been made to take this into account and thus the following values are only approximate. The values in the table refer to the after drift in every case, and the equilibrium time is arbitrarily defined as the point where the back extrapolation of temperature was begun. The values given are averages from several heat capacity points in the vicinity of the stated temperature.

TABLE IV

Approximate Equilibrium Times

Temperature	41.8 m. ² /g. Sample	78.3 m. ² /g. Sample
4°K	----	80 min.
6°	18 min.	50
8°	16	45
10°	13	28
12°	13	20
14°	10	22
16°	12	18
18°	10	20
20°	11	----

APPENDIX III

POWER CALCULATION

We wish to calculate the magnitude of the error involved in defining the average power as the average current times the average voltage. The time average power should really be given by:

$$\bar{P} = \overline{E \cdot I} = \frac{\int_0^{\Delta t} E \cdot I \, dt}{\int_0^{\Delta t} dt}$$

In practice it is more convenient to measure $\bar{E}$ and $\bar{I}$ separately.

The resultant error is given by

$$\delta = \frac{\overline{E \cdot I} - \bar{E} \cdot \bar{I}}{\overline{E \cdot I}}$$

Let us assume that E and I can be represented fairly well by a quadratic function of time.

$$E = a + bx + cx^2$$

$$I = \alpha + \beta x + \gamma x^2$$

$$\bar{E} = \frac{1}{2x} \int_{-x}^x (a + bx + cx^2) \, dx = a + \frac{1}{3} cx^2$$

$$\bar{I} = \frac{1}{2x} \int_{-x}^x (\alpha + \beta x + \gamma x^2) \, dx = \alpha + \frac{1}{3} \gamma x^2$$

$$\bar{E} \cdot \bar{I} = a\alpha + \frac{1}{3} c\alpha x^2 + \frac{1}{3} \gamma a x^2 + \frac{1}{9} c\gamma x^4$$

$$\overline{E \cdot I} = \frac{1}{2x} \int_{-x}^x (a\alpha + a\beta x + \dots + c\gamma x^4) \, dx$$

$$\overline{E \cdot I} = a\alpha + \frac{1}{3} (a\gamma + b\beta + c\gamma) x^2 + \frac{1}{5} c\gamma x^4$$

$$\overline{E \cdot I} - \bar{E} \cdot \bar{I} = \frac{1}{3} b\beta x^2 + \frac{4}{45} c\gamma x^4$$

Neglecting higher order terms, we find that the error is

$$\delta \cong \frac{1}{3} \left(\frac{bt}{a} \right) \left(\frac{\beta t}{\alpha} \right)$$

For this calorimeter a typical set of values near 6°K are:

$a = 1200 \mu v$, $\alpha = 700 \mu v$, $b = .05 \mu v / \text{min.}$, $\beta = .7 \mu v / \text{min.}$,
and $t = 10$ minutes. In this case the error δ is $.14 \times 10^{-6}$ or
.00014%.

APPENDIX IV

CURVATURE CORRECTION

The heat capacity of a substance is defined as the partial derivative of the energy with respect to temperature at constant pressure or volume. The experimental heat capacity involves finite differences.

$$C_{\text{exp}} = \frac{\Delta H}{\Delta T}$$

If one assumes an analytical form for the heat capacity a factor can be derived which relates the true heat capacity to the experimental heat capacity. This is referred to as the curvature correction since if the heat capacity were linear in temperature no correction need be applied.

In the following derivation $\bar{T}$ is the temperature at the midpoint of the heating interval and 2δ is equal to the total temperature interval, ΔT . In these experiments it is found to a fair approximation that the heat capacity can be represented by the equation:

$$C_p \equiv \left(\frac{\partial H}{\partial T}\right)_p \cong aT + cT^3$$

$$\Delta H = \int \left(\frac{\partial H}{\partial T}\right) dT = \int_{\bar{T}-\delta}^{\bar{T}+\delta} (aT + cT^3) dT$$

$$\Delta H = 2a\bar{T}\delta + 2c\delta(\bar{T}^3 + \bar{T}\delta^2)$$

$$\frac{\Delta H}{\Delta T} = a\bar{T} + c\bar{T}^3 + c\bar{T}\delta^2 = \frac{dH}{dT} + c\bar{T}\delta^2$$

$$\frac{dH}{dT} = \frac{\Delta H}{\Delta T} - c\bar{T}\left(\frac{\Delta T}{2}\right)^2$$

$$\frac{dH}{dT} = \frac{\Delta H}{\Delta T} \left\{ 1 - \frac{\left(\frac{\Delta T}{2}\right)^2 c\bar{T}}{\left(\frac{\Delta H}{\Delta T}\right)} \right\}$$

The quantity in the braces is the required one. If $\Delta T \leq .1 \bar{T}$ the factor is approximately .998 or correction of .2%.

In practice the experimental data can be plotted up to estimate the value of the constant c , and then the correction applied analytically during the calculation of the heat capacities on the computer.

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