THE ENTHALPY AND SPECIFIC HEAT OF POTASSIUM BROMIDE AND
POTASSIUM IODIDE AT HIGH TEMPERATURES

by

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SECTION I. INTRODUCTION

The detailed investigation of the variation of specific heat with temperature is of great importance for a proper understanding of the solid state of matter. Together with other experimental measurements it offers a direct experimental check on theories of the internal energy of substances. Tables of specific heats are also of interest in thermodynamics. It is the purpose of these experiments to measure the specific heat at constant pressure of two of the alkali halides, potassium bromide and potassium iodide.

The theory of the specific heat at constant volume of monatomic solids was first worked out on the basis of the quantum theory by Einstein and Debye. This work is summarized by Seitz\(^1\). Born\(^2\) extended the theory to include crystalline solids. He regarded these as being composed of many similar groups of atoms, the groups being spaced uniformly in any given direction. He found that the motion of crystalline groups as wholes could be well described by a Debye function. In addition to this motion there are other vibrations which can be thought of as being due to the vibration of atoms within groups, these being independent of atoms in other groups. For each of these modes a term in the energy of the Einstein form is used. The resulting equation reduces at high temperatures to the Dulong and Petit law.
The theories of Einstein, Debye, and Born were based upon the assumption that the forces involved are linear, or that the energy is given by a quadratic expression. It might be expected that at higher temperatures, where the vibrations are more violent, the force expression may contain terms of higher power than one, and that this would change the energy dependence upon the temperature and thus that of the specific heat. Schrödinger attacked the high temperature problem by generalizing the Hooke's law forces used previously by an expression,

\[-\mu x + \mu' x^2 + \mu'' x^3 + \ldots\]  

so that the vibrations of the atoms thus become anharmonic. The results of the calculation yield for the specific heat at higher temperatures,

\[c'_v = c_v (1 + \alpha \tau)\]  

where \(c_v\) is the specific heat of the Dulong and Petit law. The quantity, \(\alpha\), is equal to the difference of two terms, of which the positive term depends upon the coefficient of \(x^2\), and the negative term upon the coefficient of \(x^3\). Thus the additive term may be either positive or negative.

The quantity of theoretical interest is the specific heat at constant volume, \(c_v\), whereas experimentally the quantity generally measured is \(c_p\), the specific heat at constant pressure. These two are related by a thermodynamic formula as follows

\[c_p - c_v = \tau V \frac{9 \alpha^2}{\beta}\]
where $\alpha$ is the coefficient of linear thermal expansion, and $\beta$ is the compressibility. Thus measurements of $c_p$ together with linear expansion and compressibility yield values of $c_v$ which can be compared with theory.

The experimental results of specific heats at high temperatures are meagre and often inaccurate due to the difficulties of measurement. It has not yet been determined for certain what the shape of the $c_v$ curve at high temperatures actually is.

Eucken and Dannohl found that $c_v$ drops below the DuLong and Petit value for NaCl at higher temperatures. However, this result is based on the calculation of compressibilities by linear extrapolation from the room temperature values.

Hunter and Siegel have used the values of Eucken and Dannohl together with their own experimental data for the compressibility and found that for NaCl the curve actually does keep approaching the $3R$ value, not dipping down.

The experimental values of the thermal expansion at high temperatures are presumably fairly accurate. It is uncertainties in the values of specific heats at constant pressure, and of compressibilities which introduce the uncertainty in the results for $c_v$. 
SECTION II. METHOD

The ice calorimeter used in these experiments is a suitable instrument for the accurate measurement of enthalpies at high temperatures. Basically the ice calorimeter consists of a vessel containing water in the center of which is a hollow well. The water in the vessel has an interface with a quantity of mercury which is lead into the vessel thru a tube from the outside. An ice mantle is formed about the well, and the whole apparatus is immersed in an ice bath. When the heated sample is dropped into the well, some of the ice mantle is melted, resulting in a decrease in the volume of the contents of the vessel. Therefore a certain amount of mercury is drawn into the vessel. By weighing the mercury intake one can determine the heat given off by the sample in terms of the specific volume of the ice, \( v_i \), the specific volume of the water \( v_w \), the density of the mercury \( d_m \), and the latent heat of fusion of the water \( L \), by use of the relation,

\[
K = \frac{L}{(v_i - v_w) d_m}
\]

(4)

\( K \) is the calibration factor of the calorimeter, the ratio of heat input to mass of mercury intake. The density of ice, which was thought at one time not to be accurately reproducible, was carefully studied by Ginnings and Corruccini\(^7\) of the National Bureau of Standards. They determined its value accurately, and also established the fact that its density is constant.
The advantages of the ice calorimeter are that no temperature measuring device or electrical instruments need be used with it if its calibration factor is constant, and when it is properly used with an ice bath its heat leak is very small.
SECTION III. DESCRIPTION OF THE APPARATUS

1. Ice Calorimeter

A sectional view of the ice calorimeter of the same type as used by D.C. Cinnings is shown in Figure 1. The central well, $W$, into which the heated sample is to be dropped is a monel cylinder cut into two sections divided by the gate, $G$.

The purpose of this gate is to dissipate into the outer ice bath, $I$, heat radiated down the well from the hot furnace above. It consists of a flat hollow brass cylinder with a tight fitting copper gate inside it. The axis of the gate is vertical, and it can be rotated about this axis. Normally the gate is in such a position so that it intercepts radiation coming down the well from the furnace. When a sample is to be dropped into the well, the gate is rotated by the shaft, $Z$, so that the hole in the gate (of same size as the well) allows the capsule to fall thru. This hole is tear shaped so that when the gate is rotated to close the opening, the suspending wire of the capsule is caught in the corner of the tear and any heat conducted down the wire from the furnace is thus dissipated. The gate is made of copper and is chromium plated.

The bottom part of the well has 22 fins, $F$, as shown to conduct heat quickly to and from the water in the inner container. These fins are made of copper, are circularly
Figure 1.
The Ice Calorimeter
Figure 2. Furnace

Scale:
1 cm = 1 inch
shaped with two indentations to allow room for the lines B and C. These fins are separated by spacers which fit the central well snugly. The bottom 12 spacers are of copper and the remainder of brass. They are soldered to the well with tin, except for the bottom fin which is hard soldered to the well and then tin plated. The entire assembly consisting of central well, fins and spacers was coated with tin using a soldering iron, hot dipped in tin and then electroplated with tin. Experience has shown that this combination forms the least porous coating.

Tube C, of stainless steel, tin plated, allows CO₂ gas or helium to be passed thru the central well to keep moisture from condensing there. A flow of CO₂ was kept moving thru C and the well at all times by running a tube from a Dewar flask containing dry ice to the line C. Stainless steel tube T, h, and E forms a passageway for the mercury from the well of mercury inside the inner jar to the beaker h. This tube was tin plated, except for the portion which dips into the mercury which was coated with Apiezon W wax.

The inner jar, J, is of pyrex glass, and its upper end (down a distance of one inch) was ground by using abrasive so as to fit the brass fitting 3 snugly. The jar was thoroughly cleaned with KOH, HNO₃, and chromic acid cleaning solution before assembly. It is cemented in place in the fitting 3 with Apiezon W wax. This brass fitting
was coated with tin on its underside so that the water in the inner jar was exposed only to tin, mercury and a small area of Apiezon wax W.

The outer jar, K, is similar except larger as shown. It is supported by a brace attached to fitting A (not shown), and is cemented into fitting A with Universal Red Wax.

The inner jar is filled with air free distilled water 0 (described later) and with clean distilled mercury.

The whole apparatus is surrounded by the ice bath I frozen from distilled water. This bath was kept at a level L in the glass bell jar H. The whole bell jar was surrounded by bats of Styrofoam insulation (not shown).

The mercury system of the calorimeter consisted of the beaker of mercury R, valve V, capillary tube E', stainless steel tube T, stainless steel bulb D, stainless steel tube K, stainless steel tube E, and well of mercury inside the inner jar, H. As ice freezes or melts on the fins F, mercury is pushed out of the calorimeter, or sucked into it from the beaker R. The bulb D acted as a trap for water in the mercury line, or for air which got into the line accidentally; this trapped water or air could be pushed out of the system by freezing more ice on the fins. The valve V, of stainless steel, could be used to control the flow of mercury; when it was closed the beaker R could be removed for weighing. In later experiments, the valve V was
removed from the system, the capillary \( E' \) being connected to beaker \( R \) with glass capillary (0.8 mm diameter).

The metal parts of the calorimeter were soft soldered together, except for places which would be exposed to the distilled water of the inner jar which were soldered with pure tin. The glass capillary \( E' \) was attached to the mercury line \( T \) with Apiezon wax \( W \). The mercury came in contact only with water, stainless steel, Apiezon \( W \) wax and pyrex glass.

2. Description of the Furnace

Figure 2 shows a cross sectional view of the furnace. The central core of the furnace is about 22" long and about 1 1/4" in diameter, thus affording a satisfactory ratio of length to diameter. A main heater winding runs the entire length of the core, and to keep temperature gradients to a minimum, at least in the center portion of the furnace, separate top and bottom heater windings are also included. The currents in the three windings could be varied separately to allow for losses of heat out the ends of the furnace.

The main winding is wound on an alundum core \( A \). Alundum is a refractory material capable of withstanding high temperatures and does not react with platinum. The end windings were wound on the alundum core \( B \). All windings were of platinum, 90% - rhodium 10%, no 30 wire. The sample to be heated is suspended in the
central core of the furnace, C. Region D is filled with alundum powder and region F with diatomaceous earth. E is another alundum cylinder used to contain the powder. The outside of the furnace consists of galvanized sheet iron, G, and the top and bottom of the furnace are held together by the tie rods, H. On top and bottom of the furnace are transite plates, J, and iron plates, K. The cores containing the heaters can be removed from the furnace, and are held in place by the lavite fittings M (machined and baked), and the iron rings, L.

It was found that the central core of the furnace had a rough surface which when rubbed gave off a fine alundum powder, which must be kept out of the calorimeter below. Thus a stainless steel (type 304) lining, not shown, fitting the inner alundum core snugly, was placed inside the furnace. It was hard soldered to a stainless steel ring which was screwed to the iron ring L. The stainless steel lining served the additional purpose of cutting down convection currents, which occurred before due to the porosity of the alundum cores.

3. Thermocouple Assembly

The temperature of the capsule when it was suspended in the furnace was measured as follows. The furnace was lined with a stainless steel tube fitting the alundum core
of the furnace snugly. The auxiliary steel tube hard soldered to its bottom end was fitted to the tube of the calorimeter well with a one inch sylphon bellows. At the midpoint of the furnace a tube of Inconel was mounted. It was five inches long, 1/16" wall, and fitted the stainless steel tube snugly. Three thermocouples (each couple platinum to platinum 90%, rhodium 10%) had their junctions mounted in this Inconel ring. One couple was fastened at the center of the ring, and the other two at top and bottom, each two inches from the center. The junctions were attached to the Inconel ring by the use of fabricated Nichrome V screws which screwed into the Inconel ring from the inside. The junctions of the couples were thus on the inside of the ring. The main coil current and that of the two end heaters were adjusted until the three couples read approximately the same to within 0.5°C thus creating a nearly isothermal region within the Inconel cylinder. The six wires from the thermocouples were led out of the furnace and into an ice bath in a Dewar flask constituting the cold junction. Inside the furnace the pairs of leads were lead out thru double bore ceramic insulating tubing made by the McDaniel refractory company. These served the double purpose of insulating the wires, and protecting them from gases in the furnace, and contamination by evaporation from one wire onto the other. The wires were then led into pyrex glass tubes inserted into the ice bath. Each tube had
an inch or so of Hg in it. Copper wires were then fed into the mercury so as to make contact at 0° C with the platinum wires. These six copper wires were then led to the potentiometer, which could select any one thermocouple by a switching arrangement. The potentiometer was a Leeds and Northrup Wenner type capable of reading to 0.1 microvolt.

The thermocouples were certified by the Bureau of Standards before use. The standard cell used with the Wenner potentiometer was a Weston and had been certified by the National Bureau of Standards. Another certified cell was kept as a reference.

4. Vacuum System

A vacuum system was required which would serve three purposes: to evacuate the calorimeter and mercury line, to fill the calorimeter with air-free distilled water, and to be used to fill the capsule.

A standard pyrex glass vacuum system was used. The backing pump was a Megavac; the diffusion pump a Cenco mercury pump. There was a mercury barometer in the system which could be used to estimate pressures roughly, and as a valve. A McLeod gage was included in the system for measuring pressures accurately, and a thermocouple gage was later added to facilitate leak hunting. Between the McLeod gage and the system to be evacuated was a vapour trap which was filled with a dry ice acetone mixture while the mercury diffusion pump was operating. Glass stopcocks
(vacuum type) were used in the system with Dow-Silicone stopcock grease. Attached to the vacuum system was the glass system used for preparing air-free water. It consisted of a flask into which triply distilled water was placed with a connection leading to another vacuum pump. This flask was also connected by glass tubing to the vacuum system, and the whole by a glass tube to the calorimeter. The method of evacuating and filling the calorimeter with water is described later.

5. The Drop System

The method of controlling the drop of the capsule from its position in the furnace into the calorimeter is illustrated in Figure 3. A steel tube A three feet long, one inch o.d., and 1/16" wall was mounted on top of the furnace with its axis in line with the axis of the furnace. There was a metal plug C on the bottom of this tube with a 1/32" hole exactly centered. A steel plummet B was machined to fit inside the steel tube snugly, so that it could fall free inside the tube when released. Holes were drilled in the sides of the steel tube so that the plummet underwent essentially free fall, except for the last four inches where braking took place due to the air trapped by the plummet in its fall in the bottom part of the tube where there were no holes. A wire (Nichrome V, 3 & 5 gage 32) was attached to the bottom of this plummet. It ran thru the hole in the bottom plug of the tube, thru a hole in the lavite plug on
top of the furnace, P, and had the capsule and the convection shield assembly attached to its lower end. A string B was attached to the top of the plummet which ran up the tube and over a pulley mounted on the top end. Thus by pulling on the string the plummet, wire and capsule could be raised into the proper place in the furnace. Then when it was desired to lower the capsule into the calorimeter, the string was cut, and the assembly fell until the plummet hit the bottom of the tube. The length of wire was adjusted so that the capsule would then be in the proper place in the calorimeter C. Tests have shown that the time of fall is fairly constant using this mechanism.

6. Capsules

There were several practical problems involved in the design of the capsules used for holding the samples. The material of the capsule had to be hard enough so that a cutting edge capable of cutting a metal gasket could be obtained; the capsule must be chemically inert with the samples run; it must have considerable mechanical strength; it must be light enough so that its specific heat does not mask that of the sample; it must be shaped on the outside so as to touch the calorimeter well over as much area as possible; and it must be capable of prolonged exposure to high temperatures without undue oxidation and without any scaling. Nichrome V, an alloy of Driver Harris Company
containing about 80% Ni and 20% Cr was used.

The capsules were machined under the direction of D.R. Long of Tagcraft Corporation, Lancaster, Pennsylvania, and their fabrication presented a machining problem due to the extreme hardness of Nichrome V. The capsules were 1 7/8" long over-all. The body of the capsule, cylindrical in shape, had wall thickness of about 0.012". The bottom of the capsule was about 0.015" thick. The top of the body was threaded with 32 threads per inch, and a cutting edge machined on the top of the body. The cap of the capsule was threaded to fit on the body so that its outside was flush with that of the body. A gold gasket of 0.010" thickness was used.

The over-all weight of the capsule and gasket was approximately 15 grams. The method of filling the capsule with a sample is given later.

7. Electrical Wiring of the Furnace

The current thru the heater coils of the furnace was adjusted manually. Three variacs and a system of resistors were used. Power for the furnace was supplied by a Sola constant voltage transformer of 2000 va capacity. One variac controlled the current thru the main winding of the furnace. Another variac controlled the current thru the end heaters. A third variac in the line from the Sola transformer controlled the voltage to the other two variacs so that the total current could be varied with one control.
SECTION IV. PROCEDURE

1. Filling the Calorimeter with Water

Two liters of triply distilled (in a glass still) water were placed in the flask provided for that purpose in the vacuum system already described. This flask had a vacuum valve above and below the water. The top valve when open connected thru glass tubing to a vacuum pump. When this pump was turned on the pressure above the distilled water was reduced, and the dissolved air in the water then escaped from the water until its partial pressure was equal to the pressure provided by the pump, less than 1 cm of Hg. The upper valve was then closed off, giving a flask of distilled air-free water. Meanwhile the vacuum system connected to the flask thru the bottom valve had been evacuated. This system had been connected to the mercury line of the calorimeter, so that as the system was evacuated, the mercury line and inner jar of the calorimeter were also evacuated. The usual tests were used to insure that a tight vacuum system existed. After the system had been evacuated, a valve connecting it to the calorimeter was closed, and the valve underneath the distilled water flask was opened. The air-free distilled water thus flowed by gravity into the calorimeter.
2. Freezing the Ice Mantle

After the calorimeter was filled with air-free distilled water as described, some dry ice was introduced into the central well of the calorimeter. The water in the inner jar was thus cooled and ice started to form around the fin assembly. This forced water back out of the calorimeter thru the line K, Figure 1. When the fins had been completely covered with ice, and as large a mantle as was possible without cracking the jar was formed, the tip of the capillary dipping into the beaker of mercury, R, Figure 1, was broken off. At the same time, the capillary line E was shut off. Then as the ice mantle was melted, mercury was drawn into the system replacing the water. At this point the line to the distilled water flask could be disconnected as there was a layer of mercury on top of the water and thus no danger of contaminating it with air. A quantity of mercury was thus drawn from the beaker K into the mercury well, H, inside the inner jar. By repeating the mantle freezing and melting, the desired quantity of mercury could be drawn into the well. Three freezings were required in practice. Each freezing of the mantle required about 1 1/2 to 2 hours.

While the freezing and melting was in progress ice water at about 20° C was kept in the ice bath jar, I, Figure 1. When the required amount of mercury was drawn into the reservoir, a final mantle was frozen around the fins, and the calorimeter was ready for measurements. In this condition, the
distilled air-free water in the calorimeter had mercury between it and the outside beaker R. Thus heat introduced into the well, W, would be registered by the weight of the mercury drawn in.

During this process a flow of dry CO₂ was passed thru the tube C with the intent of keeping moisture from condensing inside the well. CO₂ gas, dried by passing thru a P₂O₅ trap, was kept flowing thru the well, W, at all times. A convenient source of CO₂ gas was from a supply of solid CO₂ kept in a Dewar flask.

After the mantle was frozen, the ice water was syphoned from the bell jar which was then filled with cracked ice. The whole apparatus was surrounded by blocks of Styrofoam insulation (not shown in Figure 1).

3. Filling the Capsule

The capsule containing the sample and an inert atmosphere had to be air tight. A cutting edge was turned on the capsule so that it would seal into a gold gasket. The sample was placed in the capsule as follows. The capsule, capsule top containing gold seal, and the sealed sample (of KBr or KI) was placed into a glass tube, 4 inches in diameter and a foot long. Rubber gloves were fitted over the ends of the tube so that the contents of the tube could be manipulated by hand without exposure to the atmosphere. Previously the glass tube had been filled with gas dried over P₂O₅. The sample was then placed in the capsule, the
cap screwed on, and the capsule immediately transferred to a vacuum system in which the vacuum was immediately reduced to about a mm of mercury. Since the cap was on loosely the gas in the capsule was pumped out. Then helium gas was admitted to the portion of the vacuum system containing the sample so that the capsule was filled with helium. The capsule was removed and the cap tightened down with a wrench. Thus the capsule was sealed containing the water free sample and helium atmosphere. The capsule and contents were weighed. Since a leak in the gasket would cause a change in the weight of the contents of the capsule, reweighing it would check if the gasket were tight.

4. Measurements of Enthalpy

The ice mantle was prepared as already described. If measurements were to be made soon thereafter it was necessary to premelt a little of the mantle close to the well, \( W \), to obtain a water connection to the water outside the mantle. This precaution was not necessary if the mantle was allowed to stand, over night for example, since in this case very fine filaments thru the ice from the fin side to the water side developed. These were evidently filled with water and allowed a path for water flow when melting started.

After the mantle was frozen and premelted the heat leak was tested. This was done by two methods. In the first place, the valve, \( V \), Figure 1, was closed and the position of the mercury level at \( E' \) was watched. This capillary had been
calibrated previously by adjusting the mercury in it to various levels, and weighing the amount of mercury in the beaker. Thus small changes in mercury could be read on the capillary tube $E'$, and larger changes by weighing the beaker $R$. The second method, eliminating the valve, was used principally. The valve, $V$, was removed and a capillary glass tubing leading to the beaker $R$ put in its place. A rubber tube was attached to the top of the capillary tube $E'$, a slight suction applied to it, and the beaker $R$ withdrawn. Then the mercury in the capillary tube directly above the beaker was drawn up to a prescribed level, and readings of the level of the mercury in the tube $E'$ were taken as before, with the difference that the mercury on the right was kept at a definite level. This method which dispensed with the valve, which had proved troublesome, worked satisfactorily in practice. The levels of the mercury in the capillaries was measured with traveling microscopes.

After the heat leak had settled down to a fairly constant value the calorimeter was ready for measurements. The heat leak was found to be approximately 0.4 to 0.9 calorie per hour. Variations in heat leak were attributed to moisture in the well. During this time the ice bath $I$ was kept at the level $L$, melted water being drawn from $I$ by a syphon.

Meanwhile the capsule containing the sample had been pulled into the proper place in the furnace, namely halfway up. The position of the capsule in the furnace was
checked on each run by inserting a ceramic tube up from the bottom until it touched the bottom of the capsule. The capsule thus was suspended in the middle of the isothermal region of the Inconel ring previously described. The main coil current of the furnace and the currents in the two end heaters could be manipulated so that the three thermocouples in the furnace indicated the same temperature, giving rise to a four inch isothermal region in the furnace. The readings of these couples were held as close together as possible by manipulating variacs feeding the three coils, and the whole temperature kept at a fixed value by manipulating a variac feeding all three coils at once. It was found that the temperature of the furnace could be held to about 0.1° C, and the gradients kept at or better than 1/4° C per inch.

Empty capsules were kept at the desired temperature at least 3/4 of an hour, filled capsules at least 1 1/4 hour.

The furnace was rotated about its vertical axis so that its core was lined up with the calorimeter well \( N \). The tube of the furnace and the calorimeter well were joined by a sylphon bellows. See Figure 3.

When the heat leak was steady and when the capsule had been held in the furnace the prescribed length of time, the string holding the capsule was cut.

Thus the plumb, the Nichrome V wire, and the capsule on its bottom end dropped down until the capsule was at the proper place in the calorimeter. This fall has been
described. As the capsule reached its bottom position in the furnace, (see Figure 3), the gate was closed. The gate was open about two seconds for each drop.

As the capsule gave up its heat to the calorimeter, ice melted and mercury was drawn into the system from \( R \). The levels of the mercury before and after the run at \( E' \) were noted, along with the weights of the beaker \( R \), so that the amount of mercury drawn in could be found.

For all runs recorded in the data the ice mantle was checked for intactness after each run.

A total of 93 runs was made. The ice mantle was refrozen after approximately 50 or so grams of mercury were drawn in. Thus several runs, of small heat exchange, could be made on one mantle, whereas the mantle had to be refrozen after each run for those of high heat transfer.

Runs were made with the empty capsule, and with the capsule containing the sample, and by subtracting these values; after making corrections noted later, the heat values for the sample alone could be determined. This method eliminates all experimental errors which are the same for the two cases.

In order to calibrate the calorimeter, runs were made with synthetic sapphire (\( \text{Al}_2\text{O}_3 \)) obtained from the Linde Air Products Company. The specific heat of this material, which forms a suitable standard substance for calorimetry, has been carefully investigated by D.C. Ginnings and R.J.
Corruccini\textsuperscript{9} of the National Bureau of Standards. The results of this calibration are contained in a University of Maryland (1951) M.S. thesis by George E. Hauver\textsuperscript{10}.

The pure samples of KBr and KI used were obtained from the Harshaw Chemical Company, Cleveland, Ohio.
SECTION V. DATA

Data for the runs on the empty capsule, capsule containing KBr, and capsule containing KI are listed in tables I, II, and III. The masses of mercury are corrected for buoyancy. Also, since the amount of helium in the empty sealed capsule was greater than the amount in the capsules containing the sample by an amount equal to the volume of the sample, corrections were made for this difference. The weight of the gold gasket in each case was the same. The weighted mean of the mercury mass readings is listed in the tables for each temperature. The details of the weighting are given by G.E. Hauver10. Two factors were considered in the weighting: the steadiness of the heat leak, and the magnitude of the gradient in the furnace in the neighborhood of the capsule. Weights of 2:1, 5:1 and 10:1 were used. For example, if for two different runs, both gradients were equally good, but one heat leak was considerably worse than the other, and the one gradient rather poor (that is large), a weight of 1:10 was used. Of the 36 runs included in the data, 7 means were weighted means, while in the remainder the masses averaged were weighted equally. It was found that in the later runs as technique improved there was little need for weighting.
Table 1. Data on Empty Capsule

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<th>Temperature (°C)</th>
<th>Mass of Hg corrected for buoyancy (gm)</th>
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<td>458.7°</td>
<td>14.5594&lt;sup&gt;a&lt;/sup&gt;</td>
<td>14.5652</td>
<td>-.0058</td>
</tr>
<tr>
<td></td>
<td>14.5664&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td>.0012</td>
</tr>
<tr>
<td>530.3°</td>
<td>17.0894&lt;sup&gt;a&lt;/sup&gt;</td>
<td>17.0705</td>
<td>-.0011</td>
</tr>
<tr>
<td></td>
<td>17.0821&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td>.0116</td>
</tr>
<tr>
<td>586.7°</td>
<td>19.1244&lt;sup&gt;a&lt;/sup&gt;</td>
<td>19.1531</td>
<td>-.0287</td>
</tr>
<tr>
<td></td>
<td>19.1674&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td>.0143</td>
</tr>
<tr>
<td>673.5°</td>
<td>22.4665</td>
<td>22.4685</td>
<td></td>
</tr>
<tr>
<td>728.1°</td>
<td>24.6049</td>
<td>24.6039</td>
<td>.0010</td>
</tr>
<tr>
<td></td>
<td>24.6029</td>
<td></td>
<td>-.0010</td>
</tr>
</tbody>
</table>

Mass of capsule, cap, gold gasket, helium (sealed) = 18.2400 gm

Inside volume of capsule = 7.48 cm³
Outside volume of capsule = 9.68 cm³

Masses marked <sup>a</sup> were weighted.
Table II. Data on KBr

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Mass of Hg corrected for buoyancy and Helium content (gm)</th>
<th>Mean</th>
<th>Deviation from Mean (gm)</th>
<th>Mass Hg due to KBr (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>333.4°</td>
<td>15.9935</td>
<td>16.0017</td>
<td>-.0082</td>
<td>5.6438</td>
</tr>
<tr>
<td></td>
<td>16.0129</td>
<td></td>
<td>.0112</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15.9985</td>
<td></td>
<td>-.0029</td>
<td></td>
</tr>
<tr>
<td>530.3°</td>
<td>26.3682</td>
<td>26.3492</td>
<td>.0190</td>
<td>9.2787</td>
</tr>
<tr>
<td></td>
<td>26.3475</td>
<td></td>
<td>-.0017</td>
<td></td>
</tr>
<tr>
<td></td>
<td>26.3320</td>
<td></td>
<td>-.0172</td>
<td></td>
</tr>
<tr>
<td>728.1°</td>
<td>37.9067</td>
<td>37.8840</td>
<td>.0227</td>
<td>15.2801</td>
</tr>
<tr>
<td></td>
<td>37.8938</td>
<td></td>
<td>.0098</td>
<td></td>
</tr>
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<td></td>
<td>37.8771</td>
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<td>-.0069</td>
<td></td>
</tr>
<tr>
<td></td>
<td>37.8563</td>
<td></td>
<td>-.0357</td>
<td></td>
</tr>
</tbody>
</table>

Mass of capsule + helium + KBr = 28.3263 gm
Mass of capsule corrected for buoyancy = 28.3336 gm
Mass of capsule = 18.2468 gm
Mass of helium + KBr = 10.0888 gm
Mass of KBr = 10.0862 gm
## Table III. Data on KI

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Mass of Hg corrected for buoyancy and helium content (gm)</th>
<th>Mean</th>
<th>Deviation from Mean (gm)</th>
<th>Mass of Hg due to KI (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>333.4°</td>
<td>14.7124</td>
<td>14.7266</td>
<td>0.0142</td>
<td>4.3687</td>
</tr>
<tr>
<td></td>
<td>14.7409</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>458.7°</td>
<td>20.7587</td>
<td>20.7455</td>
<td>0.0132</td>
<td>6.1803</td>
</tr>
<tr>
<td></td>
<td>20.7323</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>588.7°</td>
<td>27.1429</td>
<td>27.1402</td>
<td>0.0027</td>
<td>7.9871</td>
</tr>
<tr>
<td></td>
<td>27.1376</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>673.5°</td>
<td>31.7109</td>
<td>31.7109</td>
<td>0.0000</td>
<td>9.2424</td>
</tr>
</tbody>
</table>

- Mass of capsule + helium + KI: 28.8520 gm
- Mass of capsule + helium + KI (corrected for buoyancy): 28.8592 gm
- Mass of capsule: 18.2555 gm
- Mass of helium + KI: 10.6037 gm
- Mass of KI: 10.6030 gm
SECTION VI. METHOD OF TREATING DATA AND RESULTS

The values of mercury intake for each temperature were converted to heat values by multiplying by the calibration factor of the calorimeter, 64.638 cal/gm of mercury. The results were then divided by the mass of the samples of Hg and KI, yielding the enthalpy per gram for each temperature with respect to 0°C.

It has been common practice in thermodynamical calculations to represent the specific heat of substances above room temperature by equations in power series form,

\[ c_p = a + bT + cT^2. \]

However, it has been found that such expressions may not accurately represent the facts at higher temperatures where for many substances the specific heat is then nearly a linear function of the temperature.

In the case of KI, the data supplies values of enthalpies at five temperatures. It was decided to calculate two analytic expressions for different temperature ranges, a cubic equation (quadratic for the specific heats) for temperatures below about 400°C, and a quadratic equation (linear for specific heats) for temperatures above that value. The constants of these equations were determined by direct calculations. The data used are:
Use of the first four values was made to determine the coefficients of the equation,

\[ H = a + bt + ct^2 + dt^3 \]

These coefficients were found to be
\[ a = 0; \quad b = 0.065731; \quad c = 0.00000000207; \quad d = -0.000000003281 \]

The resulting equation for the specific heat, obtained by direct differentiation is,

\[ \alpha_p = 0.065731 + 0.0001204 t - 0.00000015984 t^2 \quad (11) \]

The specific heat is in \( \text{cal/g}^\circ \text{C} \). This equation was used for temperatures up to 400\(^\circ\) C.

The last two values in the table above, together with the value of the specific heat at 400\(^\circ\) found from equation (11) were used to obtain an equation for \( H \),

\[ H = a + bt + ct^2 \]

and the coefficients thus calculated were:
\[ a = -2.38246; \quad b = 0.085893; \quad c = 0.00000030357. \]

Thus for temperatures above 400\(^\circ\), the equation found for the specific heats was:

\[ \alpha_p = 0.085893 + 0.00000060714 t \quad (12) \]

In the case of KBr the data yielded the following values for the enthalpy:
The constants for a cubic equation for the enthalpy were found from these values to be:

\( a = 0; \quad b = 0.10478; \quad c = 0.00006426; \quad d = -0.000000014005 \)

and the resulting equation for the specific heat:

\[ c_p = 0.10478 + 0.000012852 t - 0.000000042015 t^2 \]  \quad (13)

Equations (11), (12), and (13) were then used to calculate the following values of specific heats:

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Specific heat at constant pressure (cal/gm/deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KBr</td>
</tr>
<tr>
<td>300°</td>
<td>0.1083</td>
</tr>
<tr>
<td>400°</td>
<td>0.1093</td>
</tr>
<tr>
<td>500°</td>
<td>0.1102</td>
</tr>
<tr>
<td>600°</td>
<td>0.1110</td>
</tr>
<tr>
<td>673.5°</td>
<td>0.1117</td>
</tr>
<tr>
<td>700°</td>
<td></td>
</tr>
<tr>
<td>730°</td>
<td></td>
</tr>
<tr>
<td>750°</td>
<td></td>
</tr>
</tbody>
</table>

These results are plotted in Graphs I and II.
Graph I. Specific Heat at Constant Pressure of KBr

- Cp
- cal. cal./g m. deg.

300° 400° 500° 600° Temperature (°C)
Graph II

Specific Heat at Constant Pressure of KI

$C_p$ (Cal. / gm·deg.)

0.08750
0.08800
0.08850
0.08900
0.08950

300° 400° 500° Temperature (°C)
SECTION VII. DISCUSSION OF RESULTS

An idea as to the reproducibility of the results for the enthalpy is given by the deviations from the mean of the mass of mercury readings given in Tables I, II, and III. The average deviations for all the readings is about 0.05%.

The apparatus was calibrated by O.E. Hauver by making measurements on Al₂O₃. The enthalpy and specific heat of this material have been carefully investigated by D.C. Ginnings and K.J. Corruccini of the National Bureau of Standards. Hauver calibrated the apparatus by adjusting the temperatures of his data so that his enthalpy figures agreed with those of Ginnings and Corruccini. These authors claim an accuracy for their results on the enthalpy of Al₂O₃ of 0.2%. They have taken account of a number of systematic errors which cause uncertainties in the results. Some of these errors are now listed.

The calibration factor is uncertain by an amount of about 0.02%. The capsule loses a fairly large quantity of heat in its drop from the furnace into the calorimeter. Since the heat lost by the empty falling capsule, and that lost when the capsule contained a sample is not the same at a given temperature an error is introduced, which will probably not exceed about 0.03%. Once having been oxidized, the capsule apparently did not change weight a great deal. This factor was therefore eliminated by weighing before each
set of runs. The changes in room temperature during the course of a run were small enough so that changes in the density of the mercury in the capillary line due to this cause introduced a very small error. Buoyancy corrections to the weights have already been taken account of. The effect of heat leak was accounted for in each run, by plotting a graph of heat leak before and after the run, and estimating the amount of mercury disappearing from this cause while a run was in progress. When the hot capsule is in place in the bottom of the well there is a certain conduction upwards. The amount of heat lost from the calorimeter in this way will be extremely small since the well is a poorly conducting material, and the top spacers are of brass, also poorly conducting. In addition the well is tempered its entire length by the ice of the inner jar, a distance of some seven inches. No correction was applied for this loss because it was so small and its amount not known. There will be a certain amount of heat loss up the well by convection and radiation. To reduce these effects two shields of platinum foil, of the same diameter as the capsule were mounted on a 2-inch platinum wire one-half inch apart, mounted between the top of the capsule and the Nichrome V suspension wire (see Figure 3). Experiments had shown that this effectively reduces the heat loss by convection to practically zero. The heat loss by radiation is small, and these shields reduce it still
Further. The Wenner potentiometer had been certified by the Bureau of Standards before use, and it was checked against its certified standard cell before each reading.

The calorimeter system has a certain elasticity, while for accurate measurements it should be quite rigid. If the mercury level in the line \(E'\), Figure 1, assumes different positions as mercury is drawn in this difference in head may change the readings. This effect was overcome by adjusting the mercury levels in the tube \(E'\) to approximately the same value before and after a run.

When the gate \(G\) (Figure 1) is open to allow the capsule to fall into the calorimeter in the course of a run some heat will be radiated from the furnace into the calorimeter. To make this the same for the empty and full capsule runs, the gate was kept open for the same length of time for all runs, about two seconds.

Due to the method by which the apparatus was calibrated, the uncertainties in the results for enthalpies will be equal to those of the Bureau of Standards data on \(\text{Al}_2\text{O}_3\) plus deviations from the mean of mercury readings of the present experiment. The factors which influence the accuracy of the measurements mentioned above are effectively the same for the runs using the \(\text{Al}_2\text{O}_3\) as for those with \(\text{KBr}\) and \(\text{KI}\). Thus the values of the enthalpies in the present experiments are presumed accurate to within 0.40%.

The uncertainty in the values of the specific heats will be
larger. Calculating the slopes of the two worst enthalpy curves found by using the two extreme temperature values indicates an uncertainty of about 0.8%. This figure refers to the average specific heat over this temperature range. The uncertainties of the specific heats at the upper and lower temperature values will be larger because of the difficulty in determining the slope of a curve near its end.

It was found that the samples, KBr and KI reacted chemically with the Nichrome V capsule when the former were heated above their melting points. There was no evidence of reaction below the melting points. All the data given in this report were gathered before the KBr and KI samples were heated above their melting points.

The results of these experiments yielding \( c_p \) cannot be compared directly with theory as indicated previously. However the general shape of the curves is similar to the behavior of many substances which have been measured previously\(^{11}\), and in particular to the results for NaCl of Roth and Bertram\(^{12}\) the only one of the alkali halides known to have been measured before, at high temperatures.

Magnus\(^{13}\) gives a value of the specific heat of KBr and 100° C of 0.1078 cal/mole/deg with an error of 2%. The present experiments yield a result of 0.1061 at this temperature.

As mentioned before there is no data available for KBr and KI on compressibilities at high temperatures, and therefore direct comparison with the Dulong and Petit values of...
specific heat at constant volume cannot be made. The process of extrapolating from room temperature has been shown to be very misleading in the case of NaCl by Hunter and Siegel.

In the case of KBr, the Dulong and Petit value for the specific heat at constant volume is 0.1002 cal/gm/deg. Thus the results of these experiments show that $c_p$ is greater than $c_v$ at 300°C by about 7%; at 700°C by about 11%. For KI the Dulong and Petit value is 0.0723 cal/gm/deg. Thus the measured value of $c_p$ is higher than this amount by 16% at 300°C; at 600°C by 19%. It is hoped in the near future to make measurements on the compressibilities of KI and KBr which when used with existing data on the coefficient of expansion can be used to compare the results of the present experiments with theory.
REFERENCES


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