THE THEORY OF

HIGH TEMPERATURE SPECIFIC HEAT DETERMINATION

AND

THE FORMULATION OF SPECIFIC HEAT EQUATIONS

FROM EXPERIMENTAL DATA

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INTRODUCTION

The development of metallurgical processes usually takes place in three rather orderly steps. First the basic idea is conceived, and a fairly rapid development follows. The second step, closely following the first, is the improvement of the mechanical devises used. This second step usually takes place over a fairly long period of time and runs into an inactive stage at the end. The first and last step in the development of a process is the careful investigation of the theory involved, with the purpose of refining the processes themselves.

At the present time we are approaching the end of the mechanical improvement stage and are beginning to turn to theoretical investigations. We are now searching for the possibilities and limitations of our processes under various sets of conditions. One of the easiest ways of arriving at these facts is through a study of thermodynamics.

Thermodynamic calculations are based largely upon the heat capacities of the substances under consideration. A search of the literature will reveal a deplorable lack of reliable specific heat data. It was this fact which caused us to attack the problem of specific heat determination. While we do not expect to accomplish much in the way of actual determinations, it is our hope to design and set up apparatus with which this data can be rapidly and accurately found.

DISCUSSION

At the beginning of this discussion it is necessary to define two terms - "specific heat" and "heat capacity". The specific heat of a substance may be defined as, the ratio of the heat necessary to raise the temperature of a unit weight of that substance one degree, to the heat necessary to raise the temperature of an equal weight of water one degree. Specific heat is a pure number with no units. The heat capacity of a substance is defined as the amount of heat necessary to raise the temperature of one unit to the substance one degree. The units of heat capacity are calories per gram or B.t.u. per pound. Since water is the reference material for specific heat and the units of heat are also referred to water, the values of specific heat and heat capacity are numerically equal. No real error is introduced when the terms "specific heat" and "heat capacity" are used interchangeably.

The problem of specific heat determination is, in theory, a very simple one. The heat

absorbed or evolved when a unit weight of the material changes in temperature one degree, is the heat capacity. In practice the problem is not so simple. The heat capacity usually varies slightly as the temperature rises so an equation must be evolved which will take this variation into account. Care must be taken to see that there is no loss or gain of heat during the determination, other than that absorbed or liberated by the sample; temperatures must be measured very accurately; all bodies in the setup must come to uniform temperatures, etc.

There are two methods of determining specific heat:

The drop method, or method of mixtures;

The direct method.

The second part of the problem is the formulation of specific heat equations from experimental data.

THE DROP METHOD

The drop method, or method of mixtures, of specific heat determination gets its name through the procedure followed. The sample whose specific heat is to be determined is heated in a furnace and dropped into a calorimeter. By measuring the temperature of the sample and the temperature change of the calorimeter, the heat liberated by the sample can be calculated.

The apparatus used falls naturally into three divisions:

the calorimeter;

temperature measuring devices;

the sample and its container.

THE CALORIMETER

A calorimeter is a device used for the purpose of measuring heat. In our work the heat measured is that liberated by the material whose specific heat is being determined. Any body into which the heat to be measured can be introduced and the consequent temperature change measured, will serve as a calorimeter. A bucket of water, a stirring device and a thermometer comprise a calorimeter which will give fairly good results. With such an apparatus, an accuracy of within five percent can be expected. It is when great accuracy is required that serious difficulties arise. The problems encountered increase much more rapidly than the precision.

The subject of calorimeter accuracy is best considered by discussing the possible sources of error separately. The following are the principal sources of error in calorimetry:

Conduction

Radiation

Evaporation and heat of wetting

Lags

Mechanical heat

Addition of material to calorimeter

CONDUCTION:

When attempting to improve the accuracy of the calorimeter heat losses due to conduction are probably the first factor considered. This heat loss is the result of a temperature difference between the calorimeter and the surrounding atmosphere (thermal head). The heat loss can be expressed by the equation $H = Kt$ in which H is the heat transferred, K is a constant known as the modulus of thermal leakage, and t is the thermal head. To reduce the conduction error, either of the factors K or t may be reduced. The heat transferred is also a function of time, but this can best be considered in a discussion of manipulation.

RADIATION:

While it is obvious that radiation occurs

when an object is at red heat, it is often overlooked that heat is radiated even at low temperatures. The best way to eliminate rediation errors is to surround the calorimeter with a highly polished jacket or case.

EVAPORATION AND HEAT OF WETTING:

At high temperatures or even at room temperature evaporation will cause large errors if not properly guarded against. The most successful method of suppressing evaporation is to completely surround the liquid in the calorimeter with a tight jacket. This works well to keep down evaporation but makes the calorimeter unsuited for the drop method of specific heat determination.

When a dried solid comes into contact with a liquid in which it is insoluble, the surface will become wetted. In the process of wetting a thin film of water is adsorbed to the surface with the evolution of heat.[1] The heat evolved is a function of the surface wet.

1. Industrial Chemical Calculations - Hougen and Watson, Page 285.

Normally the heat liberated, as a result of this phenomenon is small, because the surface of the sample container is small.

LAGS:

Heat lags or temperature gradients within the calorimeter are a treacherous source of error. A lag can exist without its ever being suspected, for instance, in a corner where stirring is not thorough; in some imperfection in a metal block, etc. The only method of locating lags is to test the temperature at several places in the calorimeter simultaneously. The method of combating lags is thorough stirring, in the case of a liquid calorimeter or using a material of high conductivity in an aneroid.

MECHANICAL HEAT:

The addition of heat due to work done within the calorimeter is not usually serious unless the experiment is carried out for a long time, say one hour. The heat produced by

stirring is much less than that which leaks in through the stirring rod. Heat generated by current passing through electrical temperature measuring devices is usually slight because the current is small. In any case the error is always positive and can be calculated or determined experimentally.

ADDITION OF MATERIAL TO CALORIMETER:

The addition or removal of any appreciable amount of material from the calorimeter can hardly be called an error, it is a blunder. However, it is well to mention that heating coils, cooling coils, stirring rods, covers, thermometers, etc., must not be added or removed after the water equivalent has been determined.

In the case of a liquid filled calorimeter care must be taken to avoid splashing.

TYPES OF CALORIMETERS

The more common accurate types of calorimeters are:

Adiabatic Calorimeter;

Vacuum walled Calorimeter;

Convection shield or dead air space Calorimeter;

Aneroid Calorimeter.

THE ADIABATIC CALORIMETER:

The point of distinction in the adiabatic calorimeter is that the inner vessel or calorimeter proper is completely surrounded by a bath of water or oil. The outer bath is kept at the same temperature as the inner vessel, either automatically by a thermostat or by adding heat as necessary as the inner temperature rises.

Since the outer temperature is almost the same as the inner there can be almost no heat loss due to conduction. In the equation $H = Kt$, t is very small, consequently H is small. The fact that the calorimeter is com-

pletely enclosed indicates that evaporation is at a minimum and splashing loss is eliminated.

The adiabatic calorimeter, while very accurate, is not suited to specific heat determinations. When an opening is made in the outer jacket so that the sample might be introduced, the advantage secured because of the outer bath is lost. Such a calorimeter is of necessity complicated and involves a great deal of labor in taking it apart and setting it up for each determination.

THE VACUUM WALLED CALORIMETER:

The use of a Dewar flask as the containing vessel for the calorimeter will reduce the heat loss to the atmosphere. The term "K" (modulus of thermal leakage) in the equation $H = Kt$ is made very small hence the heat loss is also very small. When using a thermos bottle a larger thermal head is allowable. Radiation is reduced to a minimum because the walls of the flask are always silvered so that they have a mirror like surface.

There are some disadvantages connected with the use of the vacuum jar. The container itself being made of glass is easily broken and therefore must be handled carefully. It is almost impossible to get an evacuated cover for the jar. The evaporation error is difficult to combat when a liquid is used.

CONVECTION SHIELD CALORIMETER:

If the central container of the calorimeter is surrounded by one or more thin metal shields it is known as a convection shield calorimeter. These shields reduce conduction losses by preventing the air in the calorimeter from circulating. This type of calorimeter usually reduces radiation as the shields can be polished. Because of the extra paraphernalia the instrument becomes bulky and difficult from which to get the sample after each determination.

THE ANEROID CALORIMETER:

The work "Aneroid" means fluidless. The aneroid calorimeter depends upon a block

of metal to absorb the heat liberated by the sample. There are two types of aneroids for different purposes - the one has a small mass compared to the sample, for use particularly for liquids, the other has a large mass in comparison to the sample for solids.

For specific heat determination, especially at high temperatures, the aneroid has several advantages over the fluid calorimeter. There are no evaporation errors and no splashing to put up with. In place of stirring, conduction is depended upon to equalize the temperature in the calorimeter. In the case of solid samples, the aneroid eliminates the danger of liquid being absorbed, with its consequent heat of wetting. The fact that the aneroid is composed only of metal makes it possible to run this calorimeter to a much higher temperature than that of liquids. There is no liquid to be measured for each determination with its consequent error.

The principal disadvantage of the aneroid is the error due to heat lags. There is a time

element involved in getting the temperature to equilibrium. If this time is too long, errors creep in. To combat this trouble the calorimeter is made of metal having a high conductivity such as copper or silver. To take care of small differences of temperature, an integrating thermometer is used, that is, the temperature read is the average from several points in the calorimeter.

TEMPERATURE MEASUREMENT

Temperature measurement is a factor which often limits the accuracy of specific heat determinations. This is especially true at high temperatures, where accurate measurements are difficult. Calorimeters can be insulated to prevent heat loss and what errors there are can either be calculated or eliminated by a careful calibration, but if temperatures cannot be measured precisely, the determinations will be failures.

There are three temperature measuring devices capable of the necessary accuracy - the mercury-in-glass thermometer, good for moderate temperatures; the electrical or resistance thermometer, good for either low or high temperatures; and the thermocouple for either low or high temperatures.

THE MERCURY-IN-GLASS THERMOMETER:

There are two classes of mercury-in-glass thermometers, the ordinary and the Beckman. The

ordinary single scale thermometer has a maximum precision of the order of .01 degrees C. For the finest work it is apparent that this is not sufficiently accurate. For a temperature change of from 10 to 20 degrees, an error of .01 degree is allowable but not for a change of 2 to 3 degrees.

The Beckman thermometer which has two scales can be read to .001 degree. An error of this magnitude is allowable even when the temperature change is only 2 degrees. One disadvantage of the Beckman is the difficulty in adjusting it and keeping it adjusted. A poor adjustment does no great harm if a temperature difference only is measured, as the amount of the maladjustment cancels out as the difference is calculated. A second disadvantage is the short range of the Beckman, a maximum of 5 degrees. A third disadvantage is the ease with which the thermometer can be broken. The fourth unfavorable quality of the Beckman thermometer is its ability to conduct heat to or from the calorimeter.

THE ELECTRICAL THERMOMETER:

While the resistance or electrical thermometer has been known for a long time, it has not been developed to the extent which its advantages seem to warrant. Consequently it is not standardized to the same point as the mercury-in-glass thermometer. Because of this lack of standardization, it is usually necessary for the experimenter to build the thermometer himself. A good axiom to observe when constructing an electrical thermometer is, "Make haste slowly". A lot of grief and trouble can be avoided by very carefully designing and building the instrument, paying particular attention to insulation and protection of fine windings from abrasion.

The principle upon which resistance thermometers are based is the change of resistance of metallic conductors with changing temperature. In its simplest form the thermometer[1] consists of a coil of wire connected

1. A complete discussion of copper resistance thermometer and the description of an interesting modification can be found in the Journal of Physical Chemistry, Vol. 34, Page 2860-2868.

with a constant source of current. The resistance change can be measured with a post office box or the RI drop can be measured with a potentiometer. Either method will give accurate results. The precision of the resistance thermometer is limited only by the delicacy of the Wheatstone bridge or potentiometer.

If the windings are insulated from solutions the resistance thermometer can be used in a liquid or an aneroid calorimeter. This type of thermometer has one special advantage - the windings can be placed in several units. With this type of construction the temperature read is an average from several points. In this way the effect of heat lags in an aneroid calorimeter can be minimized. If the thermometer is annealed to remove mechanical stresses due to winding, its calibration will remain constant indefinitely.

The platinum resistance thermometer can be used at both high and low temperatures. The copper thermometer is not suitable for use at temperatures much above 100° C. as the copper

windings will become oxidized. If either the platinum or the copper resistance thermometer becomes contaminated the calibration constants of the instrument will change. The reason platinum and copper are used for resistance thermometers is that these metals exhibit a smooth temperature - resistance curve.

THE THERMOCOUPLE:

For high temperature measurement the standard instrument is the thermocouple. The noble metal couple, Pt against Pt - Rh, is used up to 1700 degrees C. provided it is protected from smoke and soot. If the couple has been annealed for one hour at 1500 degrees C. before calibration, the calibration will not change if there is no contamination. Below 300 degrees C. the E. M. F. of the rare metal couple is so small that is is not reliable. For temperatures up to 300 degrees C. the copper-constantan couple is accurate as it produces a relatively large E. M. F. per degree. At temperatures much above 300 degrees C. the E. M. F. of the copper-constantan couple deviates rapidly from a straight line

function of temperature, so should not be used at the higher temperatures.

For precise low temperature work where a large E. M. F. per degree is desired, a multijunction couple is used. A multijunction couple is merely several couples in series. By putting a sufficient number of couples in series you can attain almost any precision you wish. The several junctions of the couple may be placed at various points in the body whose temperature is sought and in this way an average of the temperature is secured. The one objection to the thermocouple as a very precise instrument is the difficulty in securing a constant known cold junction temperature. From the difficulties encountered in getting a constant temperature in an ice bath, I doubt the reliability of thetemperature of the usual crushed ice, as the cold junction of the thermocouple. If the cold junction temperature should change .01 to .001 degrees the temperature indicated by the E. M. F. of the couple would be just that much in error.

THE SAMPLE

The care of the sample, whose specific heat is to be determined, resolves itself into three factors:

Protection;

Size;

Heating.

PROTECTION OF THE SAMPLE:

The sample must be protected from air while being heated and, unless an aneroid is used, from the fluid in the calorimeter. This protection is easily secured by sealing the sample in some suitable container. When choosing the material from whichto make the container, certain precautions must be taken. The container itself must resist oxidation at the temperature at which it is to be used. The material from which the container or bomb is made must not react with the sample at the maximum temperature to be attained. The bomb will sustain certain shocks and temperature

changes, so must have sufficient physical strength to withstand these stresses. If possible, a material having anomalies should be avoided.

The most common materials used for the bomb are platinum and gold or quartz. The precious metals, while otherwise satisfactory, are quite expensive. The disadvantages of quartz are its specific heat anomalie at 573° C. and its great weight as compared to the weight of sample which can be put into a tube of the silica.

SIZE OF THE SAMPLE:

The size of the sample used must be governed by the water equivalent of the calorimeter and the heat conductivity of the sample material. The amount of the sample and bomb should be chosen so that the heat liberated by it during a determination will cause the desired temperature change in the calorimeter. If too small an amount of sample plus bomb be used, a small error in temperature measurement in the calorimeter, results in a large percentage error in the final result. On the other hand, too large a sample causes a large temperature change

in the calorimeter with its resulting errors due to conduction, radiation, etc.

The bomb should not have a very thick cross section, otherwise a very serious temperature gradient may exist within the sample. This is especially true of a material whose heat conductivity is low. To find the magnitude of gradients in the sample, a thermocouple may be placed in the center and another at the edge of the sample. If the difference of temperature between the center and edge of the sample is 1° C., the resulting deviation from the average is .5° C. The error caused by this temperature difference at 500° C. would be .5 divided by 500 or .1%. If several tests reveal a constant temperature gradient in the sample, it should be corrected for.

HEATING THE SAMPLE:

Probably the most common error and the one most difficult to combat in specific heat determinations, is due to large temperature gradients in the heating chamber of the furnace used. In a small or poorly insulated furnace a gradient of from 10° to 15° C. over

a length of 4" is not uncommon. Assuming a 10° gradient at 500°, it is obvious that an error of about 1% will result. To maintain a precision of one per mille it is necessary to keep the gradient at 500° less than 1°.

To get the most uniform sample temperature, the heating chamber should be only a small part of a long heating tube. If in an 18" furnace tube, the heating chamber is the center 6" with the 6" ends of the tube stopped with a series of insulating plugs, a temperature gradient of less than 1° at 500° in the heating chamber should be attainable. To further promote temperature uniformity a sleeve of some good heat conducting metal, such as silver, can be placed within the furnace tube. The metal sleeve will conduct the heat from "hot spots" to the cooler portions of the tube.

THE DIRECT METHOD

The direct method of specific heat determination is based upon the measurement of the heat absorbed by the sample while it is being heated. Heretofore this method has been employed chiefly for very low temperature work but has not been developed for determinations at high temperatures. At the present time interest is developing in the direct method so that it is probable that in the future this method will be given more attention. Undoubtedly if suitable apparatus is designed this method is capable of greater speed and accuracy than the drop method.

The apparatus for the direct method is usually designed so that the sample is suspended in as near a vacuum as possible. The vacuum is to reduce conduction of heat as much as possible. The sample can be heated by a small resistance coil in or around the unknown. The temperature of the sample is measured by either a single or multijunction thermocouple.

A SUGGESTED DESIGN:

A fairly simple apparatus for measuring specific heat directly could be easily made of four concentric spheres which could be evacuated. The center sphere to contain the sample, heating coil, and thermocouple, would have to be made of some material such as platinum so that it would resist corrosion and high temperatures. Since platinum can be highly polished the central chamber would reduce the radiation. The second, and each succeeding sphere, should be made of material which can be polished. A material like nickel would do very well for the outer spheres. If four spheres in all were used this should reduce radiation and conduction sufficiently.

The construction of this apparatus would require very careful work because the spheres must be so made that they could be evacuated. So that the sample could be replaced, the spheres must be in halves and fixed so that they could be tightly sealed together.

Some complication would arise when provisions were made to bring necessary thermocouple and electrical leads from the central sphere to instruments on the outside. While this apparatus appears to be quite complicated, it should not be too difficult a task for an ingenious machinist.

The calibration of apparatus of this sort is very important. Only by a very careful calibration under conditions of use can the constants of the instrument be determined. An equation which would give the heat capacity of the device, minus the sample, very accurately over the temperature range in which it would be used, would be necessary.

Granted that the apparatus crudely described above could be built and calibrated, it would be possible to take measurements at successive steps of say 10^{o} C. This would allow the experimenter to determine rapidly the specific heat at short intervals and thus locate anomalies easily. When the drop method

is used, a large number of determinations is necessary to locate the temperature at which an anomaly occurs.

MANIPULATION

In many cases large errors creep into otherwise precise work as the result of a personal factor of the experimenter. About the only way to determine if such errors exist and locate them if they do, is to repeat a determination several times, varying the procedure one part at a time. By so doing it is possible to locate that part of the manipulation which is at fault. It often happens that by varying the procedure slightly, errors previously unsuspected are brought to light.

CALIBRATION:

The manipulations involved in calibration are probably the most important in the entire procedure. Through a careful calibration practically all of the systematic and constant errors can be eliminated. When, for example, a resistance thermometer to be used in an aneroid calorimeter is being calibrated, it should be in exactly the same position in the calorimeter as

it will be when in use. Thus if there is a lag between the calorimeter and the thermometer windings, the thermometer calibration will have this taken into account. The same holds true for the determination of the water equivalent of the calorimeter. If the procedure for the determination of the water equivalent is similar to that followed when the calorimeter is in use, errors like radiation, conduction and heat lags will be taken into account automatically. Particular attention should be given the matter of timing in calibrations. The same amount of time should be allowed for equilibrium conditions, as will be allowed when a determination on an unknown is being run. Since errors like radiation and conduction are a function of time, any difference between the times of calibration and the running of an unknown will introduce these errors into the final result.

TIMING:

The time which should be allowed during each step of a determination cannot be arrived

at by any theoretical calculation, because each instrument used will have constants slightly different from other like instruments. The best way to arrive at the timing to be followed is to observe the apparatus under operating conditions. The time necessary for equilibrium to be established, provided it is not excessive, is that which should be allowed during a determination. If the time necessary to attain equilibrium is too long, it would be better to change the design of the apparatus so that this delay can be eliminated. It would be well to state here that while simplicity of design is desirable, it is better to have apparatus of complicated construction but simplicity of operation than that of simplicity of construction but complicated of operation. Having arrived at the timing to be used, it should be followed closely in each determination.

ACCIDENTAL ERRORS:

Any experimenter should repeat each determination at least once to guard against

some blunder in reaching or recording data. If the two determinations are in close agreement with each other, their average may be used. To run a large number of determinations to preclude the possibility of an accidental error is often a waste of time, because the same man is apt to make the same mistake over and over again. Even granting that no constant error is being made, the repetitions of a reading over four or five times do not greatly increase its precision. From a study of the laws of probability it is found that the precision of the several quantities increases directly as the square root of the number of observations[1]. Thus if the mean of three readings is taken, the addition of a fourth only increases its precisim by:

$$\frac{\sqrt{4} - \sqrt{3}}{\sqrt{3}} = \frac{2 - 1.732}{1.732} = \text{about } 15\%$$

If this is further carried on to five readings, the increase of the precision would be:

1. Practical Least Squares. - Leland

$$\frac{\sqrt{5} - \sqrt{4}}{\sqrt{4}} = \frac{2.24 - 2}{2} = 12\%$$

It would be much better to have a second experimenter go through the determination. If the second person checks the results of the first, this should be sufficient assurance that no accidental error has been made.

THE CALCULATION OF SPECIFIC HEAT EQUATIONS

The data on specific heat, as obtained by the experimenter, usually consists of a series of values of the total heat liberated from a unit weight of material as it cools from an initial temperature - t° C. - to some reference point, usually 0 or 20° C. In this form the information is almost useless as it consists only of random values. To be of practical value the data must be worked into an equation from which the specific heat at any temperature can be found. The usual form of the equation expresses the specific heat as a linear function of powers of t (temperature).

The method here employed to derive an equation from the data is known as the "Method of Least Squares". The Method of Least Squares, while more laborious than other methods, yields an equation closer to the data than any other. A detailed description of the method of forming the equation can be found in - "Practical Least Squares" by Leland.

DATA

"h" is the average heat capacity in calories per gram per degree from 0^{o} to t^{o} C.

"t" is temperature in degrees C.

	h	t	
(1)	.1850	100	(I)
(2)	.1868	100	(II)
(3)	.2006	200	(I)
(4)	.2068	250	(I)
(5)	.2168	300	(II)
(6)	.2229	400	(I)
(7)	.2379	500	(II)
(8)	.2439	550	(II)

(I) Data from Weitzel
Zeitchrift Fur Anorganische Und
Allgemeine Chemie. Vol. 116, P. 71 - 1929

(II) Data from W. P. White
American Journal of Science
Series 4, Vol. 47, P. 1 - 1919.

Form of the equation[1]

$$h = a + b\,t + c\,t^{-2}$$

Substituting the values of h and t in the equation and rearranging the terms:

1. $a + 100b + .0001c - .1850 = 0$
2. $a + 100b + .0001c - .1868 = 0$
3. $a + 200b + .000025c - .2006 = 0$
4. $a + 250b + .000016c - .2068 = 0$
5. $a + 300b + .0000111c - .2168 = 0$
6. $a + 400b + .00000625c - .2229 = 0$
7. $a + 500b + .00000400c - .2379 = 0$
8. $a + 550b + .00000331c - .2439 = 0$

Letting $100{,}000\,c' = c$ and $.01b' = b$

1. $a + 1.0b' + 10.000c' - .1850 = 0$
2. $a + 1.0b' + 10.000c' - .1868 = 0$
3. $a + 2.0b' + 2.500c' - .2006 = 0$
4. $a + 2.5b' + 1.600c' - .2068 = 0$
5. $a + 3.0b' + 1.111c' - .2168 = 0$
6. $a + 4.0b' + 0.625c' - .2229 = 0$
7. $a + 5.0b' + 0.400c' - .2379 = 0$
8. $a + 5.5b' + 0.331c' - .2439 = 0$

(1) Recommended by Chas. G. Maier and K. K. Kelly Journal of the American Chemical Society, Vol. 54, P. 3243.

FORMING THE NORMAL EQUATIONS

a and a a	b' and a b'	c' and a c'	l and a l	s and a s	b' b'	b' c'	b' l	b' s	c' c'	c' l	c' s
1.0	1.0	10.000	- 0.1850	11.8150	1.000	10.000	- 0.1850	11.8150	100.000	- 1.8500	118.150
1.0	1.0	10.000	- 0.1868	11.8132	1.000	10.000	- 0.1868	11.8132	100.000	- 1.8680	118.132
1.0	2.0	2.500	- 0.2006	5.2994	4.000	5.000	- 0.4012	10.5988	6.250	- 0.5015	13.248
1.0	2.5	1.600	- 0.2068	4.8932	6.250	4.000	- 0.5170	12.2330	2.560	- 0.3309	7.829
1.0	3.0	1.111	- 0.2168	4.8942	9.000	3.333	- 0.6504	14.6826	1.234	- 0.2409	5.437
1.0	4.0	0.625	- 0.2229	5.4021	16.000	2.500	- 0.8916	21.6084	0.391	- 0.1393	3.376
1.0	5.0	0.400	- 0.2379	6.1621	25.000	2.000	- 1.1895	30.8105	0.160	- 0.0952	2.465
1.0	5.5	0.331	- 0.2439	6.5871	30.250	1.820	- 1.3414	36.2290	0.110	- 0.0807	2.180
8.0	24.0	26.567	- 1.7007	56.8663	92.500	38.653	- 5.3629	149.7905	210.705	- 5.1065	270.817

NORMAL EQUATIONS

(I) $8\,a' + 24.0\,b' + 26.567\,c' - 1.7007 = 0$

(2) $92.5\,b' + 38.653\,c' - 5.3629 = 0$

(3) $210.705\,c' - 5.1065 = 0$

SOLUTION OF NORMAL EQUATIONS

	a	b'	c'	l	s	
I	+ 8.000	+ 24.000	+ 26.567	- 1.7007	+ 56.8663	
2		+ 92.500	+ 38.653	- 5.3629	+ 149.7901	
3			+ 210.705	- 5.1065	+ 270.8185	
2		+ 92.500	+ 38.653	- 5.3629	+ 149.7901	
4		- 72.000	-79.701	+ 5.1021	-170.5989	I x $\frac{-24}{8}$ = I x (-3)
II		+ 20.500	-41.048	- 0.2608	- 21.8088	2 + 4
3			+ 210.705	- 5.1065	+ 270.8183	
5			-93.250	+ 5.6480	-191.8530	I x $\frac{-26.567}{8}$ = I x (-3.32
6			-82.178	- 0.5221	- 43.6612	II x $\frac{+41.048}{20.500}$ = II x + 2.002
III			+ 35.277	+ 0.0194	+ 35.2941	3 + 5 + 6

$$c' = \frac{-.0194}{35.277} = -0.00055$$

$$b' = \frac{.2608 - .02258}{20.5} = \frac{.23822}{20.5} = .0116$$

$$a = \frac{-24\,b' - 26.567\,c' \quad 1.7007}{8}$$

$$= \frac{1.4369}{8} = .1796$$

Since $c = 100{,}000\,c'$

$$c = 55.0$$

and $b = .01b'$

$$b = .000116 \text{ or } 1.16 \times 10^{-4}$$

Substituting the values of a, b and c, the equation reads:

$$h = .1796 + 1.16 \times 10^{-4}t - 55\ t^{-2}$$

By solving the equation for "h" at various temperatures, the following table results:

Temp. in °C. t	Ave. Sp. Ht. from 0-t °C. (observed) h	Instant. Sp. Ht. at t °C. (Calculated) h	Diff. between obs. and calc. h	Percent Deviation
0		.1796		
100	.1859	.1857	— .0002	.1%
200	.2006	.2014	+ .0008	.4%
250	.2068	.2077	+ .0009	.4%
300	.2168	.2138	— .0030	1.4%
400	.2229	.2257	+ .0028	1.3%
500	.2379	.2374	— .0005	.2%
550	.2439	.2432	— .0007	.3%

Considering that the data from which the equation was derived, came from two independent experimenters, the equation fits the experimental work closely.

Writing the equation:

$$h = .1796 + 1.16 \times 10^{-4} t - 55 t^{-2}$$

To form the equation which will yield instantaneous specific heats which are used in thermodynamic calculations:

$$C_p = \frac{dH}{dt}$$

$$H = ht = .1796 t + 1.16 \times 10^{-4} t^2 - 55 t^{-1}$$

Differentiating:

$$C_p = .1796 + 2 \times 1.16 \times 10^{-4} t - (-1) 55 t^{-2}$$

$$C_p = .1796 + 2.32 \times 10^{-4} t + 55 t^{-2}$$

Computing the values of C_p for various temperatures t:

Temp. in °C. = t	Ave.Sp.Ht. (from data) h	Instant.Sp.Ht. (Calculated) C_p
0	.1796	.1796
100	.1859	.2080
200	.2006	.2274
250	.2068	.2385
300	.2168	.2498
400	.2229	.2727
500	.2379	.2958
550	.2439	.3074

CONCLUSION

From a consideration of the preceeding theoretical discussion, we decided that our best chance of success lay in the use of the drop method rather than the direct method for specific heat determination. It was also decided that the aneroid calorimeter and differential resistance thermometer, in a Dewar flask, would give better results, for high temperature work, than any other combination.

After an aneroid calorimeter and resistance thermometer hed been built, they were found to be too crude to yield results of the desired accuracy. In light of the experience gained by working with the first apparatus, it was decided that we should design and have built a second calorimeter and resistance thermometer, and continue the work. The new apparatus is now being constructed. The results of this second attempt will appear as an addendum to this paper.