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MEASUREMENT OF SPECIFIC HEATS BY
A PULSE METHOD

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MEASUREMENT OF SPECIFIC HEATS

BY A PULSE METHOD*

by

Richard C. Strittmater and Gordon C. Danielson

ABSTRACT

A pulse heating method for measuring the specific heat of metals at all temperatures has been developed. The apparatus will deliver a current pulse of sufficient magnitude to heat a fine wire sample to its melting temperature in a short time, for example 0.1 second. Under these conditions, the energy losses from the wire are negligibly small compared with the energy input. By recording simultaneously with a dual beam cathode ray oscilloscope the current through and the potential across a sample, one can determine at any instant the power input and the resistance of the wire. From the resistance of the wire and the results of a preliminary experiment on the resistance-temperature relationship the temperature can be found. By a single heating pulse a plot of the temperature as a function of time can be made. Since the power input and the mass of the sample are known, the specific heat, at any temperature within the range of the test, can be calculated. Preliminary results are given for platinum and nickel over the temperature range 25°C to 500°C.

*This report is based on an M.S. thesis by Richard C. Strittmater submitted August 1, 1955, to Iowa State College, Ames, Iowa. This work was done under Contract with the Atomic Energy Commission.

INTRODUCTION

This investigation was undertaken in order to develop and evaluate a method, which involved less time than calorimetric methods for determining the specific heats of metals at all temperatures.

When a calorimetric method of measuring specific heat is used, laborious precautions and calculations of subtle heat transfers must be carried out in order to correct for heat losses. A method was desired in which heat losses could be neglected without affecting the accuracy of the results by more than a small fraction of one per cent. The heat losses from a fine wire heated by a current of high density can be neglected, and this accuracy maintained. This is shown in the appendix.

Other advantages of heating by this method are: the amount of heat supplied can be measured with great precision; the heat supplied is generated uniformly throughout the interior of the body under investigation; more exact information is given regarding the law of variation of specific heat with temperature than is given by methods in which only the mean specific heat over a wide temperature range is measured; the sample may be used to measure its own temperature when the resistance is measured and the resistance-temperature relationship is known.

Previous investigations using the same approach to the problem were reviewed. Kurrelmeyer, Mais, and Green (1) in 1941 suggested the use of heating rates, such that the losses could be neglected. In their experiment the wire was enclosed in an evacuated tube and placed in one arm of a Wheatstone bridge. The wire was then brought to the temperature at which the specific heat was to be determined. With the bridge balanced a charged condenser was connected across the battery terminals of the bridge. The specific heat was evaluated from the resulting ballistic galvanometer deflection. In this method the specific heat was determined at the ambient temperature of the furnace. The ambient temperature had to be varied to determine the specific heat as a function of temperature. Baxter (2) in 1944 described a method in which longer heating pulses were delivered to the wire. In this method the current through and the voltage across the wire were recorded simultaneously. This information combined with knowledge of the resistance-temperature relationship gave the specific heat. By this method the specific heat was determined for all temperatures of the wire during the pulse. Khotkovitch and Bagrov (3) made a subsequent investigation, following the suggestion of Baxter, Nathan (4) described a method which was essentially the same as the method given by Baxter, except that a thermocouple junction was spot welded to the center of the sample to record the temperature

A method similar to that of Baxter was adopted for this investigation because it was believed that the desired precision could be obtained from measurements made with readily available instruments. There was also the advantage of securing extensive data in a short time.

THEORY

When a system gains energy from an electric current and also loses energy to the cooler surroundings, the net heat energy effective in producing a temperature change is just the difference of the gain and loss. The specific heat of the system is given by the equation,

$$c = \lim_{\Delta \theta \rightarrow 0} \frac{\Delta Q_1 - \Delta Q_2}{m \Delta \theta},$$

where c is the specific heat, ΔQ_1 is the energy gain of the system in time Δt , ΔQ_2 is the energy loss of the system in time Δt , m is the mass of the system, and $\Delta \theta$ is the temperature change of the system in time Δt . In the experiment to be described the measurements are carried out at constant pressure. Therefore, the specific heat will be written c_p to denote the condition under which the temperature change occurs.

A central segment of a fine wire, heated by an electric current of high density, makes an excellent sample on which to carry out specific heat determinations. The analysis given in the appendix shows that, for such a sample, the heat losses can be neglected and the temperature of the sample is sufficiently uniform so that the specific heat can be calculated from the measurements at any time during the heating pulse. Therefore, the specific heat can be written,

$$c_p = \frac{dQ_1}{m d\theta}.$$

When the energy is supplied by Joule heating, and the current through and the voltage across a sample are measured simultaneously, the energy input, dQ_1 , in an interval of time, dt , is,

$$\frac{e i dt}{J},$$

where J is the appropriate conversion factor between electrical and calorimetric units. The current through the sample is i and the voltage across the sample is e . Therefore, from the two preceding equations,

$$c_p = \frac{e i}{J m \frac{d\theta}{dt}}.$$

It is a requirement of thermodynamics that the system be, at all times, infinitesimally near a state of thermodynamic equilibrium. How well the sample of this investigation conforms to the above requirement, especially during a transition, can be determined from observation of any change in the specific heat curve when the heating rate is varied. The investigation of the variation of the specific heat as a function of heating rate, in the neighborhood of a transition temperature, is a possible method for determining mean transition times.

PROCEDURE

A. Sample Preparation

The first metal investigated was thermometric purity platinum. The sample was in the form of a five mil diameter wire about seven inches long. Each end of the wire was clamped and copper brazed inside a hole drilled along the axis of a 1/8 inch diameter nickel rod. The nickel rods served as both current conductors and supports for the sample. The nickel rods also supported the nickel enclosure when the sample was suspended in the cylindrical furnace to determine the resistance-temperature curve. The sample and nickel enclosure, suspended in the furnace, are shown in Figure 1.

Brown and Sharpe gauge #40 platinum wire was used as voltage probes. The probes were placed at right angles to the axis of the sample and each was resistance welded approximately 5/8 inch from the position at which the sample was brazed to the nickel rod. The voltage probes and the thermocouple wire were brought out of the furnace through two souble bore alundum tubes.

The sample, when hanging within the nickel enclosure, extended approximately three inches along the axis and 3/4 inch along the radius of the furnace. It, therefore, became necessary to secure a uniform temperature zone of this size to determine the resistance-temperature curve. The radial gradient near the center of the furnace was very small and was neglected. The axial temperature distribution was investigated by scanning the furnace with a chromel-alumel thermocouple. The power inputs to the main windings and to the guard windings were each adjusted until the temperature variation across the center five inches was less than 4° C for various temperatures between room temperature and 1000°C. The results of a previous experiment indicated that this variation was reduced to a maximum of less than 1°C when the sample was within the nickel enclosure. This uniformity was considered adequate for the determination of the resistance-temperature relationship.

A chromel-alumel thermocouple, of Brown and Sharpe gauge #18 wire, was used to measure temperatures at the center of the nickel enclosure. Corrections to be applied to the standard tables were supplied by Leeds and Northrup. The thermocouple, with corrections applied, measured the temperature to within 0.3°C. The above error limitation is based on the assumption that the wire had not been handled erratically, mechanically or thermally, since calibration. Inside the nickel enclosure the thermocouple was insulated with H.I. Thompson quartz refrasil insulation. The thermocouple junction was placed approximately at the center of the sample loop.

Figure 1. Furnace with Sample and Nickel Enclosure in Position.

The top of the enclosure was attached to the nickel tubing with four 1 - 72 stainless steel screws. The furnace was sealed permanently from the bottom. A plug sealed the top after the sample had been lowered into the furnace.

B. Data Collection

Resistance values for the resistance-temperature curve were obtained from the quotient, voltage divided by current. The voltage across the sample was measured directly on a Rubicon type B potentiometer. The current through the sample was obtained from a measurement of the voltage across a one ohm Leeds and Northrup standard resistor in series with the sample. These readings were taken when the furnace was very near thermal equilibrium. In order to avoid heating the sample above the ambient temperature indicated by the thermocouple, the current through the sample was kept small (two milliamperes).

The thermocouple electromotive force was read before and after each resistance determination. The wire correction was applied to the thermocouple electromotive force and the corrected value converted to temperature by means of a Leeds and Northrup conversion table. After sufficient data had been collected to construct the resistance-temperature curve, shown in Figure 2, the sample was removed from the nickel enclosure and placed in a vacuum system.

After the pressure had been reduced to 5×10^{-4} mm. of Hg, by means of a D.P.I., three stage, fractionating, oil diffusion pump, the sample was pulsed for 55 milliseconds. A block diagram of the apparatus is given in Figure 3. A leak at the glass to metal seal of the vacuum connector prevented lower pressures from being reached. It was thought, at the time, that the pressure was low enough to neglect conduction losses through the gas surrounding the wire. However, a careful study of this problem was made later and it was found that appreciable conduction might occur at these pressures.

The details of the sequence of events during the pulsing cycle can best be understood by reference to the circuit diagram shown in Figure 4. The circuit controlled the pulsing of the sample and also directed the calibration, standard resistor, and sample voltages to the dual beam Dumont oscilloscope (type 322A). Twelve volt lead storage batteries were used as the sample power supply and a Western Electric mercury contact relay (K4 in Figure 4) was used to switch this supply.

The order of signals received by the oscilloscope can be observed by reference to the tracing, shown in Figure 5, of a photograph of the scope face during the pulsing cycle. The sequence of events reads from the left and down. The time, in milliseconds, is given below the tracing. The high

Figure 2. Resistance of Platinum Sample as a Function of Temperature

Figure 3. Block Diagram of Specific Heat Apparatus

Figure 4.

PULSING AND SWITCHING CIRCUIT

Figure 5. Tracing of Three Consecutive Sections of Film Record
Obtained during the Pulsing of the Platinum Sample.

The solid center line is a reference line, with respect to which all distance measurements were made. The traces of the A and B beams were blanked in millisecond intervals. The zero, in time, was taken at the first blanking marker after the initiation of the pulse. The first pair of traces displayed are the high calibration voltages. The traces displayed on the last half of the initial section are the low calibration voltages. The direction of increasing voltage is toward the bottom of the sections. The traces appearing closest to the reference line indicate the voltages used to calibrate the A beam. These were 9.342 V. and 8.614 V. The traces appearing farthest from the reference line indicate the voltages used to calibrate the B beam. These were 0.7581 V. and 0.3999V. The A beam trace, at the initiation of the pulse, starts near the top of the middle section and moves downward as the voltage across the sample increases with time. The B beam trace starts near the bottom of the middle section and moves upward as the voltage across a 0.1 ohm standard resistor, in series with the sample, decreases with time.

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voltage calibrators are displayed first. When the pulsing cycle has been initiated by throwing switch S1 (Figure 4) the relay, K1 closes and displays the low voltage calibrators. The DPDT switch was kept in manual position at all times. The closing of K1 completes the circuit through and closes K2. This activates K3 which switches the pulse current and voltage signals to the oscilloscope. The closing of K3 energizes K4 which closes the sample circuit initiating the pulse. The pulse is ended by the dying out of the transient current in K2. The calibration signals are again displayed after the pulse (not shown in Figure 5) in order to detect any possible drift in the oscilloscope amplifier or positioning circuits during the pulse.

The voltages used to calibrate beam B, 0.7581 volts and 0.3999 volts, are displayed toward the edges of the film strip. The voltages used to calibrate beam A were 9.342 volts and 8.614 volts.

The photograph was taken with a Leica f/1.9 lens on 35 mm. Linograph Panchromatic film. The film was driven vertically past the scope face at about 20 ft./sec. by a General Radio Corporation oscillograph recorder (type 651AE). The signals were directed to the vertical deflection plates of the cathode ray tube which had been rotated 90° to give horizontal deflections. The tube was rotated in order to take advantage of the greater sensitivity of the vertical axis amplifiers.

The following considerations were involved in order to determine the setting of the pulse duration. First it was necessary to decide the temperature range over which the specific heat was desired. From the resistance-temperature curve, the resistance, R_i , for any temperature, θ_i , was known. This resistance added to the lead resistance, resistance of the standard resistor, and the internal resistance of the sample power supply gave the total resistance of the circuit at temperature, θ_i . The sample current, I_i , at temperature, θ_i , was given by the ratio of the electromotive force of the sample power supply to the total resistance. The power input, P_i , to the sample, at temperature, θ_i , was then $R_i I_i^2$. From this, and knowing approximate values for the mass and the specific heat, c_{pi} , at temperature, θ_i , the time interval, Δt , necessary to heat the sample through a small range of temperature, about the temperature, θ_i , was calculated from the equation,

$$\Delta t = \frac{m c_{pi} (\Delta \theta)_i}{J P_i}$$

The total pulse duration is, therefore,

$$t = \sum_0^t \Delta t = \sum_{\theta_1}^{\theta_2} \frac{m c_{pi} (\Delta \theta)_i}{J P_i}$$

where θ_1 and θ_2 are the initial and final temperatures. If the pulsing is not done near the melting point temperature this is not a very critical calculation, and it is a sufficiently good approximation to replace c_{p1} by an average specific heat, c_{pav} . Also, if a small temperature range is covered the power can be considered constant and

$$t = \frac{c_{pav} m (\theta_2 - \theta_1)}{P J}$$

This value of the pulse duration was then set on the pulse length adjustment.

The sample currents when the sample temperature was θ_1 and θ_2 were calculated. From this the initial voltage, V_1 , and the final voltage, V_2 , directed to the B beam were calculated, since the B beam was connected across a 0.1 ohm standard resistor. The initial and final voltages were set on the high and low voltage calibrators and, by means of switch S2 of Figure 4, these voltages were observed on the face of the cathode ray tube. The B beam sensitivity and the horizontal positioning were adjusted until both signals were focused near opposite edges of the film. The same procedure was followed for the A beam where the initial and final voltages across the sample were used to make the adjustments.

The linear magnification of the system was such that the center two inches of the face of the cathode ray tube focused on the one inch of useable film width when a tube 8 9/16 inches long joined the oscilloscope to the recorder.

The procedure, after all preliminary adjustments mentioned before had been made, was to turn on the 1000 cycle/sec. Z axis modulating signal to provide a time reference. The film drive clutch was then engaged and, after one second to allow the film to come up to speed, the calibration and pulsing cycle was initiated by throwing switch S1 of Figure 4. One second after throwing switch S1, the film drive clutch was disengaged.

The developing process was done in a Morse (type G-3) developing tank. D - 19 developer was used for 20 minutes, stop bath (SB - 5) for 30 seconds and fixer for 15 minutes.

The calibration voltages were measured as soon as possible after completion of the run in order to eliminate errors due to a change in the terminal electromotive force of the mercury cells. These measurements were made on a type B Rubicon potentiometer. After sufficient data had been collected on the sample, the wire was cut under a microscope at the center of the voltage probe, and the mass determined by means of a microbalance. The mass of the platinum wire was 33.447 ± 0.002 milligrams.

C. Data Analysis

All measurements from the film strip were made on a Gaertner traveling microscope. All distances were measured with respect to a fixed reference line formed by the image of an illuminated slit fixed to the face of the cathode ray tube. The reason this reference line was used, rather than one edge of the film, was to eliminate errors due to relative motion of the oscilloscope face and the recorder. Measurements were made every one to ten milliseconds depending on the detail wanted in the curve of specific heat versus temperature. The conversion of distance to voltage was made on the assumption that the voltage varied linearly with distance on the film.

A curve of temperature versus time was drawn from the above measurements. In order to construct this curve the resistance value was taken from the film at a certain time, t_1 , and this was converted to temperature by the resistance-temperature curve. This curve is shown in Figure 6. The slope of this curve at time, t_1 , and the power input at time, t_1 , together with the mass of the sample, determined the specific heat of the sample at the temperature corresponding to the time t_1 . The specific heat was given by the equation,

$$c_p = \frac{e \cdot i}{J \cdot m \frac{d\theta}{dt}}.$$

The calculations are given in Table 1.

The slopes were determined graphically by means of a secant method.

The specific heat was calculated at the temperatures corresponding to the time of the millisecond markers. However, this was done purely for convenience and the method is not limited to such temperatures.

The data were collected on the nickel sample in the same way as the platinum data and are shown in Figures 7, 8, and 9, and Table 2. In Figure 8 the tracing shows only portions of the photograph of the oscilloscope face during the pulsing. This figure shows the calibration voltages, a record of the beginning of the pulse (0 - 28 milliseconds) and a record as the sample passes through the Curie temperature (90 - 118 milliseconds).

The mass of the nickel sample was 28.664 ± 0.002 milligrams.

Figure 6. Temperature of Platinum Sample as a Function of Time.

Table 1. Specific Heat Data for the Platinum Sample

t	e	i	ei	$\frac{e}{i}$	θ	$\frac{d\theta}{dt}$ $\frac{^{\circ}\text{C}}{^{\circ}\text{C}}$	c_p $\frac{\text{Cal}}{\text{Gm } ^{\circ}\text{C}}$
(Milliseconds)	(Volts)	(Amperes)	(Watts)	(Ohms)	($^{\circ}\text{C}$)	Second	
3	8.08	6.51	52.6	1.24	65	12,200	.0308
4	8.13	6.31	51.3	1.29	77	11,700	.0313
8	8.31	5.77	47.9	1.44	120	9,970	.0343
12	8.46	5.34	45.2	1.58	157	9,110	.0354
20	8.67	4.72	40.9	1.84	227	8,280	.0353
24	8.75	4.48	39.2	1.95	259	7,790	.0359
32	8.88	4.10	36.4	2.17	317	6,810	.0382
44	9.01	3.69	33.2	2.44	396	6,160	.0385
51	9.07	3.51	31.8	2.58	437	5,900	.0385
54	9.10	3.44	31.3	2.65	454	5,900	.0379

Figure 7. Resistance of Nickel Sample as a Function of Temperature.

Figure 8. Tracing of Three Sections of Film Record Obtained during the Pulsing of the Nickel Sample.

The solid center line is a reference line, with respect to which, all distance measurements were made. The traces of the A and B beams were blanked in millisecond intervals. The zero, in time, was taken at the first blanking marker after the initiation of the pulse. The first pair of traces displayed are the high calibration voltages. The traces displayed on the last half of the initial section are the low calibration voltages. The direction of increasing voltage is toward the bottom of the sections. The traces appearing closest to the reference line indicate the voltages used to calibrate the A beam. These were 9.132 V. and 8.288 V. The traces appearing farthest from the reference line indicate the voltages used to calibrate the B beam. These were 0.9736 V. and 0.3586 V. The A beam trace, at the initiation of the pulse, starts near the top of the middle section and moves downward as the voltage across the sample increases with time. The B beam trace starts near the bottom of the middle section and moves upward as the voltage across a 0.1 ohm standard resistor, in series with the sample, decreases with time. The end section shows the record of these voltages as the sample passes through the Curie temperature.

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Figure 9. Temperature of Nickel Sample as a Function of Time

Table 2. Specific Heat Data for the Nickel Sample

t	e	i	ei	$\frac{e}{i}$	θ	$\frac{d\theta}{dt}$	c_p
(Milliseconds)	(Volts)	(Amperes)	(Watts)	(Ohms)	(°C)	$\frac{^{\circ}\text{C}}{\text{Second}}$	$\frac{\text{Cal}}{\text{Gm } ^{\circ}\text{C}}$
6	8.18	8.16	66.7	1.00	94	5,160	.108
18	8.53	6.89	58.7	1.24	143	3,240	.124
30	8.74	6.05	52.9	1.44	190	3,240	.136
42	8.90	5.39	48.0	1.65	228	2,900	.138
60	9.10	4.64	42.2	1.96	277	2,580	.136
78	9.25	4.07	37.6	2.27	321	2,110	.148
90	9.33	3.78	35.3	2.47	343	1,880	.156
96	9.36	3.64	34.1	2.57	354	1,790	.159
98	9.37	3.60	33.7	2.60	358	1,760	.160
100	9.38	3.58	33.6	2.62	362	1,580	.177
102	9.38	3.56	33.4	2.63	366	1,480	.188
104	9.39	3.54	33.2	2.65	367	1,530	.181
106	9.39	3.52	33.1	2.67	371	2,160	.128
110	9.40	3.47	32.6	2.71	382	2,350	.116
112	9.40	3.44	32.3	2.73	387	2,220	.121
114	9.41	3.43	32.3	2.74	393	2,190	.123
120	9.42	3.39	31.9	2.78	401	2,190	.121
144	9.46	3.22	30.5	2.94	452	2,050	.124
162	9.48	3.11	29.5	3.05	488	1,740	.141
186	9.51	3.02	28.7	3.15	524	1,710	.140

RESULTS

The first metal investigated was thermometric purity platinum. Platinum was used because its availability in very pure form allowed the experimental results to be compared with the results obtained calorimetrically by other investigators. The sample was first pulsed in air and the results compared favorably with calorimetric determinations near room temperature. At higher temperatures the temperature gradient increased in the vicinity of the wire. The conduction through the surrounding gas became appreciable and the specific heat appeared too large when heat losses were neglected. The results at 450°C were 20 per cent higher than results obtained calorimetrically. These data are not presented.

The same sample was again pulsed with the pressure reduced to 5×10^{-4} mm. of Hg. The results were again within experimental error near room temperature and the results at higher temperatures were significantly improved. The value at 450°C was now only ten per cent higher than the calorimetric determinations (5). The specific heat as a function of temperature obtained by the pulse method is shown in Figure 10.

A qualitative spectroscopic analysis of the nickel sample showed the presence of 0.01 per cent to one per cent of manganese, cobalt, iron, and copper. The results for the nickel sample are shown in Figure 11. The results for nickel also showed agreement with calorimetric determinations at low temperatures and values too high at elevated temperatures. The specific heat curve, for nickel, obtained by the pulse method has the same general shape as the curve obtained calorimetrically by C. Sykes and H. Wilkinson (6). The values obtained under this investigation, however, were about five per cent too high.

The Curie temperature, taken from the specific heat curve was 366°C. This agreement, with Curie point determinations taken from specific heat data obtained calorimetrically, is not bad; since the second derivative of the temperature-time curve is higher in this region and the graphical measurement of the slope is therefore subject to greater error.

DISCUSSION

The most serious errors occurring in this experiment were those involved in the data collected during the pulsing of the sample. The mass and the resistance-temperature relationship could be determined very precisely. Errors made in the determination of mass could be attributed to errors in the balance or to errors in cutting the sample at the voltage probes. The mass of the platinum sample was given by the analytical group as 33.447 ± 0.002 milligrams. Hence the balance error was less than 0.01 per cent. Since three mil voltage probes were used across a sample approximately five inches long the possible error in cutting the sample was 0.003 inch or 0.06 per cent.

Figure 10. Specific Heat of Platinum as a Function of Temperature

Figure 11. Specific Heat of Nickel as a Function of Temperature

The temperatures were plotted to three or four significant figures and the resistance to four significant figures when the resistance-temperature curves were constructed. Therefore, errors made in converting resistance to temperature were probably small compared with the error in measuring the resistance during the pulse.

The errors in current and voltage can be estimated by placing an upper limit on all possible sources of error involved in the measurement of these quantities. Possible sources of error in the measurement of voltage are:

- (a) Error introduced by the optical system.
- (b) Error due to non-uniform film shrinkage during development.
- (c) Error due to non-linear voltage-deflection characteristics of the cathode ray tube.
- (d) Error in the measurement of calibrating voltage.
- (e) Error in the traveling microscope measurements.
- (f) Error due to drift in the amplifier and the positioning circuit during the pulse.

The relative probable error due to the combined effect of non-uniform film shrinkage and short term amplifier and positioning circuit drift was estimated, from measurements on the calibration voltages, to be less than 0.5 per cent.

The calibrating voltages were measured on a type B Rubicon potentiometer to five significant figures and these errors were considered negligible.

The non-linearity of deflection with voltage was not checked, but it is not expected to vary from a linear relation by more than 0.3 per cent when only the center $1 \frac{3}{4}$ inches of the oscilloscope face was used.

The relative probable error in the traveling microscope measurements, due to the uncertainty in defining the maximum density of the traces, was estimated, by comparing measurements made by different observers, to be less than 0.3 per cent.

If errors introduced by the optical system are assumed to be negligible, the relative probable error in the voltage measurement from all sources was less than 1.1 per cent.

Errors in the 0.1 ohm standard resistor can be neglected. Therefore the above estimated error also applied to the measurement of sample current.

The error in the time derivative of the temperature term contained errors arising from the following:

- (a) Errors in measuring the resistance.
- (b) Errors in making the conversion of resistance to temperature by the resistance-temperature curve.
- (c) Errors in taking the slope graphically.
- (d) Errors in the frequency standard.

The relative probable error in the General Radio Corporation tuning fork frequency standard is given as 0.2 per cent.

The relative probable error in taking the slope, by the secant method, is estimated to be not greater than 0.2 per cent. The temperature variation with time was assumed to be smooth and a large number of points were plotted. Hence, it was possible to make the error in the slope, due to random errors in the first two factors, negligibly small.

The relative probable error in the specific heat from all the above errors is approximately 2.7 per cent.

It is believed that this method is capable of giving results within two per cent of the true values, if some small refinements are made in the design of the apparatus and in the analysis of data.

The large deviations from calorimetric data at the higher temperatures can be attributed largely to heat losses. The analysis, given in the appendix, on conduction through the surrounding gas shows that this term could have been relatively large when the wire temperature was increasing at a rapid rate.

Although the pulse heating method was developed primarily for work on metallic conductors, with average or higher temperature coefficients of resistance, it has limited application for non-metals. T.E. Pochapsky (7) has pulsed a platinum wire, coated with silver bromide, and, from the combined effect, determined the specific heat of the bromide.

The specific heat curve for nickel was obtained by the pulse method, without difficulty, through the phase transition at the Curie temperature. This indicated that a major part of the disordering phenomenon at the Curie temperature, which was associated with the magnetic contribution to the specific heat, occurred so rapidly that a lag in the phenomenon could not be detected at the heating rates used.

It has been suggested by C. Sykes and H. Wilkinson (8) that the shape of the specific heat versus temperature curve is very sensitive to the presence of impurities. For pure nickel, free from strain, they suggest that the curve should drop very steeply to a minimum just above the Curie temperature, since the coordination of electron spin, even for small groups of atoms, should vanish completely at the Curie temperature. The curve obtained in this investigation seemed to drop faster, just above the Curie temperature, than the curves reported by other investigators. This may indicate that the pulse method is superior to the calorimetric methods in the determination of specific heats at such phase transitions.

RECOMMENDATIONS

This investigation was only a preliminary attempt in the development of a method to measure the specific heat of metals by a pulse method. The design and construction of a furnace-vacuum system, in which all measurements could be conducted, would eliminate the necessity of moving the sample from the furnace to the vacuum system (as was done in this investigation). The metals investigated had very low oxidation rates and it was, therefore, possible to take data for the resistance-temperature curves with the sample in air. However, future samples may require high vacuum conditions at all times. With a furnace-vacuum system the ambient temperature of the sample could be brought to any desired value before the pulse is initiated. The losses are smaller when the sample is pulsed over a smaller temperature range. Also when the sample is pulsed through small temperature intervals, the difference in initial and final current and voltage values is reduced. This allows the use of greater sensitivity on the oscilloscope amplifiers. It also improves the precision of measurement of currents and voltages.

The problem of improvement in the focusing of the cathode rays should be investigated, since this may seriously limit the ultimate precision which can be obtained by this method.

A drum camera, using wide film, would improve the precision of distance measurements made by the traveling microscope.

It is concluded from the results of the problem on heat flow through the surrounding gas, given in the appendix, that pressures be maintained less than 10^{-3} mm. of Hg if heat losses are to be maintained less than a small fraction of one per cent.

The energy loss by conduction through the voltage probes should be investigated. It may be necessary to use probes of still smaller diameter.

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