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THE HEAT CAPACITY OF IRON CARBIDE

by

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A Thesis Submitted to the Graduate Faculty
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Approved:

Signature was redacted for privacy.
In charge of Major Work

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Head of Major Department

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INTRODUCTION

The presence of iron carbide in steel has caused it to be the object of many investigations. Its formation and decomposition have been studied in various gaseous mixtures and under widely different conditions. Because of the disagreement of various investigators concerning the stability of iron carbide it is desirable to have an exact knowledge of the free energy change attending the formation of the compound from its elements as this will give some additional information concerning the stability from a thermodynamic viewpoint. If the free energy of the compound is less than that of its elements, it would be stable, but if greater we should expect it to be unstable or metastable.

The free energy, F, of a substance is defined by the equation,

$$F = H - T S,$$

where H is heat content, T is absolute temperature, and S is entropy. For a reaction at constant temperature the increase in free energy, ΔF, will be:

$$\Delta F = \Delta H - T\Delta S.$$

When a compound is formed from its elements, $-\Delta H$ is called the heat of formation and may be found by subtracting the heat of combustion of the compound from the sum of the heats of combustion of the elements in the compound.

Δ S may be found by subtracting the sum of the entropies of the elements from that of the compound. To obtain S for each substance we make use of the third law of thermodynamics, which states,[9] "Every substance has a finite positive entropy, but at absolute zero the entropy of a substance may become zero and does so become in the case of pure crystalline substances." If an infinitesimal amount of heat, dq, is added at constant pressure at any temperature, T, the increase in entropy is:

$$dS = \frac{dq}{T} = \frac{C_p dT}{T},$$

where C_p is the heat capacity at constant pressure.

The entropy at any temperature is, therefore,

$$S = S - S_0 = \int_0^T \frac{C_p}{T} dT,$$

since $S_0 = 0$, by the third law of thermodynamics.

The heat of formation of iron carbide and the entropy of iron and of carbon have been determined. With a knowledge of the heat capacity of iron carbide one could determine its entropy and calculate the free energy change attending its formation from the elements of which it is composed.

Since there is a possibility of some difference between the properties of iron carbide in the free state and as it exists in steel, the present investigation is concerned with the heat capacity of the carbide in steel samples, as such data would be of more practical significance.

HISTORICAL

The Heat of Formation of Iron Carbide

The heat of formation of iron carbide has received considerable attention. In a recent article Naeser$_{11}$ refers to fourteen different sets of determinations with values ranging from − 27500 to +8940 calories. By repeating some former work and by use of a new method he obtains results which indicate that some of the discrepancies in the literature may be ascribed to the difference in the state of the carbon used or formed. Calorimetric data were obtained using graphitic carbon, while in some earlier work carbon was produced in an amorphous state. Naeser suggests a possible range of from +8000 to −4000 cal., the value depending on whether the carbon involved is amorphous or partially or wholly graphitic. Graphitic carbon gives the lower value.

Yap and Liu$_{20}$ and Schwartz$_{18}$ consider the work of Brodie, Jennings and Hayes$_{3}$ as the most reliable. Their value of -13580 cal., which was obtained by the combustion of Fe_3C in an oxygen bomb at 25°C, agrees well with the calorimetric determination of Ruff and Gersten$_{16}$. It is also quite consistent with the results of Maxwell and Hayes$_{10}$ obtained by measurements on the composition of CO-CO_2 mixtures in equilibrium with Fe_3C and with the similar work of Schenck$_{17}$ who used hydrogen-methane mixtures as the gaseous phase.

Yap and Liu have recalculated the results of Brodie, Jennings and Hayes, using more recent data on the heats of formation of Fe_3O_4 and Fe_2O_3 and have obtained a value of -12300 cal. In subsequent calculations this value will be used, bearing in mind, however, the existence of conflicting data.

Heat Capacity and Entropy of Iron and of Carbon

The existing data on the heat capacity of iron agree quite well. As Austin[1] has pointed out, the values of Eucken and Werth[4] seem to be the most consistent among themselves and fall between those of Gunther[6] on one side and those of Rodebush and Mikalek[15] and of Griffith and Griffith[5] on the other side.

Using the heat capacity data of Eucken and Werth, Austin[2] has calculated the entropy of iron at 25°C to be 6.60 units.

The entropy of carbon is given by Lewis and Randall[9] as 1.3 and by International Critical Tables[7] as 1.39. The value 1.39 will be used here.

Heat Capacity and Entropy of Iron Carbide

The mean specific heat of iron carbide between 0°C and 650°C was determined by Oberhoffer and Meuthen[13] by using steel samples of different carbon content and extrapolating to pure iron carbide(6.67% C).

Using a water calorimeter, Levin and Schottky[8] found that the mean specific heat between 17°C and 100°C varied directly as the carbon concentration. The same was true at other temperatures. The specific heat seemed to be the same for a slowly cooled sample as for one which had been heated to 800°C and quenched. From their data they were able to calculate the heat capacity from 0° to 680°C.

Umino[19] has made similar measurements using a large number of samples of different carbon concentrations and has calculated the specific heat of iron carbide from 150°C to 850°C. He says that "The specific heat-carbon concentration curve must be linear" for annealed steels below 700°C.

Up to a year ago no data could be found on the heat capacity of iron carbide below 0°C. Recently, however, Naeser[12] has made measurements on the specific heat between -195°C and 750°C. His work differs from the present investigation in that he used pure iron carbide rather than steel samples and in that he used a water calorimeter instead of the method of electrical heating. Samples were heated (or cooled) to various temperatures and then put into a water calorimeter of known heat content and the change in temperature observed by a Beckman thermometer. From the values thus obtained he calculated the heat capacity at various temperatures. Naeser did not make any calculation of entropy.

By an indirect method based on equilibrium measurements at temperatures of 700°C and above, Yap and Liu$_{20}$ have calculated the entropy of iron carbide at 25°C to be 31.8 units. They give the value of ΔF at this temperature as 9300 cal. per mole of Fe_3C formed.

EXPERIMENTAL

Preparation of Materials

The steel samples were prepared by melting pure iron and carbon in magnesia crucibles. C. p. magnesium oxide was sintered at about 1800°C in a carbon crucible in an induction furnace. The sintered magnesia was then ground to about 100 mesh, moistened with just enough distilled water to make it stick together and made into a crucible by packing in a carbon crucible. A piece of one inch glass tubing, which was closed at one end, was held in the center of the carbon crucible to give the right inside diameter. The crucible was dried slowly at 100°C and heated to 1800°C in a larger carbon crucible. The small carbon crucible containing the one made of magnesia just fitted inside the larger carbon container.

After cooling, the magnesia crucible was filled with the required amount of iron and carbon. The iron used was Armco iron. The carbon was some in electrode form which had been tested spectroscopically and found to contain only insignificant traces of impurities.

The crucible with its contents was placed in the furnace and heated again. After the iron had melted it was stirred once. It was kept molten for at least five minutes longer and then cooled slowly in the furnace.

The slugs thus produced were polished at both ends and examined microscopically. No free carbon or inocclusions could be detected. The carbon seemed to be present as pearlite and massive cementite.

The slugs were turned down to three-quarters of an inch in diameter and two and five-sixteenths of an inch in length, leaving at the center of one end a small additional piece of metal through which a hole was bored for suspending the sample. For reference purposes, an iron sample of the same dimensions was made from three-quarter inch Armco iron rod. Each sample was wound with 40 ohms of no. 34 constantan wire and lacquered with a Bakelite lacquer to give thermal contact between the heating coil and the sample. The lacquer was baked for several hours at 100°C. After being used in heat capacity measurements, the steel slugs were made into turnings, sampled, and analyzed. The weight, carbon analyses, etc. for the samples are given in table 1. The last column gives the weight of iron which would have about the same heat capacity as the windings and lacquer.

Table 1

Sample number	Percent carbon	Weight of sample	Weight of lacquer	Iron equivalent of lacquer, etc.
0	trace	131.715	.297	1.077
1	1.43	126.007	.242	0.905
2	1.15	125.508	.339	1.212
3	1.55	129.512	.343	1.224

APPARATUS

The calorimeter was the same in principle as that used by a number of previous investigators.[4, 5, 6, 14] The outside vessel was made entirely of Pyrex glass. The lower part, A, containing the sample was 1½ inches in diameter and 7½ inches long. When a sample was to be admitted or changed the vessel was cracked apart about an inch below the constriction, B. After the sample was properly suspended and all connections made the glass was sealed back together again.

The sample, C, was suspended by a silk thread from the copper wires, E, which also served as leads for conducting the current to the sample. The wires, E, were brazed to short tungsten wires which were sealed in the glass at F. The lower ends of these wires, E, were soldered to small copper wires which were in turn soldered to the heating coil around the sample.

The thermocouple was made of no. 36 copper and no. 34 constantan wire. The wires passed through capillary tubes G and G' where an air-tight seal was made with Picene wax. One junction was soldered to the sample at D. The other was kept in ice in a Dewar flask during most runs. In a few cases it was kept in a bath which surrounded the vessel, A, in which was the sample being heated.

The electromotive force produced by the thermocouple was measured by a Leads and Northrup student potentiometer

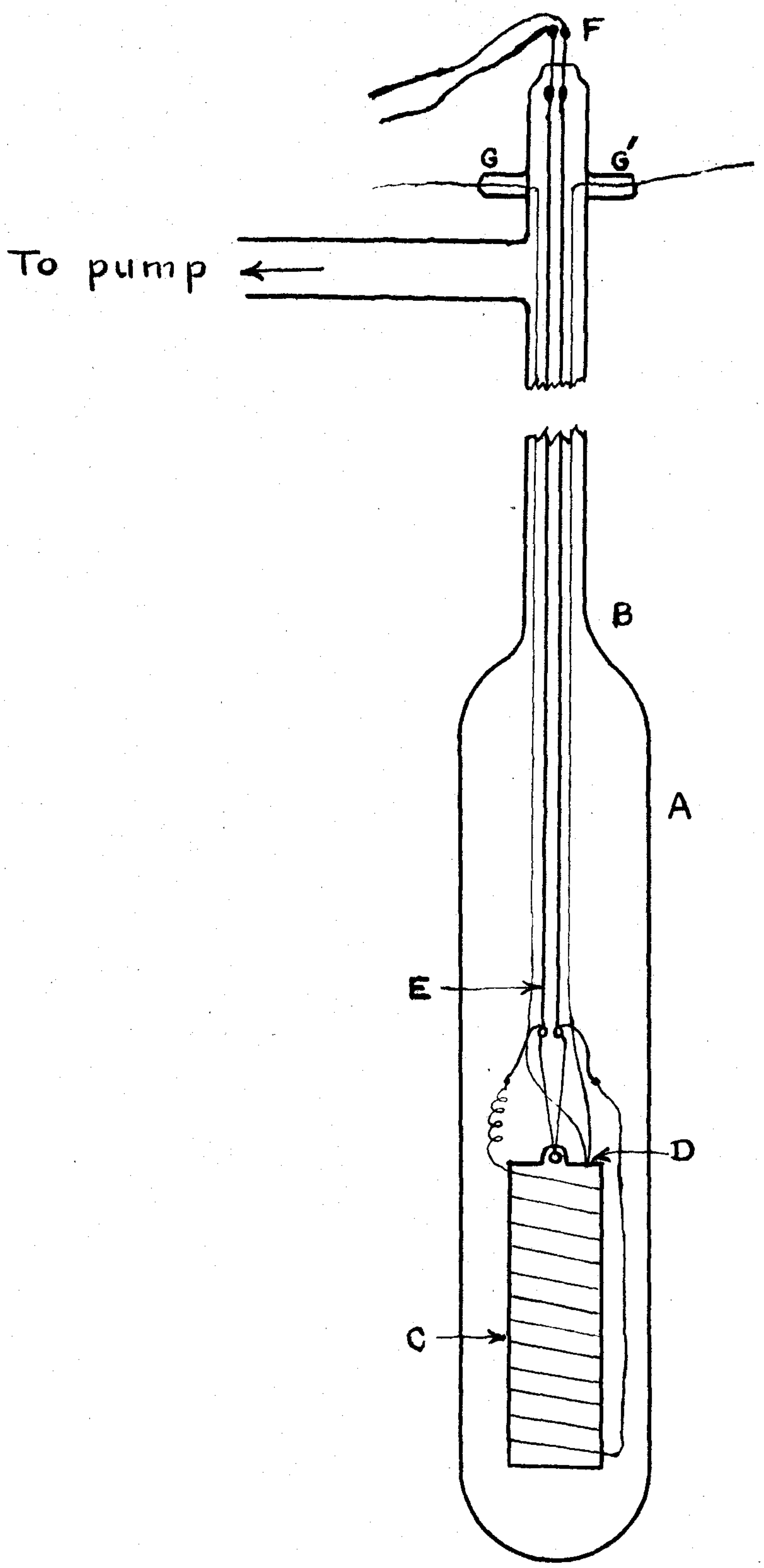


FIG. I.

which could be read to the nearest microvolt.

The thermometer which was used in some runs could be read to a hundredth of a degree. It was found to be correct at 0°C and 100°C and was therefore assumed to be correct for the temperatures at which it was used.

The calorimeter was evacuated by means of a mercury vapor pump in series with a "Cenco Megavac" mechanical pump.

A 6 volt 120 ampere-hour lead storage battery served as a source of electrical energy. The current was measured by means of a milliameter which could be read with an accuracy of one or two tenths of milliampere in the range used. The current used was ordinarily between 145 and 160 milliamperes.

During most runs the calorimeter was surrounded by a constant temperature bath. Liquid oxygen, solid carbon dioxide, and ice were used. In the runs made at room temperatures and above, the calorimeter was surrounded by a brass vessel filled with water and wound with resistance wire. An electrical stirrer kept the temperature of the water uniform and by means of a rheostat one could control the current passing through the heating coil around the brass vessel and thus keep the temperature of the water constant or change it at any desired rate.

Methods of Procedure

The milliammeter was calibrated by measuring the potential drop across a standard 10 ohm resistance in series with the milliammeter. The corrections to be applied are given by figure 2.

The thermocouple was calibrated by the usual method. The standard temperatures used were the melting point of ice, the boiling point of water, the sublimation temperature of solid carbon dioxide, and the boiling point of liquid oxygen. Figure 3 shows on a small scale the calibration curve used.

The resistance of the constantan heating coil, although not greatly affected by temperature, did nevertheless vary appreciably. The resistance was determined at a number of temperatures and the values plotted as shown on figure 4.

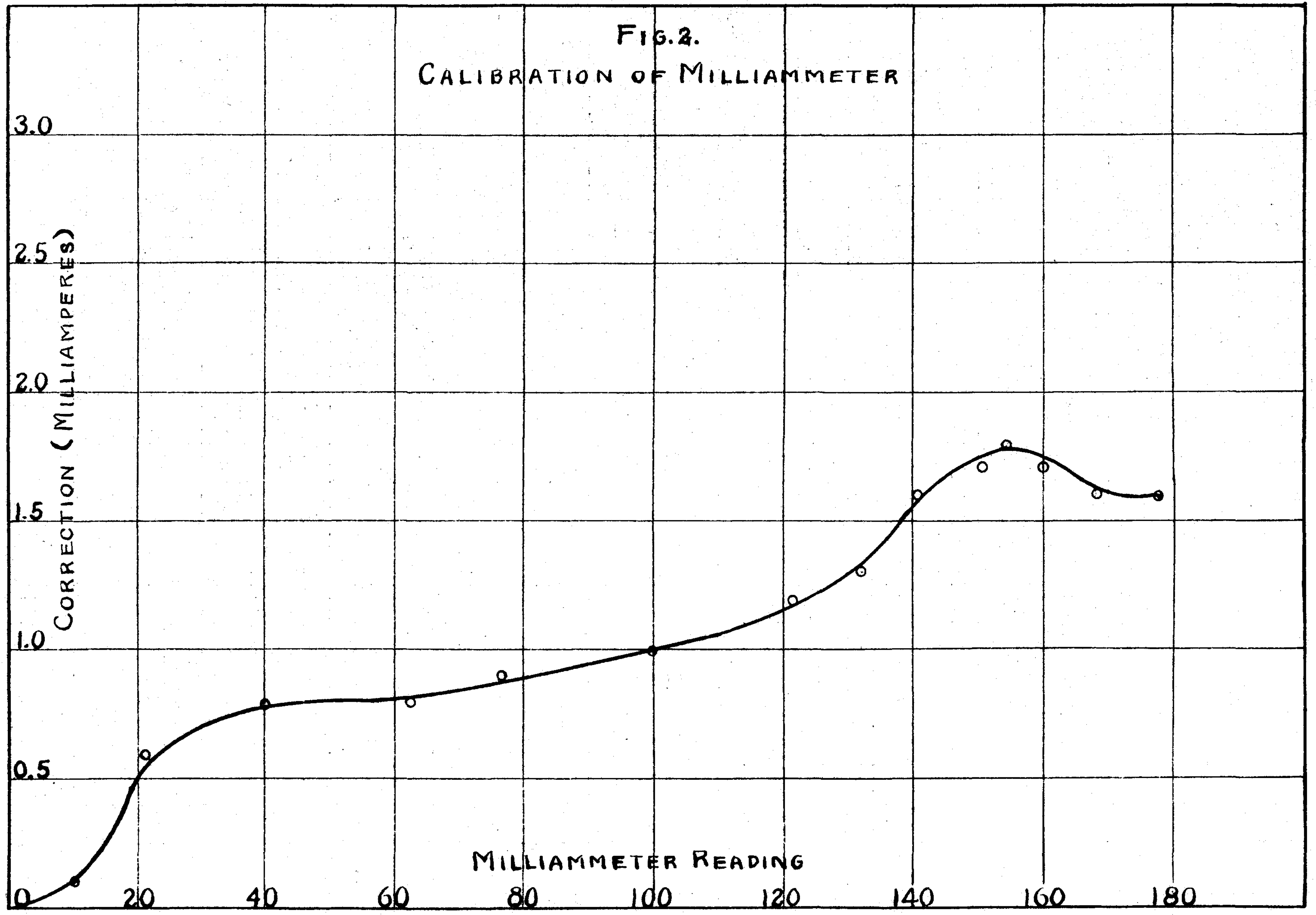
The data for calculating heat capacity were obtained by two methods.

1. Adiabatic method

At room temperatures and above, the calorimeter was surrounded by the brass vessel containing water. One junction of the thermocouple was on the sample and the other in the water. The leads were connected directly to a Leeds and Northrup, type P galvanometer. Whenever the temperature of the bath differed from that of the sample by more than a hundredth of a degree, the galvanometer would be deflected

FIG. 2.

CALIBRATION OF MILLIAMMETER



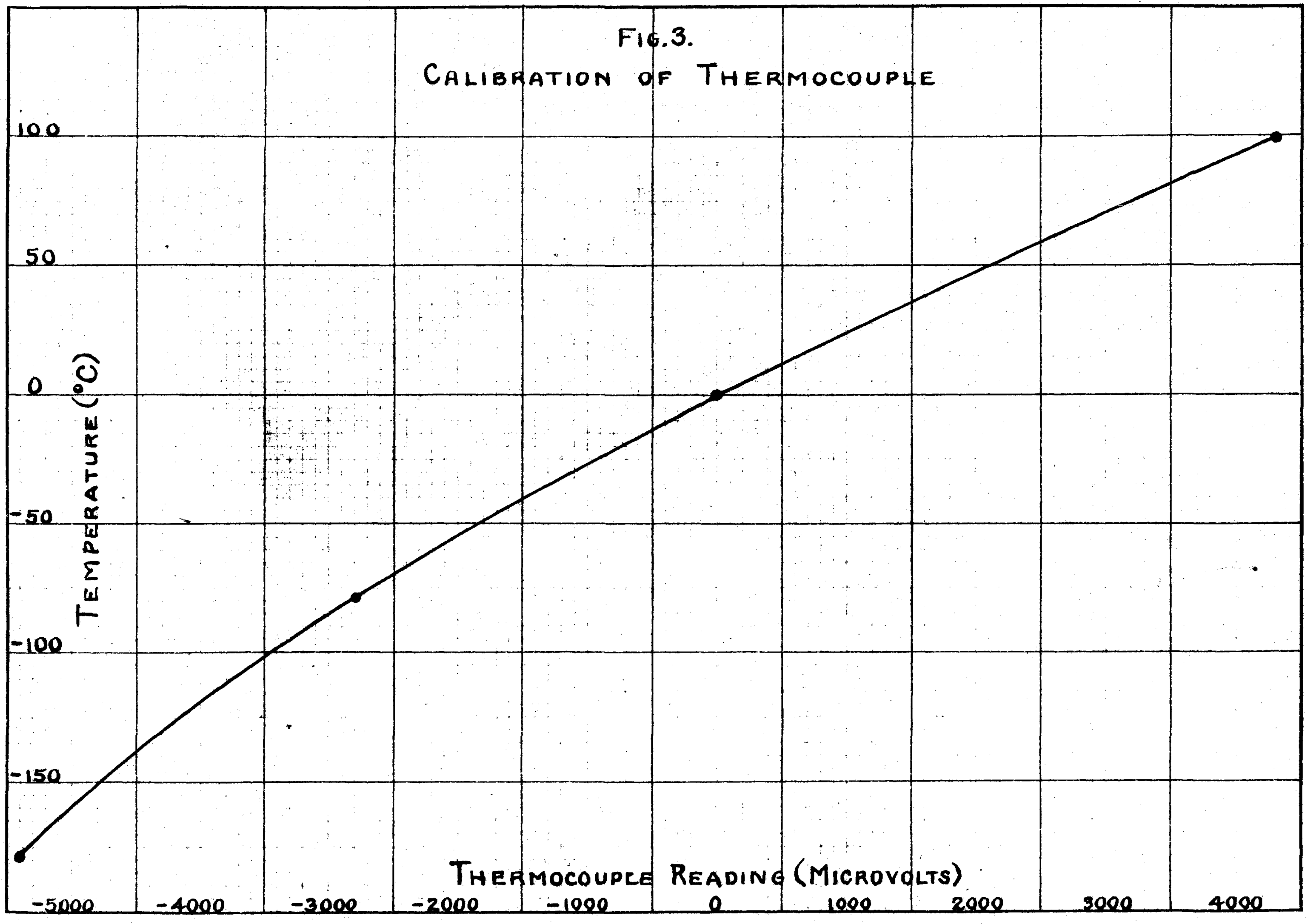
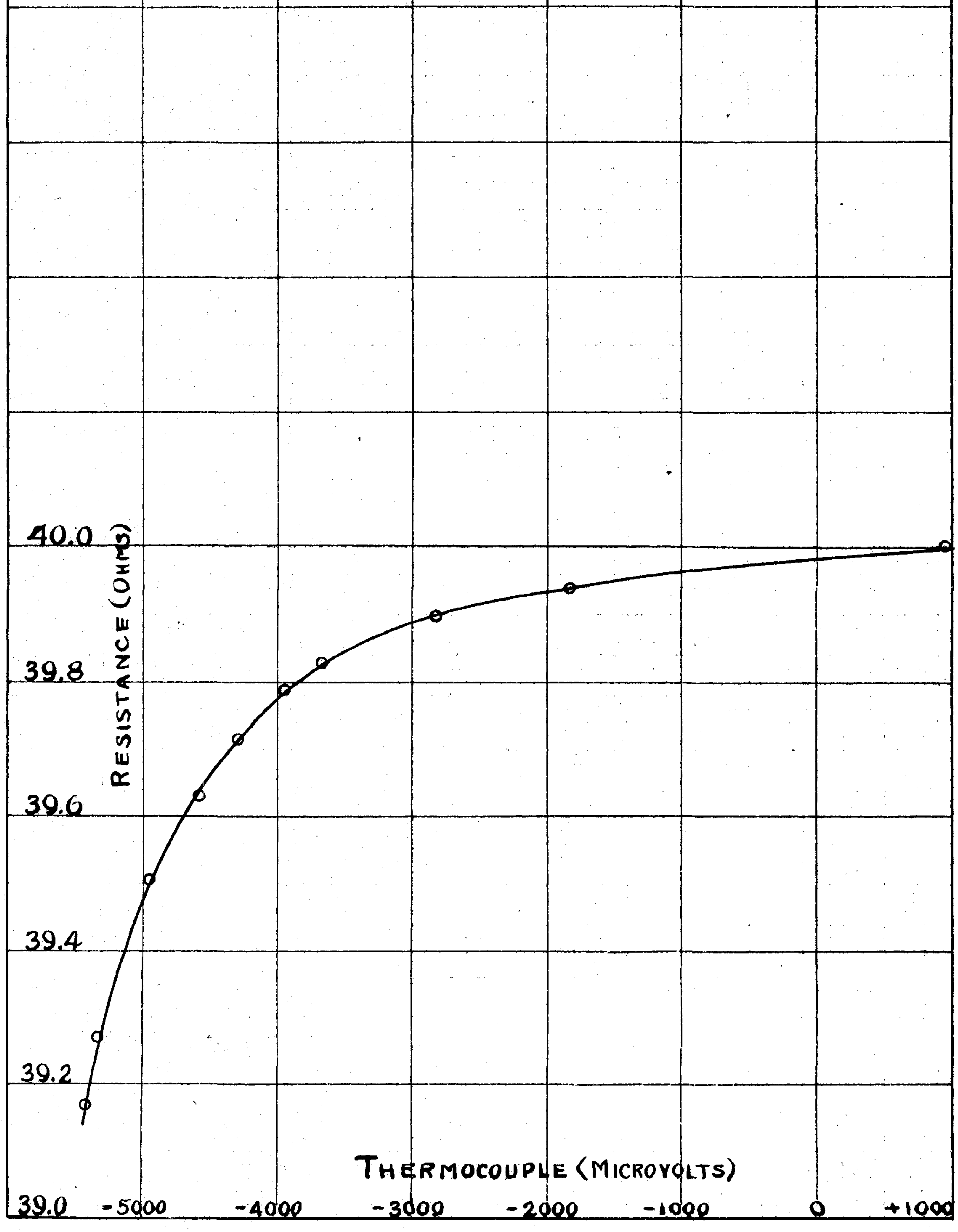


FIG. 3.

CALIBRATION OF THERMOCOUPLE

Fig. 4.

Calibration of Heating Coil



from its zero point. A thermometer in the outside bath was used to give the temperature of the sample as well as that of the bath.

The brass vessel was filled with cold water. When the steel slug was cooled to the same temperature as the bath, the calorimeter was evacuated and the sample and bath heated electrically, keeping the temperature of the two the same at all times. Readings of temperature, time, and the current supplied to the sample were taken every three or four minutes. Measurements were made by this method covering the interval 20°C to 65°C.

2. Method in which a constant temperature bath surrounded the calorimeter.

The exterior junction of the thermocouple was kept in ice. The calorimeter was filled with hydrogen and then put in the constant temperature bath. Hydrogen was used because it contained no gases that would be condensed and because the high speed of its molecules decreased the time for the sample to reach the temperature of the bath. When the sample had reached a constant temperature the calorimeter was evacuated and a current passed through the heating coil around the sample. Readings of the e. m. f. produced by the thermocouple were taken on the potentiometer every few minutes. The current was also observed every five or ten minutes. The heating was continued until a temperature was reached at which the loss of heat from the sample to the bath became fairly large. The current was then turned off and the rate of cooling observed. Two or more runs were made on each of the three steel samples and the pure iron sample using as constant temperature baths ice, solid carbon dioxide, and liquid oxygen.

Calculations and Results

Calculation of specific heat of the steel samples.

The heat capacity of a substance at constant pressure, C_p, may be defined by the equation

$$C_p = \frac{dq}{dT},$$

where dq is the heat added and dT is the rise in temperature. This may be put in the form

$$C_p = \frac{dq}{dT} = \frac{dq}{dt}\frac{dt}{dT},$$

where t is the time in minutes. The electrical energy added per minute will be

$$\frac{dq}{dt} = \frac{(I^2R)(60)}{4.1826},$$

where I is the current in amperes and R is the resistance in ohms. Therefore in the adiabatic method, where all of the electrical energy is used in heating the sample,

$$C_p = \frac{(I^2R)(60)}{4.1826}\frac{dt}{dT}.$$

$\frac{dt}{dT}$ will be the reciprocal of the rise in temperature per minute of heating, and may be obtained from a graph in which temperature is plotted against time, such as figure 5. By

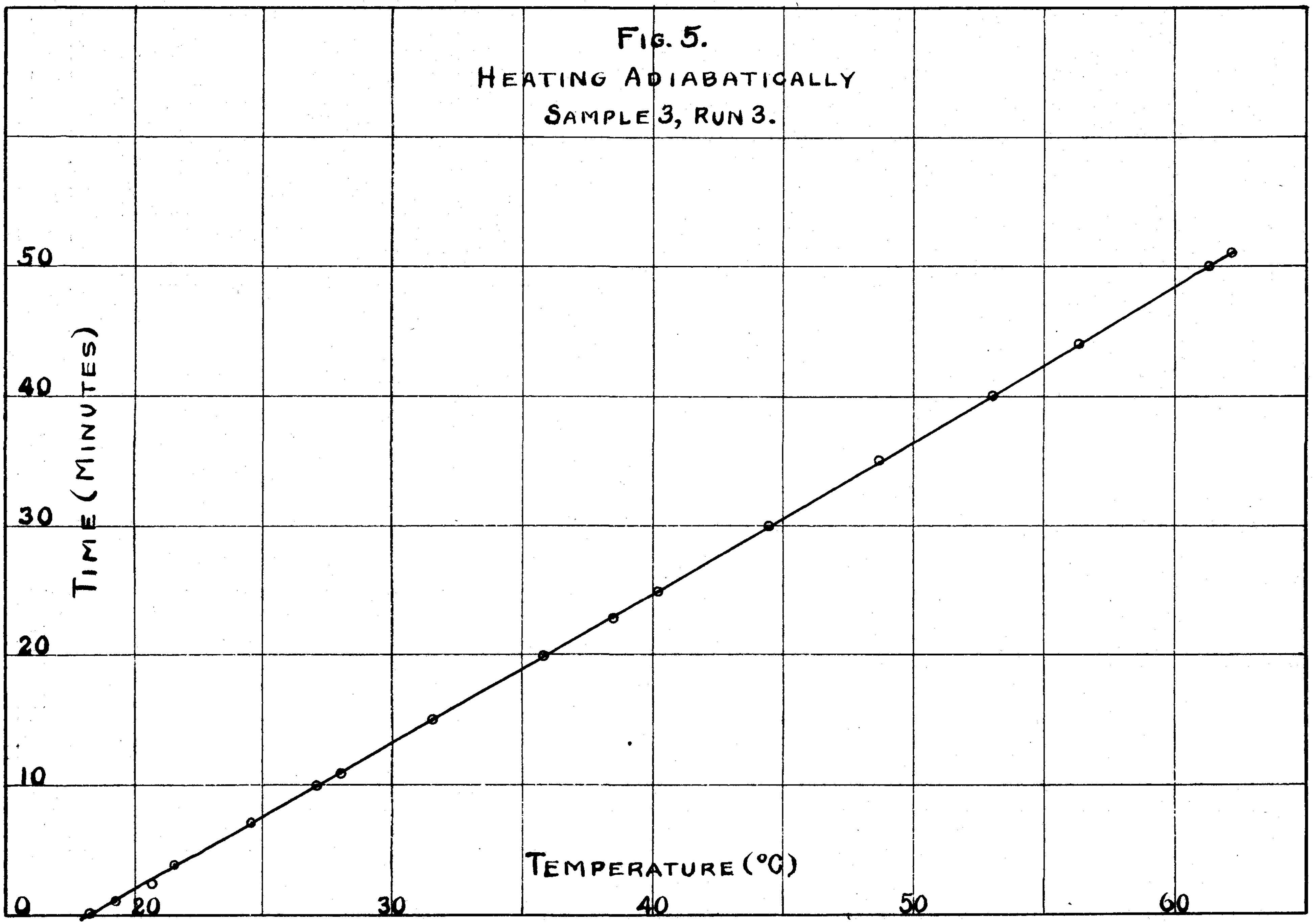


FIG. 5.
HEATING ADIABATICALLY
SAMPLE 3, RUN 3.

plotting the data and using the slope of the curve we are using the actual rate of rise of temperature for a given energy imput at a given time, and thus should obtain the actual heat capacity at a certain temperature. This also has the advantage of eliminating errors in individual readings. To obtain the specific heat of a sample, its total heat capacity was divided by its weight (including the iron equivalent of the lacquer and windings). Since the specific heat of iron is well known, it was used as a method of standardizing the apparatus. If the specific heat of iron at some temperature is .114 and the value obtained was .112, the values for runs on all the steel samples at that temperature were corrected by multiplying by .114/.112.

The rates of heating and the current used at 30°C and 50°C in a number of adiabatic runs and the values of specific heat, c_p, calculated therefrom are shown in tables 2 and 3.

For the runs in which the calorimeter was immersed in a constant temperature bath there was in most cases an appreciable transfer of heat between the sample being heated and the walls of the calorimeter, since the outside of the calorimeter was always at the temperature of the bath.

If an amount of heat, dq is added at constant pressure, part of this, dH, will be stored up and part of it, dH', will be lost.

Table 2.

Condensed Heat Capacity Data at 323.2°K

R = 40.0 ohms

Sample No.	Run No.	Current	$\frac{dT}{dt}$	Heat capacity of slug	Specific heat	Mean specific heat corrected
0	24	151.7	0.873	15.15	0.1141	0.1091
0	25	151.7	0.871	15.18	0.1143	
1	8	146.9	0.812	15.13	0.1193	0.1142
1	9	146.5	0.811	15.20	0.1198	
1	10	146.4	0.8185	15.04	0.1186	
1	13	145.3	0.794	15.25	0.1202	
2	1	151.9	0.884	14.97	0.1192	0.1137
2	2	152.2	0.889	14.96	0.1191	
2	3	152.4	0.892	14.97	0.1192	
3	1	151.0	0.828	15.81	0.1219	0.1157
3	2	152.5	0.841	15.88	0.1214	
3	3	152.6	0.842	15.87	0.1213	

Table 3.

Condensed Heat Capacity Data at 303.2°K

R = 40.0 ohms

Sample No.	Run No.	Current	$\frac{dT}{dt}$	Heat capacity of slug	Specific heat	Mean specific heat corrected
0	24	152.2	0.8935	14.87	0.1120	
0	25	152.2	0.891	14.83	0.1117	0.1081
1	8	147.6	0.831	15.03	0.1184	
1	9	147.2	0.845	14.72	0.1160	
1	10	147.2	0.842	14.76	0.1163	0.1132
1	13	145.4	0.8125	14.95	0.1178	
2	1	152.1	0.906	14.67	0.1167	
2	2	152.2	0.913	14.56	0.1158	0.1124
2	3	152.5	0.9105	14.66	0.1166	
3	1	151.5	0.854	15.42	0.1180	
3	2	152.9	0.8615	15.57	0.1191	0.1180
3	3	152.8	0.875	15.26	0.1167	

$$
\begin{aligned}
dq &= dH + dH' \\
&= \frac{dH}{dT}\,dT + \frac{dH'}{dt}\,dt \\
&= \frac{dH}{dT}\,dT + \frac{dH'}{dT'}\,\frac{dT'}{dt}\,dt \\
&= C_p + C_p\,\frac{dT'}{dt}\,dt
\end{aligned}
$$

$$\frac{dq}{dT} = C_p + C_p\,\frac{dT'}{dt}\,\frac{dt}{dT}$$

Solving for C_p we have

$$C_p = \frac{\frac{dq}{dT}}{1 + \frac{dT'}{dt}\,\frac{dt}{dT}} = \frac{\frac{dq}{dt}\,\frac{dt}{dT}}{1 + \frac{dT'}{dt}\,\frac{dt}{dT}}$$

$$= \frac{\frac{dq}{dt}}{\frac{dT}{dt} + \frac{dT'}{dt}} = \frac{\frac{(I\ R)(60)}{4.1826}}{\frac{dT}{dt} + \frac{dT'}{dt}}$$

Since the primed quantities refer to cooling, dT'/dt is the rate at which the sample would cool and dT/dt is the rate of rise of temperature with heating.

Since it is rather tedious to convert a large number of values of e. m. f. readings, E, given by the thermocouple into temperatures, one can instead plot E against t as in figure 6 and thus obtain a measure of the rate of rise (or fall) of temperature, dE/dt (or dE'/dt). The above equation can be changed slightly to use these quantities.

$$\frac{dT}{dt} = \frac{dE}{dt}\,\frac{dT}{dE} \quad \text{and} \quad \frac{dT'}{dt} = \frac{dT'}{dE'}\,\frac{dE'}{dt} = \frac{dT}{dE}\,\frac{dE'}{dt}$$

The equation for the calculation of C_p then becomes:

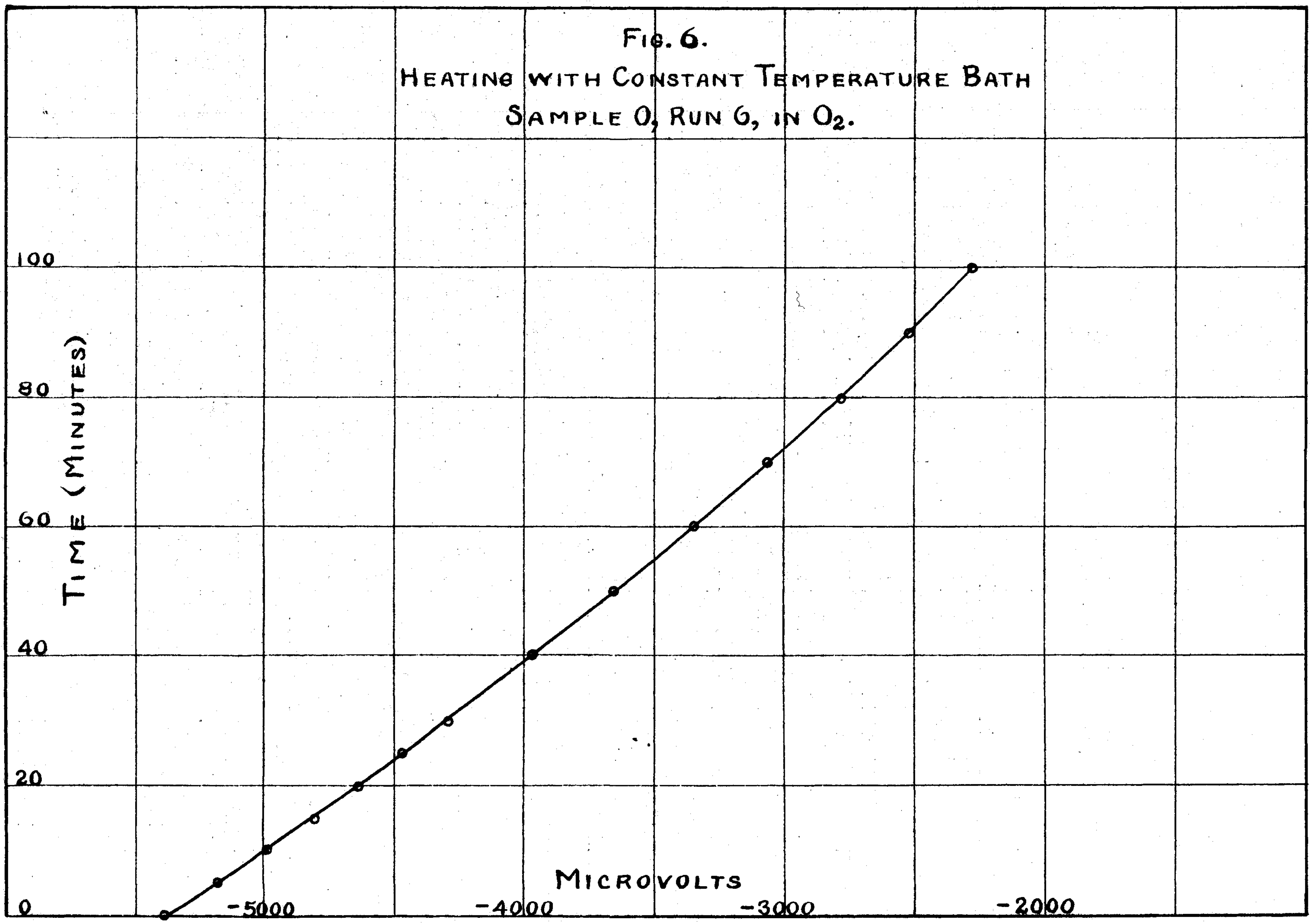


Fig. 6.

HEATING WITH CONSTANT TEMPERATURE BATH

SAMPLE 0, RUN 6, IN O_2.

$$C_p = \frac{(I^2R)(60)}{(4.1826)\left(\frac{dE}{dt} + \frac{dE'}{dt}\right)\left(\frac{dT}{dE}\right)} .$$

dT/dE is determined by finding the slope of the curve in figure 3, in which T is plotted against E.

This equation, like that used for the adiabatic runs, gives the heat capacity at a point and tends to prevent an error in a single measurement from causing an erroneous result.

The specific heat is calculated from the heat capacity of the slug as previously mentioned. Condensed data and the calculated values for specific heat are given for six different temperatures in tables 4 to 9.

Calculation of the heat capacity of iron carbide

The specific heat of iron carbide was calculated by plotting the values of specific heat at one temperature for the different slugs against percentage carbon and extrapolating to pure iron carbide (6.67% carbon). Each line on figure 7 represents a different temperature. The values thus obtained are given in the second column of table 10.

Multiplying the values for specific heat by the molecular weight of iron carbide, 179.52, we obtain the corresponding figures for molar heat capacity, $\widetilde{C}_p$. These values are given in column 3 of table 10. These same results are shown graphically by figure 8, curve 2. Curve 1 of the same figure shows the results obtained by Naeser over a similar temperature range.

Table 4.

Condensed Heat Capacity Data at 280.7° K

R = 40.0 ohms $\frac{dT}{dE}$ = 0.02435

Sample No.	Run No.	Current	$\frac{dE}{dt}$	$\frac{dE'}{dt}$	Heat capacity of slug	Specific heat	Mean specific heat corrected
0	7	154.0	33.5	4.24	14.80	0.1114	0.1060
0	8	154.0	33.5	4.24	14.80	0.1114	
0	9	155.0	33.5	4.24	15.00	0.1130	
1	5	143.5	28.4	4.40	14.80	0.1167	0.1106
2	5	153.0	34.45	4.43	14.78	0.1166	0.1105
3	8	153.6	31.7	4.30	15.45	0.1182	0.1122
3	9	155.1	32.2	4.30	15.53	0.1187	

Table 5.

Condensed Heat Capacity Data at 201.3°K

$R = 39.94$ ohms $\qquad \frac{dT}{dE} = 0.0290$

Sample No.	Run No.	Current	$\frac{dE}{dt}$	$\frac{dE'}{dt}$	Heat capacity of slug	Specific heat	Mean specific heat corrected
0	16	153.2	28.25	6.40	13.35	0.1005	
0	17	152.3	28.33	6.40	13.18	0.0993	0.0981
0	18	152.5	28.70	6.40	13.07	0.0992	
1	7	144.5	24.83	6.48	13.15	0.1036	0.1018
1	6	141.0	23.50	6.48	13.07	0.1030	
2	8	152.8	28.5	6.90	13.04	0.1028	0.1013
3	14	152.1	27.32	6.41	13.53	0.1035	0.1021

Table 6.

Condensed Heat Capacity Data at 201.3°K

R = 39.91 ohms $\frac{dT}{dE}$ = 0.0319

Sample No.	Run No.	Current (milli amperes)	$\frac{dE}{dt}$	$\frac{dE'}{dt}$	Heat capacity of slug	Specific heat	Mean specific heat corrected
0	16	154.1	33.87	0.78	12.31	0.0927	0.0928
1	7	145.1	31.4	0.79	11.75	0.0927	0.0928
2	8	154.3	34.4	0.73	12.18	0.0961	0.0962
3	14	153.2	32.6	0.78	12.62	0.0966	0.0968

Table 7.

Condensed Heat Capacity Data at 161.2°K

R = 39.82 ohms $\frac{dT}{dE} = 0.0379$

Sample No.	Run No.	Current	$\frac{dE}{dt}$	$\frac{dE'}{dt}$	Heat capacity of slug	Specific heat	Mean specific heat corrected
0	2	155.5	31.15	2.45	10.85	0.0818	
0	3	155.4	31.15	2.45	10.84	0.0817	0.0817
0	6	155.2	31.1	2.45	10.82	0.0815	
1	14	154.4	31.8	2.60	10.40	0.0820	0.0829
1	17	155.3	31.7	2.60	10.60	0.0836	
2	11	153.4	30.95	2.70	10.55	0.0832	0.0833
2	12	153.4	30.95	2.70	10.55	0.0832	
3	15	156.5	31.75	2.50	10.79	0.0826	0.0827
3	16	156.4	31.65	2.50	10.80	0.0826	

Table 8.

Condensed Heat Capacity Data at 120.5° K

R = 39.58 ohms $\frac{dT}{dE} = 0.0426$

Sample No.	Run No.	Current	$\frac{dE}{dt}$	$\frac{dE'}{dt}$	Heat capacity of slug	Specific heat	Mean specific heat correctd
0	2	156.8	35.70	0	9.18	0.06915	
0	3	156.7	35.70	0	9.17	0.0691	0.0636
0	6	155.6	35.55	0	9.08	0.0684	
1	14	156.6	36.45	0	8.97	0.0707	
1	17	157.0	36.77	0	8.93	0.0704	0.06485
2	11	154.7	35.3	0	9.035	0.07035	
2	12	154.65	35.3	0	9.025	0.07025	0.0646
3	15	157.8	35.90	0	9.25	0.0707	
3	16	157.7	35.90	0	9.23	0.0706	0.0650

Table 9.

Condensed Heat Capacity Data at 102.4°K

$R = 39.40$ $\frac{dT}{dE} = 0.0453$

Sample No.	Run No.	Current	$\frac{dE}{dt}$	$\frac{dE'}{dt}$	Heat capacity of slug	Specific heat	Mean specific heat corrected
0	2	157.7	39.2	-0.7	8.02	0.0604	0.0526
0	3	157.6	39.3	-0.7	8.03	0.0605	
0	6	157.7	39.4	-0.7	8.06	0.0607	
1	14	157.1	40.2	-0.8	7.81	0.06155	0.0535
1	17	158.1	40.8	-0.8	7.80	0.06145	
2	11	155.9	39.5	-0.9	7.85	0.0619	0.0538
2	12	155.6	39.8	-0.9	7.77	0.0613	
3	15	158.7	39.9	-0.7	8.02	0.06135	0.0533
3	16	158.3	39.8	-0.7	8.00	0.0612	
3	17	158.1	39.9	-0.7	7.96	0.06085	
3	19	158.1	39.6	-0.7	8.02	0.06135	

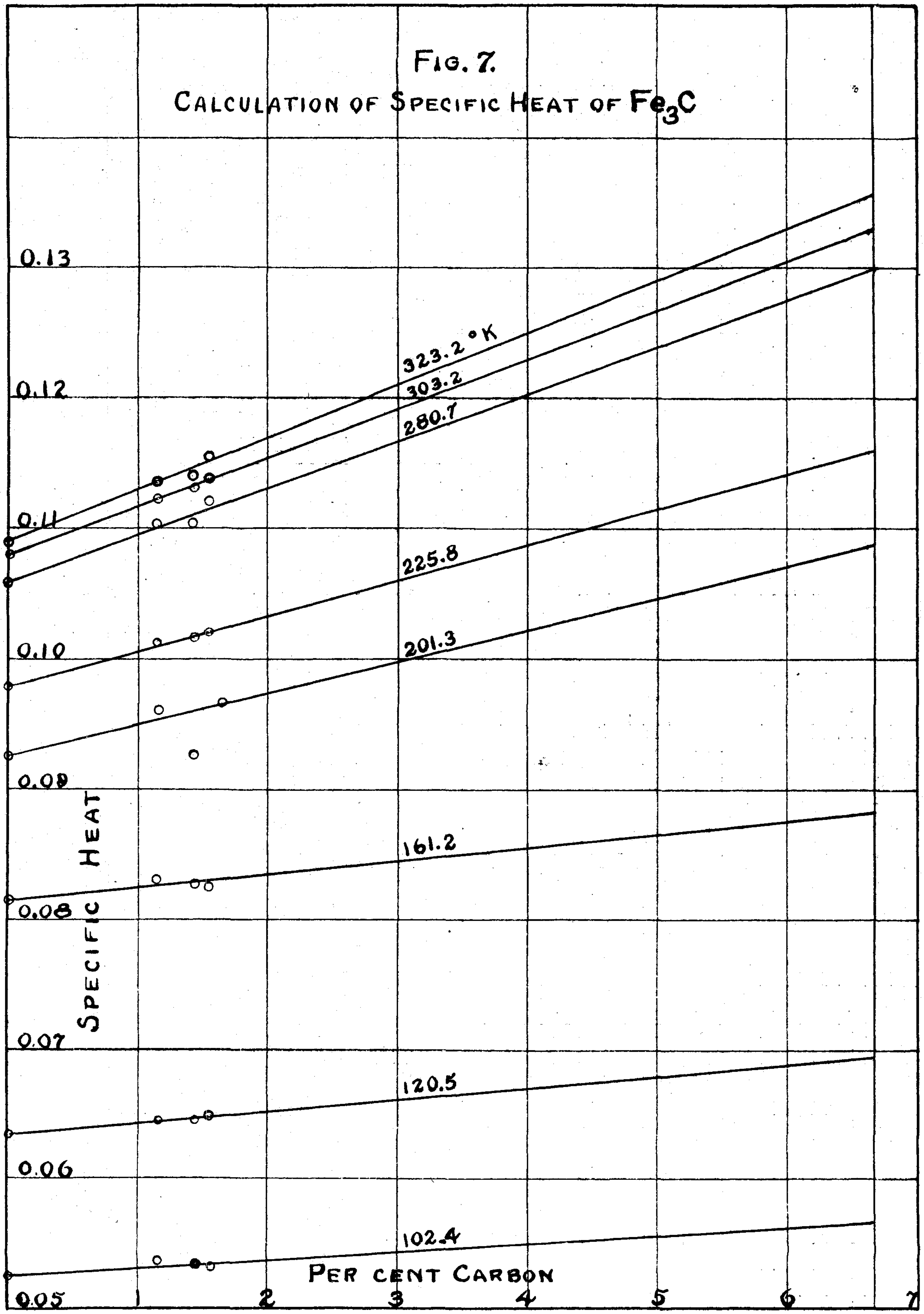


FIG. 7.

CALCULATION OF SPECIFIC HEAT OF Fe_3C

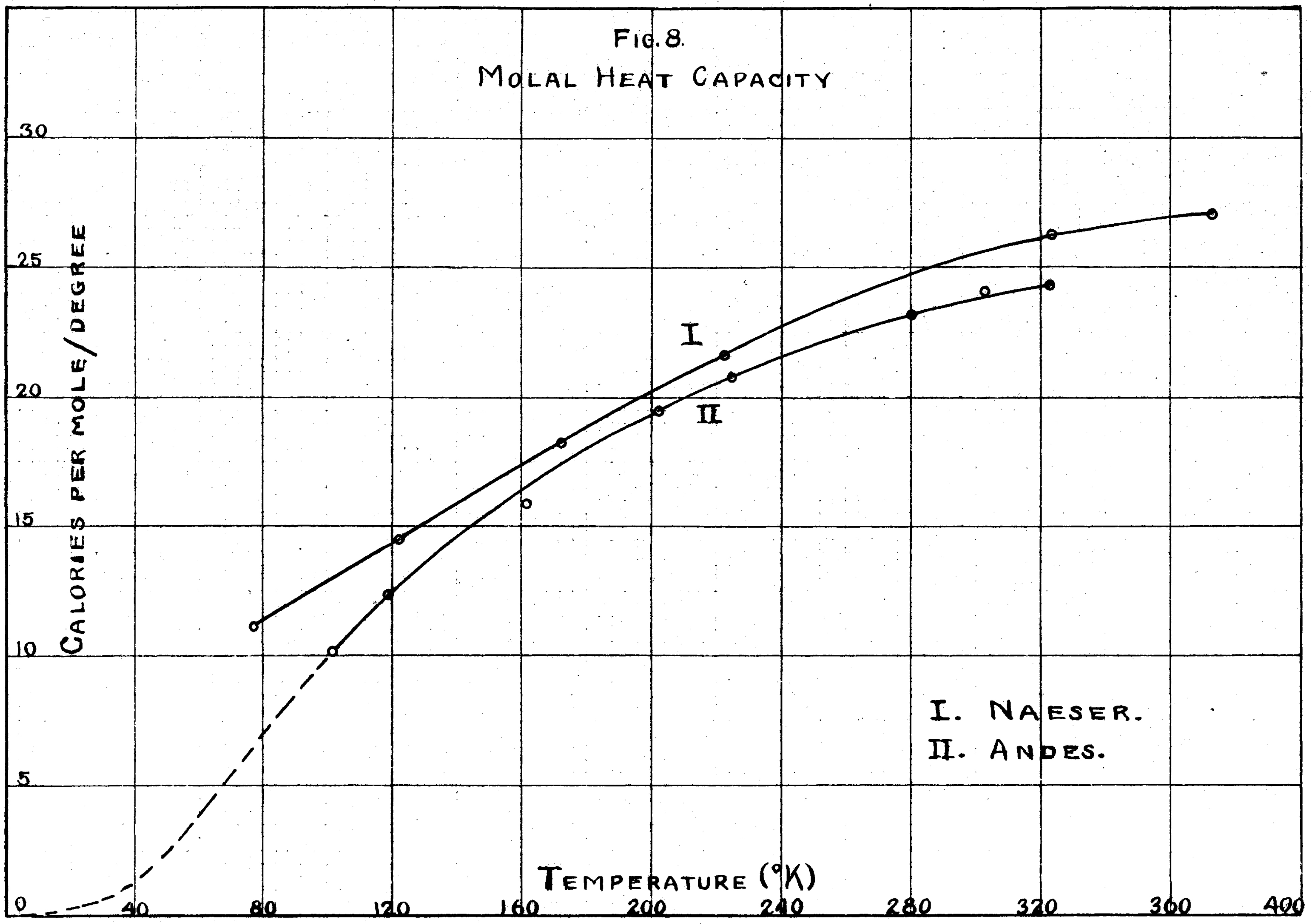
Table 10.

Specific Heat and Molal Heat Capacity of Iron Carbide

Absolute temperature	Specific heat	Molal heat capacity	$\frac{C_p}{T}$
323.2	0.1358	24.38	0.0755
303.2	0.1341	24.06	0.0794
280.7	0.1301	23.34	0.0809
225.8	0.1160	20.83	0.0923
201.3	0.1087	19.51	0.0969
161.2	0.0884	15.87	0.0985
120.5	0.0694	12.46	0.1034
102.4	0.0566	10.16	0.1008

Fig. 8.

Molal Heat Capacity



Calculation of entropy

To obtain the entropy of iron carbide the molecular heat capacity divided by the absolute temperature was plotted against the absolute temperature. The values of heat capacity below 100° absolute were obtained by comparing the specific heat of iron to that of the carbide (fig.9). It is seen that in the range investigated experimentally the specific heat of the carbide gives a curve similar to that for iron and that the two approach more closely at low temperatures. It was therefore concluded that the form of the curve for iron carbide near absolute zero could be assumed to be similar to that for iron. From the curve thus extrapolated values were obtained which gave points for the lower part of the curve in figure 10.

The value of the entropy of iron carbide at 25°C, S_{298}, was obtained by graphical integration (fig. 10).

$S_{298} = \int_0^{298} \frac{C_p}{T}\,dT =$ the area under the curve from $T = 0$ to $T = 298$.

$$S_{298} = 23.55 \text{ entropy units.}$$

Calculation of free energy

For the reaction,

$$3Fe_{(s)} + C_{(graphite)} \longrightarrow Fe\ C_{(s)},$$

$$\Delta S = S_{Fe_3C} - (3S_{Fe} + S_C)$$

$$\Delta S = 23.55 - (3x6.60 + 1.39)$$

$$= 23.55 - 21.19 = 2.36.$$

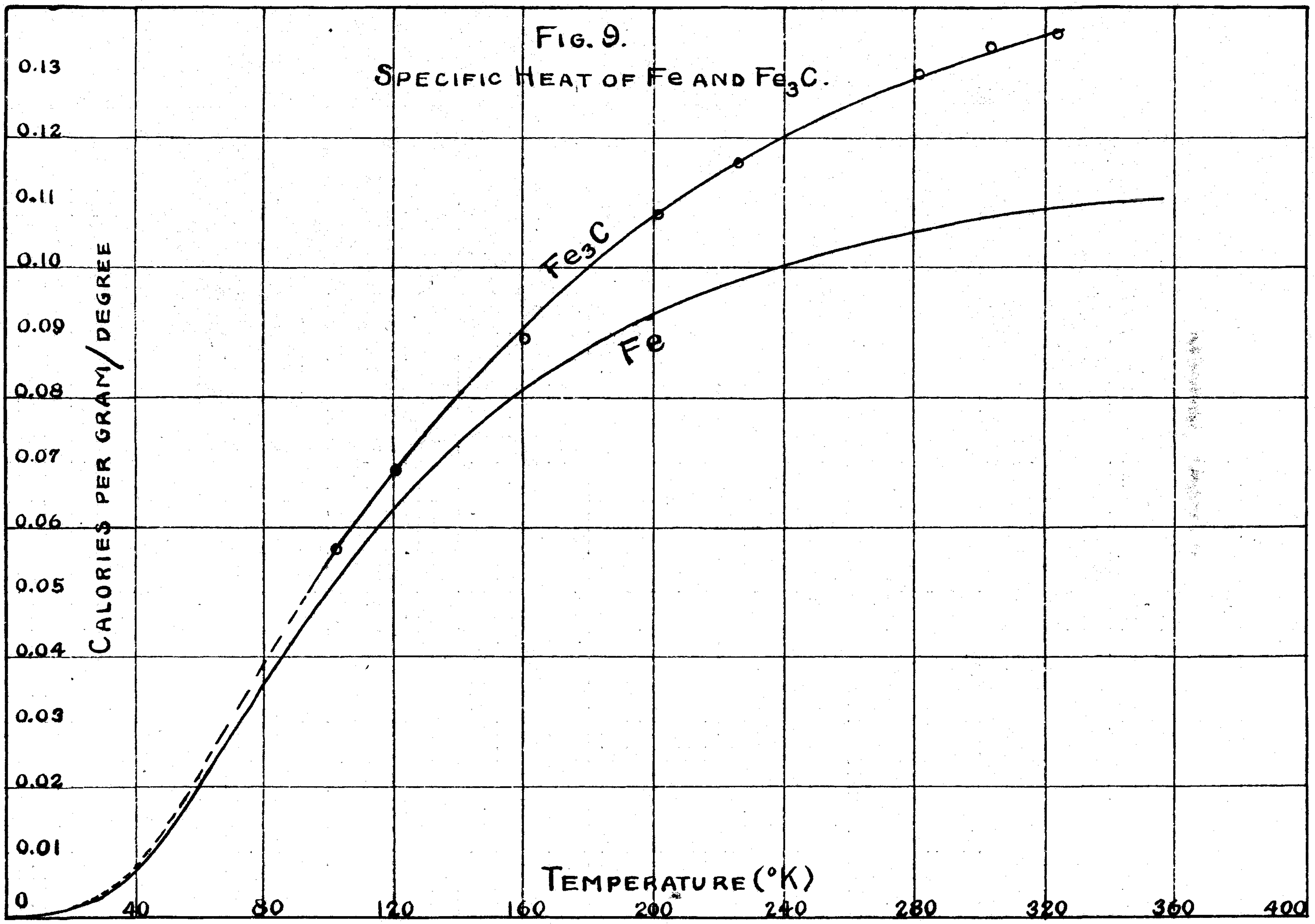


FIG. 9.

SPECIFIC HEAT OF Fe AND Fe_3C.

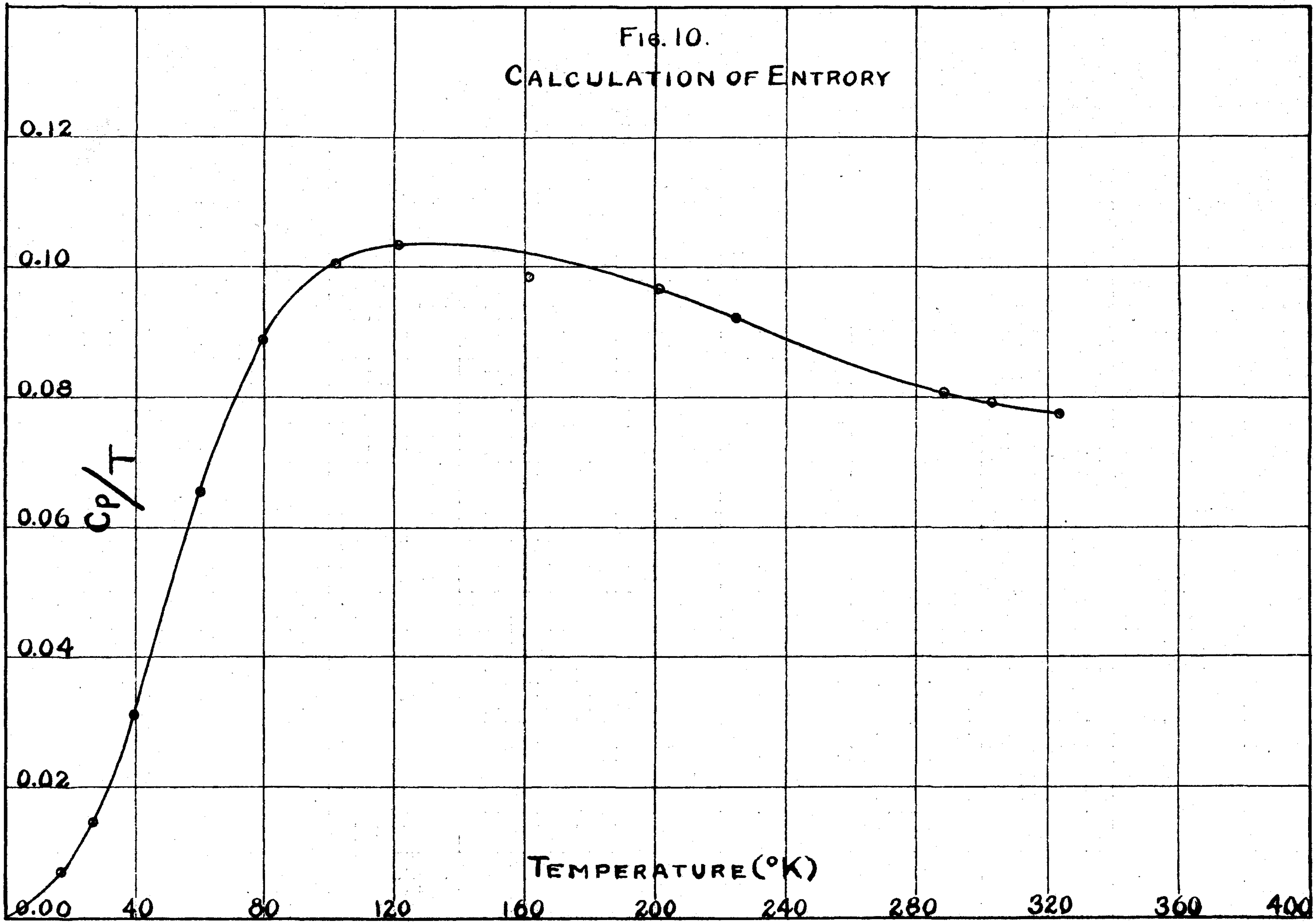


Fig. 10.
Calculation of Entropy
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Cp/T
Temperature (°K)
40
80
120
160
200
240
280
320
360
400

The increase in free energy at 25°C is:

$$\begin{aligned} \Delta F &= \Delta H - T\Delta S \\ &= 12300 - (298.16)(2.36) \\ &= 12300 - 704 \\ &= 11596 \text{ cal.} \end{aligned}$$

DISCUSSION

The accuracy of the results obtained depends largely on four factors; (1) the correctness of the heat capacity data of Eucken and Werth, (2) the correctness of certain assumptions, (3) the accuracy of the analyses and observations on the condition of the carbon in the steel samples, and (4) the magnitude of errors in calibrating instruments and in taking readings of time, current, etc.

It seems improbable that the data on the heat capacity of iron would be greatly in error.

The assumption of a straight line variation of specific heat with carbon content has been observed by Umino and by Levin and Schottky. The assumption involved in extrapolating the lower portion of the specific heat curve for iron carbide probably does not cause much error, as the form of the curves for iron and iron carbide are quite similar in the range for which experimental values were obtained.

The errors in analyses and readings do not seem to account for the variation of the data for the heat capacity of iron carbide, as found in this investigation, from the results of Naeser (see fig. 8). Therefore it is quite possible that this discrepancy may be accounted for by a difference in the heat capacity of the pure carbide and of that existing in steel.

A few measurements were made in this laboratory on the heat capacity of free iron carbide, using spheroidized cementite which analyzed 6.67 per cent carbon and 93.3 per cent iron. The data obtained, although not conclusive, seemed to be in fair agreement with the work of Naeser.

If there is a real difference, the data on the carbide as it exists in steel should be more valuable than similar information concerning the free carbide.

The value of ΔF obtained is inaccurate to the extent of the possible error in the value of ΔH which was used in its calculation. A variation of a few per cent in the heat capacity values would produce a change in ΔF which would be negligible compared to the possible error due to the uncertainty of ΔH.

Because of this uncertainty in H, the value of 11596 cal. for ΔF_{298} is not too inconsistant with the value, 9300, obtained by Yap and Liu from calculations based on equilibruim measurements at high temperatures.

If we regard ΔF_{298} as a positive quantity of the magnitude given above, iron carbide should be unstable or metastable at room temperatures, as is the opinion of most investigators.

If we should accept a negative or a small positive value for ΔH, ΔF would also be negative and Fe_3C would be stable at room temperature.

SUMMARY AND CONCLUSIONS

1. The heat capacity of iron carbide in steel has been determined from -171°C to + 50°C. The values thus obtained are given in table 10 and figure 8.

2. By the use of these results the entropy of Fe_3C at 25°C is found to be 23.55 units.

3. The results of Brodie, Jennings, and Hayes, as recalculated by Yap and Liu, for the heat of formation of iron carbide are used in calculating ΔF. The value thus obtained for the free energy change attending the formation of one mole of the compound from its elements is 11596 cal. This would indicate that iron carbide is unstable or metastable at room temperatures.

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