Contrails

A MODIFIED ADIABATIC CALORIMETER

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FOREWORD

This report was prepared by the Analysis and Measurement Branch of the Materials Laboratory, Directorate of Research, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio. It was initiated under Project No. 7360, "Materials Analysis and Evaluation Techniques," Task No. 73603, "Thermal Measurements", formerly RDO No. 616-16, "Heat Transfer and Thermal Insulation". The project engineers were 1/Lt M. W. Belaga, 1/Lt D. Coddington, and Mr. H. Marcus.

WADC TR 54-601

ABSTRACT

A modified adiabatic type calorimeter, capable of measuring the heat capacities of organic liquids (natural and synthetic) in the temperature range of 100-500°F, was designed, built, and calibrated.

In this calorimeter a fixed rate of power is supplied to the sample, and a bath which surrounds the sample container is maintained at the same temperature in order to prevent heat losses from the sample. The heat capacity of an unknown material may be calculated from measurements of the time rate of temperature rise, heat input, and mass of the sample.

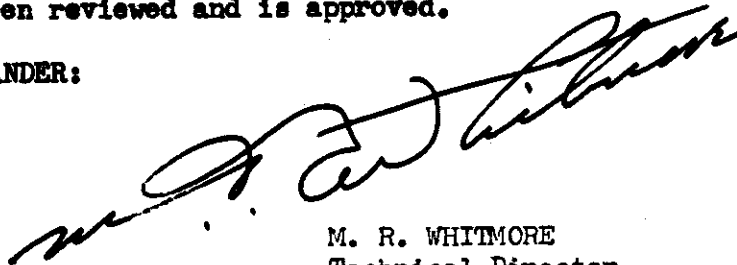The calorimeter has been designed for rapid, simple sample changing.

The calorimeter was calibrated with materials of known heat capacity (water, castor oil, and linseed oil), and the following relation between the calorimeter constant and temperature was obtained:

$$K(t) = 0.256 - 3.706 \times 10^{-5}t + 6.839 \times 10^{-7}t^2$$

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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A requirement exists for physical and thermal properties of natural and synthetic organic fluids. Of considerable importance are the heat capacities of coolants, lubricants, and hydraulic fluids.

Adiabatic calorimetry is not a new concept. However, it affords a tool of great accuracy in the measurements of various thermal properties including heat of reaction, heat of formation, and heat capacity. The adiabatic calorimeter described herein is a modification of the type first described in the literature by Barry, Richards, and White about forty years ago. The original design has been modified in light of advances in heat transfer technology as well as improved methods of temperature measurement and control.

The basis of adiabatic calorimetry is as follows:

1. A measurable amount of heat is fed into a sample and the sample container, which are the heart of the apparatus.

2. The sample container is immersed in a bath which is maintained at the same temperature as the sample in order to prevent heat losses from the sample.

3. From measurements of the rate of heat input, rate of rise of the sample temperature, sample weight, and a knowledge of calorimeter constant the heat capacity of an unknown material may be calculated from the following equation:

$$Cp(t) = \frac{1}{m} \left[F\frac{d\theta}{dt} - K(t) - L\frac{dm}{dt} \right]$$

II HISTORY

The adiabatic calorimeter was proposed and perfected by T. W. Richards and his co-workers in 1905 and has been employed in one form or another in much of the accurate thermodynamic work of recent times.

In the first adiabatic calorimeter(used in the measurements of heat of reaction) the surrounding bath contained dilute alkali and its temperature was raised in a gradual manner by the addition of acid. In later models electrical heating was employed. With the aid of relays, an amplifier, and a differential temperature sensing element, one part of which is placed in the sample and one part in the bath, the adjustment of temperature may be made entirely automatic.

The earlier designs were used to measure heats of reaction at relatively low temperatures and water was used as the bath liquid. In the present investigation, Dow Corning DC 550 fluid was used in the surrounding bath since it exhibits reasonably good heat transfer properties and is capable of withstanding cyclical heating at temperatures up to 500°F.

The heating of the sample is generally supplied by an electrical power input. A coil of known resistance is placed in the sample and a fixed voltage is applied to it for a measured time interval; the resulting temperature rise is then observed. The quantity of heat liberated is $I^2R\theta$ international joules. If the product of temperature rise and calorimeter constant is subtracted from this and if the result is then divided by the product of the temperature rise and the mass of the sample, the heat capacity of the sample is obtained.

The calorimeter constant is obtained in a similar manner by using samples of known heat capacity according to the following relationship:

$$K(t) = P\frac{d\theta}{dt} - mCp(t) - L\frac{dm}{dt}$$

The above relationship was obtained from a heat balance on the sample and sample container.

III THEORY

An equation for determining either the heat capacity of an unknown sample or the calorimeter constant may be obtained from a heat balance on a system composed of the sample and sample container. From the heat balance, the following relation is observed:

(1) Heat input = Increase in enthalpy of system   heat losses

or,

(2) $\int Q = \int dH_s + \int dH_c + \int Ldm + \int Q'$

The heat input is received from the voltage applied to the knife heater in the sample and from the stirrer agitation. The change in enthalpy of the system consists of the increase in sensible heat of the calorimeter (sample container, stirrer, thermopile well, etc.). The heat losses include conduction losses along the inlet tubes and radiation and convection losses through the inlet tubes. Additional heat is lost in the partial vaporization of the sample.

Equation 2 may be rewritten in consistent units.

(3) $Pd\theta = mCp(t)dt + K(t)dt + Ldm + Q'd\theta$

rearranging,

(4) $Cp(t) = \dfrac{1}{m}\left[P\dfrac{d\theta}{dt} - K(t) - L\dfrac{dm}{dt} - Q'\dfrac{d\theta}{dt} \right]$

or,

(5) $K(t) = P\dfrac{d\theta}{dt} - mCp(t) - L\dfrac{dm}{dt} - Q'\dfrac{d\theta}{dt}$

DT-DIFF. THERMOPILE   S-STIRRER

T - THERMOPILE   H-HEATER
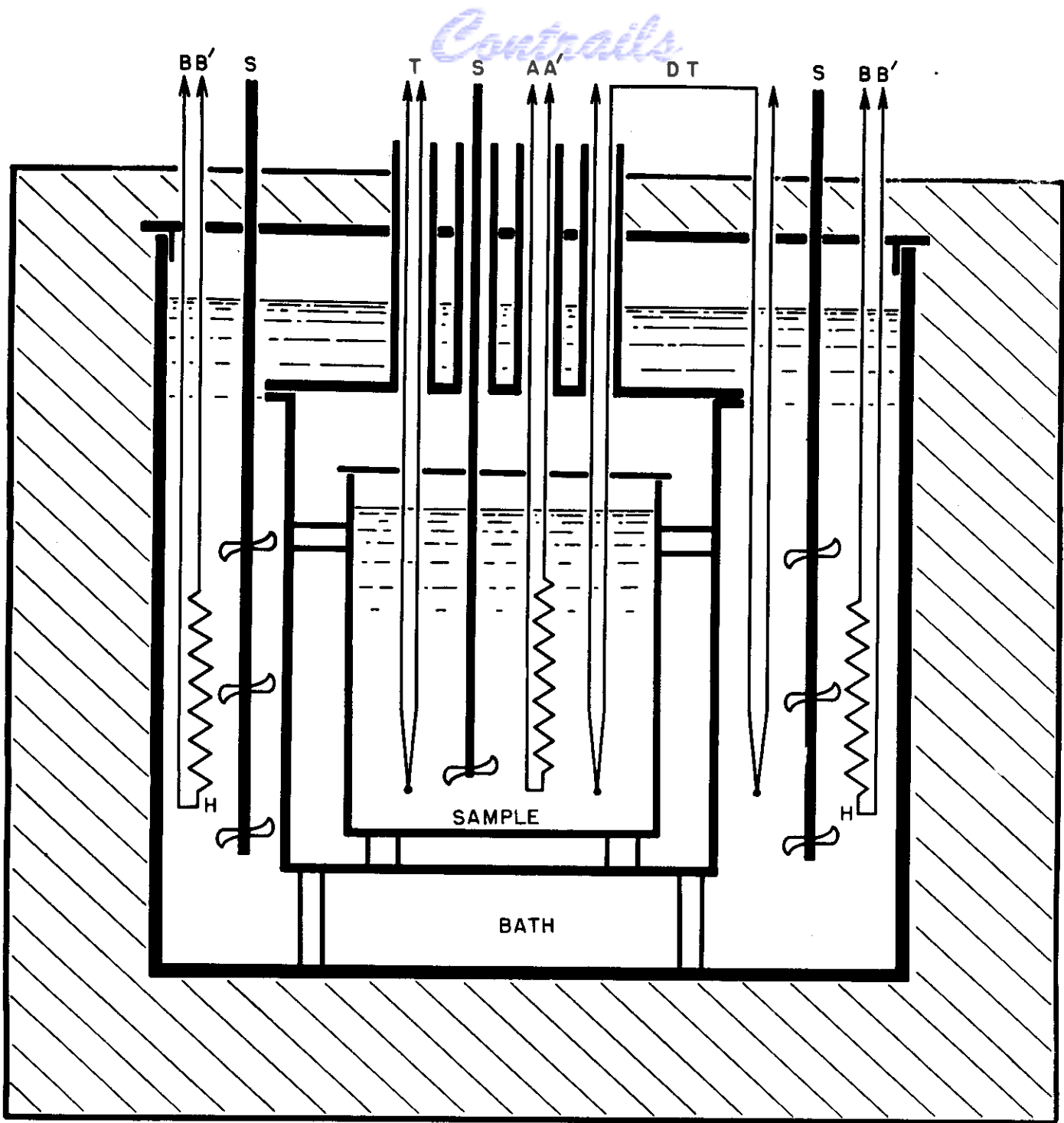
FIGURE I. SCHEMATIC OF THE ADIABATIC CALORIMETER
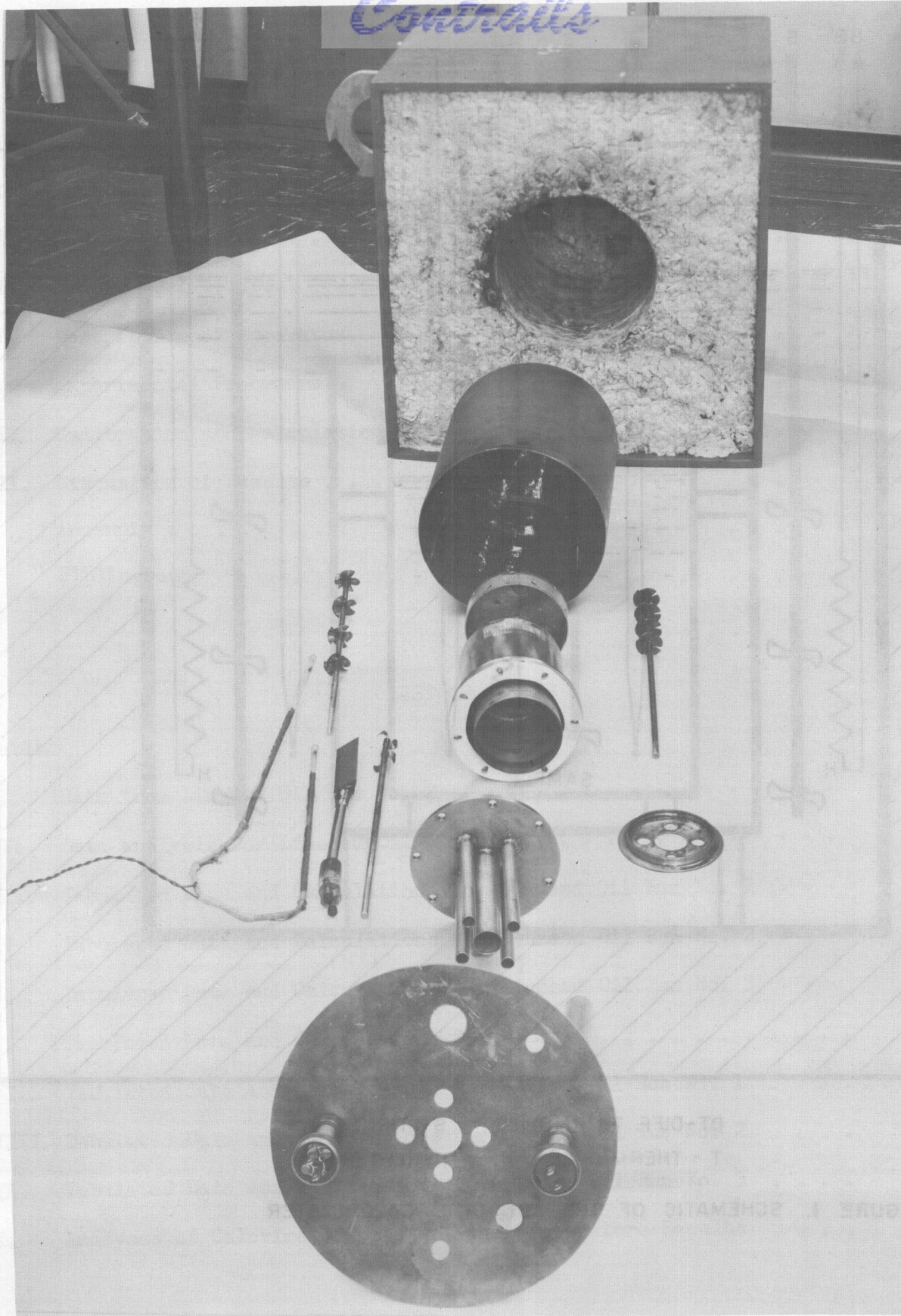
Figure 2

INTEGRAL PARTS OF CALORIMETER, DISASSEMBLED, INCLUDING
OUTER INSULATING BOX

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In the calculations, the heat losses from the system were neglected since the sample container was surrounded by a bath which was maintained within 0.25°F of the sample liquid. Further, in the calibration of the calorimeter with materials of known heat capacity the heat losses would be reflected in the calorimeter constant.

Eliminating the heat losses from equation 5 gives the following relationship:

$$(6) \qquad K(t) = P\frac{d\theta}{dt} - mCp(t) - L\frac{dm}{dt}$$

The heat loss caused by the partial vaporization of the sample becomes appreciable only when using materials of high vapor pressure and high heat of vaporization(e.g.,water). In this study the effect of castor oil and linseed oil evaporated at their estimated heats of vaporization(11) was negligible, and $L\frac{dm}{dt}$ was eliminated from equation 5 except for the calibration run with water.

The heat input from the stirrer agitation was found to be negligible relative to the power input to the sample.

IV   DESCRIPTION OF APPARATUS

Calorimeter Assembly:

The sample container is a cylindrical cup of copper with a capacity of approximately 500 cc of liquid. It is supported and held concentric relative to the intermediate cup by three stainless steel points, equally spaced laterally and welded to the intermediate cup wall. A disc of transite fitted into the base of the intermediate cup supports the bottom of the sample container.

The intermediate cup is constructed of stainless steel with a flange lip. The cup lid is fitted with five stainless steel tubes to accommodate a variable speed, motor driven stirrer, a knife heater, a thermocouple, and one leg of a differential thermopile. All of these components extend into the sample liquid. A 1/8 inch teflon gasket is inserted between the lid and cup lip to provide a liquid tight seal. The dead air space formed between the sample container and the intermediate cup reduces heat transfer outward from the sample container.

The intermediate cup is completely immersed in an oil bath consisting of approximately 2 1/2 gallons of Dow Corning DC 550 fluid. The cup assembly is supported and held concentric in the bath container by a small platform designed for this purpose. Two immersion heaters supply heating for the oil bath and two variable speed motor driven stirrers provide agitation necessary to insure uniform temperature distribution throughout the oil bath.

The entire calorimeter assembly is surrounded by a wall of rock wool contained in wooden box with a removable lid. Rock wool was packed into the box up to the height of the bath container, and two layers of Johns-Manville "Thermoflex" (1 inch thickness) are placed across the top. This provides ready access and prevents excessive loss of heat.

Auxiliary Equipment:

A fixed a.c. voltage is supplied to the knife heater in the sample through a Sola constant voltage transformer. A Weston Model 310 wattmeter is connected in the heating circuit and indicates the power supplied to the liquid sample.

The sample temperature is measured by means of an iron-constantan thermocouple connected to a Leeds and Northrup potentiometer(Catalog No. 8662). The temperature differential between the bath and sample is measured with a twenty couple iron-constantan thermopile. One leg of the thermopile is placed in the sample liquid and one leg in the bath liquid. The thermopile has a sensitivity of approximately one millivolt per $^\circ$F. The signal from the thermopile is fed into a Brown Electronik recorder and controller, which has a full scale deflection of +1.25 to -1.25 millivolts.

To minimize the temperature difference between the bath and the sample the following procedure is followed:

1. The bath heaters have an a.c. voltage applied to them so that the rate of rise of the bath temperature with time will be greater than the time rate of temperature rise of the sample. This varies between 60 and 75 volts depending on the temperature level of the calorimeter. This setting is not critical and normally requires only a single readjustment over an eight hour run.

2. The bath heater voltage is fed into the heaters through a relay, which is operated by the Brown Controller. When the amplified signal of the differential thermopile is negative(indicating that the sample is hotter than the bath) the relay is closed permitting bath heating. Since the bath heats at a greater rate than the sample, a null voltage is reached which causes the controller to open the relay and the bath heaters are shut off. The thermal inertia of the system causes a continued temperature rise in the bath with a resulting time lag before the sample temperature reaches that of the bath. When the null is again reached the bath heaters are automatically turned on and this time the inertia of the bath causes a time lag before the temperature of the bath reaches that of the sample. The result is a cyclical(approximating a sinusoidal curve) variation of temperature difference on both sides of the null temperature differential. The summation of the product of time and temperature variation from zero(i.e., the sum of the areas under the differential temperature curve) of the temperature differential averages out to zero. The temperature differential in the system is maintained within $\pm$0.25°F.

The electrical wiring diagrams of the sample and bath heating circuits are shown in Figure 3. Figure 4 is a photograph of the assembled calorimeter and the auxiliary equipment.

V EXPERIMENTAL PROCEDURE

The tared sample container is filled with sample liquid to within one inch of the top(approximately 500 grams) and weighed to 0.1 gram. The sample container with heater and stirrer is seated in the intermediate cup, and the cup lid is then bolted in place. This is then immersed, on its platform, in the oil bath. The bath heaters and stirrers are put into the bath and the assembly is closed as shown in Figure 4 with auxiliary equipment attached and connected.

Initially the stirrers and the Brown Electronik Controller are started. The Controller will indicate whether a temperature differential exists and its direction. Power is then supplied to the sample heater(about 8.5 watts) or to the bath heaters(about 60 volts) depending on which is cooler. As soon as the temperature differential has been nullified the other heater or heaters are turned on. The bath heaters are then controlled automatically.

Temperature and power readings are recorded at ten minute intervals over the desired temperature range.

VI CALIBRATION AND CALCULATION

Since data in the literature were available for the heat capacities of water, castor oil, and linseed oil, these materials were used to calibrate the calorimeter. The liquids used were of the following purities: distilled water, USP grade castor oil, and linseed oil purchased under Contract AF(33-616)52-1025LP. Measurements were made over the following temperature ranges:

a.	Castor oil:	130°-301°F
b.	Castor oil:	202-447°F
c.	Castor oil:	308°-506°F
d.	Water:	90°-162°F
e.	Linseed oil:	162°-252°F
f.	Linseed oil:	199°-335°F
g.	Linseed oil:	253-440°F

The time-temperature data were smoothed by putting the best curve through the data. The determination of the equation best fitting the time-temperature data was done both graphically and analytically(using a least squares statistical analysis of the data). Although both methods approximated each other the least least squares statistical analyses were used because they were considered to be more accurate.

Data for the heat capacities of castor oil and linseed oil were obtained from Industrial and Engineering Chemistry(3), and data for water were taken from the Chemical Engineers Handbook(15). The literature data for each material were treated by a least squares statistical analysis in order to produce curves which best fit the data.
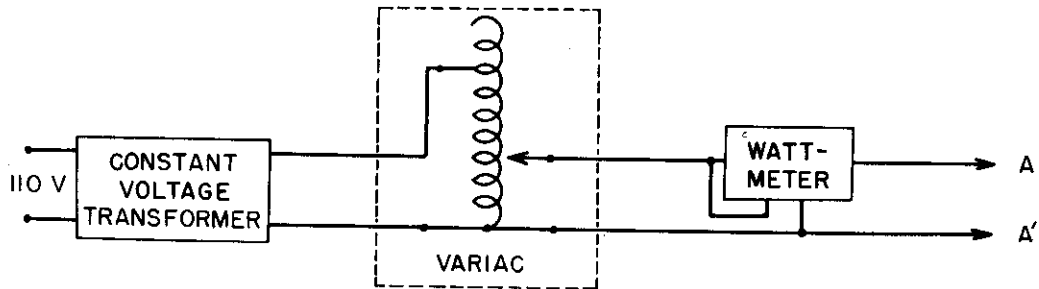
SAMPLE HEATING CIRCUIT
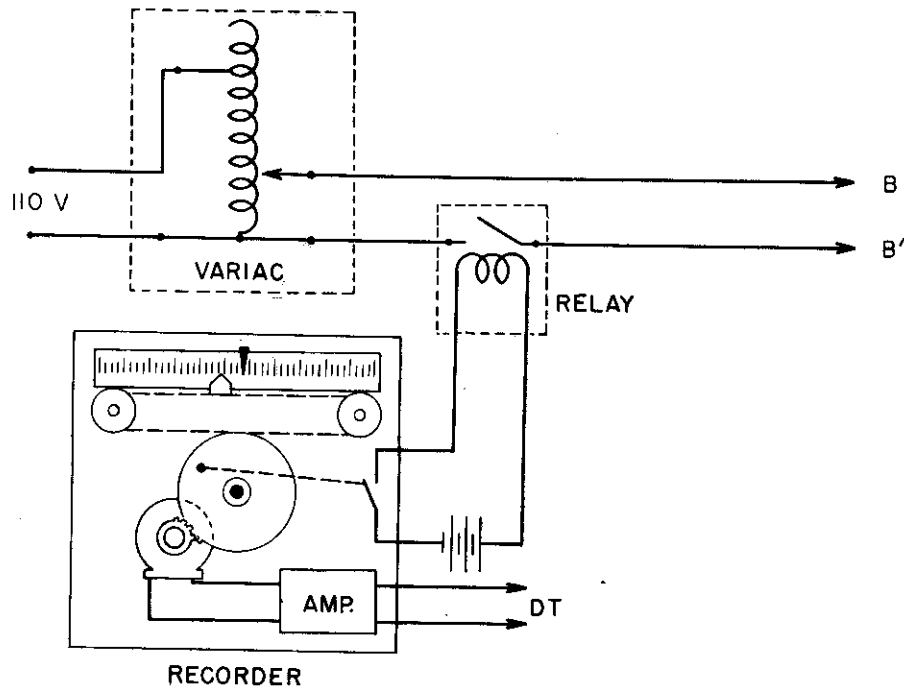
FIGURE 3. BATH HEATING CIRCUIT
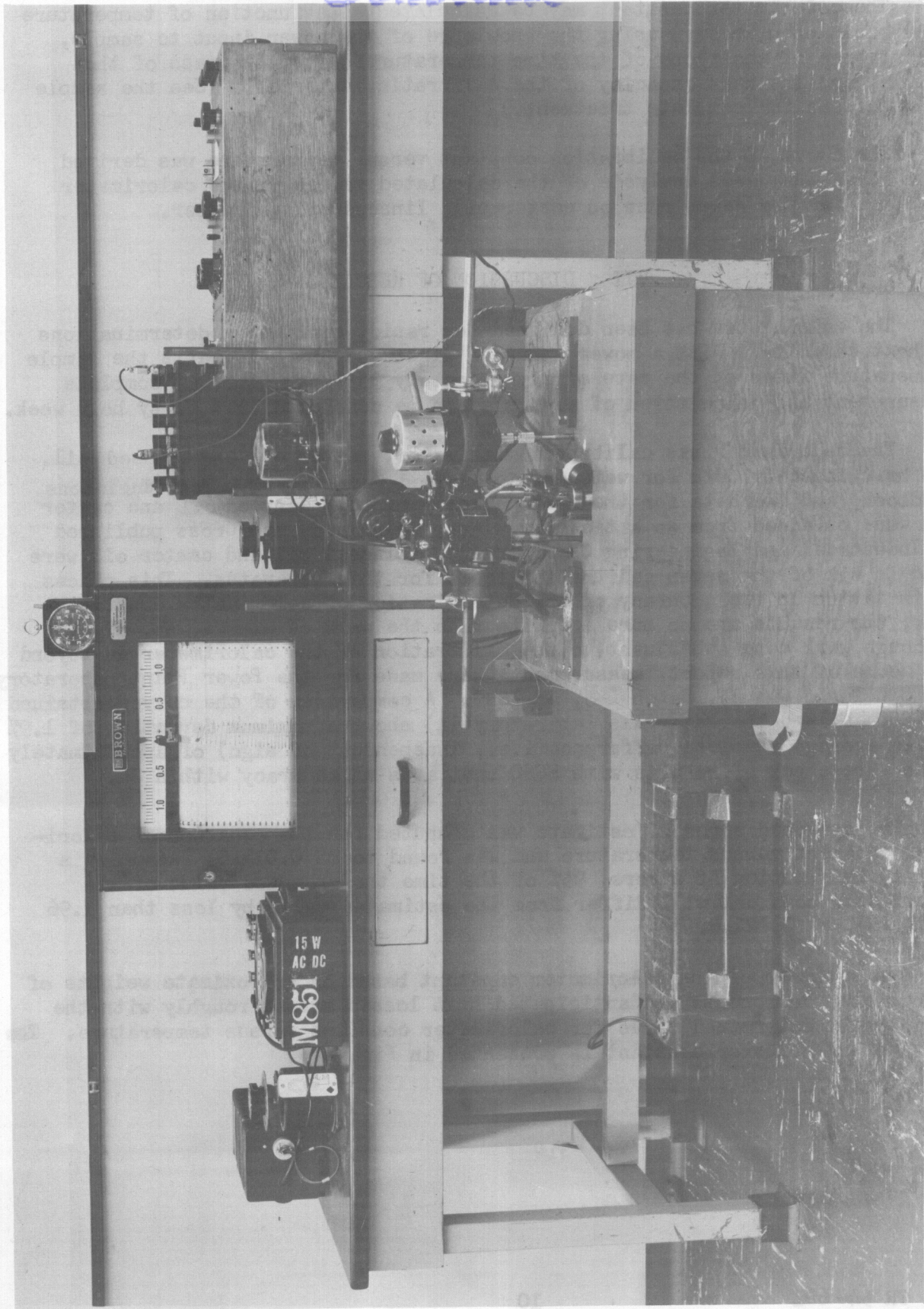
FIGURE 4 ASSEMBLED CALORIMETER AND AUXILIARY EQUIPMENT

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The calorimeter constant may be calculated as a function of temperature (see equation 6,Theory) using the knowledge of the power input to sample, the inverse of the slope of the time—temperature curve, the mass of the sample, and the heat capacity of the calibrating material. (See the sample calculations for complete treatment.)

The curve of the calibration constant versus temperature was derived from a least squares analysis of the calculated values of the calorimeter constant for the seven runs on castor oil, linseed oil and water.

VII   DISCUSSION OF RESULTS

The calorimeter has been designed for rapid, continuous determinations of heat capacity. With a power input of eight and one half watts the sample temperature rises at the rate of approximately 35°F per hour. A complete measurement and calculation of a sample can be completed in a forty hour week.

The calorimeter was calibrated with water, castor oil and linseed oil. The heat capacity data for water were obtained from the Chemical Engineers Handbook, and the data for the heat capacity of both linseed oil and castor oil were obtained from an article by Clark, Waldeland, and Cross published in Industrial and Engineering Chemistry(3). Linseed oil and castor oil were used in six of the seven calibration tests for this apparatus. This places a limitation on the accuracy of the determination of calorimeter constant, i.e., the results are no more accurate than the work of Clarke, et. al. Although work done subsequent to the calibration of the calorimeter is beyond the scope of this report, measurements were made for the Power Plant Laboratory on ESSO Turbo Oil 15, Batch L—5, CK 1889. A comparison of the curves obtained by ESSO (19)and the Materials Laboratory(14) shows a maximum deviation of 1.9% and an average absolute difference(i.e., independent of sign) of approximately 0.7%. The check of results with ESSO indicates an accuracy within 2%.

The standard error of estimate was computed for the equation of calorimeter constant versus temperature and was found to be 0.01146. Assuming a normal distribution of errors, 95% of the time the observed value of the calorimeter constant will differ from the estimated value by less than 1.96 (0.01146) = 0.02246.

An estimate of the calorimeter constant based on approximate weights of calorimeter components and anticipated heat losses agrees roughly with the empirically determined curve for calorimeter constant versus temperature. The curve of calorimeter constant is presented in Figure 5.

$$k_c = 0.256 - 0.00003706\ t + 0.0000006839\ t^2$$
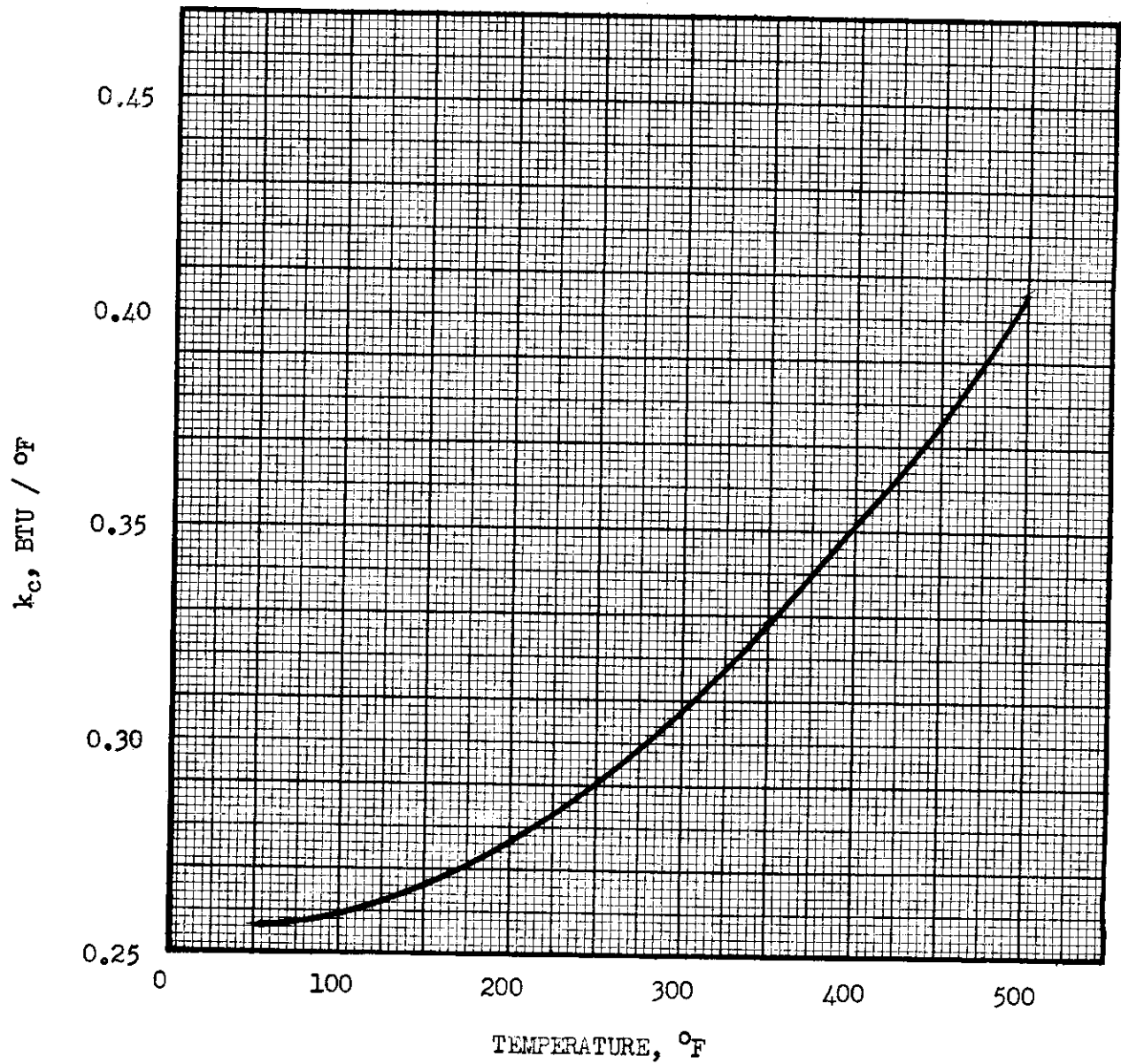
TEMPERATURE, $^{\circ}F$

FIGURE 5

CALORIMETER CONSTANT VS. TEMPERATURE

I. Sample Calculations:

A. Treatment of time-temperature data

1. It is desirable, in the calculation of the calorimeter constant, to have the variation of the change time relative to the change in temperature, i.e., $d\theta/dt$ versus θ.

During the experimental runs time, temperature and power were recorded as illustrated in Table I for Linseed Oil Run No. 2.

TABLE I

Data From Linseed Oil Run No. 2

θ,Min.	Millivolts	T,°F	P,Watts	θ,Min.	Millivolts	T,°F	P,Watts
0	4.891	199.0	8.46	110	6.849	263.7	8.39
10	5.073	205.0	8.45	120	7.021	269.3	8.39
20	5.256	211.3	8.44	140	7.366	280.9	8.37
30	5.438	217.2	8.44	150	7.532	285.7	8.37
40	5.619	223.0	8.44	170	7.870	297.3	8.35
50	5.797	229.0	8.43	190	8.202	308.1	8.35
60	5.976	235.0	8.42	200	8.370	313.7	8.35
70	6.150	240.7	8.42	210	8.537	319.3	8.33
80	6.326	246.6	8.40	220	8.699	324.4	8.33
90	6.500	252.1	8.40	231	8.877	330.3	8.32
100	6.678	258.1	8.40	240	9.018	335.0	8.32

The best curve fitting the data was obtained by a least square statistical analysis of the data. The data were fitted to a polynomial of the following general form:

$$Y = A_0 N + A_1 x + A_2 x^2 + \ldots\ldots + A_n x^n$$

It was found generally that a second degree equation satisfactorily fit the data. $d\theta/dt$ versus time was found as follows:

a. $\Sigma\theta, \Sigma\theta^2, \Sigma\theta^3, \Sigma\theta^4, \Sigma t\theta, \Sigma t\theta^2$, N were calculated(See Table II)

b. The regression coefficients were obtained by solving the following three simultaneous equations:

$$\Sigma t = A_0 N + A_1 \Sigma\theta + A_2 \Sigma\theta^2$$
$$\Sigma\theta t = A_0 \Sigma\theta + A_1 \Sigma\theta + A_2 \Sigma\theta^3$$
$$\Sigma\theta^2 t = A_0 \Sigma\theta^2 + A_1 \Sigma\theta^3 + A_3 \Sigma\theta^4$$

c.   The equation of the curve best fitting the data assumes the form

$$t = A_0 + A_1\theta + A_2\theta^2$$

and differentiating

$$\frac{dt}{d\theta} = A_1 + 2A_2\theta$$

d. $d\theta/dt$ as a function of time is

$$\frac{d\theta}{dt} = \frac{1}{A_1 + 2A_2\theta}$$

2.   Table II

Data Analysis for Linseed Oil Run No. 2

θ	θ^2	θ^3	θ^4	t	$t\theta$	$t\theta^2$
0	0	0	0	199.0	0	0
1×10	1×10^2	1×10^3	1×10^4	205.0	205.0×10	205.0×10^2
2	4	8	16	211.3	422.6	845.2
3	9	27	81	217.2	651.6	1954.8
4	16	64	256	223.0	892.0	3568.0
5	25	125	625	229.0	1145.0	5725.0
6	36	216	1296	235.0	1410.0	8460.0
7	49	343	2401	240.7	1684.9	1179 3
8	64	512	4096	246.6	1972.8	1582.4
9	81	729	6561	252.1	2268.9	20420.1
10	100	1000	10000	258.1	2581.0	25810.0
11	121	1331	14641	263.7	2900.7	31907.7
12	144	1728	20736	269.3	3231.6	38779.2
14	196	2744	38416	280.9	3932.6	55056.4
15	225	3375	50625	285.7	4285.5	64282.5
17	289	4913	83521	297.3	5054.1	85919.7
19	361	6859	130321	308.1	5853.9	111224.1
20	400	8000	160000	313.7	6274.0	125480.0
21	441	9261	194481	319.3	6705.3	140811.3
22	484	10648	234256	324.4	7136.8	157009.6
23.1	533.6	12326.16	284734.296	330.3	7629.9	176248.1
24	576	13824	331776	335.0	8040.0	192960.0

$\Sigma\theta = 2531$ $\Sigma t = 5844.7$

$\Sigma\theta^2 = 415560$ $\Sigma\theta t = 742782$

$\Sigma\theta^3 = 78034160$ $\Sigma\theta^2 t = 127424340$

$\Sigma\theta^4 = 15688403000$ $N = 22$

3. Simultaneous Equations and Solution

1. $5844.7 = A_0(22) + A_1(2531.0) + A_2(415560)$
2. $742782 = A_0(2531.0) + A_1(415560) + A_2(78034160)$
3. $127424340 = A_0(415560) + A_1(78034160) + A_2(15688403000)$

$$A_0 = 199.117$$
$$A_1 = 0.60487$$
$$A_2 = -0.00016073$$

4. Time—Temperature Equation

$$t = 199.117 + 0.60487\theta - 0.00016073\theta^2$$
$$dt/d\theta = 0.60487 - 0.0003214\theta$$
$$\frac{d\theta}{dt} = 1/[0.6049 - 0.0003214\theta]$$

5. The foregoing treatment of the time—temperature data is applied to the data obtained for three castor oil runs, three linseed oil runs, and one water run.

B. **Sample calculation of calorimeter constant**

The calorimeter constant may be determined from equation 6 as was developed in the Theory Section. The equation is as follows:

$$K(t) = P \, d\theta/dt - MCp(t) - L \, dm/dt$$

For the run on Linseed Oil No. 2 the term Ldm/dt was determined to be negligible because both the rate of mass loss with temperature and the heat of vaporization were small.

The equation then reduces to:

$$K(t) = P/[A_1 + 2A_2\theta] - (m - dm/d\theta)Cp(t)$$

The mass loss was assumed to be a linear function of time. The basis of this assumption is that vaporization occurred at the surface of the sample liquid which was in immediate contact with the sample heater and that the surface temperature of the heater is essentially constant.

For the time increment 20—30 minutes during Linseed Oil Run No. 2

$$P \text{ avg} = 8.44 \text{ watts}$$
$$\theta \text{ avg} = 25 \text{ minutes}$$
$$t \text{ avg} = 214.3 \text{°F}$$

$$P = 8.44 \text{ watts} \times 3.413 \frac{Btu}{Watt-hr} \times \frac{hr}{60 \text{ min}}$$

$$= (8.44)(0.0569) = 0.4802 \text{ Btu/Min}$$
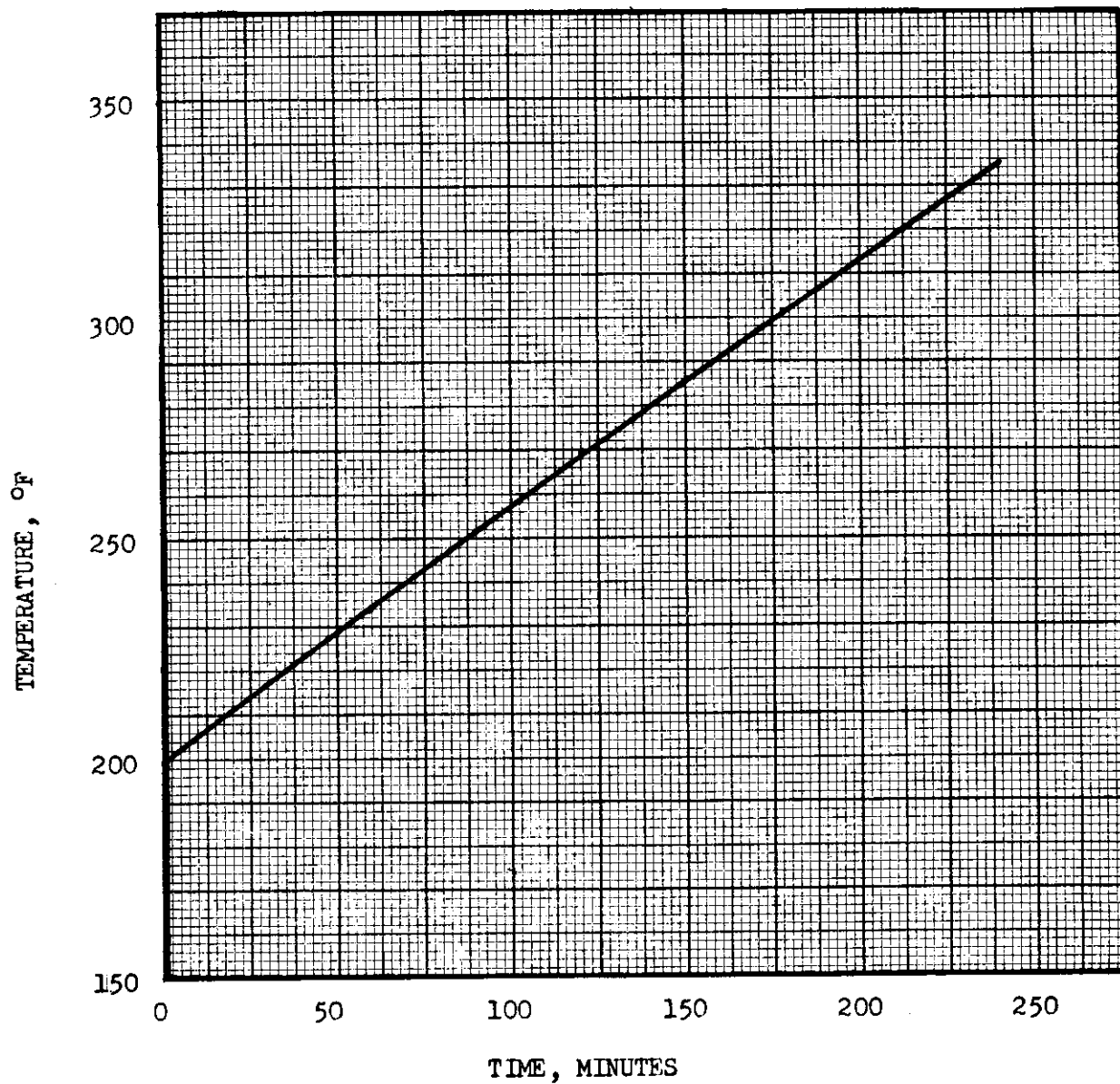
TIME, MINUTES

FIGURE 6

TIME-TEMPERATURE CURVE LINSEED OIL RUN NO. 2

Heat Capacity of Linseed Oil at t avg = 214.3°F
$$C_p(t) = 0.510 \text{ Btu/(lb)(°F)}$$

See Figure 7 for heat capacity versus temperature for Linseed Oil.

Original mass = 1.0444 pounds.

Mass loss at 25 minutes = 0.0001 pounds.

$$\frac{d\theta}{dt} = \frac{1}{0.6049 - 0.0003214(214.3)} = 1.675 \quad \frac{\text{min.}}{°F}$$

$$K(t) = (0.4802)(1.675) - (1.0443)(0.510)$$

$$K(t) = (0.272 \text{ Btu/°F at } 214.3 \text{ °F})$$

The variation of calorimeter constant versus temperature was found in the same manner as the equations of time versus temperature were obtained.

II.   Equations of time vs temperature data:

The time versus temperature relations for the seven experimental runs are listed below.

Linseed Oil Run No. 1
$$t = 161.95 + 0.6891\theta - 0.0003280\theta^2$$

Linseed Oil Run No. 2
$$t = 199.1 + 0.6049\theta - 0.0001607\theta^2$$

Linseed Oil Run No. 3
$$t = 253.4 + 0.5688\theta - 0.0001373\theta^2$$

Water
$$t = 90.2 + 0.3524\theta$$

Castor Oil Run No. 1
$$t = 131.6 + 0.5946\theta - 0.0001134\theta^2$$

Castor Oil Run No. 2
$$t = 202.7 + 0.5453\theta - 0.0007936\theta^2$$

Castor Oil Run No. 3
$$t = 308.1 + 0.5640\theta - 0.9 \times 10^{-4}\theta^2 - 0.15 \times 10^{-6}\theta^3$$

TABLE III

Tabulated Data and Calculation of Calorimeter Constant Linseed Oil Run No. 1

θ Min.	P Watts	dθ/dt Min./°F	P Btu/Min.	Pdθ/dt Btu/°F	m-dm** lbs	tm °F	Cp(s)tm* (Btu/lb)(°F)	(m-dm)Cp Btu/°F	Kc = Pdθ/dt-(m-dm)Cp Btu/°F
5	8.98	1.458	0.5109	0.7449	1.0448	165.3	0.495	0.5127	0.228
15	8.995	1.472	0.5118	0.7534	1.0447	172.1	0.497	0.5129	0.234
25	8.99	1.486	0.5115	0.7601	1.0447	178.9	0.499	0.5213	0.239
35	8.985	1.501	0.5112	0.7678	1.0447	185.7	0.501	0.5234	0.244
45	8.98	1.516	0.5109	0.7745	1.0447	192.6	0.503	0.5255	0.249
55	8.975	1.531	0.5106	0.7817	1.0446	199.1	0.505	0.5275	0.254
65	8.97	1.547	0.5103	0.7897	1.0446	205.5	0.507	0.5296	0.260
75	8.965	1.563	0.5101	0.7973	1.0446	212.0	0.509	0.5317	0.266
85	8.96	1.579	0.5098	0.8050	1.0445	218.2	0.511	0.5337	0.271
95	8.96	1.595	0.5092	0.8122	1.0445	224.5	0.513	0.5358	0.276
105	8.93	1.612	0.5081	0.8190	1.0445	230.6	0.514	0.5374	0.282
115	8.92	1.629	0.5075	0.8267	1.0445	236.8	0.516	0.5390	0.288
125	8.915	1.647	0.5072	0.8353	1.0444	242.8	0.518	0.5410	0.294
135	8.91	1.665	0.5069	0.8440	1.0444	248.8	0.520	0.5431	0.301

* Value of Cp for linseed oil obtained from the literature

** A slight loss in weight of the sample due to splashing is taken into account.

TABLE IV

Tabulated Data and Calculation of Calorimeter Constant — Linseed Oil Run No. 2

θ Min	P×0.056896 Btu/Min	dθ/dt	Pdθ/dt	** m-dm	T_m, °F	*C_p at T_m	(m-dm)C_p	*** Pdθ/dt-(m-dm)C_p
5	0.4810	1.658	0.7975	1.0444	201.6	0.505	0.5274	0.270
25	0.4802	1.675	0.8043	1.0443	214.3	0.510	0.5326	0.272
55	0.4793	1.703	0.8162	1.0442	232.0	0.515	0.5378	0.278
85	0.4779	1.731	0.8272	1.0441	249.5	0.520	0.5429	0.284
115	0.4774	1.761	0.8407	1.0441	266.3	0.525	0.5481	0.293
145	0.4762	1.791	0.8529	1.0440	283.3	0.530	0.5533	0.300
175	0.4751	1.823	0.8661	1.0439	300.0	0.535	0.5584	0.308
205	0.4742	1.855	0.8796	1.0438	316.8	0.540	0.5636	0.316
235	0.4734	1.889	0.8942	1.0437	333.0	0.545	0.5688	0.325

*   Values for C_p of linseed oil obtained from the literature
**   A slight loss in weight of the sample due to splashing is taken into account.
*** Calorimeter Constant

TABLE V

Tabulated Data and Calculation of Calibration Constant — Linseed Oil Run No. 3

θ Min	P Watts	dθ/dt	P Btu/Min	P dθ/dt	m-dm**	Tm°F	Cp at Tm*	(m-dm)Cp	$\frac{P d\theta/dt}{-(m-dm)Cp}$ ***
5	8.935	1.762	0.4776	0.8415	1.0437	259.0	0.523	0.5458	0.296
35	8.370	1.788	0.4762	0.8514	1.0436	273.4	0.527	0.5500	0.301
65	8.370	1.815	0.4762	0.8643	1.0435	290.0	0.532	0.5551	0.309
95	8.345	1.843	0.4748	0.8750	1.0434	308.0	0.538	0.5613	0.314
125	8.320	1.871	0.4734	0.8857	1.0433	323.1	0.542	0.5655	0.320
155	8.345	1.900	0.4748	0.9021	1.0432	339.0	0.547	0.5706	0.331
185	8.315	1.931	0.4731	0.9136	1.0432	354.8	0.552	0.5758	0.338
215	8.310	1.962	0.4728	0.9276	1.0431	370.5	0.556	0.5800	0.348
245	8.300	1.994	0.4722	0.9416	1.0430	385.0	0.560	0.5840	0.358
275	8.285	2.027	0.4714	0.9555	1.0429	399.8	0.565	0.5892	0.366
305	8.285	2.062	0.4714	0.9720	1.0428	414.2	0.569	0.5934	0.379

* Values of Cp for linseed oil obtained from the literature

** A slight loss in weight of the sample due to splashing is taken into account.

*** Calorimeter constant

TABLE VI

Tabulated Data and Calculation of Calorimeter Constant — Water

θ Min	P Watts	Pdθ/dt Btu/Min	** m—dm	Tm°F	* Cp at Tm	(m—dm)Cp	Pdθ/dt *** —(m—dm)Cp
10	8.495	1.371	1.0860	91.8	0.9986	1.0845	0.286
20	8.48	1.369	1.0856	95.3	0.9986	1.0841	0.285
30	8.465	1.366	1.0857	98.8	0.9986	1.0837	0.282
40	8.46	1.365	1.0847	102.4	0.9986	1.0832	0.282
50	8.455	1.365	1.0843	105.9	0.9987	1.0829	0.282
60	8.44	1.362	1.0839	109.4	0.9988	1.0826	0.279
70	8.43	1.361	1.0835	112.9	0.9989	1.0823	0.279
80	8.43	1.361	1.0830	116.5	0.9990	1.0819	0.279
90	8.425	1.360	1.0826	120.0	0.9991	1.0816	0.278
100	8.425	1.360	1.0822	123.5	0.9992	1.0813	0.279
110	8.42	1.359	1.0818	127.0	0.9994	1.0812	0.278
120	8.405	1.356	1.0814	130.6	0.9995	1.0808	0.275
130	8.40	1.356	1.0810	134.18	0.9997	1.0807	0.275
140	8.40	1.356	1.0805	137.6	0.9999	1.0804	0.276
160	8.395	1.355	1.0797	144.6	1.0003	1.0800	0.275
170	8.39	1.354	1.0793	148.2	1.0005	1.0798	0.274
180	8.385	1.353	1.0788	151.7	1.0007	1.0796	0.273
190	8.38	1.352	1.0784	155.2	1.0010	1.0795	0.272
200	8.38	1.352	1.0780	158.8	1.0030	1.0712	0.271
210	8.38	1.352	1.0776	162.3	1.0060	1.0841	0.268

   *   Values of Cp of water obtained from the literature
  ** A slight loss in weight of sample due to splashing
        is taken into account
*** Calorimeter Constant

TABLE VII

Tabulated Data and Calculation of Calorimeter Constant — Castor Oil Run No. 1

θ Min	P(0.056896)	$d\theta/dt$	$Pd\theta/dt$	m-dm **	T_m °F	Cp at T_m *	(m-dm)Cp	$\dfrac{Pd\theta/dt}{-(m-dm)Cp}$ ***
5	0.4603	1.685	0.7756	0.97907	134.5	0.525	0.5140	0.262
35	0.4603	1.704	0.7843	0.97887	152.0	0.532	0.5208	0.264
65	0.4603	1.724	0.7936	0.97862	169.6	0.539	0.5275	0.266
95	0.4603	1.745	0.8032	0.97838	187.0	0.545	0.5332	0.270
125	0.4603	1.766	0.8129	0.97814	204.0	0.550	0.5380	0.275
155	0.4603	1.787	0.8226	0.97790	221.5	0.554	0.5418	0.281
185	0.4603	1.809	0.8327	0.97765	238.0	0.558	0.5455	0.287
215	0.4603	1.832	0.8433	0.97741	253.9	0.561	0.5483	0.295
245	0.4603	1.855	0.8538	0.97717	270.2	0.563	0.5501	0.304
275	0.4603	1.879	0.8649	0.97693	286.5	0.566	0.5529	0.312
295	0.4603	1.895	0.8723	0.97677	297.2	0.568	0.5548	0.317

*   Values for Cp of Castor Oil obtained from the literature

**   A slight loss in weight of the sample due to splashing is taken into account

***   Calorimeter constant

TABLE VIII

Tabulated Data and Calculation of Calorimeter Constant — Castor Oil Run No. 2

θ Min	P, Btu/Min 0.4461	dθ/dt	Pdθ/dt	m-dm**	T_m °F	Cp at T_m *	(m-dm)Cp	Pdθ/dt÷**(m-dm)Cp
5	0.4461	1.836	0.8190	0.9768	205.3	0.550	0.5372	0.282
35		1.853	0.8265	0.9765	221.9	0.554	0.5410	0.286
65		1.869	0.8337	0.9763	238.0	0.558	0.5448	0.289
95		1.886	0.8413	0.9760	253.8	0.560	0.5466	0.295
125		1.903	0.8489	0.9758	269.8	0.563	0.5494	0.299
155		1.920	0.8565	0.9755	285.1	0.566	0.5521	0.304
185		1.938	0.8645	0.9753	300.9	0.568	0.5540	0.310
215		1.956	0.8726	0.9751	316.0	0.571	0.5568	0.316
245		1.975	0.8815	0.9748	331.0	0.574	0.5595	0.322
275		1.994	0.8895	0.9746	346.6	0.577	0.5623	0.327
305		2.012	0.8975	0.9743	361.9	0.580	0.5651	0.332
335		2.032	0.965	0.9741	376.4	0.584	0.5689	0.338
365		2.052	0.9154	0.9738	391.6	0.589	0.5736	0.342
395		2.072	0.9243	0.9736	406.0	0.594	0.5783	0.346
425		2.093	0.9337	0.9734	420.2	0.600	0.5840	0.350
455		2.114	0.9430	0.9731	434.4	0.607	0.5907	0.352
475		2.128	0.9493	0.9729	441.8	0.611	0.5944	0.355

*   Values of Cp for Castor Oil obtained from the literature

**   A slight loss in weight of the sample due to splashing is taken into account.

*** Calorimeter Constant

TABLE IX

Tabulated Data and Calculation of Calibration Constant — Castor Oil Run No. 3

θ Min	P Watts	m-dm**	CpatTm*	Tm°F	(m-dm)Cp	dθ/dt	Pdθ/dt	Pdθ/dt***/-(m-dm)Cp
5	8.50	0.9720	0.570	310.9	0.5540	1.773	0.8574	0.303
15	8.48	0.9719	0.571	316.5	0.5549			
25	8.46	0.9718	0.572	321.9	0.5559			
35	8.46	0.9719	0.573	327.3	0.5568			
45	8.455	0.9716	0.574	332.8	0.5577			
55	8.445	0.9716	0.575	338.5	0.5587	1.805	0.8673	0.309
65	8.44	0.9715	0.576	344.0	0.5596			
75	8.435	0.9714	0.577	349.5	0.5605			
85	8.43	0.9713	0.578	355.0	0.5614			
95	8.425	0.9712	0.580	360.6	0.5633			
105	8.415	0.9711	0.581	366.2	0.5642	1.845	0.8833	0.319
115	8.415	0.9711	0.583	371.7	0.5661			
125	8.415	0.9710	0.585	377.2	0.5680			
135	8.405	0.9709	0.586	382.7	0.5689			
145	8.40	0.9708	0.588	388.2	0.5708			
155	8.395	0.9707	0.590	393.5	0.5727	1.897	0.9061	0.333
165	8.395	0.9707	0.592	398.6	0.5746			
175	8.40	0.9706	0.594	403.7	0.5765			
185	8.40	0.9705	0.596	408.6	0.5784			
195	8.395	0.9704	0.598	413.6	0.5803			
205	8.385	0.9703	0.600	418.5	0.5822	1.961	0.9355	0.353
215	8.38	0.9703	0.602	423.4	0.5841			
225	8.375	0.9702	0.604	428.3	0.5860			
235	8.37	0.9701	0.606	433.2	0.5879			
245	8.365	0.9700	0.609	438.0	0.5907			
255	8.365	0.9699	0.611	442.9	0.5926	2.037	0.9695	0.377
265	8.375	0.9699	0.614	447.9	0.5955			
275	8.375	0.9698	0.617	452.8	0.5984			
285	8.365	0.9697	0.620	457.8	0.6012			
295	8.555	0.9696	0.622	462.7	0.6031			
305	8.345	0.9695	0.625	467.5	0.6059	2.127	1.0010	0.395

* Values of Cp for Castor Oil obtained from the literature

** A slight loss in weight of the sample due to splashing is taken into account

*** Calorimeter Constant

$$C_p = 0.4468 + 0.000290 \; t + 0.0000C0012 \; t^2$$
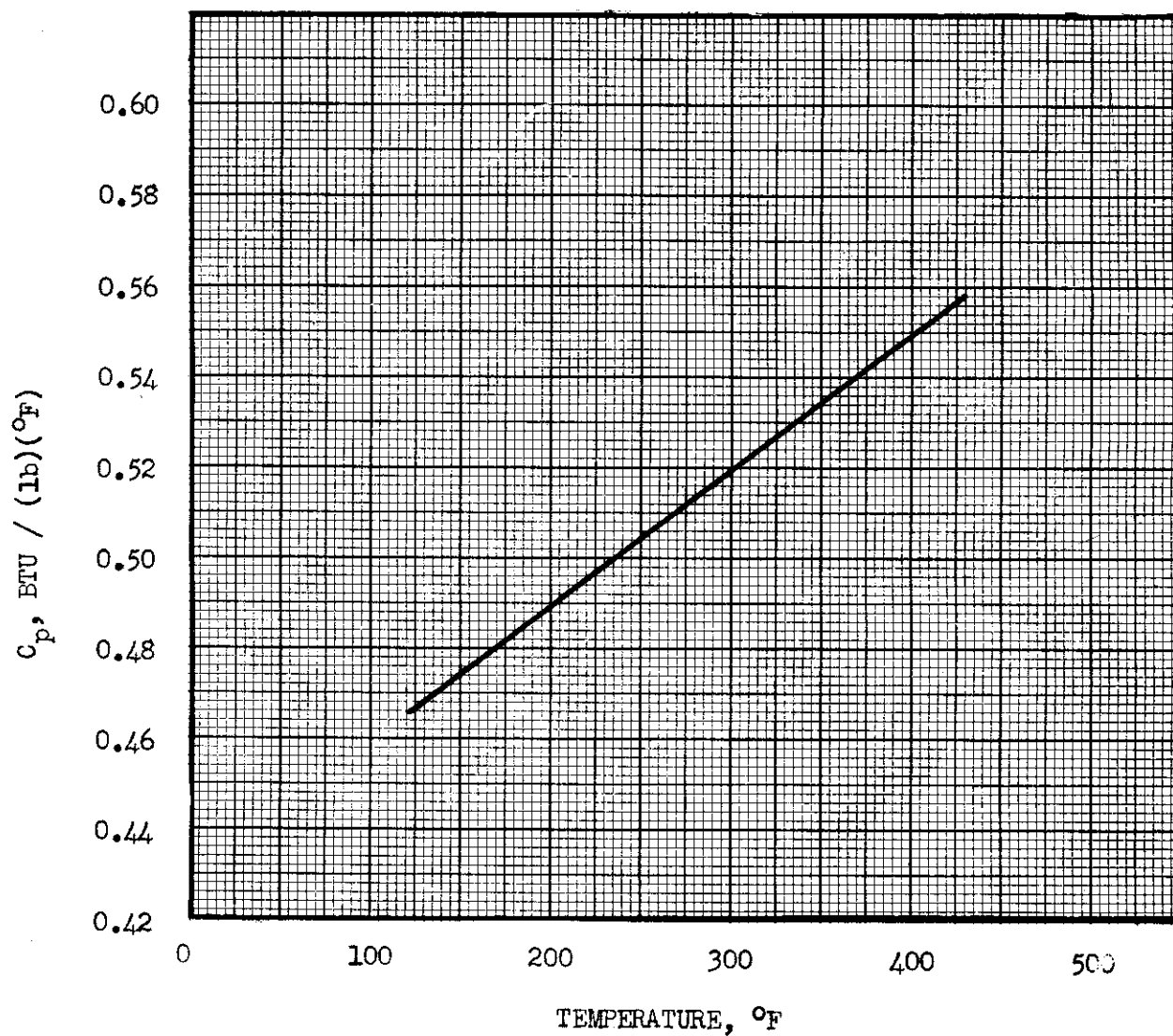

FIGURE 7

HEAT CAPACITY VS. TEMPERATURE LINSEED OIL

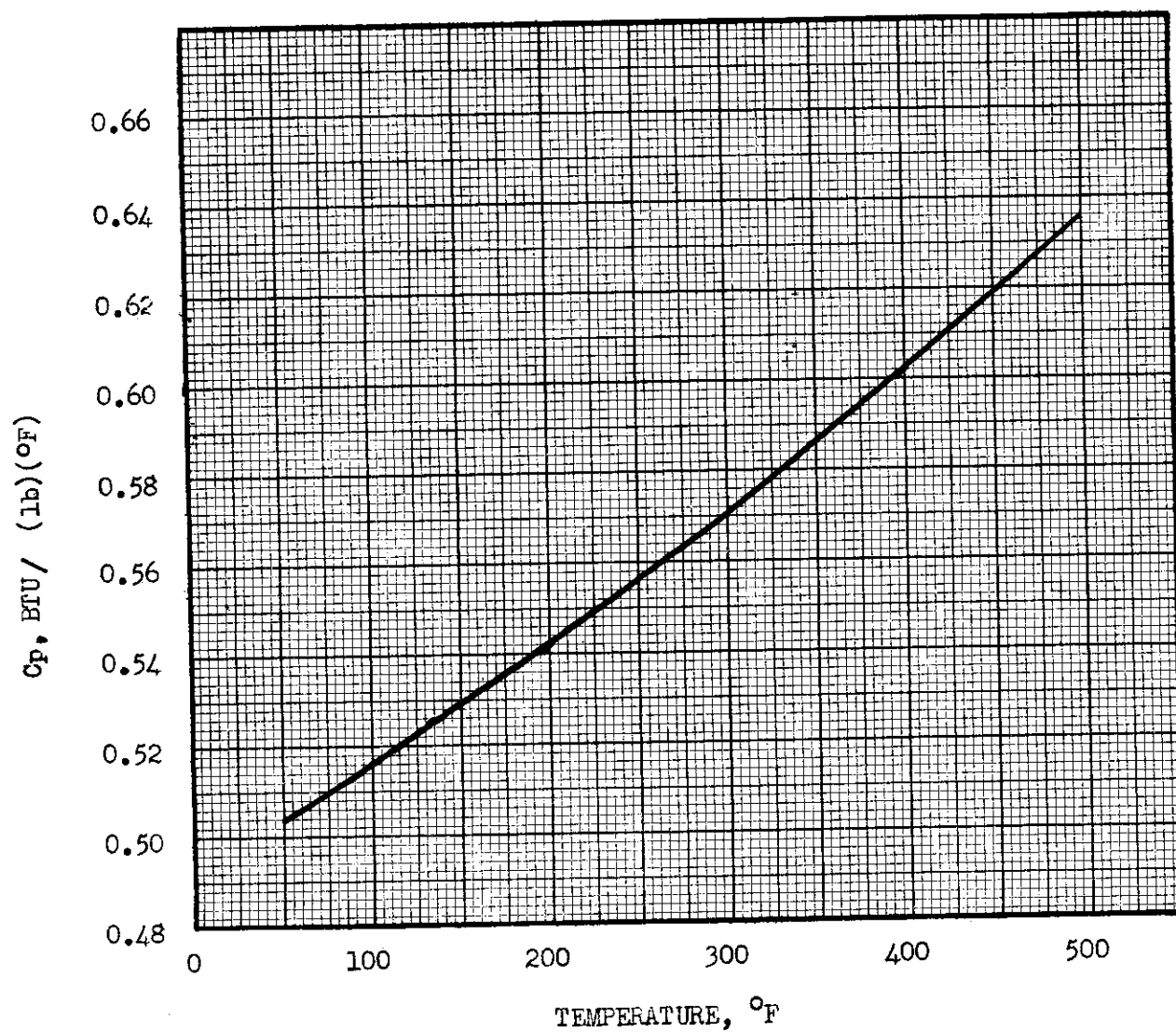$$c_p = 0.4930 + 0.0002075\ t + 0.0000001567\ t^2$$

FIGURE 8

HEAT CAPACITY VS. TEMPERATURE CASTOR OIL

Calculation of Equation of Calorimeter Constant vs Temp.

The method of least squares statistical analysis is applied to selected points of the seven runs to obtain a smoothed curve for the calorimeter constant as a function of temperature.

TABLE X

A. Calorimeter constant—temperature data analysis

t	K	t^2	t^3	t^4	tK_c	t^2K_c
134.5	0.262	1.809x10⁴	2.4331x10⁶	0.32725x10⁹	35.239	4.9376x10³
169.6	0.266	2.8764	4.8784	0.82738	45.114	7.6513
204.0	0.275	4.1616	8.4897	1.73189	56.100	11.4444
221.5	0.281	4.9062	10.8673	2.40711	63.570	14.0809
238.0	0.287	5.6644	13.4813	3.20855	68.306	16.2568
270.2	0.304	7.3008	19.7268	5.33018	82.141	22.1944
297.2	0.317	8.8328	26.2510	7.80180	94.212	27.9999
205.3	0.282	4.2148	8.6530	1.77646	57.895	11.8576
238.0	0.289	5.6644	13.4813	3.20855	68.782	16.3701
269.8	0.299	7.2792	19.6393	5.29868	80.670	21.7648
300.9	0.310	9.0541	27.2437	8.19763	93.279	28.0676
316.0	0.316	9.9856	31.5545	9.97122	99.856	31.5545
331.0	0.322	10.9561	36.2674	12.00362	106.582	35.2786
346.6	0.327	12.0132	41.6376	14.43159	113.338	39.2830
361.9	0.332	13.0972	47.3968	17.15356	120.151	43.4826
391.6	0.342	15.3350	60.0519	23.51631	130.927	52.4448
420.2	0.350	17.6568	74.1939	31.17626	147.070	61.7988
441.8	0.355	19.5187	86.2336	38.09800	156.839	69.2915
310.9	0.303	99.6658	30.0512	9.3429	94.203	29.2876
338.5	0.309	11.4582	38.7860	13.1291	104.596	35.4059
366.2	0.319	13.4102	49.1083	17.9835	116.818	42.7787
393.5	0.333	15.4842	60.9304	23.9761	131.036	51.5625
418.5	0.353	17.5142	73.2970	30.6748	147.730	61.8252
442.9	0.377	19.6160	86.8793	38.4788	166.973	73.9523
467.5	0.395	21.8556	102.1793	47.7668	184.662	86.3295
95.3	0.285	0.9082	0.8655	0.08248	27.160	2.5884
123.5	0.279	1.5252	1.8836	0.23263	34.456	4.2554
158.8	0.271	2.5217	4.0045	00.63592	43.035	6.8339

TABLE X (CONT'L)

t	K	t^2	t^3	t^4	tK_c	t^2K_c
165.3	0.228	2.7324	4.5167	0.74661	37.688	6.2299
192.6	0.249	3.7095	7.1445	1.37603	47.957	9.2366
218.2	0.271	4.7611	10.3887	2.26681	59.132	12.9026
248.8	0.301	6.1901	15.4010	3.83177	74.889	18.6323
201.6	0.270	4.0643	8.1936	1.65182	54.432	10.9735
232.0	0.278	5.3824	12.4872	2.89703	64.496	14.9631
266.3	0.293	7.0916	18.8848	5.02902	78.026	20.7783
283.3	0.300	8.0259	22.7373	6.44148	84.990	24.0777
300.0	0.308	9.0000	27.0000	8.10000	92.400	27.7200
333.0	0.325	11.0889	36.9260	12.2964	108.225	36.0389
259.0	0.296	6.7081	17.3740	4.49987	76.664	19.8560
290.0	0.309	8.4100	24.3890	7.07281	89.610	25.4869
323.1	0.320	10.4934	33.7297	10.89807	103.392	33.4060
339.0	0.331	11.4955	38.9812	13.21852	112.242	38.0613
354.8	0.338	12.5883	44.6633	15.84654	119.922	42.5483
385.0	0.358	14.8225	57.0666	21.97064	137.830	53.0646
414.2	0.379	17.1562	71.0610	29.43347	156.982	65.0219

$$\Sigma t = 13079.9 \qquad\qquad \Sigma K_c = 13.894$$
$$\Sigma t^2 = 4179518 \qquad\qquad \Sigma tk_c = 4172.617$$
$$\Sigma t^3 = 1431409460 \qquad\quad \Sigma t^2 K_c = 1370076.3$$
$$\Sigma t^4 = 516345980000 \qquad\quad n = 45$$

B. Simultaneous equations and solution

1. $13.894 = A_0(45) + A_1(13079.9) + A_2(4179518)$
2. $4172.617 = A_0(13709.9) + A_1(4179518) + A_2(1431409460)$
3. $1370076.3 = A_0(4179518) + A_1(1431409460) + A_2(516345980000)$

$$A_0 = 0.256005$$
$$A_1 = 0.0000370623$$
$$A_2 = 0.0000006839382$$

C. Variation of Calorimeter constant with temperature

$$k_c = 0.256 - 0.00003706t + 0.000006839t^2$$

D. The plot of the variation of the calorimeter constant with temperature is shown in Figure 5.

E. Computation of standard error of estimate, S_b:

$$S_b = \sqrt{\frac{(K_c - K_c^*)^2}{n-3}}$$

E.(CONT'D)

$$\sum (k_c - K_c^*)^2 = \sum (K_c)^2 - A_0 \sum K_c - A_1 \sum (t K_c) - A_2 \sum (t^2 K_c)$$

$$\sum (K_c - K_c^*)^2 = 4.344854 - (0.256005)(13.894) = 0.00552$$

$$S_b = \sqrt{\frac{0.00552}{(45-3)}} = 0.01146$$

Nomenclature

$C_p(t)$ —   heat capacity as a function of temperature, $Btu/(lb)(°F)$

H —   Sensible heat, Btu

$K(t)$ —   Calorimeter constant, $Btu/°F$

L —   heat of vaporization, Btu/lb

M —   Mass , lb.

P —   power, watts

Q —   heat input or loss, Btu

t —   temperature, °F

θ —   time, minutes
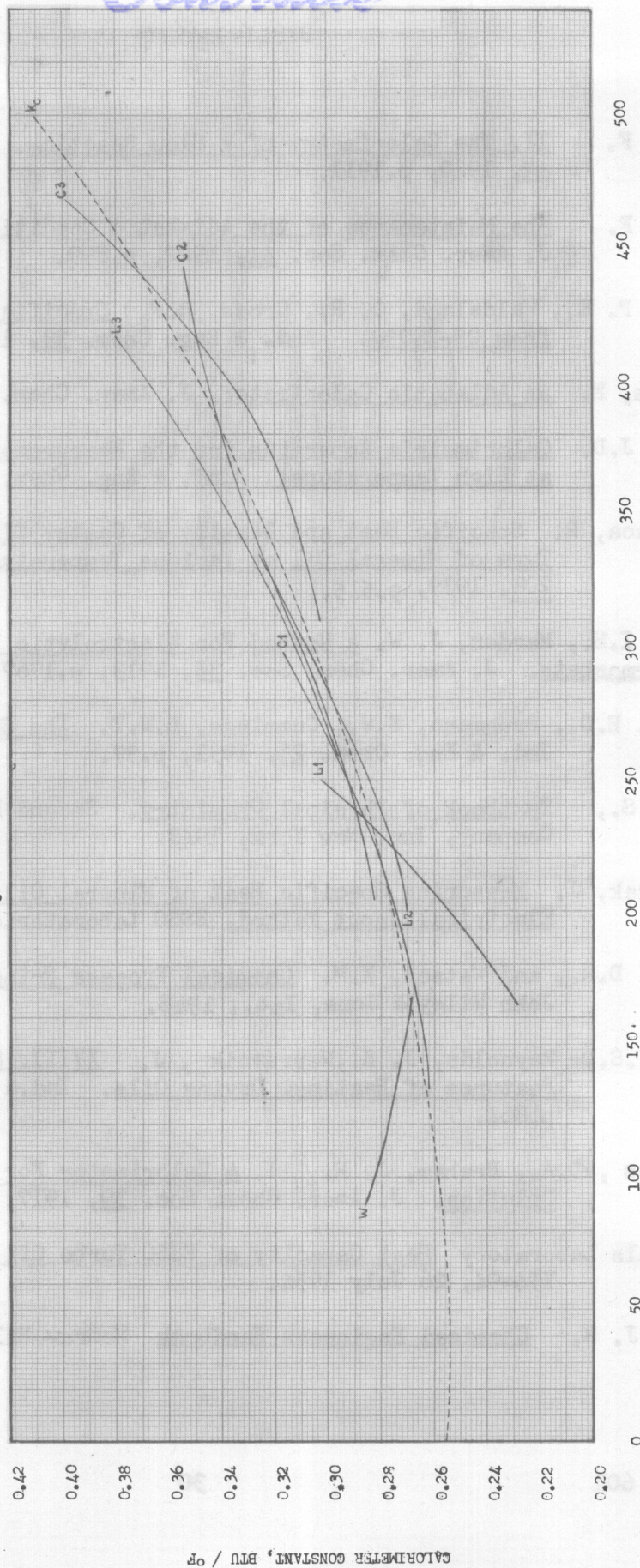
Subscripts

c —   calorimeter

s —   sample

COMPOSITE PLOT
CALORIMETER CONSTANT vs. TEMPERATURE

L1: LINSEED OIL RUN NO. 1
L2: LINSEED OIL RUN NO. 2
L3: LINSEED OIL RUN NO. 3
W: WATER
C1: CASTOR OIL RUN NO. 1
C2: CASTOR OIL RUN NO. 2
C3: CASTOR OIL RUN NO. 3

k_c, CALORIMETER CONSTANT

CALORIMETER CONSTANT, BTU / °F

TEMPERATURE, °F

FIGURE 9

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