

ISOBARIC HEAT CAPACITY AT BUBBLE POINT OF FOUR HYDROCARBONS

Thesis by

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Abstract

The isobaric heat capacity of the bubble-point liquid was determined for propene at temperatures from 80° to 160°F, and for neohexane, cyclohexane, and iso-octane in the temperature range from 80° to 200°F. An equation for obtaining the isobaric heat capacity has been derived which employs volumetric correction terms applied to the heat capacity of the substance as measured in an isochoric adiabatic calorimeter. The results are presented in both graphical and tabular form.

Introduction

The information available concerning the isobaric heat capacity of propene is limited to values below $\sim 40^{\circ}\text{F}$, while that for neohexane, cyclohexane, and iso-octane is available for temperatures up to 80°F . This investigation was carried out to supply the heat capacity data for higher temperatures.

In a constant-volume adiabatic calorimeter the energy required to heat the bomb and contents through a measured temperature interval was determined. It may be shown from the first law of thermodynamics and a material balance that the following equation obtains*.

$$\begin{aligned} C_{P_b} = & \frac{\frac{q_1}{dT} - \frac{q_2}{dT}}{m_1 - m_2} \left\{ \frac{V_d - V_b}{V_d} \right\} + T \left(\frac{\partial V}{\partial T} \right)_{P,b} \frac{dP''}{dT} \\ & + T \frac{dP''}{dT} \left[\frac{V_d \frac{dV_b}{dT} - V_b \frac{dV_d}{dT}}{V_d} \right] \\ & + \frac{V_b}{V_d} \left[C_{P_d} - T \left(\frac{\partial V}{\partial T} \right)_{P,d} \frac{dP''}{dT} \right] \end{aligned} \quad (1)**$$

Equation (1) requires a knowledge of the rate of energy addition as a function of temperature for two weights of material, $\left\{ \frac{\frac{q_1}{dT} - \frac{q_2}{dT}}{m_1 - m_2} \right\}$ which is subject to experimental measurement***.

* A detailed derivation of this equation is included in the Appendix

** Symbols used are listed at the end of the thesis

*** Since the heat capacity of the bomb is invariant with respect to the amount of material present, it may be eliminated from equation (1).

The volumetric behavior of the substance must also be known.

The volumetric data for propene were obtained from Farrington and Sage (1)*. It is estimated that these data represent the actual behavior of propene to within 0.3 per cent.

The volumetric and vapor pressure data for neohexane were taken from Kay (2). As there were no volumetric data available for the superheated region, the behavior in this region was estimated by the following method. Values of the compressibility factor (Z) were obtained from the known dew point volumes. These were then plotted vs. pressure and smooth curves drawn from the dew-point Z to the point at which Z = 1. These curves were drawn on the basis of an assumption that the behavior of the fluid was analogous to that of similar substances for which volumetric data were available. Then values of Z were taken from these curves at constant pressure and as a function of temperature. The volumes in the superheat region were then calculated from the Z values. It is believed that these data represent the actual behavior to within one per cent.

The volumetric data for cyclohexane were taken from Young (3). Volumes in the superheat region were estimated in the same manner as for neohexane. Vapor pressure data were obtained from the International Critical Tables (4).

Volumetric data for iso-octane at temperatures ranging from 80° - 200°F were not available in the literature. However, they were estimated by the following method. Accurate vapor pressure data and a value of the latent heat of vaporization at one temperature were obtained from Smith (5). Nutting (6) expressed the heat of vaporization as a function of the critical temperature

* The list of references is given following Page 11.

and temperature of the material. The critical constants for iso-octane were obtained from Gilliland and Parekh (7). By applying the Clapyron equation,

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V} \quad (2)$$

the change in volume (dew point volume less bubble point volume) may be determined. The bubble point volumes were taken from the International Critical Tables (8). The isobars in the superheat region were estimated by the law of corresponding states.

The heat capacity of the dew point gas for each of the materials was obtained from the literature (9, 10, 11, 12). These data were accurate to within 0.2 per cent. The only term of equation (1) involving a significant uncertainty is the isobaric volume temperature coefficient at dew point. The factor involving this term is multiplied by the ratio of the bubble point volume to the dew point volume. In the case of neo-hexane, cyclohexane, and iso-octane, this ratio is small, so that the entire term does not exceed 10 per cent of the total correction. Thus, if the maximum error in this coefficient is considered to be two per cent, the uncertainty introduced in the final answer is less than 0.2 per cent. In the case of propene, the ratio of the bubble to dew point volume is higher, so that the last term of equation (1) may be as high as 50 per cent of the total correction. This is compensated by the fact that the volumetric data for propene in the superheated region are directly available and the desired derivative may be determined within 0.2 per cent.

Apparatus

The calorimeter employed was described in previous publications (13 and 14). It consisted of a steel bomb, whose approximate volume was 18.3 cubic inches, which was mounted in a vacuum jacket. The bomb and jacket were immersed in an oil bath. A four-junction, copper-constantan thermocouple was mounted on the exterior of the bomb and interior of the jacket and was employed to determine the difference in temperature between them during the course of a set of measurements. A two-junction, copper-constantan thermocouple was mounted on the bomb and jacket, and was connected to a high-sensitivity, low-resistance galvanometer. The control of the addition of energy to the oil bath was by a conventional droop circuit. By this arrangement it was possible to maintain a very small temperature differential between the exterior of the bomb and the interior of the jacket. In general, the temperature difference was maintained at less than 0.3°F. The oil bath was installed in an air thermostat, which was held two or three degrees below the temperature of the oil bath. The calorimeter bomb was connected through a length of stainless steel tubing containing a needle valve, to a manifold which was used to admit the sample. All connecting lines and the needle valve were enclosed in a steam jacket to avoid any condensation in this part of the system. One side of the manifold was connected to a vacuum pump so that the bomb could be evacuated. The calorimeter was also connected through a mercury trap and an oil-filled line to the laboratory pressure balance. The pressure in the bomb was thus subject to measurement. The connecting line and the trap were also enclosed in a steam jacketed line to avoid condensation of the sample.

The heating element inside the bomb was constructed of constantan wire enclosed within a stainless steel tube. The energy added to the calorimeter electrically was measured by conventional volt box and standard resistance techniques. A type K-2 potentiometer (Leeds and Northrup) was used for this measurement. The time of addition of energy was measured by an electric timer. The differential temperature between the bomb and the jacket and the temperature of the liquid in the bomb were measured by means of a White double potentiometer.

Two weighing bombs of a type previously described (15) were used to admit and withdraw the various samples.

Large capacity storage batteries were used to supply current to the bomb heater, so that the current remained substantially constant over the period of a set of measurements.

Experimental Procedures

Samples were introduced into the bomb by high-vacuum and weighing-bomb techniques (15). The uncertainties introduced were believed to be less than 0.05 per cent. As an additional check, the samples were withdrawn at the conclusion of a set of measurements. The original weight was reproduced to within 0.1 per cent.

Energy was then added electrically to the material in the bomb. The current to the bomb heater was determined by measuring the current through the standard resistor, and correcting for the current through the volt box. The voltage across the bomb heater was determined by measuring the voltage across the volt box, correcting in this case for the resistance of the heater leads. The energy addition was known to within 0.02 per cent. The

time of energy addition was adjusted so that the temperature rise of the contents was from 5 to 7°F . A period of from 500 to 1000 seconds was then required to attain equilibrium conditions in the bomb. At the end of this period the change of temperature in the bomb with time was found to be less than 0.002°F per minute. During the energy addition and calming period, readings of the differential thermocouple (jacket to bomb) were taken every 100 seconds. The energy that the bomb lost by radiation was given by the equation:

$$\underline{Q}_R = K \int_{\theta_A}^{\theta_B} \Delta t_{\mu\nu} d\theta \quad (3)$$

The constant K was determined as follows. Equilibrium was established in the bomb and the differential thermocouple was caused to read as near to zero as possible. Keeping the temperature of the jacket constant, a known amount of energy was added to the bomb. Values of the differential thermocouple were plotted vs. time until the differential thermocouple again read zero. The results of such a determination are presented in Figure 1. White (16) showed that

$$\underline{Q} = K \left[\int_{\theta_0}^{\theta_A} \Delta t_{\mu\nu} d\theta + \int_{\theta_A}^{\theta_B} \Delta t_{\mu\nu} d\theta \right] \quad (4)$$

Where the interval 0 to A represents the period of energy addition and A to B the calming period. The areas under the curves may be computed, and with a knowledge of the energy added, the constant K may be determined.

The average value of K used in the calculations was 5.5×10^{-7} B.t.u. per microvolt-second. This value checked within one per cent, the value used by Schlinger (17), which he obtained in a different manner. The value of the radiation correction (Q_R) was usually not greater than one per cent of the total energy input. The uncertainty of the measurement of the net energy input was therefore less than 0.05 per cent.

The temperature of the contents of the calorimeter was measured at the beginning of the energy addition, and at the end of the calming period with an accuracy of $\pm 0.005^{\circ}\text{F}$. The temperature rise was adjusted so that the accuracy of its measurement was within 0.2 per cent. If one considers the small temperature interval, it may be seen that

$$\frac{q_{\text{Net}}}{dT} = \frac{Q_{\text{Net}}}{\Delta T} \quad (5)$$

The arithmetic mean of the initial and final temperature was taken as the temperature at which the heat capacity determined by equation (5) is valid.

This process was repeated until values of equation (5) were obtained throughout the temperature range of the investigation. The entire set of measurements was then repeated for a different weight of material.

The weight of material to be employed in each run was subject to two restrictions. Enough material had to be added to avoid the possibility of vaporizing all of the sample before the highest temperature of the run was reached. However, the upper limit of quantity of sample had to be known so that the possibility of having the bomb completely filled with the liquid phase could be ruled out. These extreme weights could easily be computed from a knowledge of the dew-point and bubble-point volumes

at the highest temperature expected to be reached. The critical mass to be employed lies between these limits and may be expressed as follows:

$$\frac{V}{V_b} > m_c > \frac{V}{V_d} \quad (6)$$

Materials

Propene (propylene)

The material was originally of research grade, and was purchased from the Phillips Petroleum Company, whose analyses indicated that it contained 99 mol per cent propene. This material was fractionated with a reflux ratio of 40 to 1 at atmospheric pressure in a low-temperature column packed with glass rings. Approximately 15 per cent of the overhead was discarded at the beginning of the fractionation, and about 20 per cent of the original amount was left in the kettle. The resulting material boiled within a range of 0.1°F. The propene was then subjected to a partial condensation at liquid air temperature to remove any dissolved non-condensable gases. In a similar purification Farrington (1) states that this purified material at 100°F showed less than 0.5 pound per square inch change in vapor pressure from bubble point to a quality of 0.5.

Neohexane (2,2 dimethyl butane)

The material was of technical grade, purchased from the Phillips Petroleum Company. The analysis of the substance showed that it contained not less than 95 mol per cent neohexane. It was fractionated twice at atmospheric pressure in a high temperature bubble plate column

at a reflux ratio of 5 to 1. Approximately 15 per cent of the overhead was discarded at the beginning of each fractionation. The variation of the boiling point was less than 0.1°F during the fractionation. The index of refraction was observed and agreed with values cited in the literature (18,19,20) within 0.02 per cent.

Cyclohexane (hexamethylene)

This material was of technical grade and obtained from the Eastman Kodak Company. Analyses showed it to be 97 per cent pure, with benzene as the probable impurity. It was fractionated in the same manner as was neohexane. The material boiled over a range of less than 0.1°F . The index of refraction was observed and compared with values found in the literature (20) within 0.05 per cent. It is estimated that the impurity was less than 0.1 mol per cent.

Iso-octane (2,2,4 trimethyl pentane)

This material of technical grade (97 mol per cent minimum) was obtained from the Eastman Kodak Company. It was distilled at atmospheric pressure in a Claissen flask, which was fitted with glass beads to prevent entrainment. The material boiled over a range of less than 0.1°F . The index of refraction was checked with values in the literature (20) and found to agree within 0.05 per cent. The impurity was estimated to be less than 0.1 mol per cent.

Experimental Measurements

Values of $\frac{q}{dT}$ (the heat capacity of the bomb plus contents) were obtained for two different amounts of material as a function of temperature for each of the four substances. These data are presented in tabular form (Tables 1, 2, 3, and 4) and in graphical form (Figures 2, 3, 4, and 5).

The maximum uncertainty introduced in these values due to the deviation of the experimental points from the curve is 5 per cent in the case of propene, 1.2 per cent for neohexane, 1.0 per cent for cyclohexane and 0.6 per cent for iso-octane.

Results

Values for the isobaric heat capacity of the bubble point liquid were computed as a function of temperature for the four substances and are represented graphically in Figure 6 for propene and Figure 7 for the other three hydrocarbons. In addition, these values are presented in Table 5. Upon consideration of the accuracy involved in the various measurements, the maximum uncertainty is estimated to be 5 per cent in the case of propene and one per cent for the other three substances. The large uncertainty in the case of propene was due to the fact that the difference in weight of the two samples was much smaller than in the case of the other three substances. In Figure 8 the relative effect of the volumetric correction terms is shown. The ordinate, designated by C , is dimensionless and is equal to

$$\frac{C_{P_b} - \frac{\frac{q_1}{dT} - \frac{q_2}{dT}}{m_1 - m_2}}{C_{P_b}}$$

Included in Figures 6 and 7 are values obtained by other investigators (21,22,23,24,25,27) at lower temperatures. The author's experimental data have been extrapolated to these temperatures. The extrapolation may be considered to be accurate within 0.5 per cent in the case of neohexane,

cyclohexane, and iso-octane, because the slope of the curves is nearly constant in the region of measurement. No heat capacity values were found in the literature for propene in the temperature interval from -40° to 80° F, which meant that any correlation of data below -40° F had to be made without a knowledge of the behavior in the intermediate region.

For propene, the curve is 1.5 per cent above the values of Powell and Giauque (27).

For neohexane, the curve is 0.4 per cent above the values of Kilpatrick and Pitzer (24) and 0.8 per cent above the values of Douslin and Huffman (25).

For cyclohexane, the curve is 0.5 per cent below the values of Parks, Huffman, and Thomas (21), 1.7 per cent below that of Ruehrwein and Huffman (23), and 2.6 per cent below that of Aston, Szasz, and Fink (22).

For iso-octane, the curve is 0.6 per cent above the values of Parks, Huffman, and Thomas (21).

The relative effect of the individual terms in equation (1) at four temperatures is shown by Table 6. Designating the terms by Greek letters as shown, the values of β , γ , δ , and ϵ are expressed as a percentage of the isobaric heat capacity. α is given directly as the ratio of the difference of the dew and bubble point volume to the dew point volume. Because some of the corrections are negative, it is interesting to note that the absolute magnitude of the correction terms reach as high as 80 per cent of the value of isobaric heat capacity (Propene at 160° F).

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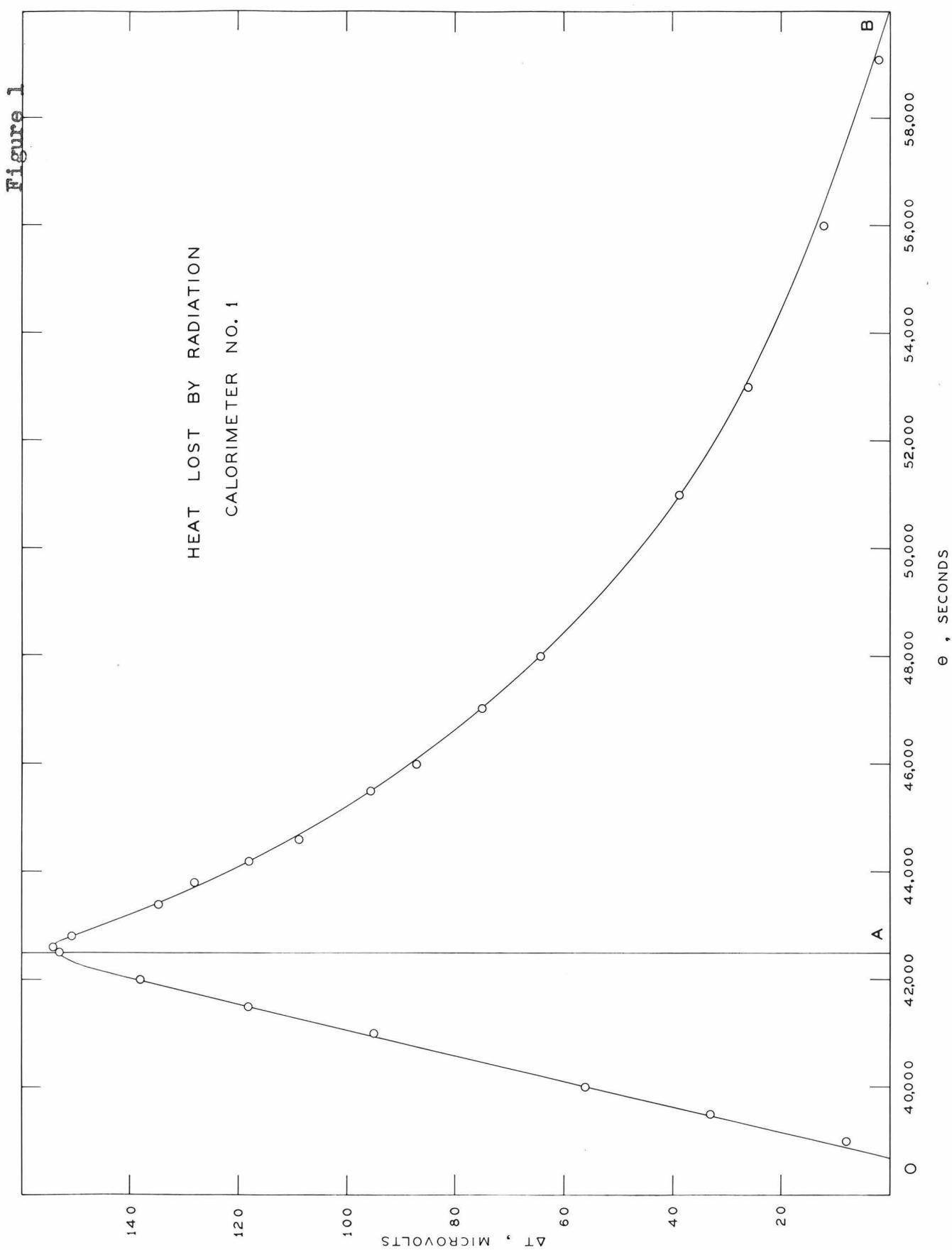
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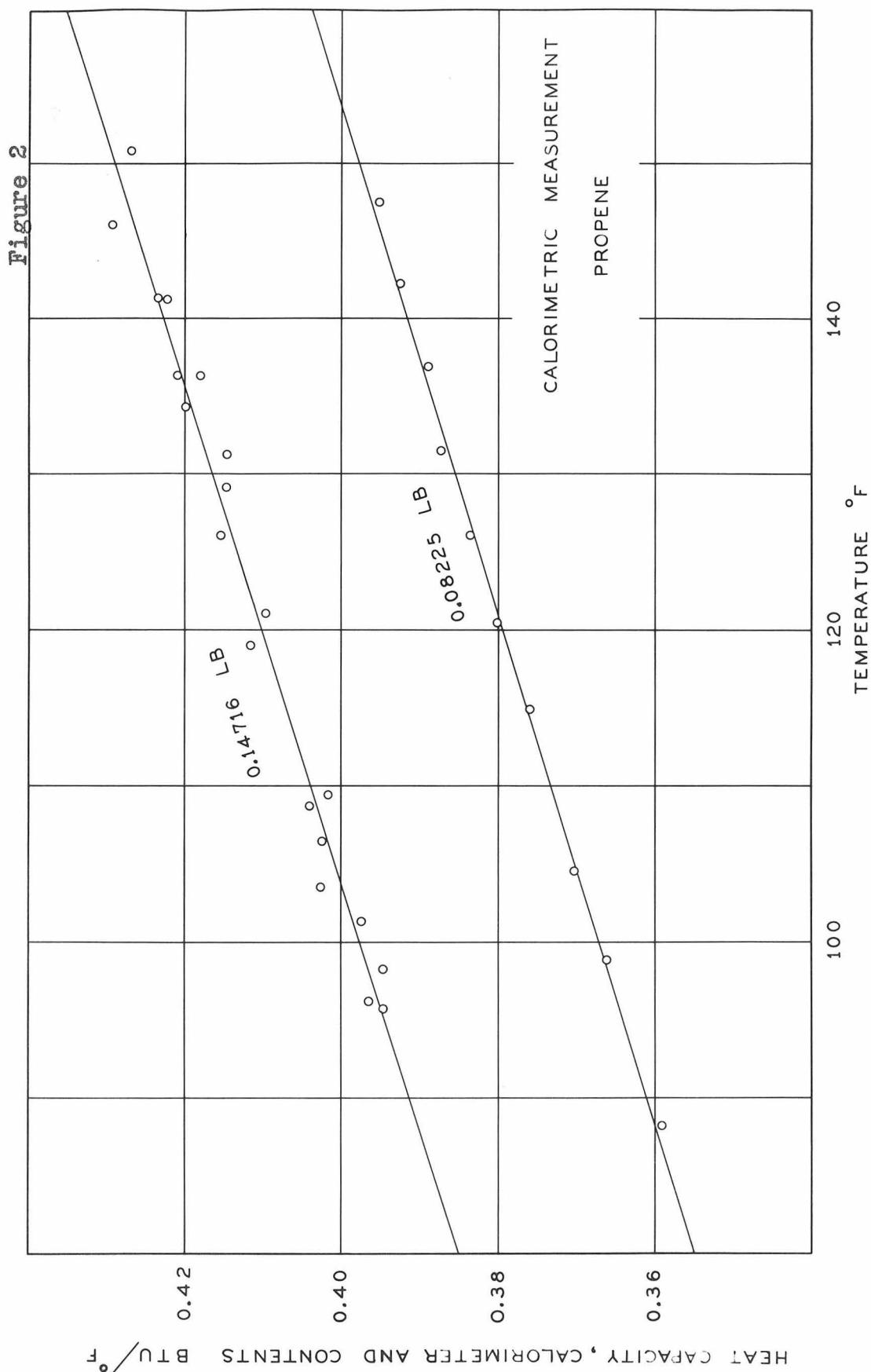
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HEAT CAPACITY, CALORIMETER AND CONTENTS BTU/°F

Figure 3

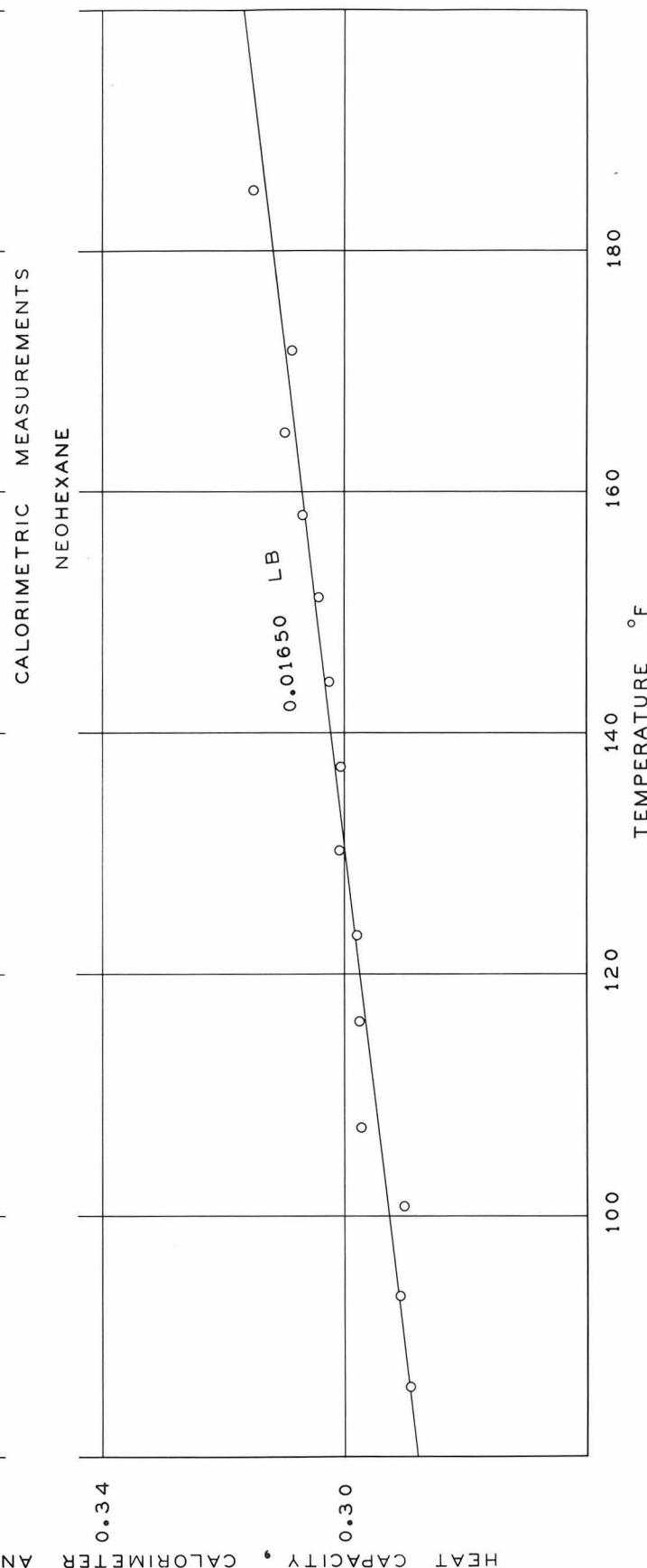
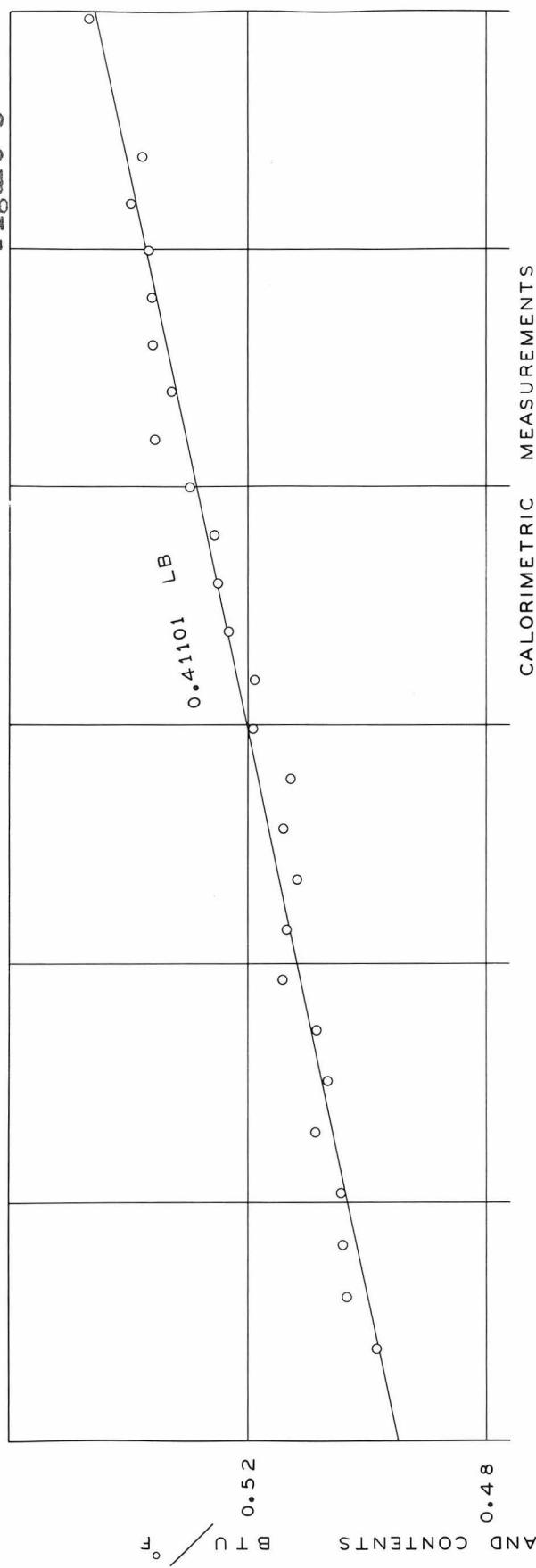
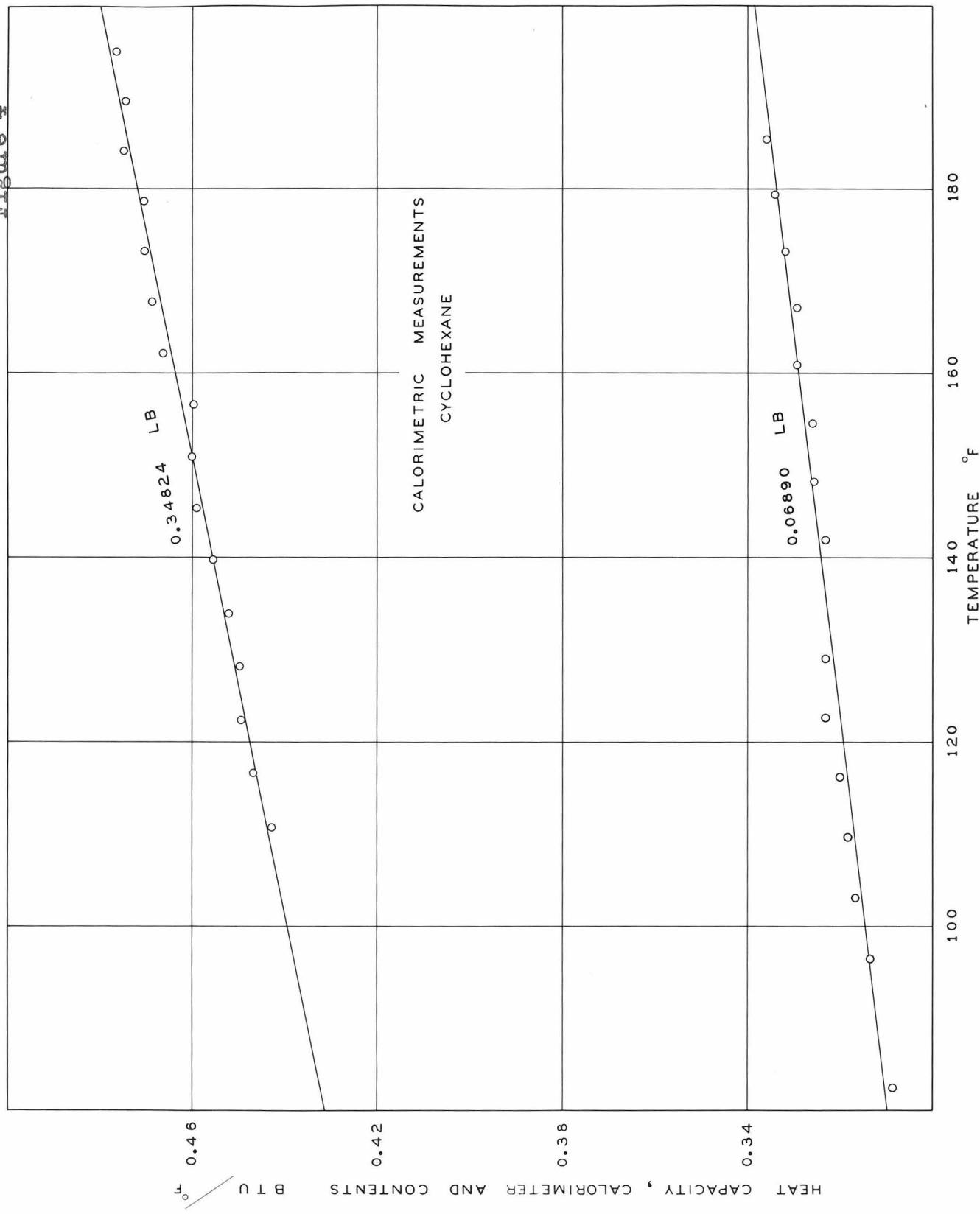
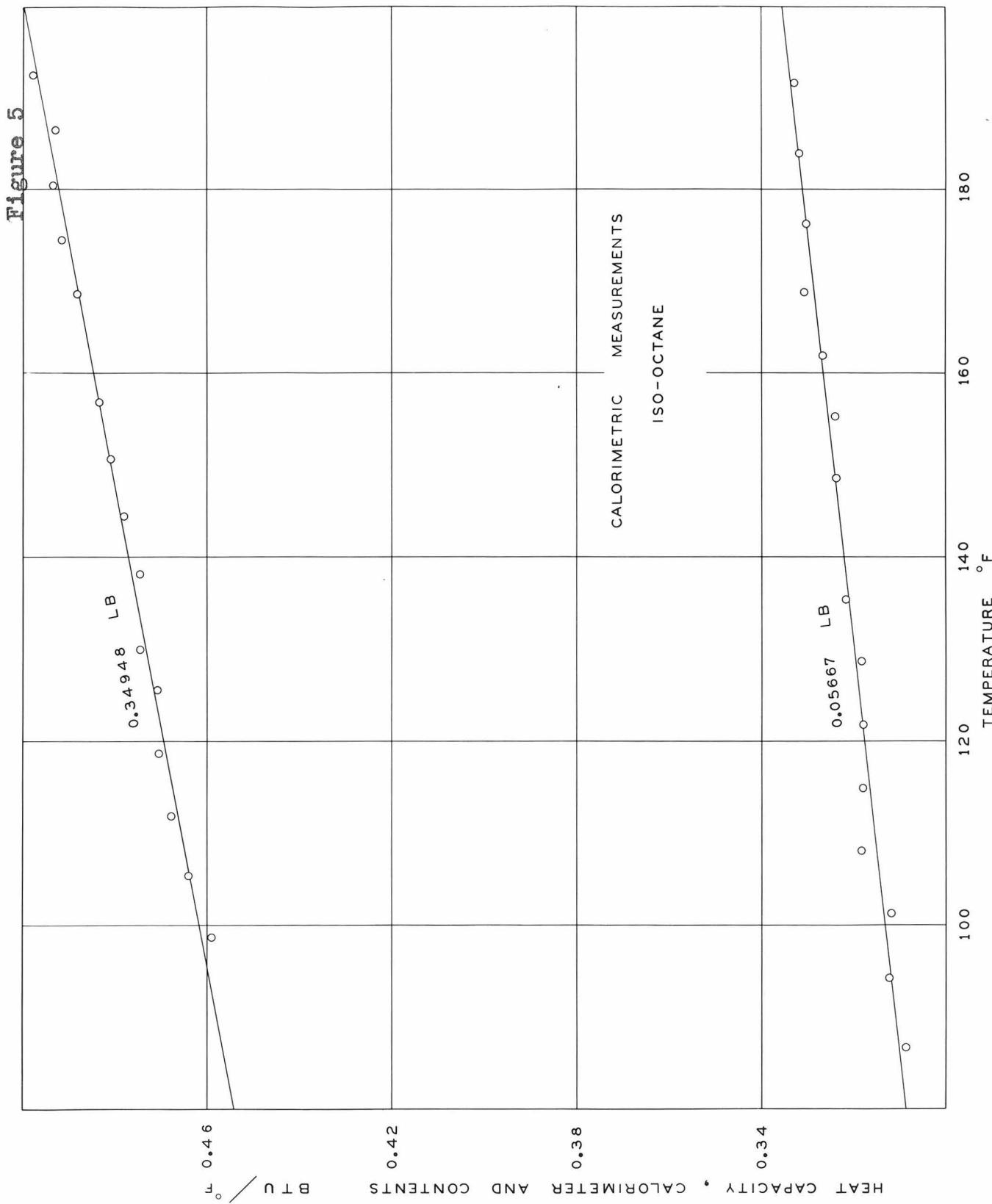
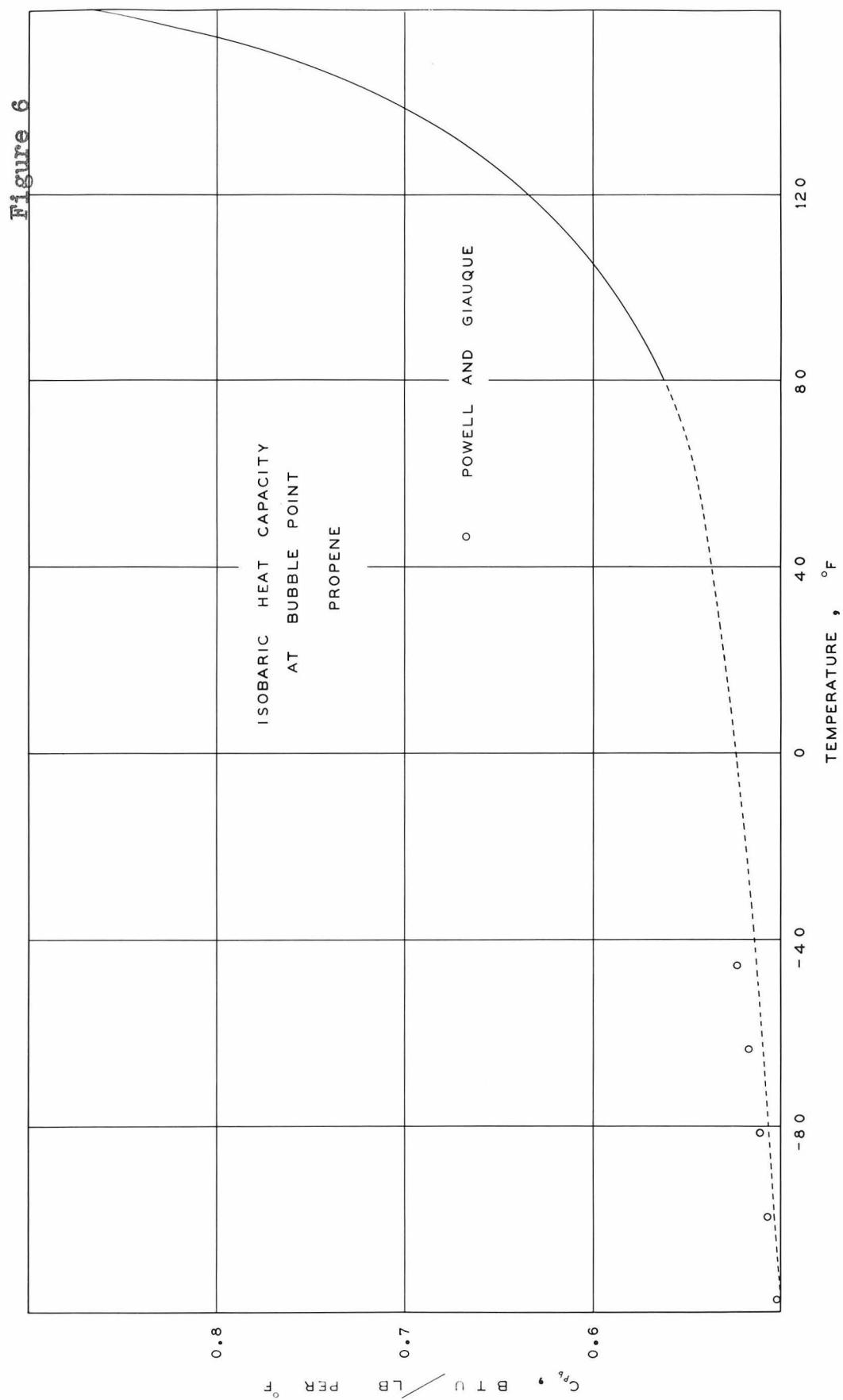


Figure 4



HEAT CAPACITY, CALORIMETER AND CONTENTS BTU





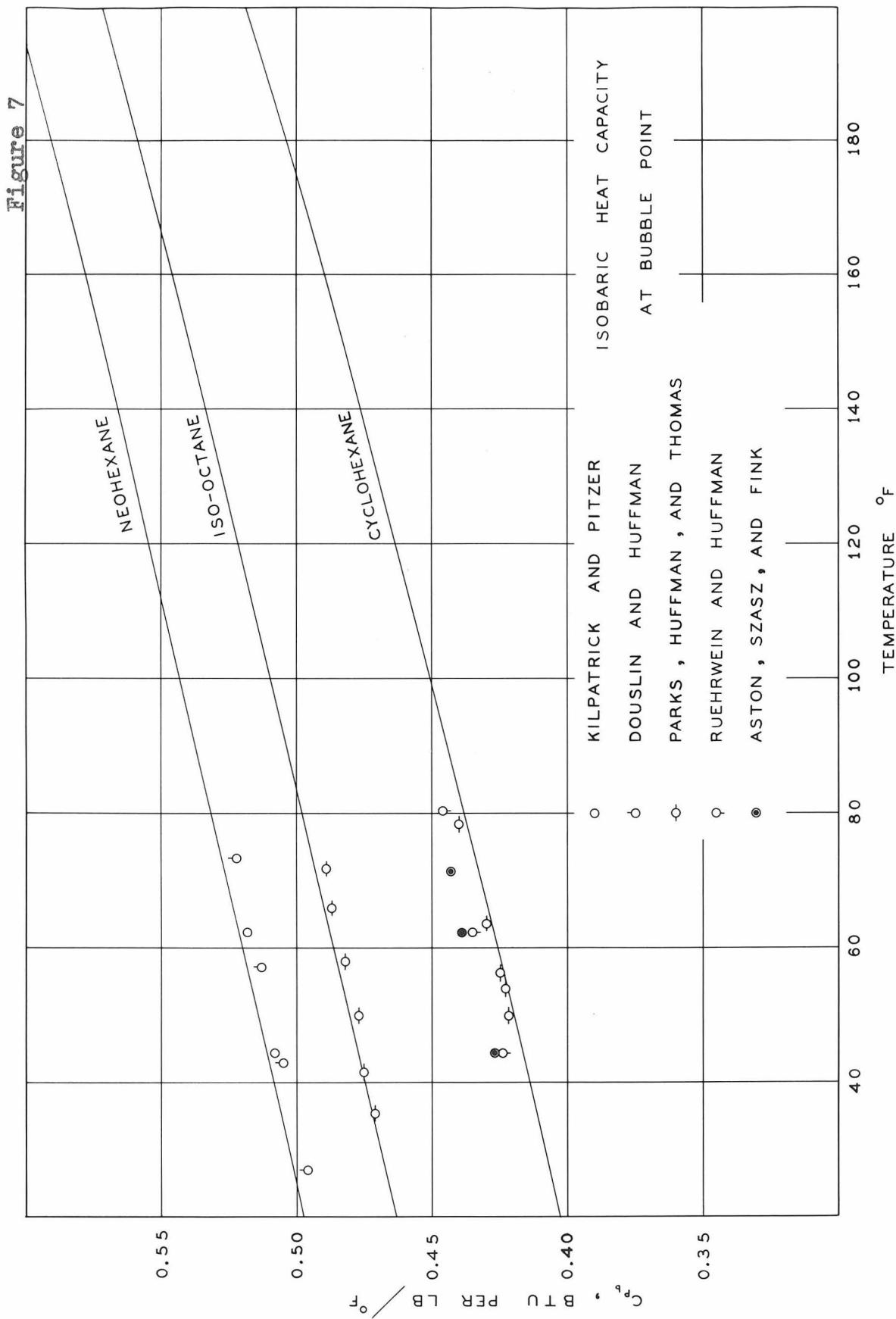


Figure 8

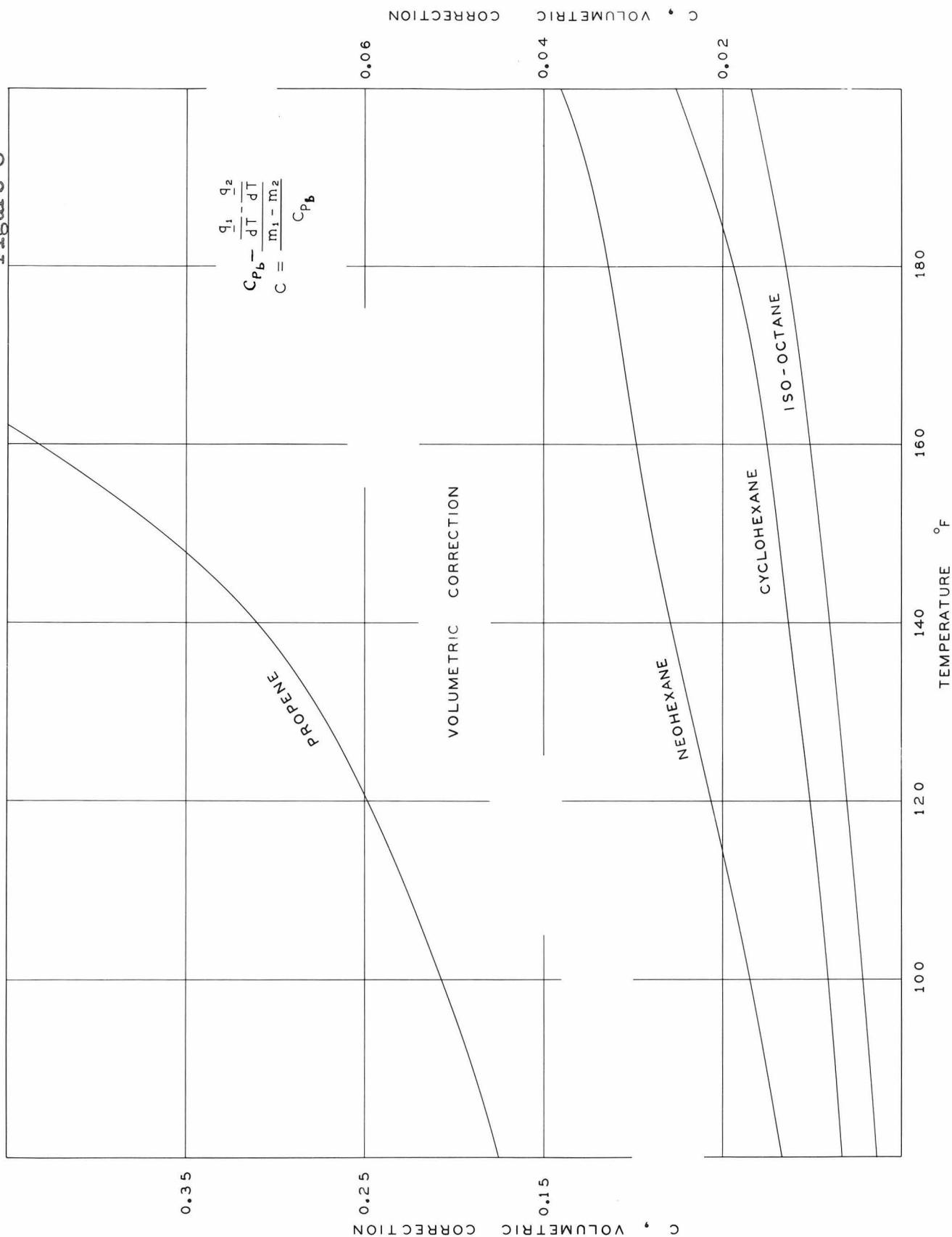


TABLE I

Heat Capacity of Calorimeter and Contents

Propene

- wt. 0.08225 lb. -

t (°F)	$\frac{q}{dt}$ (B.t.u. per °F)	t (°F)	$\frac{q}{dt}$ (B.t.u. per °F)	t (°F)	$\frac{q}{dt}$ (B.t.u. per °F)
88.288	0.3592	95.78	0.3947	126.04	0.4154
98.892	0.3662	96.26	0.3965	129.16	0.4147
104.597	0.3703	98.37	0.3947	131.22	0.4146
114.960	0.3759	101.39	0.3974	134.24	0.4199
120.539	0.3801	103.61	0.4026	136.34	0.4180
126.076	0.3835	106.47	0.4025	136.35	0.4210
131.504	0.3873	108.78	0.4040	141.20	0.4223
136.905	0.3889	109.45	0.4017	141.36	0.4235
142.252	0.3925	119.02	0.4117	146.06	0.4294
147.549	0.3952	121.06	0.4097	150.88	0.4270

TABLE 2

Heat Capacity of Calorimeter and Contents

Neohexane

- wt. 0.016497 lb. - - - - - wt. 0.411009 lb. - - - - -

t (°F)	$\frac{q}{dt}$ (B.t.u. per °F)	t (°F)	$\frac{q}{dt}$ (B.t.u. per °F)	t (°F)	$\frac{q}{dt}$ (B.t.u. per °F)
85.90	0.2892	87.78	0.4985	143.80	0.5188
93.391	0.2909	92.10	0.5034	147.84	0.5232
100.814	0.2902	96.47	0.5040	151.89	0.5250
108.30	0.2973	100.81	0.5043	155.95	0.5256
116.084	0.2975	105.94	0.5086	159.98	0.5297
123.263	0.2979	110.21	0.5065	163.95	0.5355
130.269	0.3008	114.50	0.5084	167.98	0.5328
137.209	0.3006	118.72	0.5141	171.94	0.5359
144.265	0.3025	122.92	0.5133	175.91	0.5361
151.225	0.3042	127.10	0.5116	179.86	0.5366
158.117	0.3069	131.29	0.5139	183.81	0.5396
164.913	0.3097	135.51	0.5127	187.78	0.5377
171.685	0.3086	139.68	0.5191	199.40	0.5466
185.047	0.3150				

TABLE 3

Heat Capacity of Calorimeter and Contents

Cyclohexane

	wt. 0.0688967 lb.		wt. 0.348239 lb.
t (°F)	$\frac{q}{\frac{dt}{(B.t.u.)}} \text{ per } {}^{\circ}\text{F}$	t (°F)	$\frac{q}{\frac{dt}{(B.t.u.)}} \text{ per } {}^{\circ}\text{F}$
82.49	0.3086	110.80	0.4426
96.54	0.3135	116.67	0.4467
103.06	0.3166	122.42	0.4493
109.69	0.3183	128.21	0.4496
116.23	0.3200	133.99	0.4521
122.67	0.3230	139.77	0.4554
129.09	0.3230	145.37	0.4590
135.51	0.3187	150.98	0.4600
141.95	0.3231	156.62	0.4597
148.30	0.3255	162.22	0.4663
154.58	0.3258	167.78	0.4686
160.88	0.3292	173.28	0.4702
167.08	0.3992	178.73	0.4704
173.22	0.3317	184.20	0.4748
179.38	0.3341	189.63	0.4744
185.43	0.3359	195.09	0.4764

TABLE 4
Heat Capacity of Calorimeter and Contents

Iso-octane

wt. 0.056669 lb.

wt. 0.349480 lb.

t (°F)	$\frac{q}{dt}$ (B.t.u. per °F)	t (°F)	$\frac{q}{dt}$ (B.t.u. per °F)
86.704	0.3089	98.763	0.4591
94.272	0.3124	105.458	0.4641
101.322	0.3119	111.384	0.4678
108.176	0.3183	118.741	0.4704
114.931	0.3180	125.649	0.4707
121.819	0.3179	131.966	0.4744
128.656	0.3182	138.179	0.4745
135.37	0.3218	144.479	0.4779
141.925	0.3218	150.721	0.4808
148.587	0.3237	156.904	0.4833
155.252	0.3239	168.568	0.4882
161.878	0.3266	174.545	0.4915
168.84	0.3306	180.495	0.4935
176.270	0.3302	186.529	0.4930
183.976	0.3317	192.576	0.4978
191.632	0.3328		

TABLE 5

Isobaric Heat Capacities at Bubble Point

t (°F)	Propene	Neohexane	Cyclohexane	Iso-octane
80	0.5615 ^a	0.5312	0.4378	0.4980
90	0.5747	0.5373	0.4445	0.5035
100	0.5917	0.5429	0.4505	0.5094
110	0.6102	0.5485	0.4570	0.5153
120	0.6329	0.5543	0.4641	0.5212
130	0.6607	0.5601	0.4700	0.5273
140	0.6985	0.5662	0.4764	0.5333
150	0.7607	0.5723	0.4835	0.5395
160	0.8608	0.5781	0.4899	0.5457
170	-	0.5836	0.4961	0.5525
180	-	0.5900	0.5034	0.5584
190	-	0.5960	0.5108	0.5650
200	-	0.6045	0.5189	0.5717

a B.t.u. per lb. per °F.

TABLE 6
Relative Effect of Volumetric Correction Terms

		C_{P_b}	ϵ/C_{P_b}	α	β/C_{P_b}	χ/C_{P_b}	δ/C_{P_b}	$C_{P_b} - \epsilon$
80° F	Propene	0.5615 ^a	82.6 ^b	0.9491 ^c	21.73 ^b	21.73 ^b	- 2.71 ^b	0.175 ^d
	Neohexane	0.5312	98.7	0.9976	0.05	1.3	0.18	0.0132
	Cyclohexane	0.4378	99.3	0.9995	0.016	0.68	0.016	0.0066
	Iso-octane	0.4980	99.5	0.9996	0.01	0.28	0.026	0.0028
120° F	Propene	0.6329	75.2	0.9029	5.19	33.3	- 6.29	0.249
	Neohexane	0.5543	97.9	0.9948	0.11	2.19	0.315	0.0227
	Cyclohexane	0.4641	99.0	0.9986	0.04	1.11	0.019	0.0103
	Iso-octane	0.5212	99.4	0.9990	0.027	0.63	0.052	0.00595

a B.t.u/lb. °F

b Expressed as a percentage

c Dimensionless

d Expressed as a fraction

* See Figure 8.

TABLE 6 (CONT'D)
Relative Effect of Volumetric Correction Terms

160° F	Propene	0.8606	56.7	0.8012	13.0	54.6	- 12.9	0.433
	Neohexane	0.5781	97.0	0.9897	0.206	3.48	0.28	0.0296
	Cyclohexane	0.4899	98.6	0.9972	0.072	1.68	0.02	0.0149
	Iso-octane	0.5457	99.0	0.9979	0.053	1.11	0.10	0.0106
200° F	Propene	-	-	-	-	-	-	-
	Neohexane	0.6035	96.2	0.9811	+ 0.450	5.76	- 0.562	0.0381
	Cyclohexane	0.5189	97.5	0.9948	0.14	2.76	0.125	0.0252
	Iso-octane	0.5717	98.3	0.9941	0.095	1.85	0.31	0.0168

a B.t.u./lb.° F

c Dimensionless

b Expressed as a percentage d Expressed as a fraction

* See Figure 8.

APPENDIX

Derivation for the Isobaric Heat Capacity of the Bubble-Point Liquid

From the first law of thermodynamics

$$\underline{q} = \underline{dE} + \underline{w} \quad (7)$$

$$\underline{q} = \underline{dE} + Pd\underline{V} \quad (8)$$

For a constant volume calorimeter $d\underline{V} = 0$

$$\therefore \underline{q} = \underline{dE} \quad (9)$$

$$\underline{E} = m_d E_d + m_b E_b \quad (10)$$

but $m_b = m - m_d \quad (11)$

Differentiating (11) $dm_b = - dm_d \quad (12)$

Differentiating (10) and combining with (11) and (12)

$$d\underline{E} = m_d dE_d + E_d dm_d + (m - m_d) dE_b - E_b dm_d \quad (13)$$

Another expression for the first law yields (for a constant weight system)

$$dE = C_P dT - P \left(\frac{\partial V}{\partial T} \right)_P dT + l_p dP - P \left(\frac{\partial V}{\partial P} \right)_T dP \quad (14)$$

Equation 96 page 44 Sage and Lacey (reference 26)

$$l_p = - T \left(\frac{\partial V}{\partial T} \right)_P \quad (15)$$

Combining equations (13) and (14) and remembering that equation (14) applies at both the dew and bubble point, we have

$$\begin{aligned} dE &= m_d \left\{ \left[C_{P_d} - P \left(\frac{\partial V}{\partial T} \right)_{P,d} \right] dT - \left[T \left(\frac{\partial V}{\partial P} \right)_{P,d} + P \left(\frac{\partial V}{\partial T} \right)_{T,d} \right] dP \right\} \\ &+ (m - m_d) \left\{ \left[C_{P_b} - P \left(\frac{\partial V}{\partial T} \right)_{P,b} \right] dT - \left[T \left(\frac{\partial V}{\partial P} \right)_{P,b} + P \left(\frac{\partial V}{\partial T} \right)_{T,b} \right] dP \right\} + (E_d - E_b) dm_d \end{aligned} \quad (16)$$

From the definition of enthalpy $E = H - PV$ (17)

Applied at dew and bubble point, this becomes

$$E_d - E_b = H_d - H_b + PV_b - PV_d \quad (18)$$

The Clapeyron equation states $H_d - H_b = T \frac{dP^u}{dT} (V_d - V_b)$ (19)

Combining equations (18) and (19)

$$E_d - E_b = (V_d - V_b) \left[T \frac{dP^u}{dT} - P \right] \quad (20)$$

If V is considered a function of P and T , the general equation of partial differentiation yields

$$dV = \left(\frac{\partial V}{\partial P} \right)_T dP + \left(\frac{\partial V}{\partial T} \right)_P dT \quad (21)$$

Considering equation (21) at dew and bubble point

$$PdV_d = P \left(\frac{\partial V}{\partial P} \right)_{T,d} dP + P \left(\frac{\partial V}{\partial T} \right)_{P,d} dT \quad (21a)$$

$$PdV_b = P \left(\frac{\partial V}{\partial P} \right)_{T,b} dP + P \left(\frac{\partial V}{\partial T} \right)_{P,b} dT \quad (21b)$$

Consider now the application of equations (16) and (9) to two different masses in the calorimeter bomb at the same temperature, and combine with (20), (21a) and (21b)

$$\begin{aligned} \underline{q}_1 - \underline{q}_2 &= (m_{d_1} - m_{d_2}) \left[C_{P_d} dT - P dV_d - T \left(\frac{\partial V}{\partial T} \right)_{P,d} dP \right] \\ &+ (m_1 - m_2 - m_{d_1} + m_{d_2}) \left[C_{P_b} dT - P dV_b - T \left(\frac{\partial V}{\partial T} \right)_{P,b} dP \right] \\ &+ T \left[\frac{dP^u}{dT} - P \right] (V_d - V_b) \left[\frac{dm_{d_1}}{m_{d_1}} - \frac{dm_{d_2}}{m_{d_2}} \right] \end{aligned} \quad (22)$$

$$\text{Now } \underline{V} = V_b \frac{m_b}{m_b} + V_d \frac{m_d}{m_d} = V_b (m - m_d) + V_d \frac{m_d}{m_d} \quad (23)$$

Consider now the application of equation (23) to two different masses in the calorimeter bomb

$$\underline{V} = V_b (m_1 - m_{d_1}) + V_d \frac{m_d}{m_d} = V_b (m_2 - m_{d_2}) + V_d \frac{m_d}{m_d}$$

This reduces to

$$\frac{m_{d_1} - m_{d_2}}{V_b - V_d} = \frac{V}{V_b - V_d} (m_1 - m_2) \quad (24)$$

$$\frac{m_1 - m_2 - m_{d_1} + m_{d_2}}{m_1 - m_2} = \frac{m_1 - m_2}{V_b - V_d} (m_1 - m_2)$$

$$\frac{m_1 - m_2 - m_{d_1} + m_{d_2}}{m_1 - m_2} = - (m_1 - m_2) \frac{V_d}{V_b - V_d} \quad (25)$$

Differentiating equation (23)

$$d\underline{V} = dV_b (m - m_d) + V_b (-dm_d) + V_d dm_d + m_d dV_d$$

As before

$$d\underline{V} = 0$$

$$\therefore dm_d = \frac{1}{V_b - V_d} \left[m_d dV_d + (m - m_d) dV_b \right] \quad (26)$$

Consider now the application of equation (26) to two different masses in

the calorimeter bomb

$$\frac{dm_{d_1} - dm_{d_2}}{V_b - V_d} = \frac{1}{V_b - V_d} \left[(m_{d_1} - m_{d_2}) dV_d + (m_1 - m_2 - m_{d_1} + m_{d_2}) dV_b \right] \quad (27)$$

Combining (24), (25), and (27)

$$\frac{dm_{d_1} - dm_{d_2}}{V_b - V_d} = \frac{1}{V_b - V_d} \left[\frac{V_b(m_1 - m_2)}{V_b - V_d} - \frac{V_d(m_1 - m_2)}{V_b - V_d} dV_b \right]$$

$$\frac{dm_{d_1} - dm_{d_2}}{V_b - V_d} = \frac{m_1 - m_2}{(V_b - V_d)^2} \left[V_b dV_d - V_d dV_b \right] \quad (28)$$

Substituting (24), (25), and (28) in (22) we have

$$\begin{aligned} \frac{q_1 - q_2}{m_1 - m_2} &= \frac{V_b}{V_d - V_b} \left[-C_{P_d} dT + P dV_d + T \left(\frac{\partial V}{\partial T} \right)_{P,d} dP \right] \\ &+ \frac{V_d}{V_d - V_b} \left[C_{P_b} dT - P dV_b - T \left(\frac{\partial V}{\partial T} \right)_{P,b} dP \right] \\ &+ T \left[\frac{dP}{dT} - P \right] \frac{1}{V_d - V_b} \left[V_b dV_d - V_d dV_b \right] \end{aligned}$$

$$\begin{aligned} \frac{q_1 - q_2}{m_1 - m_2} &= \frac{V_b}{V_d - V_b} \left[-C_{P_d} dT + T \left(\frac{\partial V}{\partial T} \right)_{P,d} dP \right] \\ &+ \frac{V_d}{V_d - V_b} \left[C_{P_b} dT - T \left(\frac{\partial V}{\partial T} \right)_{P,b} dP \right] \\ &+ T \frac{dP}{dT} \left[\frac{V_d dV_b - V_b dV_d}{V_b - V_d} \right] \end{aligned}$$

Rearranging, we have

$$\begin{aligned}
 C_{P_b} dT = & \frac{\frac{q_1 - q_2}{m_1 - m_2}}{\frac{V_d - V_b}{V_d}} \left[\frac{V_d - V_b}{V_d} \right] + T \left(\frac{\partial V}{\partial T} \right)_{P,b} dP + \frac{T}{V_d} \frac{dP''}{dT} \left[V_d dV_b - V_b dV_d \right] \\
 & + \frac{V_b}{V_d} \left[C_{P_d} dT - T \left(\frac{\partial V}{\partial T} \right)_{P,d} dP \right]
 \end{aligned} \tag{29}$$

Differentiating (29) with respect to temperature we have the expression for the isobaric heat capacity of the bubble-point liquid.

$$\begin{aligned}
 C_{P_b} = & \frac{\frac{q_1 - q_2}{m_1 - m_2}}{\frac{dV}{dT}} \left[\frac{V_d - V_b}{V_d} \right] + T \left(\frac{\partial V}{\partial T} \right)_{P,b} \frac{dP''}{dT} \\
 & + T \frac{dP''}{dT} \left[\frac{\frac{dV_b}{dT} - \frac{dV_d}{dT}}{V_d} \right] \\
 & + \frac{V_b}{V_d} \left[C_{P_d} - T \left(\frac{\partial V}{\partial T} \right)_{P,d} \frac{dP''}{dT} \right]
 \end{aligned} \tag{1}$$

Nomenclature

$$C = \frac{C_{P_b} - \frac{q_1}{dT} - \frac{q_2}{dT}}{\frac{m_1 - m_2}{C_{P_b}}} = \frac{C_{P_b} - \underline{E}}{C_{P_b}} \quad (\text{Dimensionless})$$

C Specific heat capacity at constant pressure (B.t.u. per lb per °F)

d Differential

δ Partial differential

E Internal energy (B.t.u.)

E Specific internal energy (B.t.u. per lb)

H Specific enthalpy (B.t.u. per lb)

K Constant for determining energy interchange between the bomb and surroundings as a result of radiation (B.t.u. per microvolt-second)

l Latent heat of pressure variation (B.t.u. per lb/lb per sq in.)

m Amount of material in bomb (lb)

m Critical mass (lb)

P Pressure (lb per sq in. absolute)

q Heat associated with an infinitesimal change in state (B.t.u.)

Q Energy added to the bomb (B.t.u.)

Q_{net} Net energy added to the bomb (Q - Q_R) (B.t.u.)

Q_R Energy gained or lost by radiation (B.t.u.)

t Temperature (°F)

T Thermodynamic temperature (°R)

t_{μv} Temperature (microvolts)

θ Time (seconds)

V Total volume (cu ft)

V Specific volume (cu ft per lb)

w Work done by the system on the surroundings by an infinitesimal change in state (B.t.u.)

Nomenclature (Cont'd)

Symbols used in Table 6

$$\epsilon = \frac{q_1 - q_2}{\frac{dT}{dT}} \quad \frac{m_1 - m_2}{m_1 - m_2}$$

$$\alpha = \frac{V_d - V_b}{V_d}$$

$$\beta = T \left(\frac{\partial V}{\partial T} \right)_{P,b} \frac{dP^*}{dT}$$

$$\gamma = T \frac{dP^*}{dT} \left[\frac{\frac{dV_b}{dT} - \frac{dV_d}{dT}}{V_d} \right]$$

$$\delta = \frac{V_b}{V_d} \left[C_{P,d} - T \left(\frac{\partial V}{\partial T} \right)_{P,d} \frac{dP^*}{dT} \right]$$

Subscripts

b Refers to bubble point

d Refers to dew point

1,2 Refers to two different quantities of material in the calorimeter bomb

A,B Refers to time A,B

0 Refers to initial time

Superscript

* Refers to conditions in which two phases are present