DETERMINATION OF SPECIFIC HEAT AND VAPOR PRESSURE OF CRUDE PINE GUM

A THESIS

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THE REQUIREMENTS FOR THE DEGREE

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APPROVED BY

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INTRODUCTION

Little, if any, work has been done on the heat constants of crude pine gum, and such information is of value in designing stills for obtaining the turpentine and rosin. Work was begun by the writer on specific heat in 1931 and was submitted for the degree of Bachelor of Science in Chemical Engineering. This work has been continued and results are given here with those on vapor pressure.

SPECIFIC HEAT:

The gum used in the crude form was from slash pine trees near Bronson, Levy County, Florida. It was secured from G. M. Owens.

The apparatus consisted of an Emerson type calorimeter with necessary thermometers and a brass container for the gum. The temperature changes of the container was measured with a 110°C thermometer graduated in tenths of a degree and calibrated against an Anschutz thermometer. The temperature change of the calorimeter was measured with a Beckmann thermometer. Since the change in temperature of the container is about ten times that of the calorimeter, it is assumed that the percentage errors with the two thermometers will

be approximately the same.

Runs were first made to determine the specific heat of the brass container. Approximately two liters of water, accurately weighed, were placed in the nickel plated iron vessel of the calorimeter. This vessel has a water equivalent of 30 grams. The container for the gum was heated in a water bath to a constant temperature. The temperatures of both calorimeter and container were read and the container quickly immersed in the water of the calorimeter. As soon as equilibrium was set up, the final temperature was read and subtractions gave the changes in the calorimeter and container. By means of data known the specific heat was calculated. Numerous runs were made for checks. Sample calculation:

2176 gms = weight of water in calorimeter

30 gms = water equivalent of nickel vessel

2206 gms = total

1677 gms = weight of brass container

1.087°C = temperature change of calorimeter

15.21°C = temperature change of brass container

Heat in = Heat out

$2206 \times 1.087 = 1677 \times 15.21 \times S$

$$S = \frac{2206 \times 1.087}{1677 \times 15.21} = .0940 \text{ cal/gram/°C}$$

Values of Specific Heat of container:

.0938	.0938	.0939
.0941	.0950	.0934
.0937	.0949	.0940
.0932	.0942	.0943
.0936		

The average value of specific heat is .0939. The container weighs 1677 grams, thus giving a water equivalent of 157.57 grams.

$$1677 \times .0939 = 157.57$$

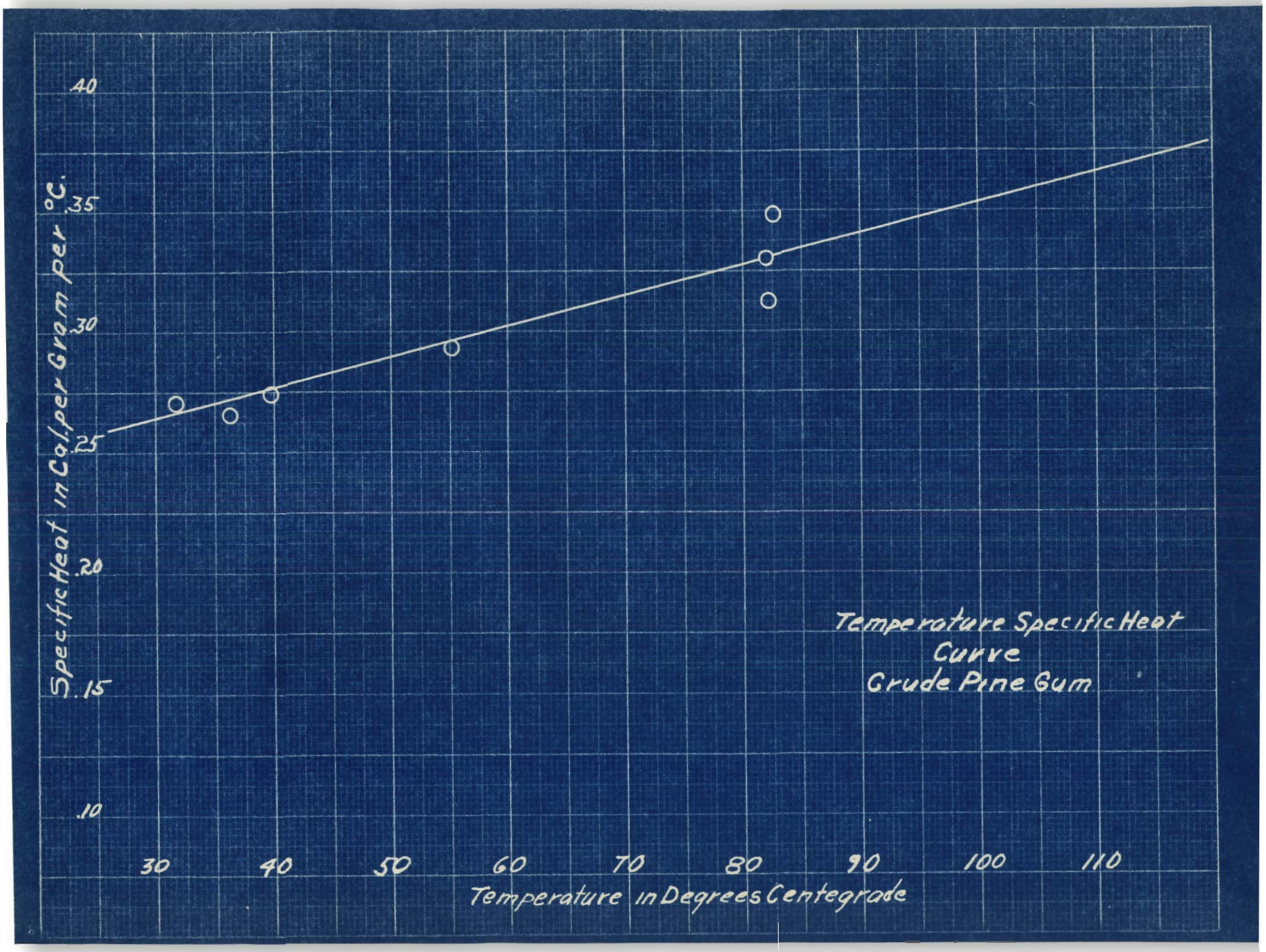
After satisfactory checks were obtained for the container, it was filled with gum and runs were made as before. The specific heat of the gum was figured as shown in the sample calculation:

2245 gms = weight of water in calorimeter
157.57 gms = water equivalent of container
241.5 gms = weight of gum
30.0 gms = water equivalent of nickel vessel
2.438°C = temperature change of the calorimeter
24.55°C = temperature change of the gum and container.

Heat in = Heat out.

$$(2245 + 30)(2.438)(1) = (157.57)(1)(24.55) - (241.5)(S)(24.55)$$

$$S = \frac{(2245)(2.438) - (157.57)(24.55)}{(241.5)(24.55)} = .2711$$


40
.35
.30
.25
.20
.15
.10
Specific Heat in Cal. per Gram per °C.
30
40
50
60
70
80
90
100
110
Temperature in Degrees Centegrade
Temperature Specific Heat
Curve
Crude Pine Gum

The experimental data are presented in table II. Specific heats at rounded temperatures as taken from the curve plotted between specific heats and temperatures are shown in table III.

Table II

Temp. °C	Specific Heat
33.6	.2711
33.4	.2455
36.0	.2651
35.2	.2355
39.3	.2729
38.7	.2460
55.0	.2925
82.0	.3099
82.2	.2629
81.7	.3487
85.6	.2774
85.2	.3291
85.2	.2712

Table III

Temp. °C	Specific Heat
30	.2650
40	.2775
50	.2900
60	.3025
70	.3150
80	.3275
90	.3400
100	.3525
110	.3650
120	.3775
130	.3900
140	.4025
150	.4150

It was noticed that successive runs using the same sample of gum gave decreasing values for the specific heats, but that runs with fresh samples checked fairly closely. Upon continued heating, the

gum apparently decomposed and a small portion of the more volatile constituents escaped. The container could not be made absolutely gas tight. It may be seen from the curve that the specific heats increase with increase in temperature.

VAPOR PRESSURE:

The gum used in the vapor pressure experiments was similar to that used for specific heats. In determining the vapor pressures, the work of John Chipman[1], which is a modification of that of Smith and Menzies[2], was followed very closely. Chipman's apparatus, as shown in Figure 1, was used.

Pressures below atmospheric were secured with a Central Scientific Company's Hivac pump, and pressures above atmospheric were secured with an ordinary bicycle pump. The pressure measurements were made by means of mercury manometers. The meter bars of these manometers were those used by Chipman which had been checked with high grade steel scales. If the pressure or vacuum became too high, adjustment could be made by cracking the relief cock "C" to let air in or out of the system as needed. An ordinary

(1) Chipman and Peltier Ind. Eng. Chem. 21,1106 (1929)

(2) Smith and Menzies J.A.C.S. 32 1412 (1910)

Sketch of Vapor Pressure Apparatus

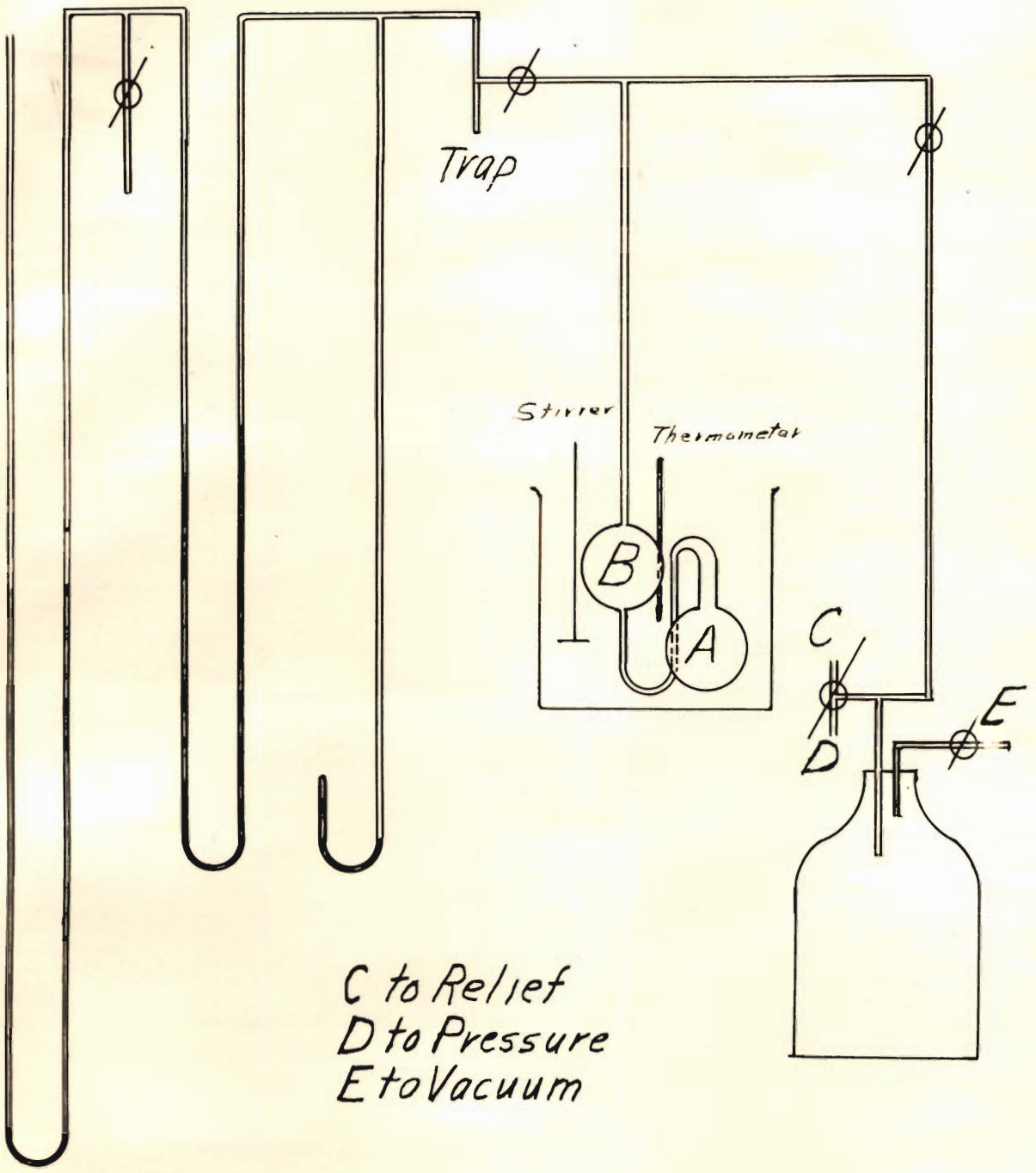


Figure 1

mercury barometer was used for determining atmospheric pressure, correction being made for temperature.

A 110°C thermometer graduated in tenths of a degree was used for temperatures up to 110°C and a 360°C thermometer for higher values. Both were calibrated against Anschutz thermometers.

The apparatus was checked by determining the vapor pressures of water. Values obtained checked within the limits of experimental error as shown in Table I.

TABLE I

Temp. °C	True V.P. In MM Hg	Exp. V.P. In MM Hg.
58.5	139	141
59.1	143	143
62.2	165	166
66.0	196	198
66.2	197	200
70.2	235	240
74.0	277	284
74.2	279	285
78.2	330	336
82.3	389	397
85.1	435	446
87.7	481	491
89.9	523	539
90.3	531	543
93.5	600	612
96.3	665	674
99.9	757	762

The bulb "A" of the isoteniscope as shown in figure I was filled with the crude gum and sealed off. The isoteniscope was then connected to the manometer system and immersed in a 1500 cc beaker of mineral oil. The bath was stirred by a small electric motor. As each run was started, the bulb "A" was boiled out to insure removal of all air. Considerable material went over into bulb "B". By careful manipulation of pressures, most of this material was forced back into "A", leaving only enough in the U tube to serve as a manometer. The level of the liquid being the same in both arms of the U tube shows that the pressure in the manometer system is the same as that over the gum. The vapor pressure is the sum of the manometer reading and the atmospheric pressure.

The temperature was held as nearly constant as possible until several readings were taken. After satisfactory checks were made, insuring a definite constant temperature throughout the gum, the bath was heated to a higher temperature and again held constant as before until readings were made. Care was necessary to be sure that the liquid in the U tube did not return to bulb "A". Should the liquid

be forced back into "A", air would also get in and it would be necessary to again completely boil out.

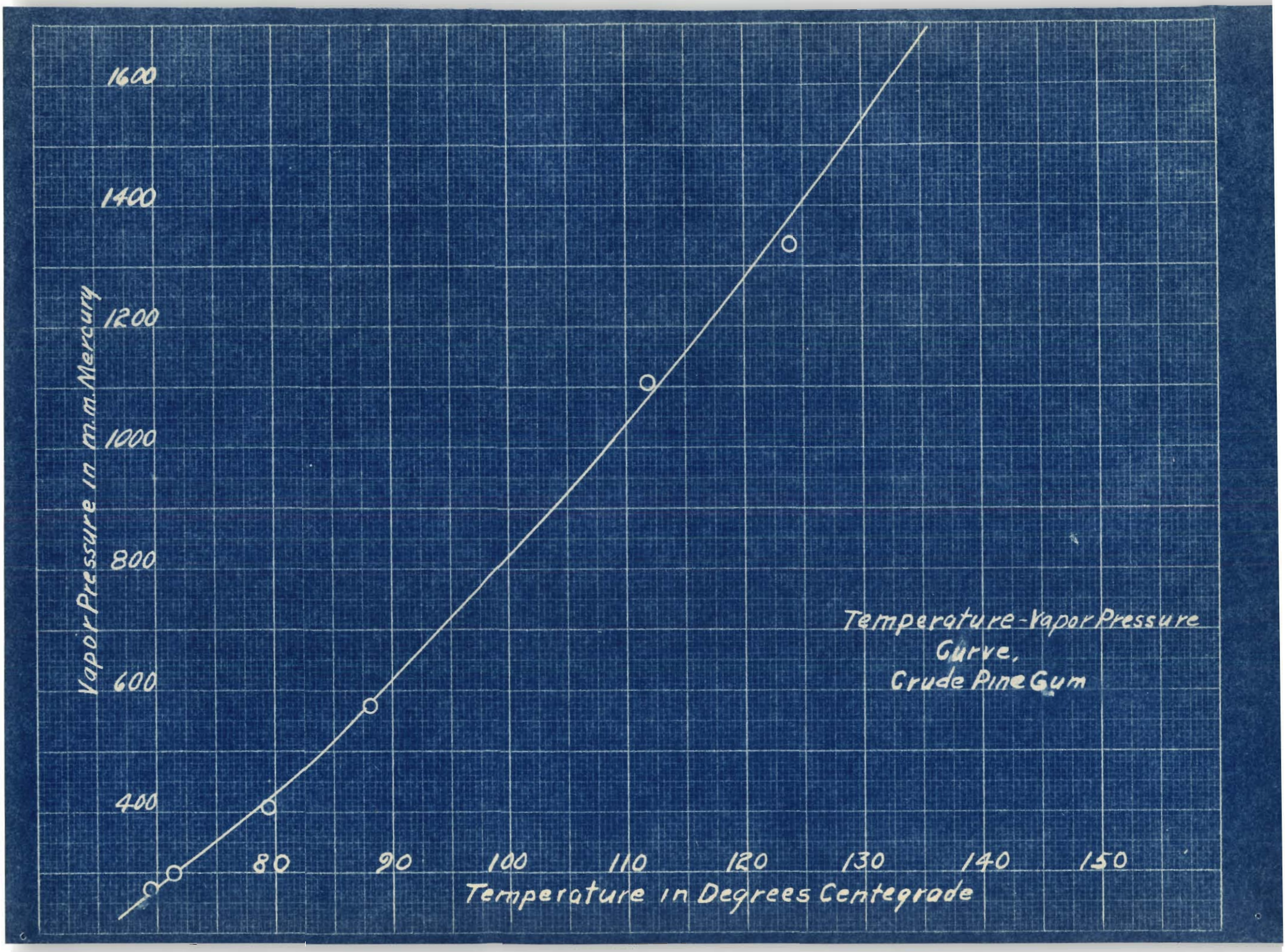
Table IV shows the experimental values of vapor pressures at different temperatures. And Table V shows vapor pressures at rounded temperatures as taken from the curve.

Table IV

Temp. °C	V. P. In MM Hg
69.7	270
71.5	296
79.5	403
88.1	570
112.1	1105
123.5	1329
84.5	445
125.0	1146
89.6	395
144.4	1599
103.0	601
124.3	789
126.1	835

Table V

Temp. °C	V. P. In MM Hg
50	130
60	200
70	275
80	426
90	610
100	813
110	1018
120	1272
130	1547
140	1810
150	2212


1600
1400
1200
1000
800
600
400
Vapor Pressure in m.m. Mercury
80
90
100
110
120
130
140
150
Temperature in Degrees Centegrade
Temperature-Vapor Pressure
Curve,
Crude Pine Gum

It was observed that checks could be easily obtained if the liquid was not allowed to return to the bulb "A". If it did return and was boiled out again, the results then obtained were considerably lower. The gum is a mixture of a number of volatile constituents. Boiling permits the more volatile ones to escape, leaving a residue which has a lower vapor pressure. Runs made with new samples checked fairly well. Table IV shows how the vapor pressure would fall off when the same sample was repeatedly used. The bath cooled at the end of each working day, thus lowering the vapor pressure of the gum and the material in the U tube was forced back into bulb "A". Boiling out was necessary at the beginning of each day's work.

DISCUSSION:

This work is done with a material which is crude -- direct from the pine tree. Each sample will be slightly different in composition and hence give slightly different values for the heat constants. Heretofore there has been no work done in this substance. Stills have been made with no regard for scientific design. Since the ones in use gave fairly good results, no one worried about the matter. The values herein contained are not submitted as true for any gum. They were obtained on this specific sample of slash pine gum. The values for other gums should approximate these. In all engineering design there is a factor of safety which would more than cover any small difference between these values and those of some other specific crude pine gum.